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W 17008
Examensarbete 30 hp
Juni 2017

Anaerobic digestion trials with HTC process water

Rötningsförsök med HTC processvatten

Erik Nilsson

ABSTRACT

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Hydrothermal carbonization (HTC) is a process where elevated temperature and pressure is used in order to convert biomass to hydrochar, a coal-like substance with good dewatering properties and many potential uses. HTC can be used to treat digestate from anaerobic digestion, but the process water that remains after the hydrochar has been recovered needs to be treated further in the wastewater treatment plant. In order to make HTC more competitive compared to other sludge treatments it is important to find a good use for the process water. The main objective of this master thesis was to investigate the effects of recirculating HTC process water to the anaerobic digestion.

To achieve the objective, both theoretical calculations and experimental trials were performed. The experimental trials were conducted with an Automatic Methane Potential Test System (AMPTS II) in order to investigate the anaerobic digestion in laboratory scale. In the first trial, three substrates, process water, hydrochar, and primary sludge were tested for their biochemical methane potential (BMP). All substrates were mixed with inoculum. Process water had a BMP of 335 ± 10 % NmL/g_{vs} (normalized CH_4 production in mL per g added VS (volatile solids)), hydrochar had BMP of 150 ± 5 % NmL/g_{vs}, and primary sludge had a BMP of 343 ± 2 % NmL/g_{vs}. The methane production was almost the same for process water as for primary sludge i.e. no inhibitory effects could be seen when process water was mixed with only inoculum.

In the second trial, a more realistic scenario was tested where process water was co-digested with primary sludge at different ratios. The results from the second trial were not statistically reliable and therefore cannot be used on their own to determine with certainty if the process water could have an inhibitory effect in a full-scale anaerobic digester. However, the combined results from both trials indicate that it is unlikely that the process water would have an inhibitory effect.

The possible increase in methane yield, if the digestate from a biogas facility was treated in full-scale implementation of the HTC process, was calculated theoretically. The produced process water would have the capacity to increase the methane production with approximately 10 % for a biogas facility. For the calculations, the BMP for process water was assumed to be 335 NmL/g_{vs} and no synergetic effects was considered.

Keywords: anaerobic digestion, HTC, process water, hydrochar, AMPTS, BMP, primary sludge, digestate

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REFERAT

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Hydrotermisk förkolning (HTC) är en process där biomassa behandlas med hög temperatur och högt tryck. Slutprodukten blir biokol, en kolliknade substans med goda avvattningsmöjligheter och många potentiella användningsområden. HTC kan användas för att behandla rötslam från biogasanläggningar, dock behöver processvattnet som uppkommer vid filtreringen av biokol behandlas vidare i avloppsreningsverket. För att göra HTC mer konkurrenskraftigt gentemot andra slambehandlingsmetoder är det viktigt att hitta ett bra användningsområde för processvatten. Syftet med det här examensarbetet var att undersöka effekterna av att återföra HTC processvatten till rötningsprocessen.

För att uppnå syftet, har teoretiska beräkningar och experimentella försök genomförts. De experimentella försöken utfördes med hjälp av en automatic methane potential test system (AMPTS II) för att undersöka rötningsprocessen i laboratorieskala. I det första försöket testades de tre substraten processvatten, biokol och primarslam för deras biokemiska metanpotential (BMP). Samtliga substrat var blandade tillsammans med ymp. Processvattnet hade ett BMP på 335 ± 10 % NmL/g_{vs} (normaliserad CH_4-produktion i mL per g tillagd VS (volatile solids)), biokol hade ett BMP på 150 ± 5 % NmL/g_{vs} och primärslam hade ett BMP på 343 ± 2 % NmL/$g_{vs.}$ Metangasproduktionen var alltså i stort sätt samma för primärslam och processvatten, d.v.s. det gick inte att se att processvatten skulle ha några hämmande effekter när processvattnet bara var blandat med ymp.

I det andra försöket var ett mer realistiskt scenario testat, där processvatten samrötades med primärslam vid olika blandningsförhållanden. Resultaten från det andra försöket kunde inte statistiskt säkerhetsställas och kan därför inte användas på egen hand för att avgöra om processvatten skulle ha en hämmande effekt på en fullskalig rötningsanläggning. De sammanvägda resultaten från båda försöken indikerar dock att det skulle vara osannolikt att processvatten skulle ha en hämmande effekt.

Den möjliga metangasökningen för behandling av rötslam från en biogasanläggning i en fullskalig HTC anläggning beräknades teoretiskt. Det producerade processvattnet skulle ha kapaciteten att öka metanproduktionen med ca 10 % för en biogasanläggning. För beräkningarna antogs BMP vara 335 NmL/g_{vs} för processvatten och inga synergistiska effekter togs i beaktning.

Nyckelord: rötning, HTC, processvatten, biokol, AMPTS, BMP, primärslam, rötningsslam

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PREFACE

This master thesis of 30 ECST credits is the final part of the Master Program in Environmental and Water Engineering at Uppsala University and the Swedish University of Agricultural Sciences (SLU). The supervisor was Maximilian Lüdtke, Swedish Environmental Research Institute (IVL) and the subject reviewer was Åke Nordberg, associate professor and senior lecturer from the Department of Energy and Technology; Division of Bioenergy at the Swedish University of Agricultural Sciences (SLU), Uppsala.

First of all, I want to thank my supervisor Maximilian Lüdtke for the support and interesting discussions during this work. Without your help, this master thesis could not have been made. Furthermore, I want to thank Åke Nordberg for your comments on improvement of the report. Moreover, I want to thank Andreas Carlsson, biogas engineer at Stockholm Vatten AB, for your help with sample material. I would also like to thank the people from C-Green, Fredrik Öhman, Lars-Erik Åkerlund and Matilda Sirén Ehrnström. Fredrik Öhman for comments on improvements of the report. Lars-Erik Åkerlund and Matilda Sirén Ehrnström for HTC sample material and information of the HTC process. Furthermore, I want to thank Christian Baresel for comments during the work and help with the administration concerning the master thesis.

I would also like to thank Bioprocess Control AB, Kävlinge kommun and Huber technology for allowing me to use same of their images in this master thesis.

Sweden, Stockholm, June 2017

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UPTEC W 17 008, ISSN 1401-5765
Published digitally at the Department of Earth Sciences, Uppsala University, Uppsala 2017

POPULÄRVETENSKAPLIG SAMMANFATTNING

Rötningsförsök med HTC processvatten

Det finns olika sätt att använda eller behandla rötslammet från rötningskammarna. Det är rötslam som blir restprodukten från biogasproduktion och består till stor del av svårnedbrutet material. En metod för att behandla rötslam är hydrotermisk förkolning, förkortat HTC. HTC går ut på att rötslam (eller annat organiskt material) utsätts för hög temperatur och högt tryck. Huvudprodukten som fås ut av denna process kallas för biokol. Biokol liknar vanligt kol och har därför också liknande användningsområden som vanligt kol. Vanliga användningsområden för biokol är som jordförbättringsmedel, fodertillskott till djur och som filtermaterial för olika slags reningsprocesser. Liksom de flesta andra processer fås också en biprodukt vilket i HTC:s fall är processvatten. Processvattnet uppkommer när biokolet filtreras för att öka torrhalten. Processvattnet innehåller lösta restprodukter från HTC processen och måste tas om hand, antingen i reningsverket eller på annat sätt.

Syftet med detta examensarbete var att undersöka effekterna av att återföra processvattnet till rötningsprocessen d.v.s. rötningskammarna där biogas produceras. För att kunna ta reda på det har småskaliga rötningsförsök gjorts i en utrustning som heter automatic methane potential test system, förkortat AMPTS II. Detta är en utrustning som har utformats för att likna en rötningsanläggning men som kan användas i laborationsskala. Två försöksomgångar gjordes, vilka var och en tog ca en månad. I det första försöket testades tre substrat; processvatten, biokol och primärslam. Substrat kallas det som mikroorganismerna använder för tillväxt och reproduktion. Primärslam fås från avloppsvatten och är bland det första som tas bort i vattenreningsverkens reningsprocesser. Det är mycket vanligt att primärslammet rötas i biogasanläggningar. Samtliga substrat blandades med ymp från Henriksdals reningsverks biogasanläggning som ligger i Stockholm. Ymp är mikroorganismer som behövs för att kunna bryta ned substraten. Förutom de tre substraten testades också ett blankprov och en positivkontroll. Blankprovet bestod enbart av ymp och testades för att kunna se hur mycket biogas som ympen kommer att bidra med när den blandades med substraten. Den positiva kontrollen bestod av cellulosa och ymp. Eftersom cellulosa har en känd biogas produktion, kunde den positiva kontrollen användas till att avgöra ympens kvalitet. Cellulosa är för övrigt en beståndsdel i trä. För att öka den statistiska säkerheten kördes alla substrat, blankprov och positivkontrol som triplikat d.v.s. varje prov hade två kopior. Samtliga triplikat placerades i AMPTS:en under omrörning. Resultaten av rötningsförsök 1 visade att biogasproduktionen var i stort sätt på samma nivå för processvatten som för primärslam. Det går därför inte att säga att processvatten skulle ha någon hämmande effekt när det blandas med ymp, tvärtom fås en biogasproduktion som liknar den från primärslams. Biokolets biogasproduktion låg ungefär på hälften av primärslammets och processvattnets biogasproduktion.

I försök 2 gjordes ett rötningsförsök i två AMPTS:er som skulle likna ett realistiskt scenario där processvatten återförs till rötningsprocessen. Det främsta substratet som används i många rötningsanläggningar är primärslam. Därför blandades primärslam, ymp och processvatten i realistiska proportioner i försök 2. Tyvärr var inte försök 2 statistiskt säkerställt. Den främsta anledningen till det var att biogasproduktionen var för låg i triplikatet för positiva kontrollen samt att biogasproduktionen varierade kraftigt

mellan proverna i den positiva kontrollen. Det går alltså inte med säkerhet att dra slutsatsen att processvatten inte skulle ha någon hämmande effekt ifall det användes i rötningsprocessen. Om ändå försök 2 ändå tas i beaktning tillsammans med de statistiskt säkerställda resultaten från försök 1 kan det antas osannolikt att processvatten skulle ha en hämmande effekt i en rötningsprocess.

I examensarbetet ingick också en teoretisk uppskattning av hur mycket en biogasanläggning skulle kunna öka sin biogasproduktionen ifall processvatten återförs. Det antogs att processvattnet skulle ha samma biochemical methane potential (BMP) som i försök 1. BMP är ett mått som används för att kunna jämföra olika substrats metanproduktion med varandra. Det vill säga hur mycket metan som fås ut av en viss massa substrat. Den teoretiska beräkningen valdes att göras utifrån 2016 värden från Henriksdals rötningsanläggning. Om allt rötslam som producerades på Henriksdals rötningsanläggning genomgick HTC och om det processvattnet som producerades från HTC processen sedan återfördes till rötningsanläggningen skulle biogasproduktionen teoretiskt kunna öka med ca 10 %.

ABBREVIATIONS AND EXPLANATIONS

AD – Anaerobic digestion

AMPTS II – Automatic methane potential test system

BMP – Biochemical methane potential

BOD – Biochemical oxygen demand

CM –Microcrystalline cellulose

COD – Chemical oxygen demand

Digestate – Anaerobic digested sludge

HC – Hydrochar

HRT – Hydraulic retention time

HTC – Hydrothermal Carbonization

IM – Inoculum

PS – Primary sludge

PTEF – Polytetrafluoroethylene

PW – Process water

RSD – Relative standard deviation

SO. **–** Scenario

SS – Secondary sludge

STP – 1.0 standard atmospheric pressure, 0 °C and zero moisture content

TOC – Total organic carbon

TS – Stand for total solids. Represents the weight of a sample after it has been dried in an oven for 20 h in 105 °C. The TS value is usually presented as a ratio between TS weight and the wet-weight

VFAs – Volatile fatty acids

VS – Meaning volatile solids and is all the organic material in a sample. The VS value is determined by combusting a dry sample in 550 °C for 2 h. What is left after the 550 °C heating is considered as the inorganic fraction of the sample. The VS weight is then the TS weight subtracted with the weight of the inorganic. VS is usually present as a ratio between VS weight and TS weight or as a ratio between VS weight and wet-weight

ww – Stand for wet-weight and is simply the sample when untreated

WWTP – Wastewater treatment plant

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1 INTRODUCTION

Anaerobic digestion (AD) of wastewater treatment plant (WWTP) sludges generates large volumes of digestate. The management of the digestate results in costs for the WWTP, mainly in form of treatment, storage and deposition of digestate to arable soils. Therefore, Henriksdals WWTP in Sweden, Stockholm, is interested in new alternative treatments of digestate.

One alternative treatment of digestate is hydrothermal carbonization (HTC). In this treatment is the digestate exposed to high temperature (180–230 °C) and high pressure (10–28 bar) (Öhman, 2017a) under an interval of time (1–72 h) (Funke & Ziegler, 2009).

The outcoming material from the HTC process has significantly enhanced dewatering properties compare to the digestate. Therefore, the volume can be reduced drastically (Öhman, 2017a). Additionally, decreased amount of digestate with ongoing microbial activity will also lead to less greenhouse gas emissions since fresh digestate emits both methane and carbon dioxide (Björkman & Lilliestråle, 2016). Furthermore, the material is hygienisated, i.e. pathogens are removed (Funke & Ziegler, 2009).

After the HTC reaction, the solid material is separated from the liquid by e.g. mechanical separation methods such as a filter press. The solid material is called hydrochar and the liquid material is called process water. The hydrochar can be used in many areas e.g. as soil amender, filter material and feed supplement for animals (Libra *et al.*, 2011). The process water contains dissolved organic compounds as well as some inorganic compounds such as nitrogen and needs further treatment before release to the recipient (Wirth *et al.*, 2012).

This master thesis will have the process water as its main focus. It will be investigated if the process water can be reintroduced to the anaerobic digestion to produce biogas. I.e. does process water have an inhibitory effect on the biogas production or not and how much biogas can be produced from process water? The process water contains a lot of dissolved organic matter and should thereby have the capacity to increase the methane yield (Wirth *et al.*, 2012).

1.1 OBJECTIVES

The objective of this master thesis is to determine the biochemical methane potential (BMP) for process water and hydrochar after HTC treatment of digestate and investigate how the biogas production at a WWTP would be affected if the process water was reintroduced to the anaerobic digestion.

1.2 RESEARCH QUESTIONS

To address this objective, the following research questions were formulated:

1. What is the biochemical methane potential (BMPs) for process water and hydrochar, respectively?
2. Would reintroduction of HTC process water to the WWTP anaerobic digestion cause inhibitory effects or increased biogas yield?
3. How would anaerobic digestion of process water affect the total methane production at a WWTP?

1.3 DISPOSITION AND DELIMITATIONS

The report begins with a theory part about wastewater treatment, anaerobic digestion and HTC. The theory is followed by a method section which describes the execution of two experimental trials that were conducted as well as the method for the theoretical calculation of the increased biogas yield in the full-scale implementation where process water is reintroduced back to the WWTP anaerobic digesters. The results are mainly presented in the form of graphs and tables in the result section of the thesis. The results from trial 1, trial 2 and the theoretical full-scale implementation are presented in various parts. The results are thereafter discussed individually, one discussion for the laboratory trials and one discussion for the theoretically full-scale implementation. The discussion is finally concluded in the conclusion.

The master thesis was delimitated to Henriksdals WWTP i.e. the objectives were not tested on any other WWTP. HTC can be used to treat any organic material but in this thesis the organic material was delimitated to digestate. In a WWTP AD several types of substrates are used but this rapport investigates only primary sludge and secondary sludge. Moreover, secondary sludge is used only to calculation of hydraulic retention time (HRT).

2 THEORY

In this section, the whole process from when the wastewater enters the WWTP to when hydrochar and process water (PW) are formed in the HTC process is described.

2.1 TREATMENT STEPS FOR WASTEWATER

2.1.1 Mechanical treatment

The treatment of wastewater includes several steps. The first step is mechanical treatment which includes three parts, bar screen, grit removal (grit chamber) and pre-sedimentation. The bar screen removes the largest fractions (Stockholm Vatten, 2015a). Thereafter, the wastewater continues to the grit chamber (EPA, 1998) where fractions bigger than 0.15 mm are removed like sand and small stones. The last part of the mechanical step is the pre-aeration where for instance bad odor is reduced (Stockholm Vatten, 2015a).

2.1.2 Chemical treatment

The second step is the chemical treatment. In this step precipitation chemicals are added; the most common precipitation chemicals are iron- and aluminum salts. The precipitation chemicals bind dissolved phosphorus in the form of poorly soluble metal phosphorus. Moreover, metal hydroxide precipitate and form flocs. The flocs tie up the metal phosphorus and other suspended compounds, for example organically bound phosphorus and other suspended materials (Stockholm Vatten, 2015a). The flocs gradually sink to the bottom of the sedimentation basins and forms primary sludge (EPA, 1998) (Figure 1). The primary sludge is removed from the basins by pumping. The sludge is then pumped to anaerobic digesters where some of the organics are converted to biogas. If the treatment plant has a well working chemical treatment, about 60 % of total-phosphorus, 60 % of chemical oxygen demand (COD) and 80 % of suspended material can be removed from the water in this step (Stockholm Vatten, 2015a).

Figure 1 The sedimentation basins at Henriksdals WWTP.

2.1.3 Biological treatment

In the third step, which is the biological treatment step, are nitrogen, suspended material, phosphorus and metals removed. About 90–95 % of the organic matter, measured in biochemical oxygen demand (BOD) is removed (Stockholm Vatten, 2015a).

A method that is used in the biological treatment is the activated sludge process. Here, air is used to hold flocs of microorganisms floating in the water. The microorganisms grow and consume organic matter that they convert into water and carbon dioxide. After the activated sludge basin, the water floats to the sedimentation basins to let the sludge settle. However, some of the sludge is pumped back to the activated sludge basin to sustain the right concentration of sludge for a well working activated sludge process (Stockholm Vatten, 2015a). The sludge not pumped back is called secondary sludge and differs in composition when compared to primary sludge as it consists mostly of settled microorganisms. As for primary sludge, secondary sludge is extracted for further treatment in an anaerobic digester (Gerardi, 2003).

2.1.4 Filtration

The last step in the biological treatment, which also is the last step in the wastewater treatment, is that the water passes a filter. The filter removes the remaining small particles. Two of the most common compounds removed by filters are nitrogen and phosphorus. The filters consist of for example sand and crushed clay beads (Blähschiefer) (Stockholm Vatten, 2015b). To get an overview over the wastewater treatment process, see Figure 2.

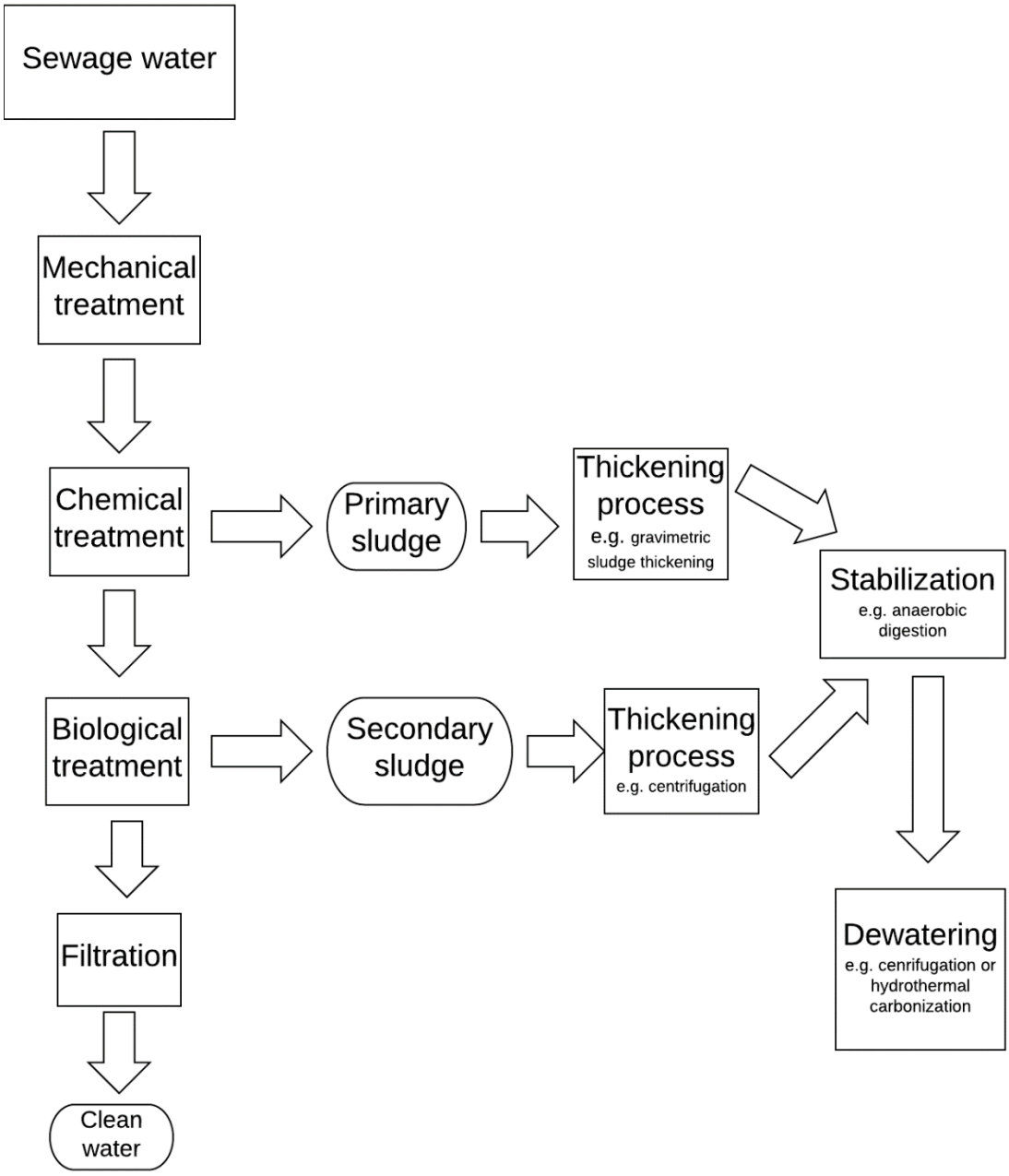

Figure 2 Flow chart over the treatment steps in a wastewater treatment plant and what types of sludge are formed in which step. Moreover, the dewatering process of primary and secondary sludge.

2.2 SLUDGE TREATMENT BEFORE ANAEROBIC DIGESTION

The treatment before anaerobic digestion usually is called sludge thickening. The most common sludge thickening methods are centrifugation and gravimetric sludge thickening, further described in section 2.3.1. and 2.3.2. It should be pointed out that anaerobic digestion is not always used, another alternative is e.g. aerobic digestion (Stockholm Vatten, 2015a).

From the wastewater treatment plant, two types of sludge are produced. These are, as mentioned before, primary sludge and secondary sludge. The primary sludge is more valuable in the perspective of anaerobic digestion since the primary sludge has a higher BMP than the secondary sludge. This is because primary sludge consists of saturated material which means that the energy content has not been consumed unlike secondary sludge for which most of the energy content has been consumed by microorganisms (Gerardi, 2003).

The primary sludge and the secondary sludge are both thickened, but separately from each other (thickening for primary sludge is not always needed). The goal is to have as high TS content in the sludge as possible, provided that the sludge still can be pumped. Untreated primary sludge has a water content of around 96–98 % and secondary sludge has a water content of about 99.5 %. After the thickening process the sludge has a water content between 94–96 %. Next, the sludge is fed into an anaerobic digester to produce biogas (Stockholm Vatten, 2015a).

2.3 WATER REMOVAL METHODS

Water is attached to the sludge in four ways; by capillary forces, adsorption and in the cells of the microorganisms. Furthermore, there is water in the cavity between the sludge particles. Most of the water is located in these cavities and requires the smallest energy amount to dewater in comparison to the other three. The cavity water together with the water which is bound by capillarity forces can be removed by mechanical water removal. To remove the water which is bound by adsorption and in the cells, a thermal treatment is needed. The best choice of water removal method depends among others things on the sludge type, since e.g. secondary sludge has a higher amount of cell-bound water than primary sludge (Baresel *et al.*, 2014).

There are many diverse types of water removal methods, thermal, chemical and mechanical. The majority of the wastewater treatment plants in Sweden only use mechanical water removal (Baresel *et al.*, 2014).

2.3.1 Gravimetric sludge thickening

One of the most used and energy effective mechanical method for sludge thickening is gravimetric sludge thickening (Figure 3). The method works by letting the sludge settle in a conic thickener. The water phase is pumped back to the inlet of the wastewater treatment plant (Stockholm Vatten, 2015a). This method is best suited for primary sludge and larger volumes of sludge is preferable since larger volumes of sludge provides a more effective sludge thickening process (Baresel *et al.*, 2014).

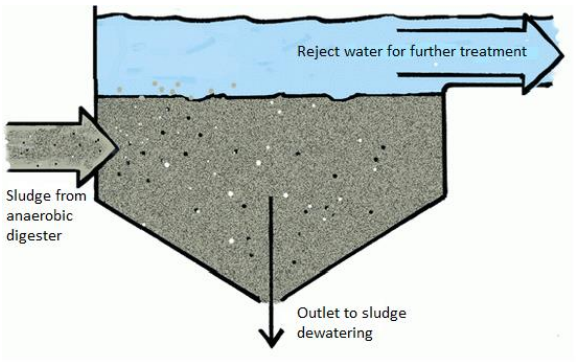

Figure 3 The image to the left show the gravimetric sludge thickening process and the image to the right show how a gravimetric sludge thickening facility can look like in reality (Kävlinge kommun, 2015).

2.3.2 Centrifugation

Another well used method is centrifugation (Figure 4). The centrifuge consists of two main parts; a screw conveyor and a solid bowl. The screw and the bowl rotates in the same direction but with slightly different speed. The solid bowl contains the sludge and the screw conveyor is contained within the bowl. The sludge is fed into the solid bowl, the great g-force which occurs when the centrifuge rotates causes the solids to settle out of the liquid. The solids can then be discharged from the centrifuge by the screw conveyor which is pushing out the solids. The centrate is discharged from another outlet. The faster the bowl turns, the better clarity of the centrate is achieved but the energy requirement will be higher (Hiller Separation & Process, 2017).

One of the advantages with water removal by centrifugation is that centrifugation is a common method. Spare parts can be found easily and many people in the business know how to use a centrifuge. It also has a small foot-print on the environment compared to other water removal equipment and there are often no odor problems associated with the centrifugation process. Furthermore, the centrifugation generates a high TS content of approximately 30 % which is significantly better than e.g. gravimetric sludge thickening which providing a TS content not higher than 10 % (Baresel *et al.*, 2014).

The disadvantages are that it is energy consuming to obtain a TS content of 30 % by centrifugation. The centrifuge is also quite noisy and is a cause of vibration which may require reinforcements of the underlying floor in some installations (Baresel *et al.*, 2014).

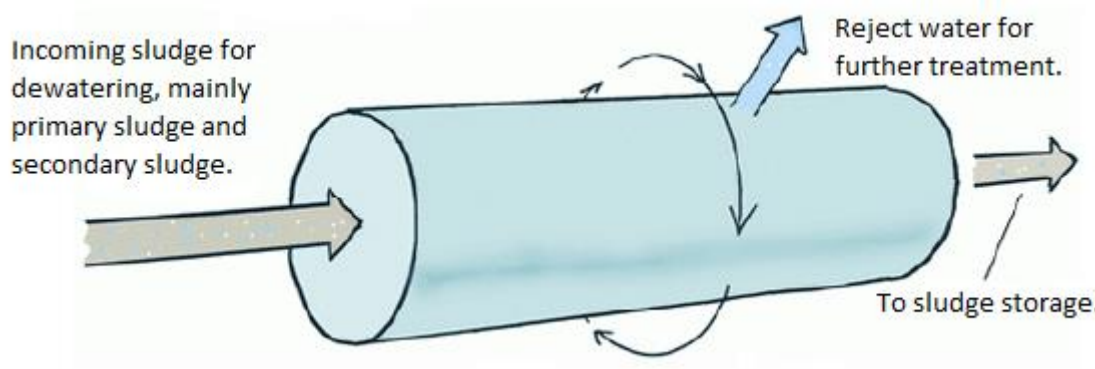

Figure 4 Simple sketch over how a centrifuge works. The primary sludge and secondary sludge are coming in. Since the reject water and the dewatered sludge have different densities, they can be separated from each other (Kävlinge kommun, 2014).

2.3.3 Pressure filtration

The third sludge water removal method which is common is pressure filtration. There are many types of pressure filtration e.g. belt filter press (Garg, 2009) (see Figure 5), vacuum filtration and screw press but it is the same basic idea. The sludge is fed into the press, where the sludge is drained with the help of a membrane, filter or cloths. The sludge is pressed against the filter, the liquid slips through the filter while the solid forms a sludge cake on the opposite side of the filter. The filtration process differs depending upon which filter technology that is being used (filter press, vacuum filtration, or screw press) but the results are comparable (Baresel *et al.*, 2014).

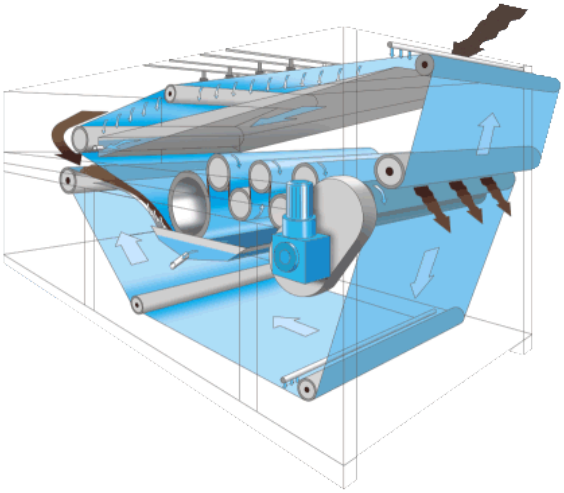

Figure 5 Illustration of a belt filter press (Huber technology, 2017).

Pressure filtration is a relatively new method for sludge treatment but the technique is well introduced in the paper industry and in manufacturing. Skilled workers can be hard to find within pressure filtration due to its short time on the market. The greatest disadvantage with pressure filtration is the low capacity but with the right pretreatment pressure filtration can obtain higher TS content than both centrifugation and gravimetric sludge thickening (Baresel *et al.*, 2014).

2.4 CHEMICAL TREATMENT

There are many chemical treatments for sludge water removal as well. Chemical treatments are most commonly combined with a mechanical method but some of the chemical treatments can be used separately too. One of the most frequently used chemical treatments is to use different types of polymers which are added to the sludge to form flocs, the flocs thicken the sludge and make it easier to drain. Many other chemical treatments have the same function. Of the three mentioned mechanical treatments, polymers are most commonly used together with centrifugation or pressure filtration (Baresel *et al.*, 2014). For gravimetric sludge thickening there is no economically viable to add polymers (Stockholm Vatten, 2015a).

Polymer addition should always be minimized; it is important not to use too much polymer since research has showed that polymer can have negative environmental impact. Polymers can e.g. contain compounds which can contaminate the sludge that later on may be spread to arable soils (Baresel *et al.*, 2014).

2.5 ANAEROBIC DIGESTION

The microorganisms represent an important part in the anaerobic digestion. The key for a working process is to have many active microorganisms which have a close cooperation. This cooperation is very sensitive and it is therefore crucial to sustain an environment where the microorganisms thrive. A disturbance in the system may in the worst case result in a shutdown of the biogas production or in better case only to less biogas production (Jarvis & Schnürer, 2009).

To sustain the biogas production, substrate needs to be fed into the anaerobic digester. In Henriksdals WWTP the three main substrates are primary sludge, secondary sludge and grease traps removal sludge which are typical substrates for WWTP anaerobic digestion. Grease traps removal sludge is an external substrate from restaurant and foodservice kitchens etc. which are co-digested with the sludge from the WWTP. It is often preferable to have a heterogenic substrate mix i.e. a substrate mix that consists of different compounds that matches the growth requirements for many different types of microorganisms. The reason for this is that a richer diversity of microorganisms makes the system more resistant against disturbances and a heterogenic substrate mix favors the microorganism diversity. It is nevertheless important that the substrate does not differ too much over time since many microorganisms are sensitive to changes in the environment. Oxygen level, pH, temperature and salinity are four factors which are essential for the biogas production. The levels of this factors need to be a compromise, so that as many microorganisms (microorganisms which are important for the biogas production) as possible thrive. The biogas process must take place in an anoxic environment (Jarvis & Schnürer, 2009). However, if smaller amounts of oxygen enters the system, it is usually not a major problem since oxygen is rapidly consumed by aerobic microorganisms (Agdag & Sponza, 2004). The pH-tolerance varies a lot between different groups of microorganisms. In general, the acid producing microorganisms are more resilient to low pH-values than the methanogens. Around pH 8 is a common pH-value in many Swedish digesters (Jarvis & Schnürer, 2009). The most common temperature intervals used to operate anaerobic digesters are 30–40 or 50–60 °C (Nordberg, 2006). In addition, it is central that the salinity level in the digester is right. Both too much and too little salinity may lead to inhibitory effects. The salts

contain important compounds for the microorganisms, e.g. potassium, sodium and chlorine. The salts which are needed for a healthy microorganisms culture are however often found in the primary sludge and the secondary sludge (Chaban *et al.*, 2006).

The degradation from substrate to methane and carbon dioxide involves four main steps: hydrolysis, fermentation, anaerobic oxidation, and methanogenesis. Diverse groups of microorganisms are active in the four processes (Jarvis & Schnürer, 2009), see Figure 6.

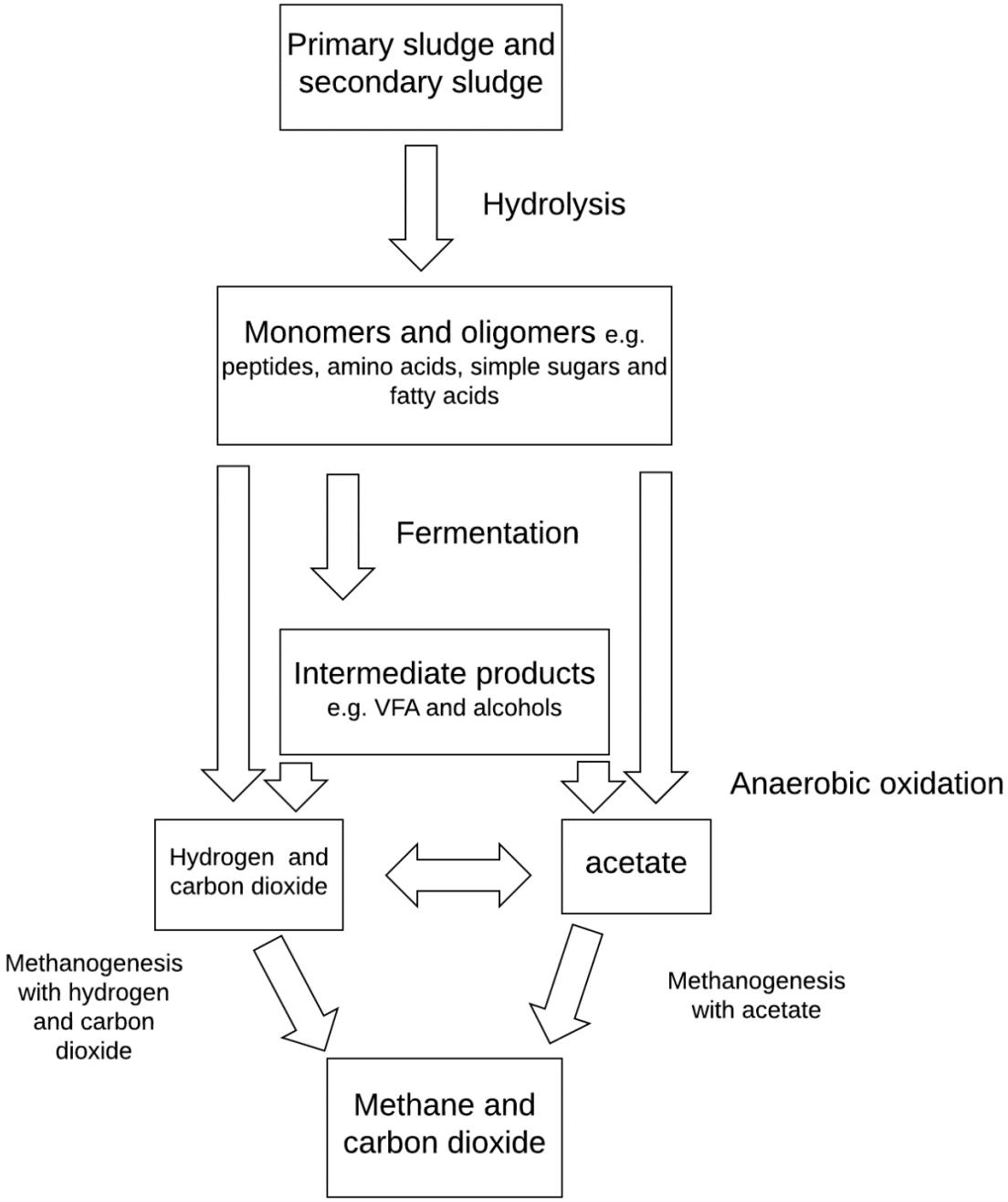

Figure 6 Flow chart over the four degradation steps from sludge to methane in an anaerobic digester.

2.5.1 Hydrolysis

In the hydrolysis macromolecules are broken down into smaller molecules. The breakdown is necessary because the macromolecules cannot be used as a nutrient source by the microorganisms. The macromolecules are simply too big to be taken up by the cell. The macromolecules can be lipids, proteins and carbohydrates and are degraded by special types of enzymes that are excreted by the microorganisms. The lipids are mainly transformed to glycerol and fatty acid (Jarvis & Schnürer, 2009). In fatty acids many compounds are included, e.g. volatile fatty acids (VFA). VFAs are characterized volatile because they vaporize in room temperature at atmospheric pressure. The VFAs consists of six or fewer carbon atoms i.e. VFAs are short-chain fatty acids (APHA, 1992).

2.5.2 Fermentation

The second step in the decomposition is the fermentation. The shorter molecule chains which have been produced under the hydrolysis are now used as a carbon and energy source by the microorganisms. However, the lipids are not used by the fermentation microorganisms and are first taken care of in the third step (Jarvis & Schnürer, 2009). Many of the microorganisms which were involved in the hydrolysis are also involved in the fermentation along with e.g. Acetobacterium, Eubacterium and Enterobacterium (Madigan & Martinko, 2006). The products which come out from the fermentation are mainly various organic acids, e.g. acetic, propionic and butyric acid but also ammonia, alcohols, hydrogen, and carbon dioxide. The composition of the products depends on the substrate, the environment and which type of microorganisms that are active (Jarvis & Schnürer, 2009).

2.5.3 Anaerobic oxidation

During the anaerobic oxidation, many products from the fermentation are converted to primarily acetate, hydrogen and carbon dioxide (Drake *et al.*, 2008). For the anaerobic oxidation to work, a close cooperation between methanogens and oxidation organisms is needed. The reason for this is that a low partial pressure of hydrogen is required otherwise the thermodynamics do not work and because of that the anaerobic oxidation can only proceed if the hydrogen is consumed by the methanogens. Microorganisms which cooperate with methanogens are e.g. genera from Clostridium, Syntrophomonas, and Syntrophus (Jarvis & Schnürer, 2009).

2.5.4 Methanogenesis

Acetate, hydrogen and carbon dioxide are transformed to methane and carbon dioxide in the last step of the biogas process, the methanogenesis. This step is driven by methanogens which includes diverse types of microorganisms e.g. methanogens which use acetate as substrate and methanogens which use hydrogen and carbon dioxide as substrate. When acetate is used as substrate, the methanogens are cleaving the acetate and in that way using one carbon to form methane and the other to form carbon dioxide. This process is usually the most energy effective and account for approximately 70 % of the methane that is created in the WWTP anaerobic digesters (Zinder, 1993). The methanogens are growing very slowly and because of that the methanogenesis is most often the rate determining step in the biogas process (Liu & Whitman, 2008).

2.6 ANAEROBIC DIGESTER TYPES

There are several types of digesters, continuously stirred tank reactor (CSTR), batch reactor, plug-flow reactor, anaerobic filter (AF), upflow anaerobic sludge blanket (UASB), expanded granular sludge blanket (EGSB) and anaerobic membrane bioreactor (AnMBR) are some examples of the most common digesters. CSTRs are the most commonly used for biogas production at WWTPs in Sweden, see Figure 7.

The CSTR:s have different shapes and contain various amount of volume. The most common shape is cylindrical with a conic roof but CSTRs with an egg shape also exists. The basic parts for a CSTR are a mixing system, the tank, a heating system and sometimes also a cover. There are two main types of CSTR systems, single tank systems where all degradation steps take place in the same tank or serial tank systems. In serial tank systems, the hydrolysis, fermentation, and anaerobic oxidation can be separated from the methanogenesis in the last tank (Nordberg *et al.*, 2007). The heating system can be designed in many ways. External heat exchangers are common as well as heating coils within the walls or inside the walls. The tanks are usually built of concrete or steel. If steel is used, stainless steel is preferred. For open top digesters, there are various types of roof design, the roof can be fixed, or floating on the digester sludge and kept steady by roller mechanisms. With the roller mechanisms, the roof can slide up and down vertically. Other roof designs are presented as well (Greene, 2014). The substrate is usually injected at the top of the CSTR and the digestate is discharged from the bottom. It is also common to have two outlets for digestate, one for high density digestate at the bottom and one for low density digestate at the top. The biogas is collected at the top and can be distributed or stored in a separated gas-holder (Gerardi, 2003).

The mixing in the digester is important for the biogas production. The mixing contributes by distributing the substrates, the nutrients and the microorganisms in the digestate as well as equalizing temperature. Altogether, this lead to a faster degradation in the digester (Gerardi, 2003).

There are different mixing techniques, gas recirculation or mechanical methods. Mechanical methods can e.g. be draft tubes, turbines or propellers. The gas recirculation can be done by gas injection, external pumps or recirculation from the roof or floor of the digester. The gas recirculation and the mechanical methods can be located in various ways, in the center, along the sides or as a combination, of the digester (Gerardi, 2003).

The CSTR is usually equipped with different meters so that, e.g. the digestate level and the temperature can be checked continually. Furthermore, the amount of digestate discharged can be controlled. The CSTR is best suited for wet fermentation, e.g. primary sludge and secondary sludge (Gerardi, 2003).

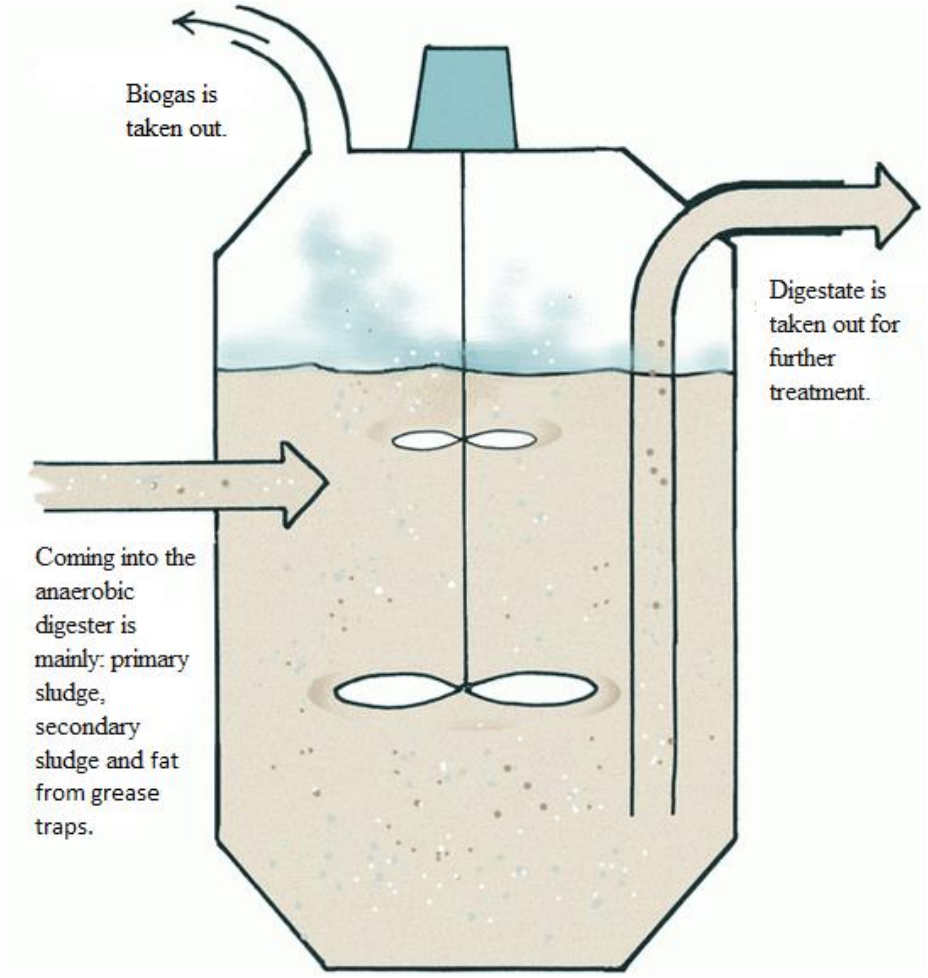

Figure 7 Simple sketch of a CSTR. Mainly Primary sludge, secondary sludge and grease traps sludge are fed into the CSTR at Henriksdals WWTP. Biogas and digested sludge are discharged at top of the digester. It is also common with a third outlet at the bottom of the CSTR for digested sludge with high density (Kävlinge kommun, 2016).

2.7 SLUDGE TREATMENT AFTER ANAEROBIC DIGESTION

After the anaerobic digestion, the water content needs to be reduced even further in order to minimize costs for e.g. storage and transportation. To do this centrifuges or belt filters can be used. After the centrifugation or belt filter treatment, the water content is between 65 and 75 % and can be stored for other usage (Stockholm Vatten, 2015a). The water removal after the anaerobic digestion usually is called dewatering. After the dewatering, additional treatments can be used, e.g. hydrothermal carbonization.

2.8 HYDROTHERMAL CARBONIZATION (HTC)

One method to treat the sludge from the anaerobic digestion is hydrothermal carbonization (HTC). HTC is not a new method, the first report about HTC came out as early as 1913. The HTC process did not make any real success though and fell into oblivion. Recently, in the 21th century the HTC process has been growing more and more popular as hydrochar is seen as an alternative to coal and petroleum (Funke & Ziegler, 2009). The basic idea of HTC is that sludge is exposed for high temperature (180–220 °C) (Funke & Ziegler, 2009) and high pressure (water under saturated pressure plus the pressure from gas formed during the reaction) under an interval of

time (1–72 h) (Funke & Ziegler, 2009). The process takes place in a reactor that the sludge is fed into. Moreover, the process is exothermic and takes place in a liquid water environment (Wirth *et al.*, 2012). At the beginning of the process the pressure in the reactor should be equal to the vapor pressure of water. When the pressure is equal to vapor pressure most of the water is in liquid phase. The reason to the high pressure is that water acquires special qualities in this condition. E.g. the water is a good solvent for polar compounds and transport properties are improved. An advantage with good transport properties is a more homogenous distribution of heat in the reactor. Moreover, when pressure is that high water behaves as a reactant and catalyst (Fiori *et al.*, 2014). To get an overview over the HTC process, see Figure 8.

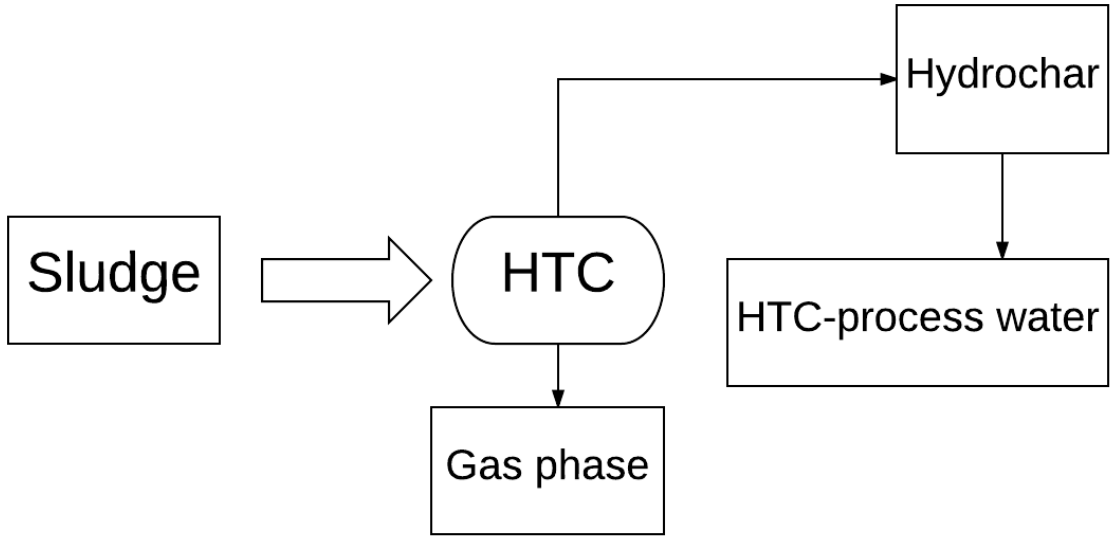

Figure 8 Incoming products and outcoming product of the HTC process.

2.8.1 Reaction mechanisms in HTC

During the HTC process, mainly five reaction mechanisms take place, hydrolysis, dehydration, decarboxylation, aromatization, and condensation. The mechanisms do not necessary need to come in this order because that depends primarily on the type of feed. In the hydrolysis biomacromolecules are broken down to smaller molecules. It is primarily the ether and ester bonds which are cleaved in the hydrolysis. During the dehydration water is drained from the biomass. The hydrogen and oxygen content is reduced from the biomass. Dehydration in the HTC process is the result of both physical processes and chemical reactions. The basic mechanism behind dehydration is the removing of hydroxyl groups. As the name decarboxylation reveals, decarboxylation is about carboxyl groups, more precisely about the partial elimination of carboxyl groups from the biomass. The carboxyl groups are rapidly transformed to carbon dioxide and carbon monoxide in temperatures over 150 °C, with an overweight of carbon dioxide produced due to the carboxyl groups. Where the rest of the carbon dioxide is coming from is not proven. The formation of aromatic hydrocarbons from the biomass are highly temperature dependent, the aromatization increases with the temperature and the temperature should at least exceed 200°C. The content of aromatic rings increases in the biomass with HTC and is very important for the structure of the HTC coal. The mechanism of condensation stands for the formation of water (Funke & Ziegler, 2009). The main outputs from the HTC are two products: a hydrochar (also called biochar) which is a coal-like solid substance and a process water (Wirth *et al.*, 2012).

2.8.2 Temperature HTC

It is not surprising that the temperature plays a significant role in the amount of hydrolyzed biomass compounds. With a higher temperature, the number of biomass compounds that can be hydrolyzed increases. Moreover, pyrolytic reactions seem to become more dominant with rising temperatures. As mentioned earlier, at high temperatures and high pressures the properties of water is changed. The water can easier penetrate porous media since the viscosity of water is reduced and this enhances the degradation of the biomass (Funke & Ziegler, 2009).

2.8.3 Residence time

HTC experiments have been performed with everything between 1 h to several days in residence time. So far, no single optimal residence time have been found as the wanted composition of the HTC products varies with the chosen application. The experiments however indicates that longer residence times yield a larger amount of HTC coal (Funke & Ziegler, 2009).

2.8.4 Water content in the feed

The water content of the feed is of great significance for the HTC process. A feed with very low water concentration, will almost be completely dissolved and almost nothing will be left as residue. The water content also has an impact on the monomer concentration and the polymerization. Higher solid loads (to a certain point) will enhance the monomer concentration, that results in an earlier start of the polymerization and thereby also a shortening of the residence time for the HTC process (Funke & Ziegler, 2009). Therefore, wet substrates often are dewatered before treated in HTC.

2.8.5 The importance of pH-value

The HTC process seems to lower the pH-value in the biomass based on HTC experiments. The experiments suggest that the reason to the reduced pH-value is that organic acids are formed. The acidic environment appears to have positive effects on the HTC process since the overall reaction rate is enhanced (Funke & Ziegler, 2009).

2.8.6 Pressure

There are two types of pressure techniques involved in the HTC process, compaction and reaction pressure. Compaction mean simply that the free space in the HTC reactor is reduced by direct force even called lithostatic pressure. Some studies indicate that compaction leads to enhanced carbon content but it is hard to say if it is due to the compaction. Furthermore, the compaction reduces the water content of the biomass and because of that, indirectly speeds up the reaction rate. Reaction pressure is applied by increasing the temperature or adding fluids. The reaction pressure turns the water to transition from gas to liquid (Funke & Ziegler, 2009).

2.8.7 Products from the HTC process

After HTC reaction, the solid material (hydrochar) is separated from the process water by e.g. mechanical separation methods such as a filter press. Compared to the original sludge, the dewatering properties are significantly enhanced which makes it possible to reach high dry content of up to 65–75 % without addition of polymers. The final products from the HTC process is hydrochar and a process water containing organic and inorganic components that are dissolved during the HTC reaction (Öhman, 2017a).

Hydrochar has a similar appearance to ordinary coal (natural bituminous coal) but has some differences. For example, hydrochar has more functional groups due to hydrothermal dewatering. Another property of the hydrochar is that it is more hydrophobic than the starting material thanks to the HTC process which removes carboxyl and hydroxyl groups (the carboxyl and hydroxyl groups contribute to a material´s hydrophilic features). It is not totally known what happens to the inorganics in the HTC process, but they most likely remain within the hydrochar. The major liquid product from the HTC process is water mixed with organic and inorganic compounds. This water is usually called process water. The process water contains a high amount of volatile fatty acids (VFA) which cause a low pH-value in the process water. Acetic acid and formic acid are often found in high concentrations. Furthermore, sugars, phenols and polycyclic aromatic hydrocarbons are common in the process water. The chemical oxygen demand (COD) usually ranges from 10 to 40 g/l and the concentration of total organic carbon (TOC) is between 5 to 20 g/l. However, if the process water is recirculating in the HTC process. The TOC level can be even higher, up to 40 g/l (Wirth *et al.*, 2012). Additionally, the process water contains nutrients and trace elements that are important for the microorganisms in an anaerobic digester. Studies have shown ammonia nitrogen concentration of 230 mg/kg and phosphorus concentration of 197 mg/l (Wirth *et al.*, 2012). Some of the compounds have a value if recovered, e.g. nitrogen and phosphorus. The most abundant gases from HTC process are carbon dioxide, carbon monoxide, methane, and hydrogen. Worth noticing, about half of the carbon dioxide is dissolved in the water and the remaining in the gas phase. The amount of gas produced is increased with elevated temperatures. On the other hand, the amount of carbon monoxide is reduced with elevated temperatures (Funke & Ziegler, 2009).

The hydrochar has many uses, most common as soil amender but hydrochar also can be used as filter material and feed supplement for animals (Libra *et al.*, 2011). The other product is the process water which contains organic matter and nutrients. It is possible that the process water can increase the yield of biogas if the process water is recirculated to the digester. The TOC concentration of up to 40 g/l however indicate that process water contains a rich source of potential substrate for AD (Wirth *et al.*, 2012).

There are many advantages with the HTC method. The hydrochar has high concentrations of phosphorus since the phosphorus is enriched in the solid phase (hydrochar). It would therefore be possible to recycle the phosphorus from the hydrochar. One way to do it is to leach the hydrochar with an acid. In the reactor, the sludge would likely be hygienized given that the temperature in the reactor is around 200 °C. The costs for sludge treatment will also be lower since the volume will be reduced after the HTC treatment. The volume reduction is due to two effects: degradation of the solid substance during the HTC reaction (about 30 % of the solid substance will dissolve or form gas) and significantly improved dewatering properties which allows dry solids contents of 65–75 % of the final product and thus much less water in the final product. A decreased amount of digestate with ongoing microbial activity will also lead to less green gas emissions since fresh digestate emit both methane, nitrous oxide and carbon dioxide (Björkman & Lilliestråle, 2016). With new technical applications it is even possible that the hydrochar in the future can be used to do nanocables, nanospheres, submicrocables, nanofibers, and submicrotubes (Funke & Ziegler, 2009).

2.9 VOLATILE FATTY ACIDS AND HTC

It has been established that VFAs are formed when digestate is used as substrate in the HTC process (Berge *et al.*, 2011). The process water contains higher concentrations of VFA when the HTC process has higher temperatures compared to lower temperatures (140–200 °C). Moreover, theoretical calculations have shown that the BMP for process water depends on the concentration of the VFAs. The higher concentration of VFAs, the higher was the methane yield (Danso-Boateng *et al.*, 2015).

2.10 BIOCHEMICAL METHANE POTENTIAL (BMP) IN GENERAL

The BMP tests were developed during the 1970s. The tests are used on organic matter to determine the methane potential and the degradability of the substrate. A BMP test is considered to be more precise than calculating the methane potential theoretically. Moreover, theoretical calculation requires that the composition of the substrate is known (Symons & Buswell, 1933). In addition, theoretical calculations tend to overestimate the methane potential since the degradability is not considered (Angelidaki *et al.*, 2009).

All organic substrates contain a certain amount of organic matter, some parts of the organic matter are easily degraded and some are persistent. The BMP-test shows how much of the organics that can be transformed to methane (Angelidaki *et al.*, 2009).

Practically the BMP-test is performed by mixing inoculum (microorganisms) with the substrate of interest in a vial. The test is done in the absence of oxygen and the methane production is followed over time. The accumulated methane production is calculated and usually is expressed as either NmL methane/g COD or NmL methane/g VS (Carlsson *et al.*, 2011).

For a well working BMP-test it is important that the used inoculum has a rich flora of microorganisms. Ideal is to use an inoculum that is adapted to the substrate to test. The inoculum e.g. can be taken from a WWTP anaerobic digester or from a previous laboratory trial. Even liquid manure can be used, but usually is a poorer alternative compared to the other two (Angelidaki *et al.*, 2009). The microorganisms are sensitive to variations in temperature. Therefore, it is important that the temperature used in the BMP-test is the same as the original temperature of the inoculum (Carlsson *et al.*, 2011).

For the substrates, it is important to have a larger amount than is required for the actual BMP-test (the amount substrate that is put into the vials). Some substrate must be left to characterize the substrate. A quite large amount also is required to ensure a representative sample. The substrates should be stored in room temperature as shortly as possible. In particular substrates with high moisture content (although very dry substrate can be stored in room temperature). In room temperature, the microorganisms thrive and therefore begin to consume the organic matter in the substrate. Freezing should be avoided since the structure of substrates can be changed (Carlsson *et al.*, 2011).

2.11 AMPTS II

AMPTS II stands for automatic methane potential test system and is an on-site lab equipment for methane potential analysis. AMPTS II is built to imitate an anaerobic

digester that can be used in laboratory scale. It is possible to measure methane potential without an AMPTS II, other methods have been used for long time. The problem is that those methods involve a lot of steps and that it is cumbersome to get continuous measurement of the methane production. Moreover, many traditional methods require expensive laboratory equipment and good laboratory experience. Additionally, the majority of the traditional methods are labor- and time-consuming in comparison. The AMPTS II however, is very user friendly and do not require a lot of laboratory work or expensive equipment. E.g. the recording of data is completely automatic when the experiment is running. Furthermore, the software does some calculations automatically which can be used to extract kinetic information of the degradation process (Bioprocess Control Sweden AB, 2013).

The AMPTS II consists of three main parts, part 1, part 2 and part 3. Part 1 includes a water bath, 15 bottles and 15 rotating agitators. The 15 vials (500 mL) are placed in the water bath and on top of every vial is an agitator that mixes the content in the vial. The temperature in the water bath can be adjusted and therefore the temperature in the vials can be regulated to a required temperature. Every vial has two metal tubes one for gas flow and one for manual measurements. Part 2 contains 15 bottles (100 mL) and a bottle holder. The bottles hold sodium hydroxide and the pH-indicator (Thymolphthalein). The function of part 2 is to clean the biogas from mainly carbon dioxide and H_2S. The goal is that only methane should slip through. When the liquid turns from blue to colorless the adsorbing ability is reduced and the sodium hydroxide and pH-indicator need to be changed. Part 3 is a gas volume measuring device whose function is to determine the amount of gas (methane) coming from part 2. Part 3 can measure gas volumes with an accuracy of 10 mL and all measurements are recorded of an integrated embedded data acquisition system. The result can be displayed in a web browser with help of built-in software. The AMPTS II setup can be seen in Figure 9 (Bioprocess Control Sweden AB, 2013).

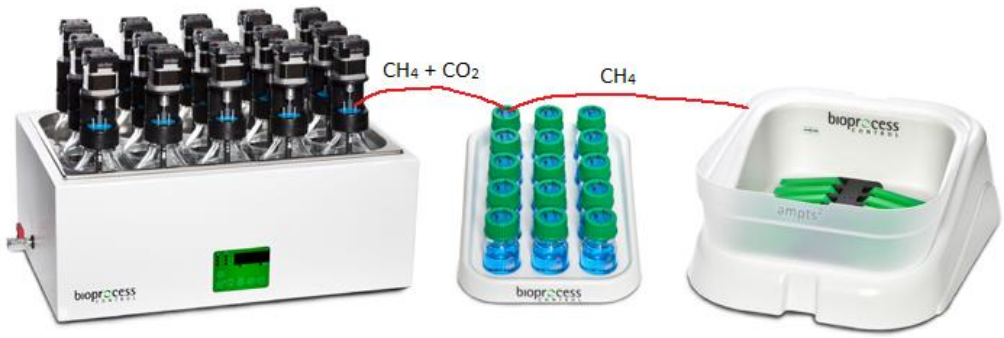

Figure 9 The device to the left is part 1, the device in the middle is part 2, and the device to the right is part 3 (Bioprocess Control Sweden AB, 2017).

3 MATERIALS AND METHODS

In order to answer research question 1 & 2, laboratory experiments were conducted, see section 3.2. In order to answer research question 3, theoretical calculations were performed on a hypothetical full-scale implementation of the HTC process where all the HTC process water was assumed to be reintroduced back to the digesters, see 3.3. Moreover, research question 3 also was tested with laboratory experiments, see 3.2. In section 3.1. the various substrate and inoculum used during trial 1 and trial 2 is described.

3.1 SUBSTRATE AND INOCULUM

Four types of substrates were used during the first anaerobic digestion trial (trial 1), primary sludge, process water, cellulose microcrystalline and hydrochar. The substrates were mixed with inoculum from Henriksdals wastewater treatment plant (WWTP). In the second anaerobic digestion trial (trial 2), the following substrates were used: process water, primary sludge and microcrystalline cellulose. Two types of inoculum were used: ordinary inoculum from Henriksdals WWTP and adapted inoculum. The adapted inoculum is described in section 3.1.6.

Figure 10 Three image of three different substrates. The image to the left is primary sludge, middle image is process water and the image to the right is microcrystalline cellulose.

3.1.1 Primary sludge

Primary sludge (Figure 10, left) was taken from Henriksdals wastewater treatment plant for both anaerobic digestion trials. The primary sludge had a TS content of 3.8 % for the first trial and 3.4 % for the second, presented as a ratio between weight after 105 °C oven (excluding mold) and wet-weight. The VS value was 77.7 % for the first test and 80.8 % for the second, present as a ratio between the weight after 550 °C and weight after 105 °C.

3.1.2 Process water

The process water (Figure 10, middle) was a product from hydrothermal treatment of digestate from a Swedish WWTP at 200 °C and a residence time of 1 h in a laboratory scale HTC batch reactor, followed by separation of the hydrochar from the process water using a simple Buchner funnel and was provided by the company C-Green. The process water had a TS content of 3.3 %, a VS content of 94.1 % (ratio between VS weight and TS weight), a VS content of 3.1 % (ratio between VS weight and wet-weight) and a pH-value of 7.7 (Åkerlund & Sirén Ehrnström, 2017). Process water from the same HTC composite sample (consisting of 6 batch reactions combined) was used

for both the first and the second anaerobic digestion trial. The process water was stored in 4 °C for almost a month between the two trials. Any effect of the storage was not investigated but is presumed to have been negligible according to previous observations by C-Green (similar samples stored over months in room temperature) and due to the fact that the sample was not biologically active.

3.1.3 Microcrystalline cellulose

Microcrystalline cellulose (Figure 10, right) was used as positive control for both anaerobic digestion trials due to its known biochemical methane potential (BMP) (Holliger *et al.*, 2016). The microcrystalline cellulose had a TS content of 96 % (SERVA, 2017) and a VS content of 100 % (Björkman & Lilliestråle, 2016).

Figure 11 Two substrates and one inoculum. The image to the left is hydrochar, the middle image is ordinary inoculum from Henriksdals WWTP and the image to the right is adapted inoculum.

3.1.4 Hydrochar

The hydrochar (Figure 11, left) was provided by C-Green and was a product by the HTC process. The TS content was 31.2 % and the VS content was 56.9 % (Åkerlund & Sirén Ehrnström, 2017). The hydrochar that was used was produced from the same series of HTC batch reactions as the process water and was stored in 4 °C between trials.

3.1.5 Inoculum

The inoculum (Figure 11, middle) was collected from Henriksdals wastewater plant, more precisely from Anaerobic digester 1 for both occasions. The anaerobic digesters are fed with approximately 16 % secondary sludge, 78 % primary sludge and 6 % other substrates (values from 2016). The digester maintain a temperature of 37 °C (Carlsson, 2017b). The inoculum had a TS content of 2.2 % and a VS content of 67.8 % for trial 1 and 2.3 % TS and 72.0 % VS for trial 2.

3.1.6 Adapted inoculum

After the termination of trial 1, the inoculum/hydrochar and the inoculum/process water samples were mixed together and used as inoculum in trial 2. The mix was called adapted inoculum (Figure 11, right). The adapted inoculum had TS value of 2.1 % and a VS value of 63.4 %. The TS and VS values are summarized in Table 1 and Table 2 for trial 1 and trial 2.

Table 1 TS and VS content for substrate and inoculum for trial 1.

Substrate/inoculum	TS %	VS (% of TS)	VS (% of wet-weight)
Inoculum	2.2	67.8	1.5
Process water	3.3	94.1	3.1
Hydrochar	31.2	56.9	17.8
Microcrystalline cellulose	96.0	100.0	96.0
Primary sludge	3.8	77.7	2.9

Table 2 TS and VS content for substrate and inoculum for trial 2.

Substrate/inoculum	TS %	VS (% of TS)	VS (% of wet-weight)
Inoculum	2.3	72.0	1.7
Process water	3.3	94.1	3.1
Adapted inoculum	2.1	63.4	1.3
Microcrystalline cellulose	96.0	100.0	96.0
Primary sludge	3.4	80.8	2.7

3.2 LABORATORY-SCALE EXPERIMENTS

3.2.1 HTC

The process water and the hydrochar were provided by the company C-Green that were produced by a method called HTC. The feed (the material which were fed into the HTC reactor) consisted of dewatered anaerobic digested sludge and reject water from the wastewater plant SYVAB Södertälje (the anaerobic digested sludge had first been treated by centrifugation). The sludge had been stored frozen and was thawed in room temperature before it entered the HTC reactor. The dewatered sludge had a TS content of 24.7 % and the reject water had a TS content of 0.2 %. The dewatered sludge was diluted before usage. The reject water was used as diluent and the sludge was diluted to about 12 % TS. Moreover, the sludge was homogenized with an ordinary kitchen electrical whisk for about 2 and a half minutes. The sludge slurry was weighed before and after the heating. The ratio between the wet-weight and the dry weight is TS. Then the average was taken of the two sample in terms of TS (Åkerlund & Sirén Ehrnström, 2017).

The equipment used for the HTC process was a batch reactor of model Berghof BR-50 with an insert of PTFE, the volume of the PTFE insert was 0.4 L. PTFE stands for Polytetrafluoroethylene, more known as Teflon. Teflon has a high tolerance to elevated temperatures and therefore is good material to use for HTC. The sludge slurry was fed into the PTFE insert and filled to 0.4 L and placed in the reactor. The sludge slurry was continuously mixed in the PTFE insert. The sludge slurry had 1h residence time. After 1 h, the reactor was cooled to approximately 60 °C and the overpressure was vented to the atmosphere. Thereafter the PTFE-inset was removed and weighted. Two samples of the HTC slurry were taken to determine TS. More details can be seen in Table 3. The setup of the experiment can be seen in Figure 12 (Åkerlund & Sirén Ehrnström, 2017).

Table 3 Parameter values of the reactor.

Parameters	Value
Sludge slurry mass	350 g
Dry content sludge slurry	12 %
Temperature	200 °C
Residence time	1h
Mixing velocity	250 rpm

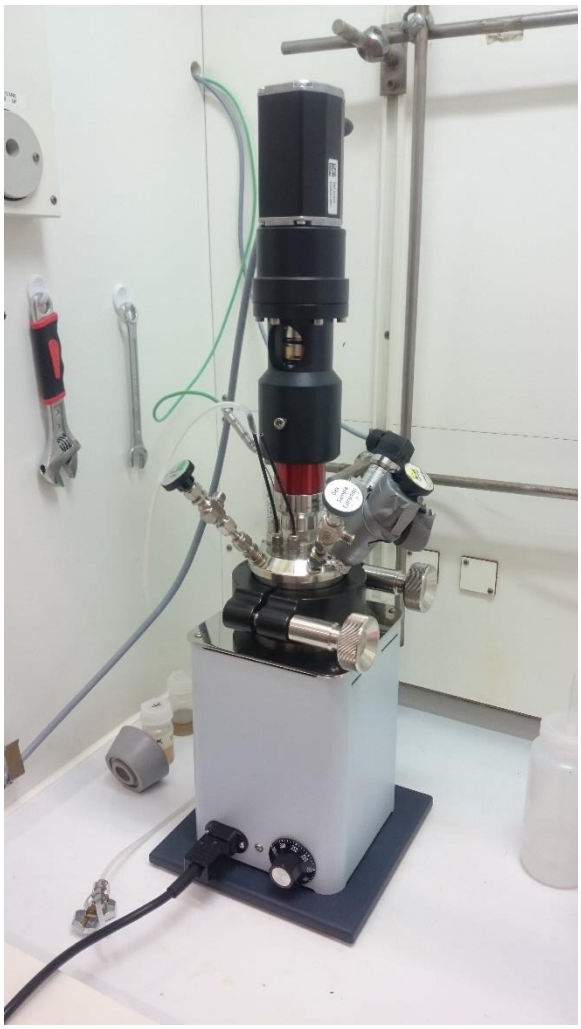

Figure 12 The laboratory scale HTC batch reactor (Åkerlund & Sirén Ehrnström, 2017).

To extract the process water from the HTC slurry a Büchner funnel was used. The funnel had a dimeter of 7 cm and double filter paper was used (Munktell no 3, pore size 6 µm). The Büchner funnel was connected to a suction flask and the suction flask was connected to water-jet pump and a pressure gauge. The filter paper was wetted with tap water and thereafter the funnel was filled with HTC slurry. With a pressure of circa 75 kPa was the process water separated from the HTC slurry. Both the process water and the sludge cake were weighed afterwards. The HTC slurry was weighed before the filtration as well (Åkerlund & Sirén Ehrnström, 2017).

Enough process water was extracted after 6 HTC batches. The PTFE insert had a small volume of 0.4 L. The wanted amount process water was approximately 1 L. The process water was pooled from the 6 batches and the same was done with the sludge cakes. TS and VS were determined for the total amount process water and for the total amount sludge cake. More information can be found in Table 4 (Åkerlund & Sirén Ehrnström, 2017).

Table 4 Combined products from the HTC batch runs.

	Value
Number of runs	6
Total amount process water	1220g
Total amount sludge cake	450g

All TS values and VS values were based on averaged from double samples. Moreover, after the 105 °C oven and the 550 °C oven were the samples incubated in a desiccator to cooled down before weighted. The TS for the samples were determined by putting the sample in a 105 °C oven over the night. Thereafter, the TS weight are noted. The content from the TS determining were placed in crucibles. The crucibles were first incubated in the 105 °C oven without content and thereafter with the TS content for a couple of hours, each time. Finally, the VS value for the samples were determined by incubating the crucibles with TS content in the 550 °C oven over the night. Thereafter, the weight was noted.

3.2.2 Trial 1 and trial 2

In trial 1 BMP-tests for process water, hydrochar and primary sludge were made, see Table 5. All substrates were mixed with inoculum. The tests were made to answer research question 1, but trial 1 also can be used for research question 2. Trial 2 was BMP-test with mixes of process water, primary sludge and inoculum made. The mixes were tested in different ratios. In total 4 different scenarios were tested. Scenario 1 (SO1) and scenario 2 (SO2) were designed on the basis of information from Henriksdals WWTP anaerobic digestion facility, information from 2016. With the information, a realistic ratio between primary sludge and process water was calculated. The ratio would correspond to a case where all digestate from the digesters at henriksdals WWTP went through HTC and the process water produced was reintroduced to the anaerobic digestion. The difference between scenario 1 and 2 were, in scenario 1 was ordinary inoculum used and for trial 2 was adapted inoculum used. In scenario 3 (SO3) was a greater ratio between primary sludge and process water used compare to scenario 1 and 2. Furthermore, in scenario 4 (SO4) was a smaller ratio between primary sludge and process water used compare with scenario 1 and 2. In both scenario 3 and scenario 4 ordinary inoculum were used. With this setup for trial 2, it would be possible to answer research question 2. For more detailed information of the 4 scenarios, see Table 6. In the following sections (3.2.2 to 3.2.6) a detailed description of the execution of trial 1 and trial 2 can be seen.

Table 5 The 3 triplicates were mixed 2:1 compare to inoculum in terms of VS weight.

Triplicate	Ratio (inoculum/substrate)
Process water	2:1
Hydrochar	2:1
Primary sludge	2:1

Table 6 Ratios for the various scenarios in trial 2. The ratios are calculated in VS weight. Substrate is in this case the combined weight of primary sludge and process water.

Triplicate	Ratio (inoculum/substrate)	Ratio (primary sludge/process water)
Scenario 1	2:1	10.72
Scenario 2	2:1	10.72
Scenario 3	2:1	12.45
Scenario 4	2:1	8.93

3.2.3 Preparation of the substrate and the inoculum, trial 1

To calculate the correct volume ratio between inoculum and substrate, it was needed to calculate the ww, TS and VS for the substrates and the inoculum. The ww, TS and VS were already determined for hydrochar and process water by C-Green. The microcrystalline cellulose is a positive control that is frequently used, values for ww, TS and VS were used from a previous trial. Ww, TS and VS analysis for primary sludge and for inoculum were performed at Hammarby sjöstadsverk. The primary sludge and the inoculum were taken from Henriksdals wastewater plant. Approximately 1 L of thickened primary sludge and 10 L of inoculum were sampled. The first step was to weigh four cake molds. The samples were filled into the cake molds, two samples of inoculum and two samples of primary sludge. The weights were noted. In order to take a representative sample, the inoculum and the primary sludge both mixtures were stirred well. Furthermore, the inoculum and the primary sludge were poured out rapidly into the cake molds to keept the samples more homogenous and minimize sedimentation. The four samples were placed in a 105 °C oven for 20 h.

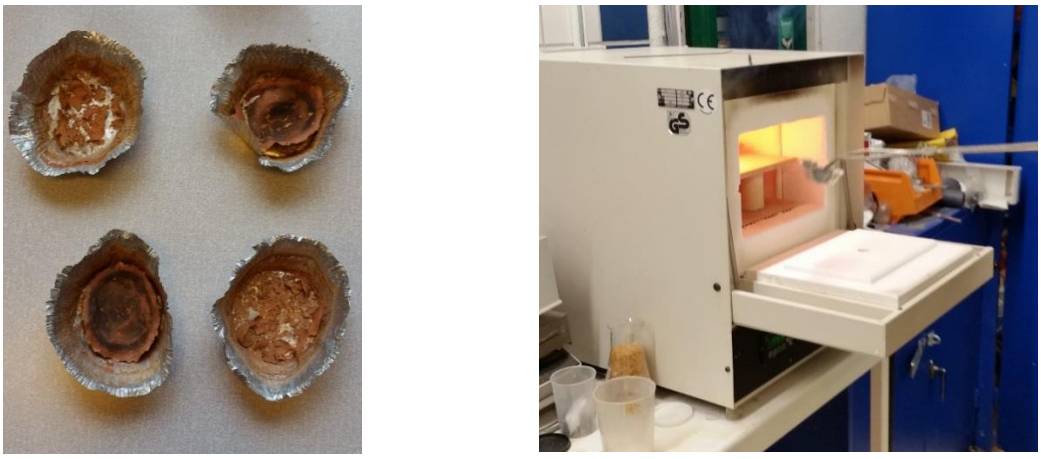

Figure 13 Left: The samples after 2 h in 550 °C and Right: One sample on its way into the 550 °C oven.

The weight of the dry samples was noted and placed in another 550 °C oven, this time for 2 h. The burnt samples weight was noted, see Figure 13. The TS value was calculated according to Equation 1 and the VS value was calculated according to

Equation 2. All the measured values can be seen in Table 7. To achieve a representative TS and VS value an average was taken between the samples with the same content. The inoculum cannot be stored and therefore the same inoculum cannot be used for the determination of TS and VS, as for the anaerobic digestion trials since the determination of TS and VS take about 24 h. Therefore, two more inoculum samples were taken the day after to calculate TS and VS. I.e. the TS and VS values were calculated for another inoculum than was used for the anaerobic digestion trials. However, these TS and VS values were nevertheless used to calculate the amount of inoculum to the anaerobic digestion trials. The values for samples 2, 4, 5 and 6 were though almost the same which make the source of error minimal.

Table 7 All values for the 6 samples.

Numbers	Parameters	Cake mold (g)	Sample (g)	After 105 °C oven (g)	After 550 °C oven (g)	TS %	VS %	Average Duplicate TS %	Average Duplicate VS %
1	Primary sludge	0.8	20.0	1,5	0,9	3.8	77.6	3.8	77.7
2	Primary sludge	0.7	19.4	1.4	0.9	3.8	77.7		
3	Inoculum 1	0.7	21.1	1.2	0.9	2.1	68.0	2.1	68.0
4	Inoculum 1	0.8	19.3	1.2	0.9	2.2	68.1		
5	Inoculum 2	0.8	20.3	1.2	0.9	2.2	67.7	2.2	67.7
6	Inoculum 2	0.8	13.7	1.1	0.9	2.2	67.8		

The TS value was calculated according to Equation 1 and the VS value was calculated according to Equation 2. The VS value is expressed as a ratio between VS weight and TS weight. Moreover, the VS value can be expressed as a ratio between VS weight and the wet-weight (ww), Equation 3 can then be used.

Cake mold = *A* Sample (untreated) = *B* After 105 °C oven = *C* After 550 °C oven = *D* VS_{ww} = ratio between VS weight and wet-weight

$$TS = \frac{C-A}{B-A} \quad (1)$$

$$VS = 1 - \frac{D-A}{C-A} \quad (2)$$

$$VS_{ww} = VS \times TS \quad (3)$$

3.2.4 Experimental set-up, trial 1

The ratio between inoculum and substrate was decided to be 2:1 according to VS measured in g according to literature recommendations (Holliger *et al.*, 2016). The vials can hold 500 mL and the mix between inoculum and substrate was determined to 400g which are a common weight to use for 500 mL vials (Bioprocess Control Sweden AB, 2013). To obtain the right ratio between inoculum and substrate were Equation 4, 5 and 6 used. The result can be seen in Table 8: All samples were made as triplicates i.e. every three vials had the same content. Moreover, the density of sludge was assumed to be 1 kg/L i.e. weight and volume were considered 1:1. This assumption was applied consistently through the report.

m_I = mass inoculum

VS_I = VS inoculum, presented as a ratio between VS and ww in g

m_s = mass substrate

VS_s = VS substrate percent as a ratio between ww and VS in g

$$\frac{(m_I \cdot VS_I)}{(m_s \cdot VS_s)} = 2 \quad (4)$$

$$m_I + m_s = 400 \text{ g} \quad (5)$$

Eqs 4 and 5 combined give:

$$\frac{800 \text{ g} \cdot VS_s}{VS_I + 2VS_s} = m_I \quad (6)$$

Table 8 Calculated amounts of substrate and inoculum per bottle for trial 1.

Triplicate	Inoculum/Substrate	Mass (g)	Mass VS (g)
1	Inoculum	400	5.8
	-	-	-
2	Inoculum	320	4.7
	Primary sludge	80	2.3
3	Inoculum	323	4.7
	process water	77	2.4
4	Inoculum	397	5.8
	Microcrystalline cellulose	3	2.9
5	Inoculum	384	5.6
	Hydrochar	16	2.8

Samples, trial 1

To achieve reliable results, every sample was replicated in triplicate and since the AMPTS II device can take 15 vials, only 5 different substrates/inoculums could be tested at the same AMPTS II device at the same time. One triplicate was used as positive control and one was used as blank. The positive control consisted of microcrystalline cellulose and inoculum in trial 1. The microcrystalline cellulose is a known compound and could therefore be used as positive control to decide e.g. the quality of the inoculum. In other words, the appearance of the graph for microcrystalline cellulose in terms of biogas production is known. If the graph of microcrystalline cellulose would look odd, there is probably something wrong with the inoculum. The blank consisted of inoculum alone. The blank was important, because otherwise it would not have been possible to deduce how much of the total methane that was coming from the inoculum and how much was coming from the substrate. The methane production for the inoculum was given from the blank. Using this number, the methane production contribution from the added inoculum in the other triplicates could be calculated since the added amount inoculum in each triplicate was known. When the blank and the positive control were excluded, three triplicates were left. Since this master thesis is about process water and anaerobic digestion there was self-evident that one triplicate should consist of inoculum and process water. Moreover, there would be interesting to test hydrochar and inoculum. If both hydrochar and process water are tested can the combined BMP for the HTC products be calculated which is the reason to

test hydrochar. Additionally, one sample consisted of primary sludge and inoculum as primary sludge is a very common substrate and therefore interesting to compare with.

Water bath and gas measuring device

The water bath was filled with de-ionized water and set to 37 °C. The gas measuring device was filled with Milli-Q water, see Figure 14. The Milli-Q water is ultra-pure and therefore reduces microbial grow which make the gas measuring device easier to clean.

Figure 14 Left: The water bath. The temperature in the water bath could be regulated, during the trials the temperature was set to 37°C. The water bath was constructed with 15 holes, where the vials could be placed. Right: Gas measuring device, when enough gas has entered under the green flaps, they are lifted and the released volume is registered (Bioprocess Control Sweden AB, 2017).

Carbon dioxide-fixing unit

2 L NaOH/thymolphthalein solution was prepared. 240 g NaOH and 10 mL thymolphthalein were added to an Erlenmeyer flask. The Erlenmeyer flask was filled with de-ionized water up to 2 L under magnetic stirring. The solution had a concentration of 3M. 15 100 mL glass bottles were filled with the solution up to 80 mL. The bottles were provided with rubber stoppers with 2 metal tubings and sealed with plastic screw caps with hole. All the bottles were placed on the bottle holder. The bottle holder can be seen in Figure 15.

Figure 15 Left: 15 CO2-fixation bottles placed in the bottle holder. Right: Close-up of a CO2-fixation bottle and the alkaline solution.

Sample incubation unit

The substrates and inoculum were distributed according to the calculated ratios. A scale was used to achieve the right amount inoculum and substrate. All samples were prepared in triplicate. The primary sludge, the process water and the inoculum were mixed well before weighing. The mixing was made to avoid non-representative sampling due to sedimentation of the substrate and the inoculum. The substrate and inoculum were also filled as quickly as possible into the vials to receive a representative sample. The microcrystalline cellulose and the hydrochar were not mixed since they were already considered homogeneous and well-mixed. After the vials were filled with the inoculum and the substrate the vials were flushed with nitrogen gas to get rid of the oxygen, to form an anaerobic environment in the vials. The bottles were provided with rubber stoppers with 2 metal tubings and sealed with a plastic screw thread caps. A mixing device was also mounted to the vials to achieve a proper mixing of the inoculum and substrate inside the vial. All the 15 vials were placed in the water bath. One of the metal tubings on each rubber stopper was then sealed with a plastic stopper. The other metal tubings were attached with a plastic tubing (Tygon®) which was attached to the carbon dioxide-fixing unit i.e. all the vials were attached with its respective CO_2-fixing bottle with the help of plastic tubing. The other metal tubing of the CO_2-fixing bottles were attached to their respective gas measuring cells on the gas measuring device with the help of 15 plastic tubings. Trial 1 was run for 26 days. It was not possible to weigh the exact amounts of inoculum and substrate according to the calculations. The actual amounts can be seen in Table A1 (Appendix) and images of the sample incubation unit can be seen in Figure 16.

Figure 16 Left: The sample incubation unit consisting of the water bath and the 15 vials. Right: A close-up of one vial with sample within. The red little plastic piece is a gas stop i.e. it prevent gas from leaking out (Bioprocess Control Sweden AB, 2017).

Gas data collection

All the methane flow data was registered and stored in the gas measuring device. No calculations or further laboratory tests were needed, normalization to STP and compensation for flush-gas (N_2) was made automatically by the gas measuring device. Graphs showing flow rate and accumulated methane production for each bottle could be monitored throughout the experiment time via a laptop connected to the device. Completed gas reports were downloaded regularly for more detailed information and data analysis.

3.2.5 Preparation of the substrate and the inoculum, trial 2

The TS and VS value were predefined for microcrystalline cellulose and process water. The TS and VS value for process water were decided by the company C-green and values for microcrystalline cellulose can be found in the literature (SERVA, 2017). Furthermore, TS and VS for primary sludge, inoculum and adapted inoculum were decided exactly in the same way as in trial 1. The laboratory execution was also done in the same way as trial 1. One thing worth mentioned was the dealing of the adapted inoculum. The TS and VS value were decided separately for hydrochar inoculum and process water inoculum. Since adapted inoculum consists of a mix of one volume part hydrochar inoculum and one volume part process water inoculum, were VS and TS for adapted inoculum decided by taking the average between VS for hydrochar inoculum and VS process water inoculum. The TS value was decided in the same way. All the TS and VS values for substrate and inoculum for trial 2 can be found in Table 9.

Table 9 Values for the TS and VS determination in trial 2. The adapted inoculum only has values for "Average Duplicate TS %" and "Average Duplicate VS %" since it is calculated from PW inoculum and hydrochar inoculum.

Numbers	Parameters	Cake mold (g)	Sample (g)	After 105 °C oven (g)	After 550 °C oven (g)	TS %	VS %	Average Duplicate TS %	Average Duplicate VS %
1	Primary sludge	0.7	17.4	1.3	0.8	3.4	80.6	3.4	80.8
2	Primary sludge	0.7	16.7	1.3	0.8	3.4	80.9	-	-
3	Inoculum1	0.8	17.1	1.1	0.9	2.1	65.7	2.1	65.6
4	Inoculum1	0.8	19.9	1.2	0.9	2.1	65.4		
5	Inoculum 2	0.8	20.6	1.2	0.9	2.2	71.5	2.3	72.0
6	Inoculum2	0.8	21.5	1.3	0.9	2.4	72.5		
7	PW inoculum	0.8	20.1	1.1	0.9	1.6	67.1	1.6	67.1
8	PW inoculum	0.8	20.2	1.1	0.9	1.6	67.1		
9	Hydrochar inoculum	0.8	21.9	1.3	1.0	2.5	59.8	2.5	59.6
10	Hydrochar inoculum	0.8	22.7	1.3	1.0	2.5	59.5	-	-
11	Adapted inoculum	-	-	-	-	-	-	2.1	63.4
12	Adapted inoculum	-	-	-	-	-	-	-	-

3.2.6 Experimental set-up, trial 2

In the second trial, a scenario was designed in that all process water was returned to the anaerobic digestion process at Henriksdals WWTP. This scenario was based on the laboratory execution in section 3.2.3. The total amount of digested sludge was 38439 m^3 and the inflow of secondary sludge and primary sludge was 91.5 m^3/h at Henriksdals WWTP 2016 (Carlsson, 2017b). That inflow corresponded to a hydraulic retention time (HRT) of 17.5 days. Assuming the inflow was the same as the outflow gives an outflow of 1.7 ton_{TS}/h digested sludge, see Equation 9. For the HTC process, an approximate TS of 12 % is required to keep the material pumpable which corresponds to 14.1 m^3/h if all the digested sludge at Henriksdals WWTP is dewatered, see Equation 10. Approximately 60 % of the sludge in the HTC process was converted into process water and 20 % into hydrochar in the laboratory scale experiments. The remaining 20 % are losses e.g. due to that some material always remains in the HTC batch reactor. The calculation can be seen in Equation 7 and the values are taken from Table 3 and Table 4. If all the digested sludge would go to the HTC process, 8.19 m^3/h of process water would be produced. If that amount process water was returned to the anaerobic digestion process, the HRT would have decreased to 16.1 days, See Equation 14. Furthermore, the ratio between (primary sludge plus secondary sludge) and (process water) was 10.7 measured in ton VS/h. There should therefore be 10.7 times more primary sludge and secondary sludge than process water measured in VS. Since there was considerably more primary sludge than secondary sludge an approximation has

been done. All the secondary sludge was considered as primary sludge in trial 2. In trial 2 more than 15 samples were needed. Therefore, two AMPTS devices were set up in parallel. The AMPTS devices were used in the same way as in trial 1. Most of the values in trial 2 are presented in Table 10.

S=TS_{Sludge} = 1.2 % T = VS_{PS} = 2.5 % U = VS_{SS} = 3 %

PS = primary sludge and SS = secondary sludge

Ratio between outcoming PW and incoming sludge;

$$K = \frac{Outcoming\ PW}{sludge} = \frac{1220\ \text{g}}{(350\times6)\ \text{g}} \approx 0.58 \quad (7)$$

$$L = HRT\ (\text{day}) = \frac{Total\ volume}{\text{Inflow PS and SS}} = \frac{38439\ \text{m}^3}{91.5\ \text{m}^3/\text{h}*24} \approx 17.5\ \text{days} \quad (8)$$

Outflow digestate;

$$M = \text{Outflow digestate}\times TS_{\text{Sludge}} = 91.5\ \text{m}^3/\text{h} * 0.012 \approx 1.7\ \text{Ton}_{\text{TS}}/\text{h} \quad (9)$$

$$\text{N} = Sludge\ Dry\ content_{12\ \%} = \frac{M}{0.12} \approx 14.1\ \text{m}^3/\text{h} \quad (10)$$

$$O = Inflow\ PS = Inflow\ PS\times VS_{PS} = 75.5\ \text{m}^3/\text{h}\times\text{T} \approx 2.2\ \text{Ton}_{\text{VS}}/\text{h} \quad (11)$$

$$P = Inflow\ SS = Inflow\ SS\times VS_{ss} = 16.0\ \text{m}^3/\text{h}\times\text{U} \approx 0.5\ \text{Ton}_{\text{VS}}/\text{h} \quad (12)$$

$$\text{Q} = Inflow\ PW = N\times K = 14.1\ \text{m}^3/\text{h}\times0.58 \approx 8.2\ \text{m}^3/\text{h} \quad (13)$$

HRT (day) with added PW;

$$R = \frac{Total\ volume}{\text{Inflow PS, SS and PW}} = \frac{38439 m^3}{(91.5\ m^3/h+8.2\ m^3/h)*24} \approx 16.1\ \text{days} \quad (14)$$

Table 10 Total volume was the total volume sludge in all anaerobic digesters. The ”Inflow PS and SS m^3/h” were the inflow to the reactor. The inflow and outflow were assumed to be the same. “Inflow PW m^3/h” is the amount PW that can be added to the anaerobic digestion if all digested sludge is treated with the HTC process. “HRT (day) with added PW” is what the HRT is estimated to be if the PW is used in the anaerobic digestion process.

Total Volume (m^3)	38439
Inflow PS and SS (m^3/h)	91.5
Outflow digested sludge (m^3/h)	91.5
HRT (day)	17.5
Outflow digested sludge (ton_{TS}/h)	1.7
Digested sludge $TS_{12\ \%}$ (m^3/h)	14.1
Inflow PS (m^3/h)	75.5
Inflow SS (m^3/h)	16.0
Inflow PS (ton_{vs}/h)	2.2
Inflow SS (ton_{vs}/h)	0.5
Inflow PW and SS (ton_{vs}/h)	2.7
Inflow PW (m^3/h)	8.2
Inflow PW (ton_{vs}/h)	0.25
Ratio (PS+SS)/PW	10.7
HRT with added PW (day)	16.1

Samples, trial 2

The ratio between inoculum and substrate were like in trial 1, 2:1 in terms of VS. All samples were filled with substrate and inoculum or only inoculum, 400g in total. The ratio between substrates were adjusted to be correct in terms of VS. In one of the AMPTSs there were 5 triplicates and in the other AMPTS, 3 triplicates. The AMPTS with 5 triplicates consisted of two triplicates blank. One triplicate with only ordinary inoculum from Henriksdals WWTP and one triplicate with adapted inoculum. One triplicate positive control consisted of inoculum and microcrystalline cellulose. Two triplicates consisted of inoculum, primary sludge and process water. One was with ordinary inoculum (scenario 1 abbreviated to SO1) and one was with adapted inoculum (scenario 2 abbreviated to SO2). The relationship between inoculum and substrate was as mentioned before 2:1 in terms of VS. The relationship between primary sludge and process water was 10.72 in terms of VS, see Equation 15. The AMPTS with 3 triplicates consisted of one positive control and two triplicates with inoculum, primary sludge and process water. For the two triplicates with inoculum, primary sludge, and process water different ratios between primary sludge and process water have been made compare with scenario 1 and 2. In one of these triplicates (scenario 3 abbreviated to SO3) another determination was assumed for the HTC process. Instead of 58 % process water yield another scenario has been assumed with 50 % process water yield. This scenario probably is more likely if not advanced filtration devices is used for filtration of hydrochar. Advanced filtration is e.g. pressure filtration, see section 2.3.3. The ratio between inoculum and substrate was as usual 2:1. The ratio between primary sludge and process water was 12.45, see Equation 17. Moreover, the HRT (day) was 16.3. In the other triplicate (scenario 4 abbreviated to SO4) the amount of process water was increased with 20 % to investigate if an increase of process water could lead to an inhibition. The ratio between primary sludge and process water was 8.93, see Equation 18. Additionally, HRT was 15.8. The last triplicate was a positive control consisted of inoculum and microcrystalline cellulose. The reason to have two positive controls was to make sure of that no differences between the two AMPTS devices existed. A compilation of the samples can be viewed at Table 11.

From Table 10 there can be seen that the inflow of primary sludge and secondary sludge was 2.68 ton_{vs}/h rounded to two decimals (in Table 10 2.7 ton_{vs}/h) and the inflow of process water was 0.25 ton_{vs}/h. All values in *Samples, trial 2* are from Henriksdals WWTP (2016). It would be too complicated to do BMP test with both secondary sludge and primary sludge. Therefore, the amount of secondary sludge in 2.68 ton_{vs}/h was assumed to be primary sludge in trial 2. In Equation 15 the ratio between primary sludge and process water is calculated for scenario 1 and scenario 2.

$$Scenario\ 1\ and\ 2 = \frac{PS}{PW} = \frac{2.68\ \mathrm{ton_{VS}/h}}{0.25\ \mathrm{ton_{VS}/h}} \approx 10.72 \quad (15)$$

From Equation 10 it can be seen that 14.1 m^3/h digestate was produced with a TS of 12 %. In scenario 3, 14.1 m^3/h is multiplied with 0.5 (Equation 16) instead of 0.58 as in scenario 1 and scenario 2. In Equation 17 the ratio between primary sludge and process water is calculated for scenario 3.

PW_{VS} = 3.1 %, see Table 1

$$PW_{50\,\%} = 14.1\ \frac{\mathrm{m^3}}{\mathrm{h}} \times 0.5 = 7.05\ \frac{\mathrm{m^3}}{\mathrm{h}}, 7.05\ \frac{\mathrm{m^3}}{\mathrm{h}} \times PW_{VS} \approx\ \ 0.21 \ldots \frac{\mathrm{ton_{VS}}}{\mathrm{h}} \quad (16)$$

$$Scenario\ 3 = \frac{PS}{PW} = \frac{2.68\ldots\ \mathrm{ton_{VS}/h}}{0.21\ldots\ \mathrm{ton_{VS}/h}} \approx 12.45 \quad (17)$$

The inflow of process water was 0.25 ton_{vs}/h, see Table 8. In scenario 4, 0.25 ton_{vs}/h is simply multiplied with 1.2.

$$Scenario\ 4 = \frac{PS}{PW} = \frac{2.68\ldots\ \mathrm{ton_{VS}/h}}{0.25\ldots \times 1.2\ \mathrm{ton_{VS}/h}} \approx 8.93 \quad (18)$$

The substrates and the inoculums were heterogeneous except for the microcrystalline cellulose. Meaning the substrates and the inoculums needed to be poured as quickly as possible when being mixed. Therefore, it was hard to get the sample amount exactly as in Table 11. The real values from trial 2 can be seen in Table A2 (Appendix).

Table 11 Calculated amounts of inoculum/substrate for each triplicate. AMPTS 1 or AMPTS 2 corresponds to which of the two AMPTS devices that was used.

Triplicate	Inoculum/Substrate	Mass (g)	Mass VS (g)
1) Blank (AMPTS 1)	Inoculum	400	5.59
	-	-	-
	-	-	-
2) Blank (AMPTS 1)	Adapted inoculum	400	5.21
	-	-	-
	-	-	-
3) Positive control	Inoculum	397.10	5.55
(AMPTS 1)	microcrystalline cellulose	2.89	2.77
	-	-	-
4) Scenario 1	Inoculum	318.75	4.45
(AMPTS 1)	Primary sludge	75.03	2.04
	Process water	6.22	0.19
6) Scenario 2	Adapted inoculum	323.20	4.21
(AMPTS 1)	Primary sludge	70.97	1.93
	Process water	5.88	0.18
7) Scenario 3	Inoculum	318.70	4.45
(AMPTS 2)	Primary sludge	75.92	2.06
	Process water	5.41	0.17
8) Scenario 4	Inoculum	318.90	4.46
(AMPTS 2)	Primary sludge	73.80	2.00
	Process water	7.34	0.22
9) Positive control	Inoculum	397.10	5.55
(AMPTS 2)	Microcrystalline cellulose	2.89	2.77
	-	-	-

3.3 THEORETICAL ESTIMATION

3.3.1 Theoretical application of the HTC process at Henriksdals WWTP

The HTC process in industrial scale would be similar to Figure 17. The quantities are of course not realistic though for a HTC process used in industrial scale. However, the mass balance relationships between ingoing substrate and outgoing products and design are realistic. Incoming sludge would have a high dry content. The dry sludge would be diluted by process water from the filtration. The dilution is necessary, because the sludge must not exceed a certain dry content. Otherwise the sludge cannot be pumped and if the sludge cannot be pumped, it cannot enter the HTC treatment. The process water not used for dilution can be used as a substrate in anaerobic digestion.

Trial 2 has been based on the laboratory experiment, see section 3.2.1, 3.2.6, and 4.1.2. This section will investigate the outcome if the theoretical values in Figure 17 were applied for the anaerobic digestion facility at Henriksdals WWTP. The amount of process water produced in the HTC process that can be fed into the anaerobic digesters is presented in Table 12. Furthermore, all values in Table 12 are based on information from Henriksdals WWTP. The information was averages from 2016 (Carlsson, 2017a).

It can be seen from Equation 19 and Figure 17 that the ratio between outcoming process water and incoming sludge (25 % dry content) was approximately 73 %. The average

HRT at the anaerobic digestion facility at Henriksdals WWTP was 17.5 days during 2016, see Equation 20. The outflow of digestate was converted to Ton_{TS} per h, see Equation 21. The value for TS_{Sludge} was given from Henriksdals WWTP (Carlsson, 2017a). Thereafter, the digestares wet-weight could be recalculated to 25 % TS which is the same content that the sludge is supposed to enter the HTC process (see Equation 22). PS, SS, and PW can be converted from m^3 to ton_{vs} by multiplying with the VS value for the substrate (Equation 23 and Equation 24). The theoretical amount process water that can be produced is showed in Equation 25. The volume sludge (dry content 25 %) produced in 2016 is known by Equation 22. How much of that amount (in percent) that would leave as process water is known from Equation 19. The theoretical weight of process water that can be produced by the HTC process with the sludge from 2016 can then be determined by Equation 25. Finally, changes in the digesters HRT if the process water produced was fed into the anaerobic digesters at Henriksdals WWTP can be calculated with Equation 26. The assumptions which have been made for this section are: The VS value (ratio between VS weight and TS weight) for the process water is the same in laboratory scale as in the industrial scale.

S = total solids for digestate = $TS_{digestate}$ = 1.2 %

T = volatile solids for primary sludge presented as a ratio between wet-weight and VS weight = VS_{PS} = 2.5 %

U = volatile solids for secondary sludge presented as a ratio between wet-weight and VS weight = VS_{SS} = 3 %

Total volume = The total volume sludge for all digesters at Henriksdals WWTP.

PS = primary sludge, *PW* = process water, *SS* = secondary sludge, *HRT* = Hydraulic retention time

Ratio between outcoming PW and incoming sludge;

$$K = \frac{Outcoming\ PW}{sludge} = \frac{127.6292\ \text{g}}{173.96\ \text{g}} \approx 0.73 \quad (19)$$

$$L = HRT\ (day) = \frac{Total\ volume}{\text{Inflow PS and SS}} = \frac{38439\ \text{m}^3}{91.5\ \text{m}^3/\text{h}*24} \approx 17.5\ \text{days} \quad (20)$$

Outflow digestate;

$$M = \text{Outflow digestate} \times TS_{digestate} = 91.5\ m^3/h * 0.012 \approx 1.7\ Ton_{TS}/\text{h} \quad (21)$$

$$\text{N} = Sludge\ Dry\ content_{25\ \%} = \frac{M}{0.25} \approx 6.8\ \text{m}^3/\text{h} \quad (22)$$

$$O = Inflow\ PS = Inflow\ PS \times VS_{PS} = 75.5\ \text{m}^3/\text{h} \times \text{T} \approx 2.2\ Ton_{VS}/\text{h} \quad (23)$$

$$P = Inflow\ SS = Inflow\ SS \times VS_{ss} = 16.0\ \text{m}^3/\text{h} \times \text{U} \approx 0.5\ Ton_{VS}/\text{h} \quad (24)$$

$$Q = Inflow\ PW = N \times K = 6.8\ \text{m}^3/\text{h} \times 0.73 \approx 5.0\ \text{m}^3/\text{h} \quad (25)$$

HRT (day) with added PW;

$$R = \frac{Total\ volume}{\text{Inflow PS, SS and PW}} = \frac{38439 m^3}{(91.5\ \text{m}^3/\text{h} + 5.0\ \text{m}^3/\text{h})*24} \approx 16.6\ \text{days} \quad (26)$$

Table 12 Same as table 10, but dry content has been changed from 12 % to 25 % and ratio between outcoming PW and incoming sludge are 73 % instead of 58 %. Otherwise, the condition is the same.

Total Volume (m^3)	38439
Inflow PS and SS (m^3/h)	91.5
Outflow digested sludge (m^3/h)	91.5
HRT (day)	17.5
Outflow digested sludge (ton_{TS}/h)	1.7
Digested sludge $TS_{25\ \%}$ (m^3/h)	6.8
Inflow PS (m^3/h)	75.5
Inflow SS (m^3/h)	16.0
Inflow PS (ton_{vs}/h)	2.2
Inflow SS (ton_{vs}/h)	0.5
Inflow PW and (SS) (ton_{vs}/h)	2.7
Inflow PW (m^3/h)	5.0
Inflow PW (ton_{vs}/h)	0.31
Ratio (PS+SS)/PW	8.7
HRT with added PW (day)	16.6

Figure 17 is made by C-Green and is translated to English (Öhman, 2017c). The figure describes a hypothetical industrial scale HTC mass balance for sludge, hydrochar and process water. The quantities would of course be lager but the relative relationships are realistic. Incoming sludge can for example be dewatered digested sludge from an anaerobic digester. Thereafter, the sludge is diluted to make the sludge possible to pump. There are same losses in the HTC step mainly as gas. After the HTC step the hydrochar is filtered out. One part of the process water is returned to the HTC process and is used as a diluent. The other part is leaving the system and can be used as a substrate in the anaerobic digestion process. For explanation of solid hydrochar and process water see Table 13.

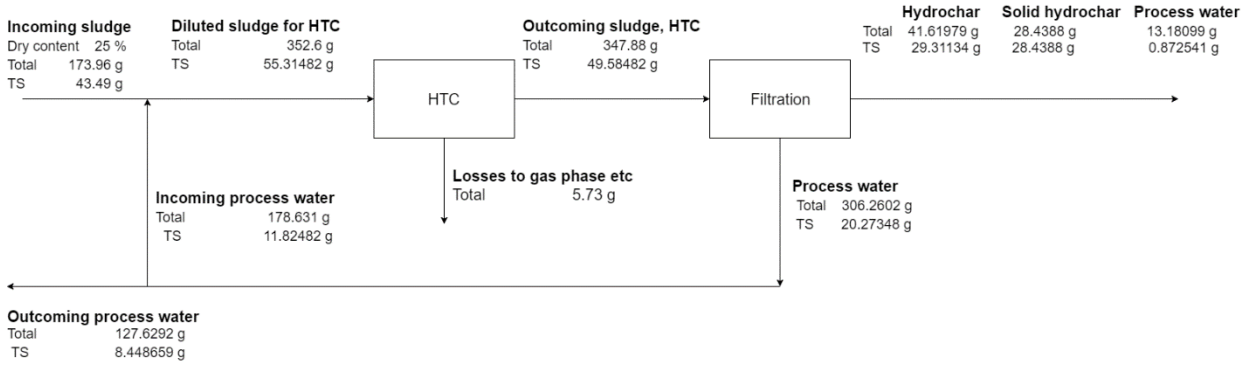

Figure 17 Mass balance for a realistic design of the HTC process in full-scale. All values are present as total weight and as the TS amount of the total weight.

3.3.2 Bound process water to hydrochar

All process water cannot be filtered out from the hydrochar so some of the process water remains in the hydrochar, see Table 14. The values in Table 14 has been calculated with help of information from the company C-Green (Öhman, 2017b). The information is presented in Figure 18. Some of the values in Equations 27–35 are taken from Figure 18. In trial 1, 16 g hydrochar was added to each sample in the triplicate, see

Table 8. The amount process water bound to the total hydrochar was calculated according to Equation 29 and the amount solid hydrochar of the total hydrochar was calculated according to Equation 34. The VS weight was determined with help of the values from Table 1 and were calculated with Equation 31 and Equation 32. The BMP for process water can be seen in Table 16 and with that value the methane production of the process water, can be calculated with Equation 33. The total methane production for hydrochar was 150 mL, see Table 16. 131 mL of methane was produce by process water and the remining methane was produced by solid hydrochar, see Equation 34. BMP for solid hydrochar is 7.8 mL/g_{vs}, see Equation 35. One made assumption is that the filtered process water had the same VS value as the process water bound to the hydrochar.

Table 13 Explanations of the three types of hydrochar is used in section 3.3.2.

Total hydrochar	When the sludge (or other waste) has been used in the HTC process and been filtered. This hydrochar is referred to as total hydrochar. The total hydrochar consists both of solid hydrochar and process water which is bound to the solid hydrochar. It should be noted that total hydrochar is only named total hydrochar in this section (3.3.2) to avoid conceptual confusion. In the rest of the report total hydrochar is just called hydrochar.
Solid hydrochar	When all process water that is bound to the total hydrochar is removed, it is only the solid hydrochar left. I.e. solid hydrochar is the solid matter in the total hydrochar. Solid hydrochar is almost the same as the TS value for total hydrochar.
Process water	Process water is the liquid matter that is bound to the solid hydrochar. A certain quantity of the process water, bound to the total hydrochar can be filtered out with a more advanced method than was used by C-green in the laboratory scale experiments but some of the process water is always left. For information about the filtering method see section 3.2.1. It should be noted that process water only has this definition in section 3.3.2. In the rest of the rapport process water is simply the filtrate from the HTC process.

Equations 27–35 describe the partitioning of solid matter and liquid matter in the total hydrochar.

I = 16 g = amount total hydrochar added to each sample in the triplicate for trial 1.

J = 335 mL/g_{vs} = BMP for process water

K = 150 mL/g_{vs} = produced methane by total hydrochar

L = VS process water = 0.0305825 %

M = VS hydrochar = 0.177528 %

Ratio process water;

$$A = \frac{weight\ process\ water}{weight\ total\ hydrochar} = \frac{113.01\ \text{g}}{141.45\ \text{g}} \approx 0.8 \quad (27)$$

Ratio solid hydrochar;

$$B = \frac{weight\ solid\ hydrochar}{weight\ total\ hydrochar} = \frac{28.44\ \text{g}}{141.45\ \text{g}} \approx 0.2 \quad (28)$$

Amount process water;

$$C = ratio\ process\ water \times I = 0.8 \times 16\ \text{g} \approx 12.8\ \text{g} \quad (29)$$

Amount solid hydrochar;

$$D = ratio\ solid\ hydrochar \times I = 0.2 \times 16\ \text{g} \approx 3.2\ \text{g} \quad (30)$$

Amount process water$_{\text{VS}}$;

$$E = C \times VS_{process\ water} = 12.8\ \text{g} \times 0.0305825 \approx 0.4\ \text{g} \quad (31)$$

Amount solid hydrochar$_{\text{VS}}$;

$$F = \left(I \times VS_{Total\ hyrochar}\right) - E = (16\ \text{g} \times 0.177528) - 0.4\ \text{g} \approx 2.4\ \text{g} \quad (32)$$

Produced CH4 by process water;

$$G = J \times E = 335\ \text{mL/g}_{\text{VS}} \times 0.4\ g \approx 131\ \text{mL} \quad (33)$$

Produced CH4 by solid hydrochar;

$$H = K - G = 150\ \text{mL} - 131\ \text{mL} = 19\ \text{mL} \quad (34)$$

$$BMP_{Solid\ hydrochar} = \frac{H}{F} = \frac{19.04\ \text{ml}}{2.44\ \text{g}} \approx 7.8\ \text{mL/g}_{\text{vs}} \quad (35)$$

Table 14 Solid hydrochar is the solid part of the hydrochar. Process water is the liquid which are bound to the hydrochar. Ratio is the percental distribution (by weight) between the total amount hydrochar and solid hydrochar respective process water, see Equation 27 and Equation 28. The weight of solid hydrochar and process water are expressed in gram and gram per VS. The methane production is expressed in mL and in percent between solid hydrochar and process water.

Components of hydrochar	Ratio % (g)	Amount g	Amount g_{vs}	CH_4 (mL)	CH_4 (%)
Solid hydrochar	20 %	3.2	2.4	19	13
Process water	80 %	12.8	0.4	131	87

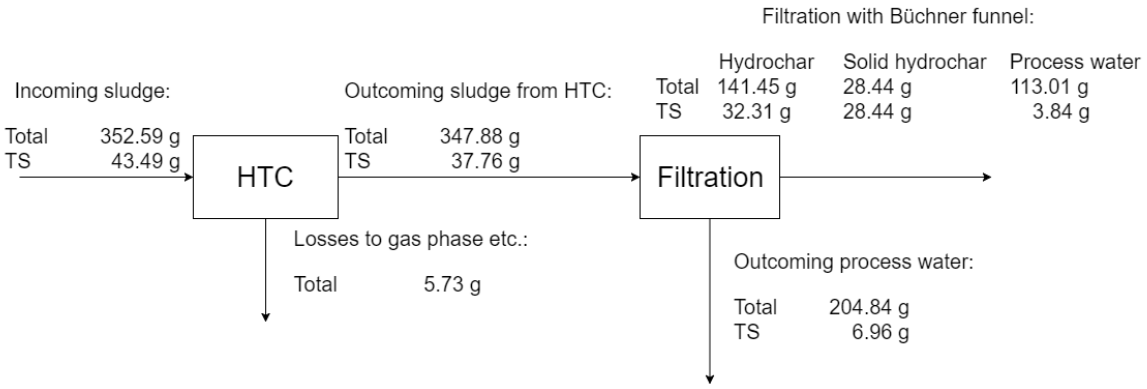

Figure 18 Modified figure from C-Green (Öhman, 2017b). The dewatering ratio (by weight) between outcoming process water and incoming sludge has been changed from approximately 70 % to approximately 58 % to better replicate the conditions in this master thesis.

3.4 CALCULATION OF RSD AND UNCERTAINTY FACTOR

The approach recommended by (Holliger *et al.*, 2016) was used. The relative standard deviation (RSD) was calculated according to Equation 36. Where S is the standard deviation and $\bar{x}$ mean. The mean and the standard deviation was calculated from the terminal methane production per g VS for the substrates and the inoculum for each triplicate. The uncertainty factor and the methane production per g VS were calculated according to Equation 37. $BMP_{substrate}$ is the total methane production per g VS for the substrate with the uncertainty factor included $BMP_{average}$ is the average methane production for each triplicate. S_{blank} is the standard deviation for the inoculum triplicates methane production per g VS and $S_{substrate}$ is the standard deviation for each substrate triplicate in terms of methane production per g VS. RSD values criteria´s for BMP test can be seen in Table 15.

$$RSD = \frac{S}{\bar{x}} \times 100 \quad (36)$$

$$BMP_{substrate} = BMP_{average} \pm \sqrt{(S_{blank})^2 + (S_{substrate})^2} \quad (37)$$

Table 15 A BMP test need to fit in these criteria's otherwise the result must be rejected (statistical test can be used to remove single outliers) (Holliger *et al.*, 2016). The values in the table have been used in this master theses to evaluate the result in trial 1 and trial 2.

	Value
Heterogeneous substrate	10 % > RSD
Homogenous substrate	5 % > RSD
Blank (inoculum)	5 % > RSD
Positive control	85 % < BMP < 100 %

4 RESULTS

This section covers the results from trial 1 and trial 2, and the results from the theoretical calculations of the hypothetical full-scale implementation of the HTC process where all the HTC process water was assumed to be reintroduced back to the digesters.

4.1 RESULTS, LABORATORY-SCALE

4.1.1 Trial 1

Trial 1 was finished after 26 days. The experiment could have been terminated after 23 days according to the recommendation, "BMP tests…. should only be terminated when daily methane production during three consecutive days is <1 % of the accumulated volume of methane (i.e. BMP1 %)" (Holliger *et al.*, 2016). The experiment was going on 3 days extra because trial 2 had to be prepared properly before trial 1 could be terminated. Figure 19 shows the total accumulated methane production during 26 days with the methane production from the inoculum included. It can be seen in Figure 19 that the methane production was very fast in the beginning and then declined. The great majority of the methane had been produced during the first five days. On the x-axis is the unit NmL written. The "N" stands for normalized, which means that the methane production has been normalized STP i.e. 1.0 standard atmospheric pressure, 0 °C and zero moisture content (Bioprocess Control Sweden AB, 2013).

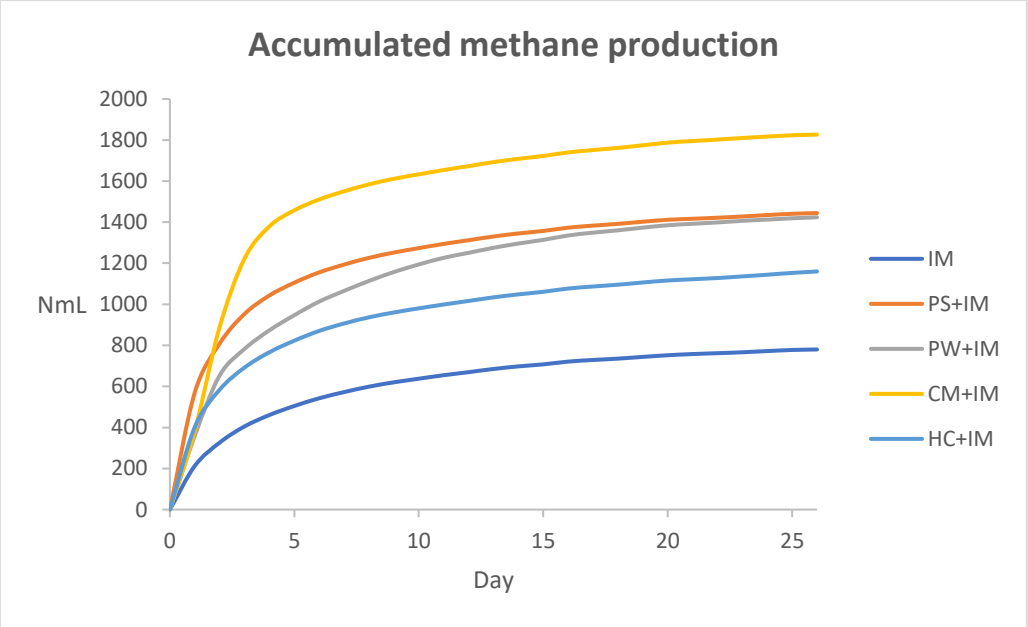

Figure 19 Total accumulated methane production for the substrates in trial 1 together with the inoculum. IM: Inoculum, PS: Primary sludge, PW: Process water, CM: Microcrystalline cellulose, and HC: Hydrochar.

In Figure 20, each sample has been divided with the sample VS weight. The methane production was accumulated and the inoculum was included. The same trend for the methane production is demonstrated in Figure 20, as in Figure 19 and 21. The methane production is fairly equal for primary sludge, process water and microcrystalline cellulose. However, the methane production for inoculum and hydrochar are considerably lower. The average methane production from the inoculum samples were 133 mL for 26 days per g VS. If uncertainties are included the methane production for

the inoculum can be expressed as 133mL ± 4 %. Moreover, the inoculum has a relative standard deviation (RSD) at 4 %. The RSD must not exceed 5 % (Holliger *et al.*, 2016).

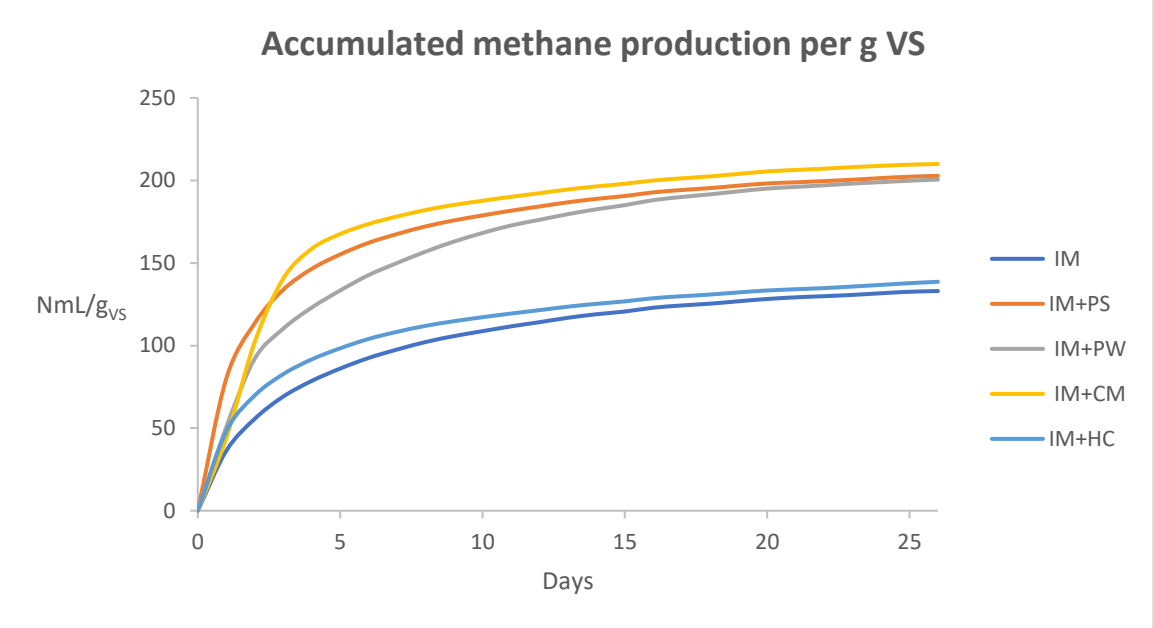

Figure 20. In this graph has VS been taking in account otherwise, it is the same graph as Figure 19.

In Figure 21, the difference in BMP of the substrates is visible since the methane production from the inoculum was excluded. The methane production was quite similar for primary sludge, process water and microcrystalline cellulose. However, the methane production for the hydrochar was rather low compared with the three others. The terminal amount CH_4 for the triplicates (substrates) can be seen in Table 16 and the terminal amount CH_4 for each sample can be seen in Table A3 (Appendix). Formulas for uncertainty factor and RSD are demonstrated in the method. The RSD must not exceed 10 % which is guideline value for heterogeneous substrates (Holliger *et al.*, 2016). Table 16 show that no one of the substrates exceeded 10 % RSD (microcrystalline cellulose is not a heterogenic substrate). The RSD for the blank or positive control must not exceed 5 %. Moreover, the positive control should be between 85 % and 100 % of the theoretical BMP (Holliger *et al.*, 2016) The positive control in trial 1 was microcrystalline cellulose and 85 % to 100 % correspond to 352 mL/g_{vs} to 414 mL for microcrystalline cellulose. According to Table 16, microcrystalline cellulose fit in that interval.

Table 16 The average amount of produced methane for the four substrates and the inoculum triplicates and their standard deviations. The methane production is for 26 days and is g per VS.

Substrate	Amount methane (NmL/g_{vs})	RSD (%)
Primary sludge	343 ± 2 %	1
Process water	335 ± 10 %	9
Hydrochar	150 ± 5 %	4
Microcrystalline cellulose	363 ± 3 %	2
Blank (inoculum)	133 ± 4 %	4

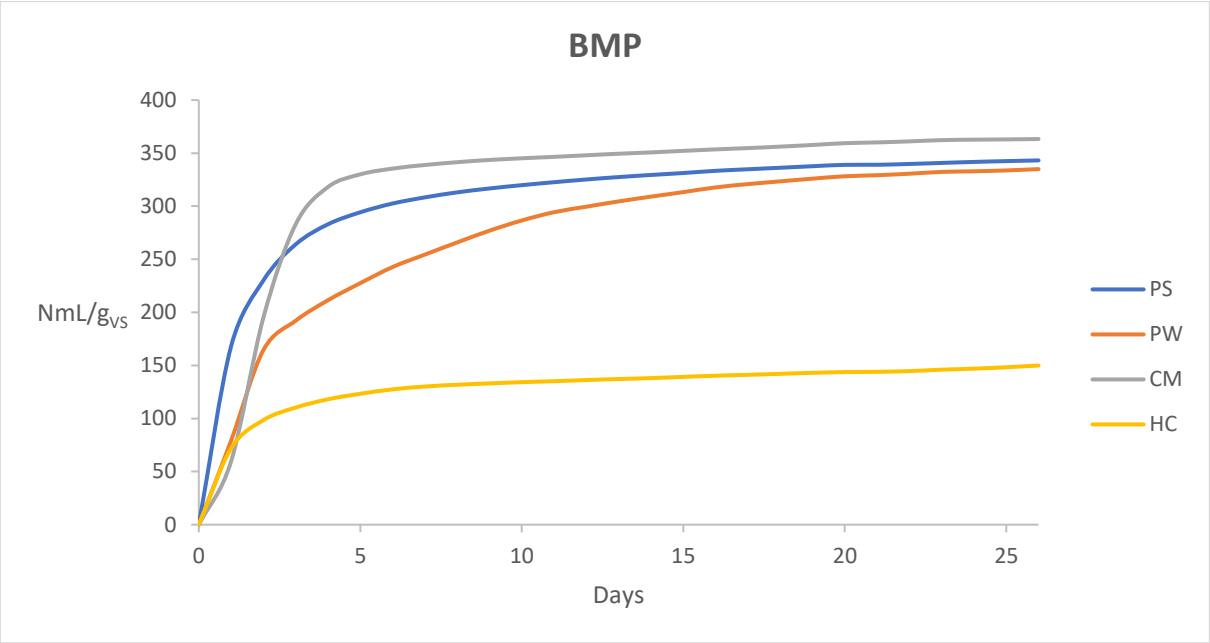

Figure 21 Methane production for each substrate divided with the substrates´ VS weight. (Methane production from the inoculum excluded).

Figure 22 shows the intensity expressed as a percentage of the total methane production during the 26 days. Primary sludge and hydrochar had the fastest degradation profile while the process water had the slowest and the microcrystalline cellulose was somewhere in between. Overall, the methane production was the greatest between days 1–3.

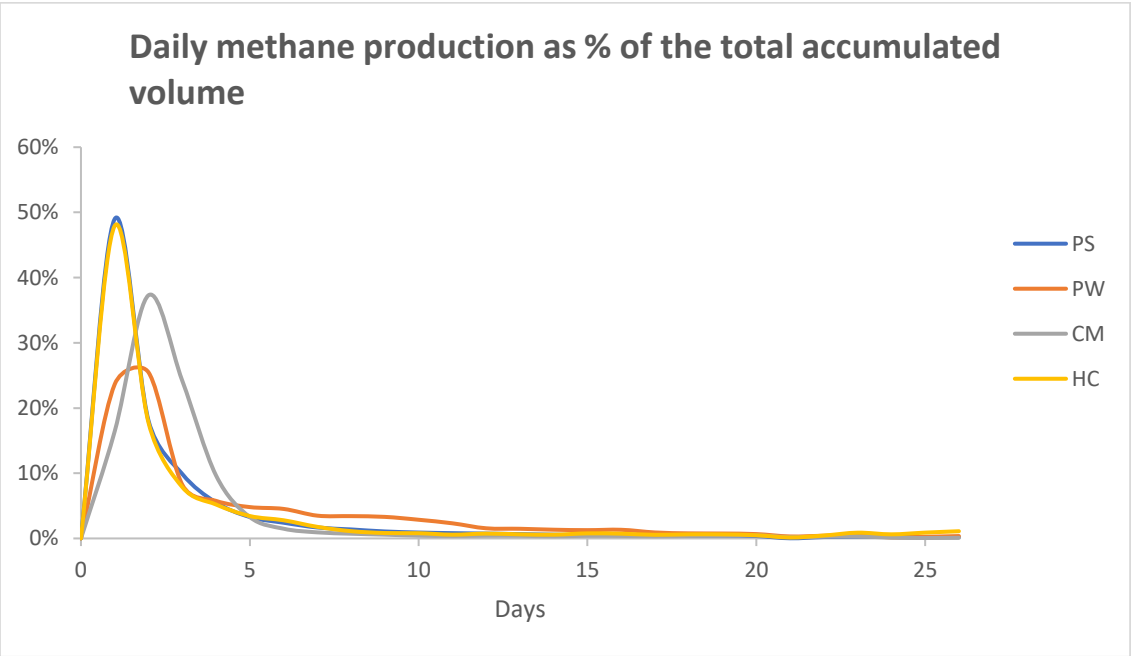

Figure 22 Daily methane production as percent of the total accumulated volume. The graph for primary sludge is hard to see but the graph is right behind the hydrochar graph.

9050000 Nm^3 methane was produced at Henriksdals WWTP during 2016 (Carlsson, 2017b). The BMP for process water was 335 mL/g_{vs}, see Table 16. 0.25 ton_{vs}/h process water can theoretical be produced from the digested sludge at Henriksdals WWTP

(values from 2016). 0.25 ton_{vs}/h process water correspond to 8.19 m^3/h process water. See section 3.2.6. 0.25 ton_{vs}/h process water has been calculated with the help of values produced by the laboratory experiment. See section 3.2.1.

VS_{PW} = 3.1 % (ratio between VS weight and wet-weight) see section 3.1.2.

D = 8.19 m^3/h

VS = Expressed as ton_{vs}/h or g_{vs}/year

$$VS = D \times VS_{PW} = 0.25 \frac{\text{ton}_{\text{VS}}}{\text{h}} = 2.19 \times 10^9 \frac{\text{gvs}}{\text{year}} \quad (38)$$

If all the process water was added to the anaerobic digestion process at Henriksdals WWTP, how much methane could theoretically be produced? 0.25 ton_{vs}/h can be expressed as 2.19×10^9 g_{vs}/year. The methane produced from the process water is hence:

$$2.19 \times 10^9 \frac{\text{gvs}}{\text{year}} \times 335 \frac{\text{mL}}{\text{gvs}} = 7.3365 \times 10^{11} \text{ mL} = 733650 \text{ Nm}^3 \quad (39)$$

If the produced methane from 2016 is used together with the theoretical amount from the process water, the total amount become 9780000 Nm^3. That would correspond to 8.1 % increased methane yield.

4.1.2 Trial 2

All figures in trial 2 are presented as an average of the samples in each triplicate. From Figure 23 it can be deduced that the two positive controls had the highest methane production. The inoculum was included and added VS has not been considered. Adapted inoculum and scenario 2 had the lowest production and the other triplicate lying somewhere in between.

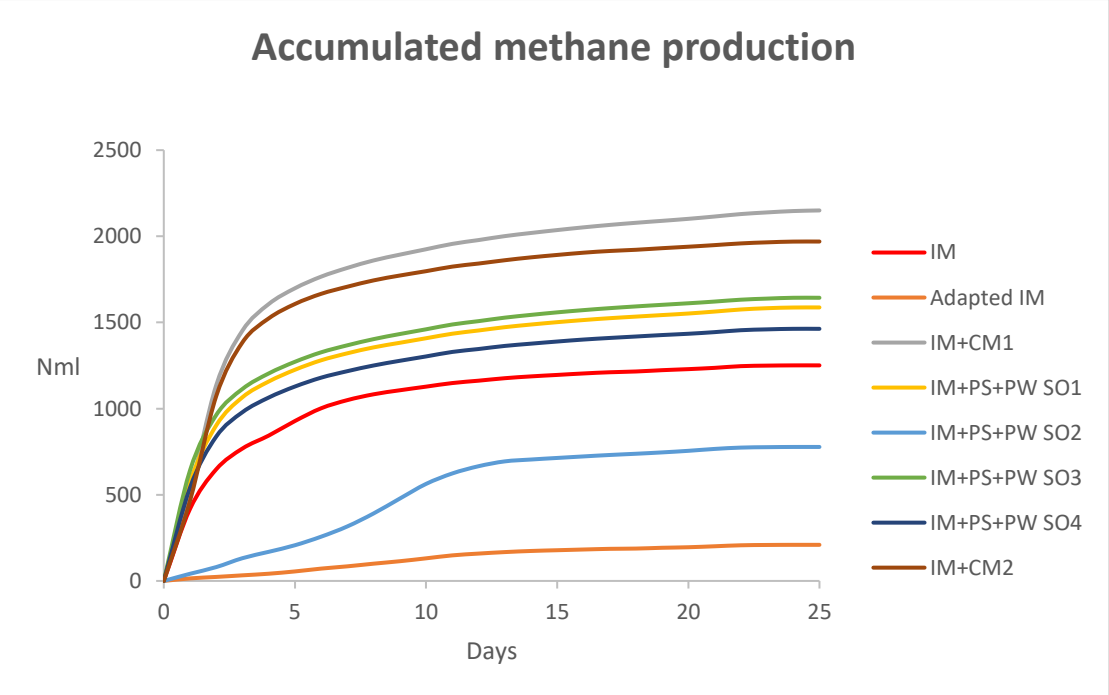

Figure 23 The total accumulated methane production for each triplicate with the inoculum included. SO is short for scenario and describes the ratio between PS and PW. The ratios are 10.72 for SO1 and SO2, 12.45 for SO3 and 8.93 for SO4. The ratios are calculated with the VS value. Other abbreviations

correspond to which type of inoculum are used. There is ordinary inoculum for all triplicates except for SO2, where Adapted inoculum was used. More information can be found in the method and in Table 11.

When added amount VS is considered and the inoculum is included (Figure 24), most of the triplicates had similar methane production. Two of the triplicates were considerably lower, scenario 2 and adapted inoculum.

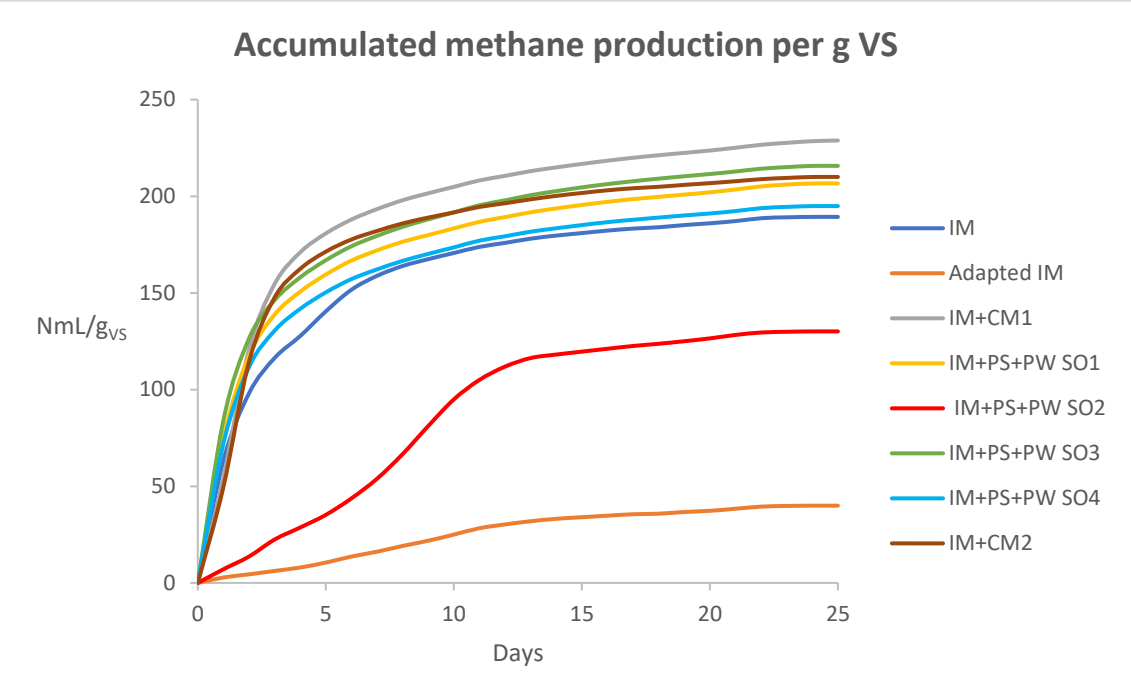

Figure 24 The total accumulated methane production divided with the added amount VS weight. The inoculum is included.

The methane production between the two positive controls (CM1 and CM2) differed a lot (Figure 25). The highest amount of methane was produced in SO2 (except for CM1) that had the adapted inoculum instead of the ordinary inoculum. The shape of the SO2 graph differs compared to the other graphs. The SO2 had almost a linear methane production from day 0 to day 13 while the other five had an exponential production from day 0 to day 4.

Both positive controls had too low methane production, the minimum value for microcrystalline cellulose is 352 mL/$g_{vs.}$ Additionally, the RSD was too high for CM1, the RSD must not exceed 5 %. The blanks exceeded the RSD too, the RSD must not be higher or equal than 5 % for blanks. The RSD limit for heterogenic substrate is 10 %, i.e. if the RSD is higher or equal to 10 % the result for that substrate is not reliable. Therefore, SO1 and SO2 was reliable, SO3 and SO4 was not. All RSD-values and methane production with uncertainty factor can be find in Table 17.

Table 17 The terminal methane production for the substrates mixes, the two positive controls and the two inoculums. The methane production for the triplicates are expressed as an interval. The size of the interval is based on the uncertainties for each triplicate. Moreover, the RSD is in percent and are calculated for each triplicate. The uncertainties factor cannot be calculated for blanks.

Substrate/inoculum	Amount methane (NmL/g_{vs})	RSD (%)
CM1	323 ± 18 %	14
PS+PW SO1	244 ± 16 %	6
PS+PW SO2	309 ± 4 %	4
PS+PW SO3	275 ± 17 %	10
PS+PW SO4	208 ± 21 %	12
CM2	259 ± 15 %	3
Inoculum	189 ± 19 %	19
Adapted inoculum	40 ± 7 %	7

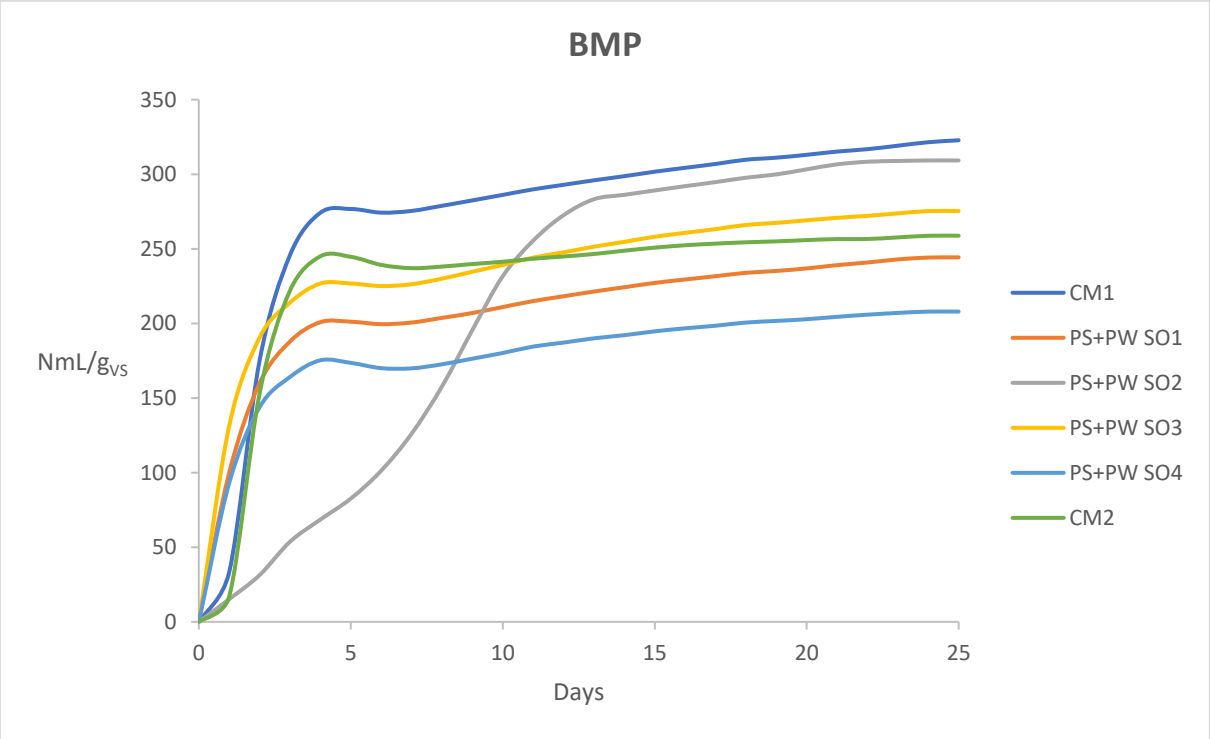

Figure 25 The methane production for each substrate triplicate. The inoculum is excluded and added VS is considered.

The two positive controls had a slower methane production in the beginning than SO1-SO3 which can be seen in Figure 26. All the substrate mixes (except SO2) had in common that almost all the methane was produced during the first 5 days. The SO2 diverged very much compared to the other substrates. SO2 had the highest production in approximately 10 days. Furthermore, SO2 had a more even production for the first 13 days than the other substrate mixes. SO2 was the only one with adapted inoculum. The reason to the negative percentages close to 5 days is, in that period was the methane production higher for the inoculum than for the substrates.

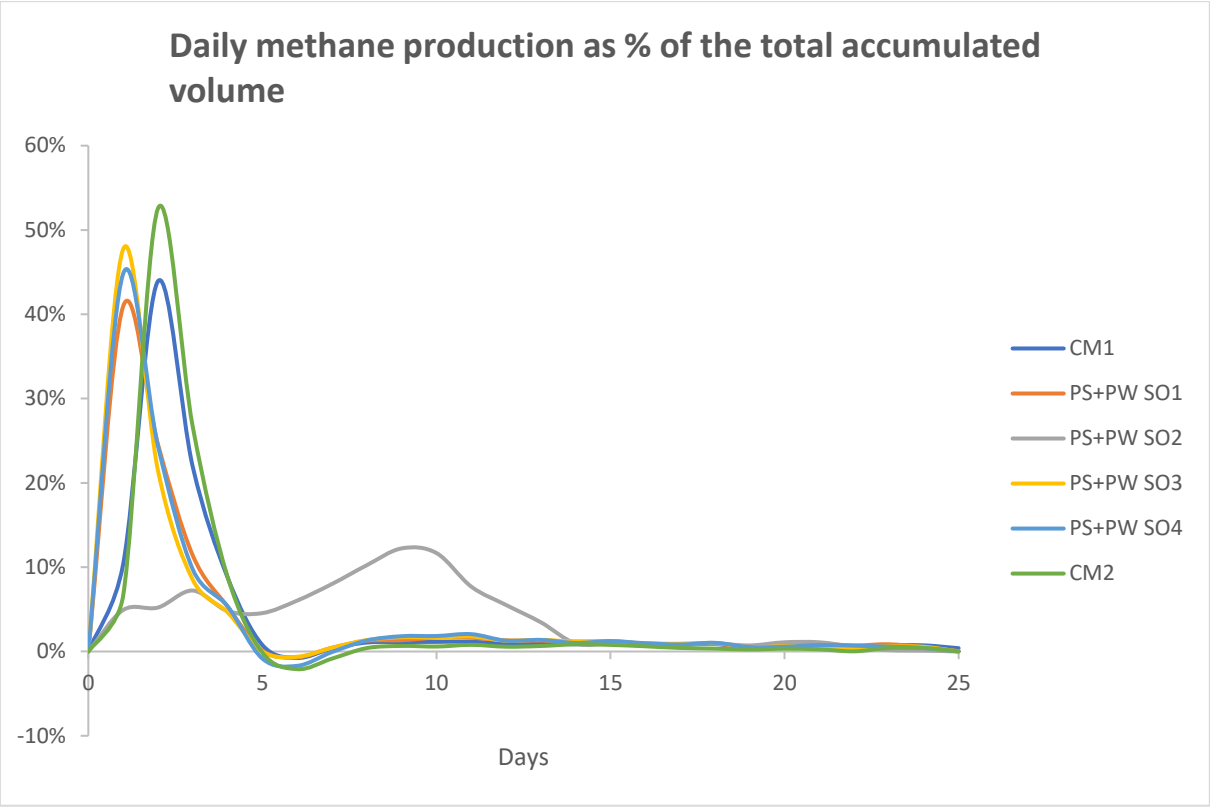

Figure 26 The total accumulated methane production per day, presented in percent.

4.2 RESULTS, THEORETICAL ESTIMATION

9050000 Nm^3 methane was produced at Henriksdals WWTP during 2016 (Carlsson, 2017b). The BMP for process water was 335 $mL/g_{vs,}$ see Table 16. From the full-scale scenario, 4.97 m^3/h process water can theoretically be produced, see section. 3.3.1 That can be converted to 0.31 ton_{vs}/h or 2.71×10^9 g_{vs}/year (Carlsson, 2017b).

αVS_{PW} = 94.1 % (ratio between VS weight and TS weight) from section 3.1.2

C = 4.97 m^3/h

$TS_{PW} = \frac{8.45\ g}{127.63\ g} = 6.6\ \%$ (8.45 g and 127.63 g are values from outcoming process water Figure 17) (40)

$\beta VS_{PW} = \alpha VS_{PW} \times TS_{PW} = 6.2\ \%$ (ratio between VS weight and wet-weight) (41)

VS = Expressed as ton_{vs}/h or g_{vs}/year

$$VS = C\frac{m^3}{h} \times \beta VS_{PW} = 0.31\frac{ton_{VS}}{h} = 2.71\times10^9\ \frac{gvs}{year} \quad (42)$$

If all the process water was added to the anaerobic digestion process at Henriksdals WWTP, how much extra methane could theoretically be produced? 0.31 ton_{vs}/h can be expressed as 2.71×10^9 g_{vs}/year. The methane produced from the process water is hence:

$$2.71\times10^9\ \frac{gvs}{year} \times 335\ \frac{mL}{gvs} = 9.0850\times10^{11}\ NmL = 908498\ Nm^3 \quad (43)$$

If the produced methane from 2016 is used together with the theoretical amount from the process water, the total amount becomes approximately 9960000 Nm^3. That would correspond to 10.0 % increased methane yield

5 DISCUSSION

This section is divided in two parts, 5.1 and 5.2. In 5.1 the laboratory results from 4.1 is discussed. In section 5.2 the theoretical estimation of the methane yield from 4.2 is discussed.

5.1 DISCUSSION LABORATORY-SCALE

From Figure 21 and Table 16 it can be observed that the total CH_4 production was almost as high for process water as for primary sludge. It should be pointed out that the process water had the highest standard deviation of the substrates. The difference between process water and primary sludge can hence be greater in terms of methane production but it is also possible that methane production per g VS could be higher for process water than for primary sludge. The process water had a slightly different production curve compared to the primary sludge. The primary sludge had a rapid production for the first 5 days which decreased thereafter. The process water had a rapid production for approximately 2 days which flattened out thereafter but more slowly than the primary sludge. This indicates that the primary sludge was easier degradable than the process water for the microorganisms but in the end, the methane production per g VS was almost the same. This can be seen even more clearly in Figure 22. According to trial 1, no inhibitory effects were seen for process water when process water was digested with inoculum alone. Considerably lower methane production for hydrochar compared to the other three substrates can be deduced from Figure 21, indicating that most of the biologically available energy from the HTC products was stored in the process water rather than in the hydrochar.

That was confirmed by Figure 18 and Table 14 which show that minimal amounts of methane were produced by the actual hydrochar. Most of the methane was instead produced by the process water in the hydrochar, to be exact 87 %. It should be noted that the VS value for process water and the VS value for the process water bound to the hydrochar have been assumed to be the same. It is likely that the process water bound to the hydrochar do not have the same VS value than the process water which could be filtered. That would mean that the methane production of the actual hydrochar (solid hydrochar) could be lower or higher.

To determine if the results were reliable and the uncertainty in the terminal methane production for the substrates, the following source was used (Holliger *et al.*, 2016). The source defines compulsory elements for validation of BMP results. This was stated during workshop in Switzerland with over 40 attendees from 30 laboratories around the world. There can be seen from Table 16 that trial 1 fit in the criteria's and is therefore reliable.

No conclusions could be drawn based on trial 2 since the methane production for both positive controls were under the minimum level at 352 $mL/g_{vs.}$ Moreover, positive control 1 had a RSD on 14 % which is substantially higher than the limiting value at 5 %. All results from trial 2 can be seen in Table 17. It was also remarkable that the methane production differed a lot between the two positive controls. It does not matter that the two positive controls were in various AMPTS devices, because the BMP of the positive controls should be the same.

It is interesting to compare the inoculums from trial 1 and trial 2 since the methane production was much higher for the inoculum from trial 2 than trial 1. This can be seen by comparing Figure 19 from trial 1 and Figure 23 from trial 2. The figures show the total accumulated methane production. Furthermore, Figure 20 and Figure 24 show the total accumulated methane production per VS. In both cases the inoculum methane production was higher for Figure 23 and Figure 24, both from trial 2. The reason for the big differences in methane production can probably be found in that the harvested inoculum had noticeable differences already at harvest time for trial 1 compared to trial 2: When the inoculum was taken from the anaerobic digester, there was observed that the conditions was different for trial 1 and trial 2. When inoculum was taken for trial 2 the sludge level was lower in the reactor compared, when inoculum was taken for trial 1. Moreover, the inoculum used for trial 2 was more porous and foamy than for trial 1. It is possible that it was foaming in the reactor when inoculum was taken for trial 1.

Therefore, it would be most interesting to know what types of compounds that were located on the surface layer of the digester when the inoculum was taken. Probably there were considerably more fatty acids in the surface layer when inoculum was taken for trial 2 than there was at trial 1. That would explain why the methane production was higher in trial 2 since fatty acids have a high BMP. Moreover, fatty acids contain a certain amount of volatile fatty acids (VFAs). It is known that VFAs evaporate in a 105 °C oven (Vahlberg *et al.*, 2013) and an increased amount of VFA would therefore not be included in the VS weight for trial 2 although it is an organic compound. In other words, the VS value for the inoculum in trial 2 should have been greater than is showing in Table 2. From this follows that the VS amount of inoculum added in the samples in trial 2 was in fact higher than what is shown in Table 11. Hence, BMP (measured per g VS) the methane production should have been lower for the triplicates in Figure 23 and Figure 24 except for the blanks in Figure 23 since the blank did not related to any substrate.

The overestimated methane production for the inoculum in trial 2 should not have any impact on the figures where the inoculum was excluded, since the same inoculum were in the blank triplicate as in the other triplicates for trial 2 (except for the triplicates with adapted inoculum). When the inoculum was excluded there was the other way around though. There was higher methane production in trial 1 than trial 2 for all substrate triplicate (except for hydrochar), see Figure 21 and Figure 25. Both positive controls had lower methane production in trial 2 than the positive control in trial 1. It also can be seen that all substrates in Figure 21 had higher methane production than the substrates in Figure 23, expect for the substrate with adapted inoculum and the substrate with hydrochar that was not tested in trial 2. However, it is difficult to draw any conclusions since the triplicates in trial 2 were mixes of process water and primary sludge whereas only single substrates were tested in trial 1. The adapted inoculum from trial 2 seem to have an inhibitory effect on the substrate´s methane production based on Figure 25. But once again the results in trial 2 are not statistically reliable.

From Figure 25 (SO1, SO3 and SO4) it can be established that the triplicate with the smallest amount process water (SO3) had the highest methane production per g VS and the triplicate with the greatest amount process (SO4) had the lowest methane production per g VS. SO1 that had more process water then SO3 but less process water than SO4

was between SO3 and SO4 in terms of methane production per g VS. That would indicate that the process water had an inhibitory effect when mixed with primary sludge. The exception was when primary sludge and process water were mixed with adapted inoculum (scenario 2). Scenario 2 had the highest methane production apart from one of the positive controls (CM1). The first conclusion which could be drawn based on Figure 25 was that process water had an inhibitory effect when mixed with primary sludge and ordinary inoculum was used. The second conclusion was that process water did not have inhibitory effects when adapted inoculum was used. The adapted inoculum was adapted since the adapted inoculum had been used to anaerobically digest process water and hydrochar earlier in trial 1. The bias against that process water had an inhibitory effect at all, was in trial 1 (Figure 21), no inhibitory effect could be noted for the substrate process water. See Table 8 for the approximate amount process water added to the samples and for the exactly amount process water added to the samples, see Table A1.

It should be pointed out that the BMP value for process water presumably might be an overestimation compared to if the methane production had been normalized against another parameter than VS, the reason for that is the same as for the inoculum in trial 2. In the HTC process, long carbon chains are broken down to smaller which also included fatty acids chains. Many of the short fatty acids are VFAs. Hence, process water contains significantly higher concentration of VFAs than for example primary sludge. That would have most effect on the process water triplicate in trial 1, Figure 21. The other triplicates that included process water in trial 2, had smaller amounts of process water and would therefore not be affected to the same degree.

It can be seen from Figure 25, that triplicate SO2 have different appearance compared to the other triplicates in Figure 25. SO2 had a methane production which was almost linear whereas the other had a production process that were more expected. Moreover, it can be seen from Figure 26 that SO2 had the maximum production around 9 days, all the other triplicate had the maximum production between 1 to 3 days. The difference with SO2 was that the adapted inoculum was used instead of ordinary inoculum. There is difficult to come up with an adequate explanation for SO2 distinctive appearance. One explanation for the linear appearance could be that only a small group of the microorganisms accounted for the greater majority of the methane production. This group of microorganisms had, for some reason, problems with reproducing or were otherwise inhibited which the capped the maximal methane production rate compared to the other samples.

5.2 DISCUSSION THEORETICAL ESTIMATION

If all digestate underwent HTC treatment and the process water produced was returned to the anaerobic digestion process, the methane production could theoretically increase with 8.1 % (section 3.2), if no synergetic effects are considered. See Equation 39. A precondition for this, is that the anaerobic digesters can handle the extra load of process water. No synergetic effect from trial 2 can be concluded, in terms of the mixes of primary sludge and process water. Additionally, trial 2 is not statistically reliable. The methane production would probably become a bit smaller than 8.1 % increase since the

HRT will decrease with an increase of substrate to the anaerobic digester. In other words, the level of degradation of the substrate will decrease when the microorganisms have less time to decompose it. Henriksdals WWTP had an HRT of approximately 18 days during 2016. This calculation is based on primary sludge and secondary sludge fed into the reactor during 2016. These are the two primary substrates, but there is also a small amount of other substrate e.g. lipids which was fed into the reactor. Grease trap removal sludge has not been taken into account when the HRT was calculated. Therefore, the HRT would in the practice be a little bit smaller than 18 days. It can be seen from Figure 21 that the methane production for primary sludge was very low after 15 days. The reduction of HRT therefore would therefore likely only have minimal impact on the methane production.

The result from the theoretical full-scale scenario in section 4.2 show that the methane production at Henriksdals WWTP could increase with 10 % if all produced digestate was used in HTC process and if the produced process water was recirculated into the digesters. It was expected that the theoretical full-scale scenario would have a larger methane production than the laboratory scenario because the theoretical full-scale scenario had a more effective dewatering of hydrochar. In the theoretical full-scale scenario, TS for process water (in percent) was recalculated according to Equation 41. In the laboratory scenario TS was 3.1 % and in theoretical full-scale scenario TS was 3.2 %. However, it was assumed that the VS value (ratio between VS weight and TS weight) was the same for the laboratory scenario and theoretical full-scale scenario. This assumption was necessary because no process water from a full-scale HTC facility was available since a full-scale HTC facility do not exist in Sweden for the moment. This assumption would probably disfavor the theoretical full-scale scenario because in theoretical full-scale the digestate is diluted with process water (see Figure 17). The literature is indicating that inorganic in the digestate remains within the hydrochar (see section 2.8.7). Therefore, when process water is used for dilution, the inorganic in the process water has several chances to end up in the hydrochar. That would suggest that the process water in the full-scale scenario would have a higher VS (ratio between VS weight and TS weight) compared with the laboratory scenario. Furthermore, in the full-scale scenario a more advanced filtration technique would be used, like filter presses. It is possible that a more advanced filtration will enhance the VS value (ratio between VS weight and TS weight) for the process water.

The recirculation of process water for dilution of digestate in the theoretical full-scale scenario will change the properties for the process water compare with the process water from the laboratory scenario. The enhanced TS value, 3.1 % for laboratory scenario process water and 6.2 % for the theoretical full-scale scenario process water, is already mentioned. It is also possible that inhibitory compounds are accumulated in the process water for the theoretical full-scale scenario because of the recirculation. In the BMP test with process water in trial 1 and trial 2, laboratory process water was used and in laboratory scale there is no recirculation of process water. Therefore, it cannot be excluded that recirculated process water has an inhibitory effect if anaerobic digested. BMP test for recirculated process water is therefore needed.

It should be noted that Figure 17 which was used for the calculations for theoretical full-scale scenario is based on estimations by C-Green. How well this estimation correspond to the actual situation can first be seen when C-Green is done with their pilot plant.

6 CONCLUSION

It can be concluded from trial 1 that process water had no inhibitory effects when mixed with inoculum. On the contrary, process water had almost the same BMP as primary sludge. It cannot be concluded if process water would have an inhibitory effect if it was added to an anaerobic digester. Because the results from the co-digestion experiments designed to simulate the full-scale scenario with a mix of process water and primary sludge in trial 2 were inconclusive. However, according to these trials it would be unlikely that process water had inhibitory effects. The BMP for hydrochar was 150 ± 5 % NmL/g_{vs} and the BMP for process water was 335 ± 10 % $NmL/g_{vs.}$ The process water would have a positive effect on the methane production at a WWTP if it is assumed that process water had the same BMP as in trial 1. The calculated estimated increase in methane production for Henriksdals WWTP would be between 8.1 % and 10.0 % for 2016, depending on the degree of dewaterability of the HTC hydrochar.

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8 APPENDIX

In Table A1 and Table A2 the amount of inoculum and substrate for each sample are described. Table A1 is for trial 1 and Table A2 is for trial 2.

Table A1 All weighted substrate and inoculum.

Number	Description	Substrate (g)	Inoculum (g)
1	Inoculum	0	400
2	Inoculum	0	407
3	Inoculum	0	400
4	Inoculum+Primary sludge	79	330
5	Inoculum+Primary sludge	82	318
6	Inoculum+Primary sludge	81	332
7	Inoculum+process water	77	328
8	Inoculum+process water	77	322
9	Inoculum+process water	79	324
10	Inoculum+microcrystalline cellulose	3	398
11	Inoculum microcrystalline cellulose	3	399
12	Inoculum microcrystalline cellulose	3	396
13	Inoculum+hydrochar	16	386
14	Inoculum+hydrochar	16	385
15	Inoculum+hydrochar	16	385

Table A2 Weighed amounts of substrate and inoculum for trial 2. Substrate1 is either microcrystalline cellulose or primary sludge. Substrate 2 is process water.

Name	Sample	Inoculum (g)	Substrate1 (g)	Substrate2 (g)
Inoculum	1	399.20	-	-
Inoculum	2	398.90	-	-
Inoculum	3	395.00	-	-
Adapted inoculum	4	407.41	-	-
Adapted inoculum	5	398.50	-	-
Adapted inoculum	6	400.30	-	-
Inoculum+Microcrystalline cellulose	7	396.23	2.89	-
Inoculum+Microcrystalline cellulose	8	398.35	2.89	-
Inoculum+Microcrystalline cellulose	9	402.09	2.89	-
Inoculum+PS+PW Scenario 1	10	316.88	87.32	5.57
Inoculum+PS+PW Scenario 1	11	317.77	76.71	5.89
Inoculum+PS+PW Scenario 1	12	318.30	79.43	8.50
Adapted inoculum+PS+PW Scenario 2	13	325.14	71.31	6.19
Adapted inoculum+PS+PW Scenario 2	14	334.26	70.10	11.28
Adapted inoculum+PS+PW Scenario 2	15	249.61	54.43	5.23
Inoculum+PS+PW Scenario 3	16	318.29	85.50	5.06
Inoculum+PS+PW Scenario 3	17	318.44	76.12	6.53
Inoculum+PS+PW Scenario 3	18	317.13	77.51	5.25
Inoculum+PS+PW Scenario 4	19	320.73	72.80	7.27
Inoculum+PS+PW Scenario 4	20	318.76	72.85	7.68
Inoculum+PS+PW Scenario 4	21	317.08	73.95	7.17
Inoculum Microcrystalline cellulose	22	397.79	2.89	-
Inoculum Microcrystalline cellulose	23	396.61	2.89	-
Inoculum Microcrystalline cellulose	24	399.22	2.89	-

The methane production for each sample in trial 1 can be seen in table Table A3 and the methane production for each sample in trial 2 can be seen in Table A4

Table A3 The amount of weighed VS in each sample and the total CH_4 production for each sample. The methane production is presented as final yield and BMP. The values in final yield have not been divided with the VS weight and the values in BMP have been divided with the VS weight.

Number	Description	Feeding amount (g VS)	Final yield (NmL) CH_4	BMP CH_4 (NmL/g_{vs})
1	Inoculum	5.8	764	131
2	Inoculum	5.9	824	139
3	Inoculum	5.8	752	129
4	Primary sludge	2.3	802	346
5	Primary sludge	2.4	816	339
26	Primary sludge	2.4	816	344
7	Process water	2.4	732	310
8	Process water	2.3	872	371
9	Process water	2.4	779	324
10	Microcrystalline cellulose	2.9	1029	355
11	Microcrystalline cellulose	2.9	1057	363
12	Microcrystalline cellulose	2.9	1081	372
13	Hydrochar	2.8	407	148
14	Hydrochar	2.8	400	145
15	Hydrochar	2.8	433	157

Table A4 The terminal amount of CH_4 present as final yield and BMP. Moreover, the substrate and inoculum in VS. Substrate/IM can be IM, adapted IM, CM 1, PS or CM 2. Substrate is strictly PW. IM, CM, PS, PW stands for inoculum, Microcrystalline cellulose, primary sludge and process water. The number before CM describes which AMPTS device the positive control was located in. 1 was the AMPTS device with 5 triplicate and 2 was the AMPTS device with 3 triplicate.

Number	Description	Substrate/IM (g VS)	Substrate (g VS)	Final yield (mL) CH_4	BMP CH_4 mL/g_{vs}
1	IM	6.6	-	1449	219
2	IM	6.6	-	1333	201
3	IM	6.6	-	971	148
4	Adapted IM	5.3	-	208	39
5	Adapted IM	5.2	-	196	38
6	Adapted IM	5.2	-	224	43
7	CM 1	2.8	-	925	334
8	CM 1	2.8	-	1004	362
9	CM 1	2.8	-	757	273
10	PS+PW (SO 1)	2.4	0.17	642	253
11	PS+PW (SO 1)	2.1	0.18	575	254
12	PS+PW (SO 1)	2.2	0.26	547	226
13	PS+PW (SO 2)	1.9	0.19	677	318
14	PS+PW (SO 2)	1.9	0.34	703	312
15	PS+PW (SO 2)	1.5	0.16	480	293
16	PS+PW (SO 3)	2.3	0.15	752	304
17	PS+PW (SO 3)	2.1	0.20	614	271
18	PS+PW (SO3)	2.1	0.16	563	249
19	PS+PW (SO 4)	2.0	0.22	465	212
20	PS+PW (SO 4)	2.0	0.23	403	182
21	PS+PW (SO 4)	2.0	0.22	513	230
22	CM 2	2.8	-	703	253
23	CM 2	2.8	-	743	268
24	CM 2	2.8	-	708	255