

**Master's thesis**

**Effects of biochar addition on anaerobic digestion and  
comparison of different biochar qualities**

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## TIIVISTELMÄ

Tässä pro gradu -työssä tutkittiin, voidaanko anaerobisen mädätyksen toimintaa parantaa lisäämällä mädätysprosessiin pieniä määriä biohiiltä. Anaerobista mädätystä tutkittiin laboratoriomittakaavan biokaasukokeilla, joissa biokaasureaktoreita käsiteltiin sekä pyrolyyttisesti että hydrodermaalisesti tuotetulla biohiilellä. Biohiilen mahdolliseen kykyyn lievittää ammoniakki-inhibitiota kiinnitettiin huomiota. Seitsemän pyrolyyttisen ja yhden hydrodermaalisesti tuotetun hiilen ominaisuuksia vertailtiin, jotta voitaisiin määrittää soveltuvia biohiiliä anaerobiseen mädätykseen. Biohiilistä analysoitiin ammonium-adsorptiokapasiteetti, irtoavan liukoisen orgaanisen kokonaishiilen (DOC) ja liukoisen kokonaistypen (DTN) määrä sekä PAH-yhdisteiden määrä.

Ammonium-adsorptiokapasiteetin mittaukset osoittivat, että biohiilet kykenevät adsorboimaan ammonium-ioneja, mutta tunnettuun ammonium-adsorbenttiin zeoliittiin verrattuna adsorptio oli vähäisempää. Zeoliitin ja biohiilten adsorptio vaihteli välillä 5,0–17,3 mg/g ja 0,8–4,4 mg/g adsorbenttien konsentraatiosta riippuen. Korkea adsorptiokapasiteetti olisi hyödyllinen ammoniakki-inhibition lievittämisen kannalta. Irtoavat DOC- ja DTN-määrät olivat välillä 8,9–6397 mg/l ja 0,83–2705 mg/l. Biohiilten PAH-määrät vaihtelivat välillä 1,6–190 mg/kg ja joidenkin näytteiden korkeat arvot osoittivat, että haitta-aineisiin tulee kiinnittää huomiota, jos mädäte hyödynnetään maanparannusaineena. Biohiilten ominaisuuksien todettiin riippuvan valmistusprosessista ja -materiaalista, ja näitä optimoimalla voi olla mahdollista valmistaa anaerobiseen mädätykseen paremmin soveltuvia biohiiliä.

Biokaasukokeiden perusteella pyrolyyttisellä biohiilellä ei ollut merkittävää vaikutusta metaanin tuotantoon, kun taas hydrodermaalinen biohiili paransi sitä. Hydrodermaalista biohiiltä lisättiin sekä normaaliin että ammoniumilla lisättyyn syötteeseen. Molemmissa olosuhteissa hydrodermaalinen biohiili lisäsi metaanintuotantoa kontrolleihin verrattuna (15 % ja 26 %). Koska biohiilten ammonium-adsorptiokapasiteetti oli rajallinen, hyvät vaikutukset voivat johtua muista mekanismeista. Hydrodermaalinen biohiili on biohajoavampi pyrolyyttiseen biohiileen verrattuna, mikä voi selittää tuloksia. Lisätty hiilimäärä oli 4,5 % syötteen tuorepainoon verrattuna, ja tällaisella määrällä todettiin olevan vaikutuksia metaanintuotantoon. Toisaalta kokeissa oli tilastollisia epävarmuustekijöitä, joiden vuoksi tuloksia tulee tulkita varovaisesti. Jatkotutkimuksia useammilla rinnakkaisilla näytteillä tulisi tehdä havaintojen varmistamiseksi ja tilastollisesti pätevien tulosten saamiseksi.

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Key words: anaerobic digestion, biochar, hydrochar, pyrolysis, hydrothermal carbonization, biogas, bioenergy, methane, ammonia inhibition, ammonium adsorption, waste management, organic waste, digestate, PAH compounds

## ABSTRACT

In this thesis, the effects of biochar addition on anaerobic digestion were studied to find out could biochar enhance the methane production. Both pyrolytic biochar and hydrothermally carbonized hydrochar were applied to anaerobic digesters in laboratory scale biogas experiments. The possible ability of biochar to mitigate ammonia inhibition was addressed. Seven pyrolytic biochars and one hydrochar were compared to find suitable biochars for anaerobic digestion. The ammonium adsorption capacity, nutrient release in respect of dissolved organic carbon (DOC) and dissolved total nitrogen (DTN), and polycyclic aromatic hydrocarbons (PAHs) were analyzed from the biochar samples.

Ammonium adsorption capacities showed that biochars could adsorb ammonium ions but compared with a well-known ammonium adsorbent zeolite the adsorption was lower. The adsorption in zeolite varied between 5.0–17.3 mg/g and in biochars 0.8–4.4 mg/g depending on the adsorbent concentration. High adsorption capacity could be useful in mitigating ammonia inhibition. All the biochars released DOC and DTN in the range of 8.9–6397 mg/l and 0.83–2705 mg/l. The PAHs in the biochars varied in the range of 1.6–190 mg/kg and high levels in some biochars showed that focus on contaminants must be considered, if the produced digestate is utilized as soil amendment. Characteristics of biochars seemed to vary depending on the feedstock and manufacturing methods, and therefore the optimization of biochars could be beneficial when considering their use in anaerobic digestion.

In biogas experiments the pyrolytic biochar did not have a significant effect on the methane production, while the hydrochar seemed to enhance it. Hydrochar was applied to normal feedstock and to feedstock with increased ammonium concentration. In both conditions the cumulative methane production was higher in hydrochar treated groups (15 % and 26 % respectively). Due to the limited ammonium adsorption capacities of the biochars it is possible that the good effects of the hydrochar were based on other mechanisms. Hydrochar has higher biodegradability compared with pyrolytic biochar and this could explain the better results. The applied hydrochar dosage was 4.5 % compared to the feedstock fresh weight and with this kind of dosage differences in the methane production were observed. On the other hand, the experiments have statistical limitations and the results must be interpreted with a high caution. Further experiments with more replicates and statistical analyses should be done to ensure the observations and get scientifically reliable results.

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Appendix 1. The values of biochar ammonium adsorption capacities.

Appendix 2. The values of nutrient release (DOC and DTN) from biochars.

Appendix 3. The values and composition of 15 PAHs in biochars.

## **ABBREVIATIONS**

BMP	Biomethane potential
COD	Chemical oxygen demand
DIET	Direct interspecies electron transfer
DOC	Dissolved organic carbon
DTN	Dissolved total nitrogen
HTC	Hydrothermal carbonization
ISR	Inoculum to substrate ratio
SCOD	Soluble chemical oxygen demand
PAH	Polycyclic aromatic hydrocarbon
TAN	Total ammoniacal nitrogen
TKN	Total kjeldahl nitrogen
TS	Total solids
TOC	Total organic carbon
VFA	Volatile fatty acid
VS	Volatile solids
WWTP	Waste water treatment plant

## 1 INTRODUCTION

Earth is facing major problems in the near future. A clear majority of the scientists in the world approves that climate change is happening and that it can have severe effects on the world we know today (Chiras 2013). Climate change results mainly from the anthropogenic use of fossil fuels which has increased the amount of carbon dioxide, which acts as a greenhouse gas in our atmosphere (Boyle 2004). To prevent the threatening climate change, greenhouse gas reductions in the range of 60-80 % are needed in the end of the 21st century and ultimately, a switch to low- or zero-carbon energy sources (Boyle 2004). Renewable energy sources include solar, wind, hydro, tidal, geothermal and bioenergy. Bioenergy is energy that is produced from biological sources, for example from plants or biological wastes (Wall et al. 2008). One form of bioenergy is biogas made with anaerobic digestion from biological materials and it can be used in the production of heat and electricity or fuel in biogas cars (Abbassi et al. 2012). Additionally anaerobic digestion plays an important role in the waste management since in addition of energy recovery it is a method for organic waste management and pollution control (Chen et al. 2008). In Finland since the beginning of 2016 the legislation (2013/331) has forbidden the placement of organic waste (over 10 % organic material) to the landfills, so there exist legal obligations to treat the organic waste separately. Additionally, with separate treatment of the organic waste and anaerobic digestion it is possible to reduce environmental impacts on the landfills and use waste to generate energy (Williams 2006). The remaining digestate from the process can be used as a fertilizer or feedstock for composting since it is rich in nitrogen and phosphorus (Holm-Nielsen et al. 2009).

Energy production with anaerobic digestion can be described as a mature technology, since it has been established already for some decades and the research around the topic has been intense (Mata-Alvarez et al. 2000). Even though the idea is not new, there still exists the problem that commercial anaerobic digestion processes are often operated below their optimal performance (Ward et al. 2008). By optimizing the process in different ways, for example controlling the carbon-nitrogen ratio of the feedstock or by using additive materials, it is possible to improve the yield and the quality of produced biogas (Ward et al. 2008). These results as resource efficiency, improved economic sustainability, and increased amount of renewable energy, and therefore the methods that improve the process are worth to study.

Biochars are stable and solid carbon-rich material obtained from thermochemical conversion of biomass in oxygen-limited environment (IBI 2012) and in recent years there has been a lot of discussion about their applications related to soil amendment, waste management, and energy production (Lehmann & Joseph 2015). Lately biochar has also been studied as an additive material in anaerobic digestion. This is relatively new topic but already some research in this field exists. According to these studies (Cai et al. 2016, Luo et al. 2015, Mumme et al. 2014) the possible effects of biochar on anaerobic digestion process in terms of stability, higher biogas yields and inhibition problems are worth studying.

The integration of biochar and biogas production promises several synergies, for example the digestate from anaerobic digestion could be a suitable feedstock for biochar production (Mumme et al. 2014) and the remaining biochar in the digestate could serve as a soil improver if the digestate is composted (Luo et al. 2015). These kinds of systems would promote nutrient recovery and circular economy, which are important concepts in Finland and globally at the moment. Together with the government the Finnish Ministry of Environment has launched a key project relating to nutrient recovery and one main theme is the utilization of organic wastes and digestate derived soil amendments (Finnish Ministry of Environment 2016). Also, the European Commission has set an action plan for the circular economy, which highly promotes waste management, food waste utilization and from waste to resources philosophy (2015/614/COM). Also these make the research of issues of these kind relevant.

In this thesis, the effects of biochar addition to anaerobic digestion were studied and different biochars were compared. The thesis was made as a collaboration between the University of Jyväskylä and the Helsinki Region Environmental Services Authority (HSY) and it was a part of the Material Value Chains (ARVI) research program. The objective of ARVI program is to research systemic assessment of material recovery and recycling opportunities. The program consists of 29 organizations and it includes both companies and research and public organizations. In addition, the effects of biochar on composting had been studied before as a part of HSY Kombi-project and based on this the effects in anaerobic digestion also wanted to investigate.

## 2 BACKGROUND AND THEORY

### 2.1 Principles of biogas formation via anaerobic digestion

Anaerobic digestion is a process, where micro-organism break down and convert organic material into biogas in the absence of oxygen (Ryckebosch et al. 2011). Anaerobic digestion occurs naturally in soils and in lake and ocean sediments (Koyama 1963) but nowadays industrial biogas is also produced for example in sewage treatment plants, landfills, and waste digestion plants (Ryckebosch et al. 2011). Biogas consists mainly on methane (55–70 %) and carbon dioxide (30–40 %) and small traces of other gases, for example nitrogen, water vapour, ammonia, and hydrogen sulphide (Rasi et al. 2007). Methane has a high calorific value compared with the other components of the biogas and in some cases it can be separated from the other gases to get biomethane, which is suitable for fuel or for injection in the natural gas grid (Ryckebosch et al. 2011).

Biogas production with anaerobic digestion is a complex process that can be roughly divided into four phases called hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Abbasi et al. 2012). Each phase is carried out by different micro-organism group (Deublein & Steinhauser 2011).

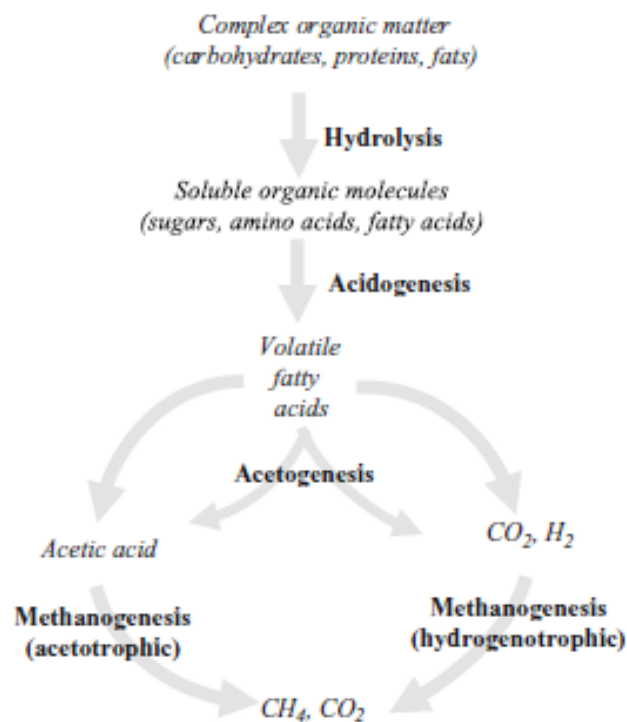


Fig. 1. The phases of biogas production through anaerobic digestion (Abbasi et al. 2012).



In hydrolysis the complex compounds of organic material are broken down by micro-organisms into smaller water soluble molecules called monomers (Angelidaki & Sanders 2004). Long-chain carbohydrates are broken down into short-chain sugars, proteins into amino acids, and fats into fatty acids and glycerin (Deublein & Steinhauser 2011). In the acidogenic phase, the monomers formed previously are degraded by anaerobic bacteria (Deublein & Steinhauser 2011). The resulting products are short-chain organic acids, alcohols, hydrogen, carbon dioxide, nitrogen oxide, and hydrogen sulphide (Deublein & Steinhauser 2011). In the acetogenic phase, the previous products serve as substrates for acetogenic bacteria via two pathways (Deublein & Steinhauser 2011). Acetogenic bacteria can reduce  $\text{CO}_2$  by  $\text{H}_2$  to acetic acid or they can formate acetate by oxidising short-chain organic acids or alcohols and as a by-product  $\text{H}_2$  and  $\text{CO}_2$  is formed (Deublein & Steinhauser 2011). The final phase is methanogenesis, where methane formation takes place via carbonate respiration (Abbasi et al. 2012). Two main pathways are aceticlastic and hydrogenotrophic methanogenesis (Wall et al. 2008). Hydrogenotrophic pathway occurs when methane is generated by reduction from  $\text{CO}_2$  by  $\text{H}_2$  (27–30 % of production) and aceticlastic pathway occurs when methane is generated by reduction from acetate in the presence of water (70 % of production) (Deublein et al. 2011). Also some other minor pathways exist, for example methyl-type formation (Wall et al. 2008).

## **2.2 Factors affecting the anaerobic digestion**

### **2.2.1 Overview**

The conditions in the anaerobic digester must be suitable for the micro-organism to keep the process working properly (Deublein & Steinhauser 2011). Therefore, a variety of parameters must be taken into consideration and especially the needs of the methanogenic bacteria must be fulfilled with care, since they are very sensitive to environmental factors and have a low growth rate (Weiland 2010). The most important parameters include pH, the temperature, substrate type and composition, and operational parameters like volume load, cultivation and mixing (Zhang et al. 2014).

### **2.2.2 Temperature**

Anaerobic digestion can be divided into mesophilic (35–42 °C) and thermophilic (45–60 °C) process because two temperature optimal for different micro-organisms exist (Weiland 2010). Methanogenic diversity is greater at mesophilic temperatures and therefore thermophilic process is more sensitive to rapid temperature changes (Deublein & Steinhauser 2011, Weiland 2010). Even variations in the range of  $\pm 2$  degrees °C can cause significant

changes in microbial activity (Deublein & Steinhauser 2011). Both thermophilic and mesophilic conditions are widely used in anaerobic digestion plants. Thermophilic conditions possess higher degradation rate of the organic solids (Kim et al. 2002) and better microbial activity (Deublein & Steinhauser 2011), which result in higher biogas yields. It also serves better in the deactivation of pathogens (Song et al. 2004) and additional hygienic procedures are not necessarily needed (Deublein & Steinhauser 2011). On the other hand, mesophilic conditions possess better process stability since micro-organisms are not so sensitive to environmental changes (Zhang et al. 2014). Mesophilic process also has better energy balance and reduced ammonia inhibition due to the lower free ammonia production (Deublein & Steinhauser 2011).

### 2.2.3 pH

Methane formation occurs in the range of 6.5–8.5 and the optimal pH for the micro-organisms is 7.0–8.0 (Weiland 2010). If the pH decrease below 6.0 or rises above 8.5 the process is inhibited and microbial activity decreases, which result as lower biogas yields (Weiland 2010). The main mechanism that affects the pH is the fermentation products that release free hydrogen ions into solution, for example the acidification of hydrocarbons, proteins and fatty acids (Deublein & Steinhauser 2011). There are natural buffering systems that resist the pH change. The bicarbonate buffering system prevents too strong acidification and the ammonia buffering system too strong basification (Deublein & Steinhauser 2011, Ward et al. 2008). Both systems can be overloaded for example by feeding too acid or toxic substances, by a decrease in temperature, or by a too high loading rate (Deublein et al., 2011). Increased pH value can often be linked to ammonia accumulation whereas decreased pH results from VFA accumulation (Weiland, 2010). Usually, a first sign of acidification is an increasing propionic acid concentration and ultimately this leads to a fall in the pH-value and a rise in the CO<sub>2</sub> in the biogas, which is a sign of inhibition in the process (Deublein & Steinhauser 2011).

### 2.2.4 Substrate type and composition

All kinds of biomass that contain carbohydrates, proteins, fats, cellulose or hemicellulose as the main components can be used in anaerobic digestion (Weiland 2010). The time and difficulty of the degradation depends on the composition of substrate (Deublein & Steinhauser 2011) and determines whether they are suitable for anaerobic feedstock. For example, lignified organic substances (e.g. wood) degrade very slowly and are not good feedstocks for anaerobic digestion (Weiland 2010). Some substances, for example short chain

sugars and carbohydrates, degrade in very short time while for others, like substances rich in cellulose and hemicellulose, it might take as much as 20 days (Deublein & Steinhauser 2011). Different feedstocks provide different amounts of biogas and this can be estimated with biomethane potential (BMP) test (Ward et al. 2008).

The composition of the feedstock is important since micro-organisms need enough macronutrients (C, N, P, and S), micronutrients, and trace minerals (Deublein & Steinhauser 2011). If an important substrate component runs out, the micro-organisms stop their metabolism and therefore it is useful to feed the process with possibly lacking substances (Deublein & Steinhauser 2011). A rough estimate for the optimal nutrient balance is the C:N ratio since these are the most important macronutrients in the process (Wang et al. 2014). The ratio should be well balanced to keep the process working properly and the recommended value is 15:1–25:1 (Weiland 2010). A too low ratio can lead to ammonia accumulation and inhibition and on the other hand too high ratio means the lack of nitrogen for the micro-organisms (Deublein & Steinhauser 2011).

#### 2.2.5 Operation parameters

The most important operation parameters include reactor type, volume load, residence time, and mixing (Deublein & Steinhauser 2011). Reactors are usually classified between the batch and continuously fed reactors. In batch reactors, the digester is filled once and during the residence time no substrate is added or taken out, whereas in the continuous process the reactor is constantly fed and material is taken out (Deublein & Steinhauser 2011). The volume load in continuous processes is expressed as organic loading rate, which is the daily recommended feedstock supply in TS or VS per digester volume. High organic loading rates are ideal for the cost reasons and for the maximum volume of biogas (Ward et al. 2008) but on the other hand they should be reasonable to prevent reactor overload and to get the best possible output (Deublein & Steinhauser 2011). Residence time is expressed as hydraulic retention time and it tells how long the feedstock stays in the reactor before it is taken out as a digestate (Abbasi et al. 2012). The retention time should be long enough to cover the whole methanogenesis to prevent biogas losses (Deublein & Steinhauser 2011). Usually hydraulic retention times of 15–20 days or even more are required, depending on the degradation rate of the feedstock (Deublein & Steinhauser 2011). Mixing is usually applied to ensure the efficient transfer of organic material for the active microbial biomass, to release gas bubbles and to prevent the sedimentation of denser matter (Ward et al. 2008).

## **2.3 Wet and dry digestion**

Based on the medium total solids in the reactor anaerobic digestion can be separated into wet and dry digestion. In wet digestion, the total solids content in the reactor is usually less than 15 %, while in dry digestion the total solids in the reactor feed is 15–40 % (Bolzonella et al. 2006). Wet digestion offers more possibilities for suitable substrates and is especially applicable to substrates with high water content, whereas dry digestion is suitable for substrates with higher dry matter content (Deublein & Steinhauser 2011). Wet digestion is easier to regulate in terms of different process parameters, for example by pH and dry matter content (Deublein & Steinhauser 2011). Due to the greater water content, wet digestion offers better mixing possibilities and the substrate is easier to transport using pumps and allows easier application of multi-stage processes (Deublein & Steinhauser 2011).

A major drawback in wet digestion is the formation of digestate that requires dewatering and the amount of wastewater, which are significantly larger than in dry digestion (Guendouz et al. 2010). The more solid digestate resulting from dry digestion is easier to handle than liquid digestate from the wet process and it can be refined for example to the fertilizer or pelletized fuel (Li et al. 2011). Dry digestion is less energy intensive and it consumes less than 15 % of the energy produced, while in wet digestion this number can be 30–45 % (Guendouz et al. 2010). Also the advantages of dry digestion include smaller reactor size because it enables a higher organic loading rate (Guendouz et al. 2010). On the other hand, the retention times are usually slower and the feedback of inoculum to the fresh feedstock to speed up the reaction processes is sometimes necessary (Li et al. 2011).

## **2.4 Inhibition of the anaerobic digestion**

### **2.4.1 Overview**

Some substances even at very low concentrations have reported being inhibitory for anaerobic digestion (Chen et al. 2008). The inhibition depends on the concentration of the inhibitor, the composition of the substrate, and the adaption of the bacteria (Deublein & Steinhauser 2011). Usually, the bacteria needs the low concentrations of the inhibitors as their trace elements but high concentrations lead to inhibition (Deublein & Steinhauser 2011). Inhibition can disturb the anaerobic digestion and lead to the instability of the reactor, decreased biogas yield and even to a complete failure (Abbasi et al. 2012), which results in economic losses. Inhibitory substances are often found out to be the leading cause for process instability (Chen et al. 2008).

#### 2.4.2 Ammonia inhibition

In the digestion of nitrogen rich substrates, for example source separated biowaste, ammoniacal compounds play a vital role in the performance and stability of the process (Rajagopal et al. 2013). They are formed naturally in the degradation of nitrogen containing compounds, for example proteins (Deublein & Steinhauser 2011). It has been showed that small amounts of ammoniacal compounds are essential nutrients for bacterial growth but in higher concentrations they may inhibit the process leading to smaller biogas yields (Yenigün & Demirel 2013). Two principal ammoniacal compounds are free ammonia ( $\text{NH}_3$ ) and ammonium ion ( $\text{NH}_4^+$ ) and both can directly and indirectly cause inhibition (Yenigün & Demirel 2013). Particularly free ammonia is a powerful inhibitor and with larger concentrations it can even be toxic, while ammonium ion is not so harmful (Deublein & Steinhauser 2011).

The most important factors affecting the ammonia inhibition are initial nitrogen concentrations depending on the substrate, pH, and process temperature (Rajagopal et al. 2013). The extent of ammoniacal compounds depends on the pH because in higher pH the proportion of free ammonia increases, while in lower pH ammonium ion is the dominant form (Fig. 2). The equilibrium between free ammonia and ammonium ion is also temperature dependent (Fig. 2). The increase in the temperature shifts the equilibrium for the favor of free ammonia and therefore the inhibition increases with a rising temperature (Deublein & Steinhauser 2011). Ammonia is a more powerful inhibitor than ammonium ion, and therefore the effects of pH and temperature must be considered carefully (Sung & Liu 2003). Several methods of controlling the ammonia inhibition have been studied and the most known solutions are pH and temperature control, acclimation of microflora, the adjustment of the C:N ratio, and different additives (Rajagopal et al. 2013). According to Rajagopal et al. (2013) ammonia inhibition can exist already with TAN concentrations of 1500 mg/kg.

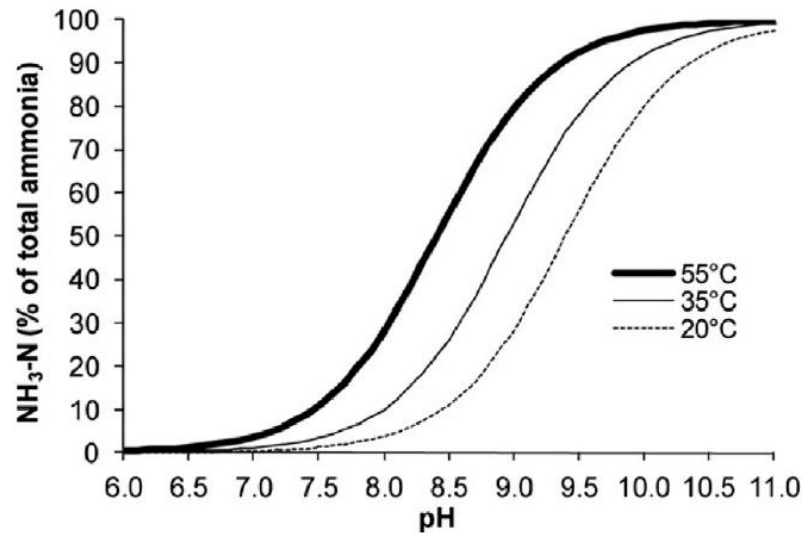


Fig. 2. The pH dependency of free ammonia in solution at 20, 35, and 55 °C (Rajagopal et al. 2013)

#### 2.4.3 Organic acids and volatile fatty acids (VFAs)

VFAs are degraded into acetic acid that serves as a substrate for a major pathway of methane production, but even though VFAs are essential for the process, too high concentrations can lead to the inhibition (Wang et al. 2009). Inhibition might occur due to hyperacidity, where the pH of the reactor decreases (Deublein & Steinhauser 2011). This can result from the too intensive feeding of the bioreactor, which leads to the accumulation of VFAs, which again leads to depletion in the buffering capacity and a decrease in pH (Chen et al. 2008). Ultimately, this leads to the distortion of the degradation and methanogenic microbial community (Chen et al. 2008). The phases of anaerobic digestion are closely linked with each other and if the first and second phases run too fast, the acid concentration rises due to fatty acids and pH-value drops (Deublein & Steinhauser 2011). It has been showed that even if pH would remain quite normal due to buffering capacity, the accumulation of VFAs may contribute to a reduced level of the hydrolysis of the solid substrate or even to an inhibition at very high levels (Siegert & Banks 2005).

#### 2.4.4 Other inhibition factors

In addition to these two main inhibition factors other sources of inhibition exists. Sulphur compounds have been found inhibitory because sulfate reducing bacteria that naturally occur in the system, competes over resources with methane forming micro-organisms (Chen et al. 2008). In addition high amounts of sulfide are toxic to various bacteria groups (Chen et al. 2008). Some light and heavy metal ions (for example sodium, potassium, lead,

and nickel) can also have toxic effects on higher concentrations, even though they are useful as trace elements (Deublein & Steinhauser 2011). Other sources of inhibition also exist, but they are not discussed further here.

## **2.5 Biochars and their production and properties**

### **2.5.1 Overview and production methods**

The International Biochar Initiative (IBI) has defined biochar as a stable and solid carbon-rich material obtained from the thermochemical conversion of biomass in an oxygen-limited environment (IBI 2012). Biochar is a relatively new scientific term, but the origins of biochar are said to be in the ancient human populations in the Amazon region where manmade rudimentary biochar was used to create dark soil called Terra Preta (Lehmann & Joseph 2015). Later research in these soils has revealed that biochar truly can act as a soil amendment and this has enhanced the research around biochars (Lehmann & Joseph 2015). In addition to acting just as a soil amendment, biochar is recognized as a significant tool in environmental management for example in the fields of waste management, climate change mitigation, and energy production (Lehmann & Joseph 2015).

Usually two different methods called pyrolysis and hydrothermal carbonization (HTC) are discussed when talking about the production of biochars. In addition of solid biochars, also liquid bio-oil and gaseous syngas (Table 1) is co-produced in both processes (Libra et al. 2011, Mohan et al. 2006). Pyrolysis is the most well-known and the used method in biochar production and it means the thermal decomposition of biomass in the temperature of 200–1000 °C with little or no oxygen (Demirbas & Arin 2002). Pyrolysis can be divided by the means of temperature and residence time and based on this it can be talked about fast pyrolysis, where residence time is only seconds, and slow and intermediate pyrolysis, where residence time is from a few minutes to several hours or even days (Mohan et al. 2006). The temperature between slow, intermediate and fast pyrolysis can vary, but in generally the faster the pyrolysis the higher the temperature (Table 1). Two special cases of pyrolysis are torrefaction, which is mild pyrolysis in the temperature of 230–300 °C (Prins et al. 2006) and gasification that happens in the temperatures above 800 °C in controlled oxygen/steam environment and results mainly in gaseous end-products (Mohan et al. 2006).

Table 1. Pyrolysis processes and their product distribution (Ahmad et al. 2014).

Process	Temp. (°C)	Residence time	Products		
			Liquid (bio-oil) %	Solid (bio-char) %	Gas (syn-gas) %
Fast	300-1000	Short (< 2 s)	75	12	13
Intermediate	≈ 500	Moderate (10-20 s)	50	25	25
Slow	100-1000	Long (5-30 min)	30	35	35
Gasification	> 800	Moderate (10-20 s)	5	10	85

HTC, sometimes called liquid pyrolysis, is also a thermochemical decomposition of biomass in the absence of oxygen but it is carried out under pressure and in the presence of a subcritical liquid phase (Libra et al. 2011). Usually, the temperatures are 180–250 °C and corresponding pressure up to approximately 20 bar (Libra et al. 2011). The biggest advantages of HTC are that the suitable feedstocks include biomasses with greater water content, for example sludge, and during the process the most of the feedstock used is transported into solids (Libra et al. 2011). Solids produced via HTC are usually referred to hydrochars to make a difference to biochars, because these two chars differ widely in chemical and physical properties (Bargmann et al. 2013).

Biochars made from different materials with different methods have unique properties, and one type of biochar may not be suitable for all purposes. The properties of biochars are mainly affected by production methods and these include pyrolysis temperature, residence time, heat transfer rate, and feedstock type. The most important properties governing the use of biochars are surface area, pore size distribution, and ion exchange capacity. In general the high pyrolysis temperatures favor biochars that are effective in adsorbing organic contaminants by increasing surface area, microporosity and hydrophobicity. On the other hand, biochars produced in low temperatures are better in removing inorganics and polar organic compounds by ion exchange capacity, electrostatic attraction, and precipitation (Ahmad et al. 2014).

### 2.5.2 Hydrochar from anaerobically digested sewage sludge

In recent years, anaerobic digestate has been studied as a feedstock material for hydrochar production and HTC is said to be a new and alternative method of treating different sludge materials and improve their properties (Libra et al. 2011). In HSY region approximately 85 000 t/a of dried sewage sludge digestate are produced and the number is expected to increase, since the population in the area grows (Castren et al. 2015). A new wastewater treatment plant (WWTP) called Blominmäki with high treatment capacity will be complet-



ed at 2020, and it will replace the older Viikinmäki WWTP (Castren et al. 2015). Currently, the dried sewage sludge digestate from WWTPs is composted and utilized as a soil amendment (Castren et al. 2015). HTC treatment of sludge digestate would be an interesting possibility alongside the traditional composting. It would not need an additional removal of the water from the sludge (Berge et al. 2011) but on the other hand, the treatment itself produces process water. Wirth & Mumme (2014) noted that the wastewater from HTC could be treated anaerobically, but in their case it was derived from corn silage. If the derived water has been subjected to anaerobic degradation before, probably the biogas yields are not very remarkable. There still exist some unsolved challenges but implementing the hydrochar production as a part of sludge and organic waste management could be potential, especially if the value of hydrochar could be increased for example in anaerobic digestion or composting.

According to the literature, it seems that anaerobically digested sludge is challenging feedstock, since the ash content of the sludge is usually high, which results in a low carbon content of the hydrochar. Kim et al. (2014) studied the HTC treatment of anaerobically digested sludge from a WWTP and their feedstock had carbon and ash contents of 38.55 and 26.06 %. The amounts of carbon and ash in the ultimate product were 39.98–48.45 % and 29.35–40.02 % depending on the HTC temperature (Kim et al. 2014). They suggested that 220 °C was the optimal temperature for HTC process based on the energy recovery efficiency (Kim et al. 2014). Berge et al. (2011) studied the HTC of different municipal waste streams including dried anaerobic digestate. The carbon and ash content in the feedstock were 32.6 and 35.9 % and in the hydrochar 27.8 and 55.8 % (Berge et al. 2011). On the other hand Mumme et al. (2011) produced hydrochar with relatively high carbon content from anaerobically digested maize silage. Different temperatures were applied and they found out that the yield and surface areas were the highest at 190 °C (Mumme et al. 2011). The carbon content in the feedstock was 45.8 % and in the hydrochar 59–79 % (Mumme et al. 2011). It seems that certain optimization potential in manufacturing exists.

### 2.5.3 Biochars as ammonium adsorbents

The ability of biochars to remove ammonium ions from matrices with high concentration has been addressed in few studies. This would be beneficial in anaerobic digestion since by adsorbing ammonium ions biochars could reduce the effects of ammonia inhibition. Kizito et al. (2015) studied the adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry with slow pyrolyzed wood and rice husks. The adsorption was studied in

leachate water separated from piggery slurry and in pure  $\text{NH}_4\text{Cl}$ -solution. They found out that the maximum adsorbed amount and removal percentages by wood biochar were 54.84 mg/g (73 %) from pure solution and 44.64 mg/g (60 %) from piggery slurry and with rice husk biochar 44.64 mg/g (60 %) and 39.8 mg/g (53 %) respectively (Kizito et al. 2015). The initial ammonium concentrations were 1400 mg/l and added biochar dosages 1–20 g/l (Kizito et al. 2015). On the other hand, some studies suggest lower values, so differences between biochar adsorption capacities exist. Sarkhot et al. (2013) studied effectiveness of biochar to adsorb ammonium from dairy effluent (ammonium concentration 0–1000 mg/l, biochar dosage 5 g/l) and they found out that up to 5.3 mg/g (18 %) of ammonium was adsorbed by the biochar. Also studies with lower initial ammonium concentration exist. Zhu et al. (2012) studied the removal of ammonium from aqueous solution by using activated carbons made from rice husks with initial ammonium concentrations of 40 mg/l. In their study, the adsorption varied between 2.04 and 0.97 mg/g depending on the biochar dosage (1–20 g/l) (Zhu et al. 2012).

The difference between the biochar ability to adsorb ammonium ions can depend on various factors. According to Kizito et al. (2015) increase in initial ammonium concentration, the temperature, smaller particle size, and contact time increase the adsorption. The adsorption decreased in low and alkaline pH and the best adsorption was found in the range of 6.5–7 (Kizito et al. 2015). The decrease in alkaline conditions can result from the conversion of ammonium to ammonia, which cannot be adsorbed very well onto biochars (Kizito et al. 2015). The manufacturing and feedstock also have a significant role in biochar characteristics (Ahmad et al. 2014) and especially biochars made in lower temperatures (250–400 °C) has been found suitable for removing inorganic and polar contaminants (Gai et al. 2014).

#### 2.5.4 Biochar nutrient release

Lehmann et al. (2011) suggests that the positive effects of biochar as a fertilizer are usually proposed due to biochar ability to adsorb and retain nutrients or also to nutrient release straight from the biochars themselves. According to Chan & Xu (2009) biochars are extremely variable in nutrient composition and the availability of these depends highly on the used feedstock and pyrolysis condition. If the biochars release useful nutrients in soil, the same kind of approach could work in the anaerobic digestion environment. This could enhance the productivity of anaerobic micro-organisms in the digester.

Mukherjee & Zimmerman (2013) studied the organic carbon and nutrient release from different biochars and they found out that biochars release nutrients into aqueous solution and that most of these are in organic form. The amounts of released DOC, nitrogen and phosphorus from three different biochars in simple horizontal shake experiment (0.5 g biochar in 40 ml leaching with speed of 150 rpm, 1 day incubation) were 355–4429 mg/kg, 0–302 mg/kg, and 187–1255 mg/kg (Mukherjee & Zimmerman 2013). They also noted that the release of nutrients depends on the manufacturing temperature and feedstock (Mukherjee & Zimmerman 2013). According to Knicker et al. (2010), the lower amounts of releasing nitrogen have been related to the minor amounts of nitrogen present in biochar. Chan & Xu (2009) suggest that to promote the use of biochars more consistent products with higher nutrient values and improved nutrient retention are desired. These kinds of biochars would probably be more beneficial also when considering the use in anaerobic digestion.

#### 2.5.5 Polycyclic aromatic hydrocarbons in biochars

Recently the possible contaminants and their bioavailability in biochars have also gained interest. Contaminants found in biochars are for example polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls, and some dioxins (Bucheli et al. 2015). Especially PAHs are the most widely discussed potential pollutant in biochars, since they are formed during combustion and pyrolysis and biochars are known to contain them sometimes significant amounts (Hale et al. 2012). Bucheli et al. (2015) highlights that if biochar is used as a soil improver or in any other purpose it must meet all applicable legislator demands. In recent years, IBI has published standards for the biochar definition and characteristics and they suggest the PAH guideline value of 6 mg/kg for biochars (IBI 2012). European Biochar Certificate (EBC) has published its own voluntary certificates and their value is 12 mg/kg for a basic grade biochar (EBC 2016). In Finland, the legislative values for contaminated soil can regulate the use of biochar. The lower and upper guideline values for PAHs are 30 and 100 mg/kg (2007/214). So far legislative values for PAHs in digestate and compost have not yet been implemented in Finland. According to Finnish Water Utilities Association (VVY 2013) the third draft of European Union directive 86/278/ETY suggests a value of 6 mg/kg. These are the guidelines, that can regulate the use of biochar in anaerobic digestion.

## **2.6 The use of additives and biochar in anaerobic digestion**

### **2.6.1 Overview**

Additives are substances that are fed to the anaerobic digester in low amounts. Their main task is to increase the efficiency of the process, but due to their low amount of biomass the additives itself contribute only marginally to an increase in the biogas yield (Deublein & Steinhauser 2011). Additives are for example trace minerals, micro- and macro-nutrients, buffering agents, compounds able to mitigate ammonia inhibition, and substances with high biomass immobilization capacity (Romero-Güiza et al. 2016). In generally it is possible to increase the biogas yield by 20–30 % by using additives (Deublein & Steinhauser 2011).

By adding trace minerals and micro- and macro-nutrients it is possible enhance the metabolism and promote the growth of bacteria, that results as an increase in the digester capacity, the general improvements of the digestion, and an increase in the biogas yield (Deublein & Steinhauser 2011). From additives that prevent ammonia inhibition especially zeolite has been studied and it has been found as a suitable material to improve the ammonia and ammonium ion equilibrium via adsorption (Montalvo et al. 2012). In addition, zeolites have proved to have high capacity for the immobilization of micro-organisms (Montalvo et al. 2012). According to Tada et al. (2005) the application of natural zeolite for anaerobic digestion containing high ammonia loads is beneficial. Almost all the natural zeolites studied could remove significant amounts of ammonium from the sludge and some of these enhanced also the methane production (Tada et al. 2005). Especially with high ammonia loads (4500 mg/l) natural modernite zeolite increased the biogas production more than four times compared to the control (Tada et al. 2005). A variety of other materials, for example carbon and charcoal, sand, polyurethane, and some synthetic membrane materials, has also been introduced to promote biomass immobilization in anaerobic digesters (Montalvo et al. 2012). Watanabe et al. (2013) studied the effects of cedar charcoal on anaerobic digestion of crude glycerol and found out improvement in microbial communities and the increase in the biogas yield.

### **2.6.2 Biochar as an additive in anaerobic digestion**

In recent years the research around biochars has been intense and focused especially in the use of biochar as a soil amendment (Lehmann & Joseph 2015), but recently the use as an additive in anaerobic digestion has also gained interest. According to Mumme et al. (2014) the high costs of biochar production are a major drawback to their broader use and one

way to overcome this could be to expand the biochar value chain in other applications, like as an additive in anaerobic digestion. Activated carbon has been studied as an additive material in anaerobic digestion with good results and according to Luo et al. (2015) biochar could have similar properties. Compared with activated carbon where the drawback is the even higher price, biochar is made in lower temperatures without activation, which results in less specific surface area but significantly cheaper price (Lehmann & Joseph 2015). Luo et al. (2015) suggests that biochar could provide relatively high surface area to immobilize micro-organisms and reduce inhibition via adsorption. In addition, the residual biochar in digestate could serve as soil improver if the digestate is composted or used as a fertilizer (Luo et al. 2015). The possible positive effects of biochar addition on biogas production would result in terms of process stability, higher methane yields, and fewer inhibition problems (Mumme et al. 2014).

The use of biochar in anaerobic digestion is a relatively new thing but already some research in this field already exists. Possible mechanisms to promote anaerobic digestion are for example the adsorption of inhibitive compounds, promoting direct interspecies electron transfer (DIET), and acting as an effective microbial immobilization method (Luo et al. 2015). Similarly, Mumme et al. (2014) and Cai et al. (2016) suggested that biochar could improve the immobilization of micro-organisms. Zhao et al. (2015) found out that biochar improved the methane production and accelerated the syntrophic metabolism of ethanol. Mumme et al. (2014) also pointed that biochar could be used to remove inhibitive ammonia and ammonium ions through adsorption and ion exchange on their reactive surfaces with feedstocks containing high amounts of nitrogen. Lü et al. (2016) also studied the effect of biochar on ammonium inhibition in anaerobic digester. Chen et al. (2014) suggested that biochar can promote DIET and this can help explaining why biochar may enhance methane production from organic wastes under anaerobic conditions.

In previous studies, the addition of pyrolytic biochar has usually had positive effects on anaerobic digestion. Luo et al. (2015) found out that pyrolytic biochar shortens the methanogenic lag phase and enhances the methane production rate and similar observations are also noted by Cai et al. (2016) and Lu et al. (2016). On the other hand, the effects of biochar on the overall methane yield in available studies (Cai et al. 2016, Lü et al. 2016, Luo et al. 2015) have been quite limited. Based on their results it seems that pyrolytic biochar effects the process by selectively enhancing microbial activity but does not affect that much the methane production. Studies also suggest that biochar could enhance the produc-

tion and degradation of intermediate and volatile fatty acids (Cai et al. 2016, Lü et al. 2016, Luo et al. 2015). In some studies, the biochar potential to mitigate ammonia inhibition has been addressed. Mumme et al. (2014) studied the effect of both pyrolytic and hydrochar to anaerobic digestion with several different TAN concentrations. Pyrolytic biochar had the ability to mitigate mild ammonia inhibition (2100 mg/kg TAN) but stronger inhibitions (3100-6600 mg/kg TAN) were not mitigated and in some cases the biochar containing fermentations followed the trend toward more serious inhibition (Mumme et al. 2014). The biochar-associated mechanisms that prevent ammonia inhibition are suggested being limited in their capacity (Mumme et al. 2014). Lü et al. (2016) found out that biochars of different particle sizes alleviate the ammonium inhibition up to 7 g-N/l during anaerobic digestion of 6 g/l glucose.

Also studies with limited or no effect of pyrolytic biochar on the gas production exist. Mumme et al. (2014) found out that pyrolytic biochar did not have clear effect on the biogas production while hydrochar increased methane yields. On the other hand, pyrolytic biochar had the ability to increase the bacterial and archaeal gene copy numbers and mitigate mild ammonia inhibition, but overall effects on the gas production were negligible (Mumme et al. 2014). Mumme et al. (2014) suggested that the ability of hydrochar to enhance the methane production results mainly from the larger fraction of anaerobically degradable carbon. According to their study, the hydrochar possessed a labile fraction of 10.4 % while for pyrolytic biochar this was 0.4 % (Mumme et al. 2014). Based on this hydrochar could act as better additional feedstock in the reactor. Mumme et al. (2014) estimated that their hydrochar made from anaerobically treated wheat straw digestate had a methane yield of 19 ml/g VS. The value is relatively low, but on the other hand the feedstock has already been subjected to the biogas production. The higher degradability of hydrochars has also noted in other studies. Bai et al. (2013) studied the degradation kinetics of pyrolytic biochar and hydrochar in soils and found out that hydrochar was readily biodegradable while pyrolytic biochar was more stable. Pyrolytic biochar had one order of magnitude slower degradation compared with hydrochar (Bai et al. 2013).

The amounts of biochar applied to anaerobic digesters in previous studies has some variation and the experiments have been done in wet conditions. Luo et al. (2015) had a biochar concentration of 10 g/l in a digester inoculated with crushed granules, and Lu et al. (2016) used the same concentration. Zhao et al. (2015) had a biochar concentration of 2.5 g/l in an up-flow anaerobic sludge blanket reactor. Mumme et al. (2014) applied biochar with a

mass based ratio of 6.67 % compared with the feedstock fresh weight. Cai et al. (2016) used several biochar concentrations in the range of 0.25–2.5 g/g-TS waste. They suggested that the optimal dose of biochar depends on inoculum amount (Cai et al. 2016).

## 2.7 Biochars and the partial flow digestion process

According to several sources (Libra et al. 2011, Mumme et al. 2011, Roberts et al. 2009) the high costs of biochar production limits their wider use. Mumme et al. (2014) also adds that to overcome this issue, new applications with economic benefits are needed. He suggested that the use of biochar in anaerobic digestion could be one method of expanding the value chain (Mumme et al. 2014). Luo et al. (2015) and some other studies related to biochar and anaerobic digestion highlights that the remaining biochar in the digestate can act as a soil improver if it is composted. In HSY partial flow digestion (Fig. 3) the upcoming biowaste is separated into two fractions, the fine and the coarse fraction, with a sieve with a pore size of 80 mm. The fine fraction is treated in the anaerobic digester to produce biogas for energy production and the coarse fraction is composted alongside with the digestate and bulking materials to produce soil amendment (Mönkäre et al. 2015). The plant is a mesophilic dry digestion plant and it is designed to treat up to 60 000 metric tons of source separated municipal and commercial biowaste per year from Helsinki metropolitan area (Mönkäre et al. 2015). In this case, the biochar could benefit both the anaerobic digestion and composting. Additionally, biochar production from anaerobically digested sewage sludge could be a new and innovative method for sludge utilization.

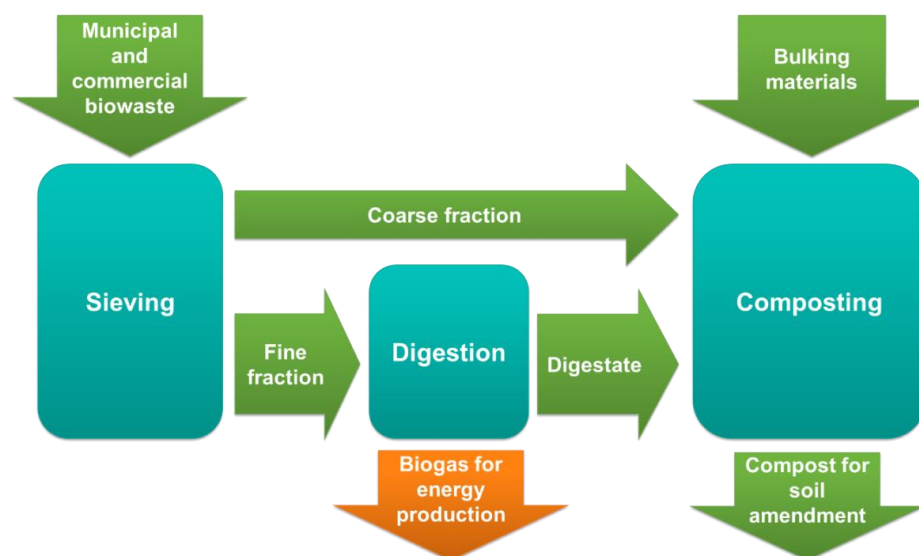


Fig. 3. The operation of the HSY partial flow digestion process (Mönkäre et al. 2015).

Meyer et al. (2011) made a comparison of the data costs of the biochar production and the values varied from 51 US\$/t (pyrolytic biochar from yard waste) to 386 US\$/t (retort charcoal). During that time, very little information about HTC with relevance was published and no information on the production costs were available (Meyer et al. 2011). Nowadays more research about HTC exists but still the manufacturing seems to be so small that the values for the production costs are hard find. Therefore, the approximate estimations need to be done with the prices of pyrolytic biochars. If the production costs are estimated according to the values presented by Meyer et al. (2011) and the biochar is applied to the feedstock (60 0000 t/a) by a mass based ratio of 5 % compared with fresh weight (based on literature values), the annual need for biochar in the HSY digestion plant would be 3 000 t. The production costs for this amount according to Meyer et al. (2011) would be 153 000–1 158 000 US\$. Therefore, it is essential, that the production costs are as low as possible. The possibly increased biogas yield could at least for some part cover the biochar production costs. Additionally Mäkinen (2016) studied the effects of biochar addition to the HSY composting process with promising results. Biochar increased the degradation of organic material and stabilization of the compost and reduced the ammonia volatilization (Mäkinen 2016). This could further increase the biochar value in HSY process.

### **3 OBJECTIVES**

This thesis had two main objectives. One was to compare biochars produced from different materials and based on this to evaluate what kind of biochars would be suitable for anaerobic digestion. This was done by determining three different characteristics of the biochars. Ammonium adsorption capacity was studied to find out that could biochar stabilize the ammonium levels in the anaerobic digester and thus prevent the formation of free ammonia. Biochar nutrient release in respect of dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) were studied to find out could biochar enhance anaerobic digestion by releasing nutrients and organically degradable material into digestate. PAHs were analyzed to describe the quality of the product against the guidelines.

Another main objective of this study was to find out how the addition of biochar affects to the anaerobic digestion process. The issue was addressed especially from the perspective of HSY anaerobic digestion process. Feedstocks were collected from the HSY biogas plant and dry conditions were simulated. The biogas plant treats source separated biowaste and



therefore the possible ability of biochar to mitigate ammonia inhibition was addressed. These issues were studied in the laboratory scale with biogas batch experiments, where different amounts of biochars were applied to the digesters and the volume and composition of produced biogas and the characteristics of the feedstocks and digestates were determined.

## **4 MATERIALS AND METHODS**

### **4.1 Samples and sampling**

#### **4.1.1 Biowaste and feedstock samples**

One biowaste sample (BIO) and the feedstocks (FEED1 and FEED2) used in the batch biogas experiments were collected from the HSY biowaste processing plant. It is a mesophilic dry digestion plant and treats source separated biowaste with partial flow digestion (Fig. 3), as explained previously.

The BIO sample was taken from the fine fraction of the biowaste after the sieving and before the fine fraction was fed into the anaerobic plug flow reactor by an automatic conveyer. Approximately 60 liters of biowaste was taken with a shovel from the conveyer and placed in the plastic containers. The sample was taken on the 10<sup>th</sup> of May 2016. On the next day from the sample taking the biowaste was homogenized with a meat grinder and mixed carefully in the laboratory. Homogenized biowaste was weighted by accuracy of  $(2000 \pm 10)$  g into resealable 2 l plastic bags and put to the freezer in the temperature of -20 °C. After a week, one bag was thawed and total solids (TS), volatile solids (VS), total kjeldahl nitrogen (TKN), and total ammoniacal nitrogen (TAN) were measured. The feedstocks used in the batch biogas experiments (FEED1 and FEED2) were taken from the beginning of the plug flow reactor via the sample taking pipe. The feedstock samples were pretreated in the field by sieving them first through 32 mm sieve and after that through 16 mm sieve to make it as homogeneous as possible. Approximately 40 liters of feedstock was sieved in both cases and they were placed in the plastic containers. FEED1 was taken on the 7<sup>th</sup> of July 2016 and FEED2 on the 19<sup>th</sup> of October 2016. During the next two days from the sample taking the TS, VS, TKN, TAN, and pH were measured for the feedstock samples. Feedstock samples were stored in plastic containers at room temperature until the start of the experiments (approximately one week). The biowaste and feedstock samples were transported from Helsinki to Jyväskylä on the same day as the samples were taken.

#### 4.1.2 Biochar samples and reference materials

Altogether eight different biochar samples were collected and studied. Seven of them were made with pyrolysis and one with HTC. Two biochars were obtained from a small-scale Finnish manufacturer and they were produced from birch (BC 1) and pine (BC 2) at a temperature of 350 °C. From other Finnish small-scale manufacturer two biochars made from the willow in the temperatures of 320 °C (BC 3) and 420 °C (BC 4) were obtained. One biochar sample was commercial charcoal made for barbecue usage (BC 5). From a German large-scale company two different biochars were obtained and they were made from wood production screenings (BC 6) and from food production wastes (BC 7). Manufacturing temperature for these two biochars were not submitted. The Technical Research Centre of Finland (VTT) manufactured the hydrochar (BC8) in a pilot scale reactor. Anaerobically digested sewage sludge was used as a feedstock and manufacturing temperature was 210 °C with 3 h residence time. Commercial synthetic zeolite (ZEO) made was used as a reference material in the ammonium adsorption capacity experiments (Table 2).

Table 2. Biochar samples and reference materials.

Sample type	Label	Feedstock	Temperature (°C)
Pyrolytic	BC1	Birch	350
Pyrolytic	BC2	Pine	350
Pyrolytic	BC3	Willow	320
Pyrolytic	BC4	Willow	420
Pyrolytic	BC5	Broadleaved trees	450
Pyrolytic	BC6	Food production residues	-
Pyrolytic	BC7	Wood residues	-
HTC	BC8	Digested sewage sludge	210
Zeolite	ZEO	-	-

All the biochars and reference material were dried overnight at 40 °C prior to the experiments. The granulate size of biochars and zeolite varied and therefore all of them were homogenized by mashing and sieving into the granulate size of below 1 mm.

#### 4.1.3 Process water

Process water from the HSY digestion plant was taken to characterize it and to compare the results with the previous analyses. The sample was taken on the 10<sup>th</sup> of May 2016. Process water is wastewater that is collected from the different phases of the organic waste treatment, for example from waste reception, pretreatment and composting plant. One fraction of process water is the water that drains from the digestate during the composting pro-

cess. A part of process water is used to irrigate the compost and the surplus is directed to the WWTP. The water samples were taken from the collection pipe and stored in barrels and transported from Helsinki to Jyväskylä on the same day as the samples were taken. During the night, samples were stored in a cold room at the temperature of 4 °C and on the next day they were filtrated with 0.125 mm sieve to remove the solids. The samples were stored in a cold room at a temperature of 4 °C until analyzed (approximately one week).

## **4.2 Experimental setups of the biochar studies**

### **4.2.1 Biochar ammonium adsorption experiments**

One objective of this thesis was to study the possibility of biochar to mitigate ammonia inhibition in anaerobic digestion especially when working with feedstocks containing high nitrogen loads. This issue was addressed by studying the biochar ammonium adsorption capacity in the liquid phase. The basic idea was that if biochar could act as adsorbent for ammonium ions it could stabilize the ammonium levels in the anaerobic digester and thus prevent the formation of free ammonia, which is a major inhibitor for the process. The adsorption capacities were studied with simple horizontal shake experiments. Adsorption experiments were also done with well know ammonium adsorbent zeolite to get reference results.

The experiments were done in a synthetic ammonium solution in 250 ml erlenmeyer flasks with a liquid volume of 100 ml. The solution was made by diluting ammonium chloride into Milli-Q water. The biochar and zeolite concentrations in the adsorption experiments were 20, 50, and 100 g/l. In the solution derived from the ammonium chloride the initial ammonium nitrogen concentration was  $\approx 600$  mg/l due to the measuring range of the ammonia selective electrode. This is rather high value, but also greater concentrations exist in anaerobic digesters. Every concentration was sampled as a duplicate and measurements were done in triplicates.

The samples were put into Heidolph Unimax 2010 shaker with a speed of 140 rpm. The experiments were kept on for 24 hours in room temperature and a control group without biochar was included to exclude the ammonium reduction from other reasons than adsorption. After the shaking the suspensions were filtrated on a vacuum through 1.6  $\mu$ m filter paper (VWR Glass Microfibres filter 691) to remove the solid biochar. The TAN was measured from the solutions with an ammonia selective electrode.

#### 4.2.2 Biochar nutrient release

Another hypothesis was that biochar could enhance anaerobic digestion by releasing nutrients and organically degradable material into digestate. This issue was addressed by studying the quality of biochar leachate in respect of DOC and DTN. Additionally, this gives information about biochar stability in the liquid phase.

The biochar leachate quality was also studied with simple horizontal shake experiment. The experimental design was similar as in ammonium adsorption experiments but the biochars were extracted in Milli-Q water with a liquid-solid ratio of 2 (liquid volume 100 ml and biochar concentration 100 g/l). After the experiments, the suspensions were filtrated through 0.45  $\mu\text{m}$  filters (Whatman ME 25) to leave only dissolved material originating from biochars. DOC and DTN were measured from the solutions.

#### 4.2.3 Other measured parameters

The PAHs were measured to describe the quality of the product against the guidelines. The sum of 15 PAHs was measured for all the biochar qualities. From hydrochar, the manufacturer provided yields and elemental composition.

### **4.3 Experimental setups of the biogas experiments**

#### 4.3.1 Overview

Two different sets of mesophilic anaerobic batch experiments were made to study the effects of biochar to the biogas yield and composition. One was made with two pyrolytic biochar concentrations and another with one hydrochar concentration and with normal feedstock and feedstock with increased ammonium concentration. The increased ammonium concentration was included because the ability of HTC biochar to mitigate strong ammonia inhibition was tested. Control groups without the biochar or ammonium addition were included. The volume and composition of produced biogas were determined and the characteristics of the feedstocks and digestates were studied. BIO sample was first planned to use in the biogas experiments with the presence of inoculum but ultimately they were replaced with FEED1 and FEED2 that acted both as a substrate and inoculum in the reactor. The use of FEED1 and FEED2 were thought to simulate the HSY biogas plant better.

#### 4.3.2 Batch experiments with pyrolytic biochar treatments

FEED1 was used both as a substrate and as an inoculum in the first biogas batch experiment. No additional inoculum was used because the feedstock was taken from biogas reac-

tor and it was already degrading and producing biogas. The FEED1 was assumed to produce enough substrate for the anaerobic digestion so therefore no additional substrate was fed. TS, VS, TKN, TAN, and pH was measured from the feedstock prior to the experiments. BC5 biochar was used in this experiment, because similar biochar was also used in another HSY research project related to the use of biochar in composting (Mäkinen 2016).

Anaerobic digestion experiments were carried out in batch experiments with 5 l glass reactors with a feedstock working weight of 4 kg (not including the biochar). The experiments were carried out under mesophilic conditions (37 °C) and the temperature in the reactors was maintained by keeping the reactors in the incubation room. Biochar treatments in the reactors were applied at g-BC/g-TS-feedstock based ratios of 0.25 and 0.5, which equals approximately mass based ratios of 3 % and 6 % compared with the fresh weight (labels BC 3 % and BC 6 %). In addition, control reactors including only the feedstock was made (label CTRL). Each treatment was sampled as a duplicate, so altogether six reactors were in operation. The pH of the feedstock was adjusted to  $7.3 \pm 0.1$  by adding 0.1 M HCl but no additional buffer was used in the reactors, because the effect of the biochar was wanted to study as natural conditions as possible. The reactors were mixed continuously with magnetic stirrer and in addition manually for 30 seconds during the weekdays. The produced biogas was collected into 10-liter aluminum gas bags (Fig. 4).



Fig. 4. Picture of the biogas experiments set up.

The produced biogas volume and composition in respect of methane and carbon dioxide were measured three times in a week for most of the experiment. When the gas production started to decrease, the measurements were done less frequently. The experiments were carried out until the daily biogas rate was less than 1% of the total biogas volume. After the experiments pH, TS, VS, TKN, TAN, and VFAs were measured from the digestates.

#### 4.3.3 Batch experiments with hydrochar treatments and ammonium addition

In the second batch experiments, FEED2 was used as feedstock. The experimental design was similar to described above with some exceptions. The working weight in the reactors was reduced to 3 kg, because the first experiment showed that with 4 kg the reactors were pretty full. A little bit smaller working weight was thought to increase the mass transfer between the biochar and the feedstock in the reactor. In this series, only hydrochar (BC8) and one concentration were used. Treatments with additional TAN were included to simulate a situation with the ammonium overload and digestion of nitrogen rich substances.

The ability of hydrochar to mitigate strong ammonia inhibition was tested by increasing the ammonium concentration artificially by adding of ammonium carbonate (reactors  $\text{NH}_4^+$  CTRL and  $\text{NH}_4^+$  HTC). The total ammonium concentration was increased by 3000 mg/kg. The conditions without ammonium addition were included (reactors CTRL and HTC). For both conditions control reactors were made. Hydrochar treatments in the reactors were applied at a g-BC/g-TS-feedstock based ratio of 0.35, which equals approximately a mass based ratio of 4.5 % compared to the fresh weight. Each treatment was sampled as a duplicate, so altogether eight reactors were in operation.

The operation and measurements from the reactors and biogas were done similar as in the first experiment except VFAs were not analyzed due to technical problems.

### 4.4 Analytical methods

#### 4.4.1 Total solids and volatile solids

TS and VS for substrates, inoculum, and biochars were analyzed according to Finnish standard methods (SFS 3008). All the measurements were done at least in triplicates. Glass excicators were used to cool down the samples.

#### 4.4.2 pH and COD

pH was measured with Metrohm 774 pH-meter using electrodes suitable for either liquid or solid samples. Measurements were done immediately after each sampling. COD was analyzed according to Finnish standard methods (SFS 5504).

#### 4.4.3 Nitrogen and carbon analyses

TKN and TAN from solid samples and TKN from liquid samples were analyzed with Tecator AB Kjeltac 1002 -distillation unit. Analyses were done according to Tecator application note (Perstorp Analytical Tecator 1995). TAN from liquid samples was measured with Thermo Scientific Orion High Performance Ammonia Electrode 9512HPBNWP. DOC and DTN from liquid samples were analyzed with Shimadzu TOC-L analyser equipped with a TNM-L total nitrogen unit.

#### 4.4.4 Biochar PAH-analysis

The sum of 15 PAHs was analyzed from the biochars. Each biochar sample (1 g) was weighted into the cellulose extraction thimble and soxhlet extracted in toluene (100 ml) with Buchi B-811 soxhlet extraction device. A soxhlet warm method and 20 extraction cycles were used. After the extraction the volume of the remaining extract was determined and 1 ml sample was taken for the PAH-analysis. PAH-determination was done with gas chromatographic mass spectroscopy (Shimadzu GCMS-QP2010, ZB5 capillary column 30 m x 0.25 mm x 0.25  $\mu\text{m}$ ). Oven temperature in the beginning was 60 °C with one-minute hold and increased to 300 °C (20 °C  $\text{min}^{-1}$ ) with five-minute hold. The source temperature of the mass selective detector was 200 °C and transfer line was 260 °C and it was operated at single ion monitoring. Helium was used as a carrier gas.

#### 4.4.5 Volatile fatty acids

VFAs were analyzed with a gas chromatograph equipped with flame ionization detector (Perkin Elmer Autosystem XL, PE FFAP column 30 m x 0.32 mm x 0.25  $\mu\text{m}$ ). The operation conditions were following: oven temperature was 100-160 °C (25 °C  $\text{min}^{-1}$ ), detector and injector temperature was 225 °C, and helium was used as a carrier gas. The preparation of the samples were done as described by Bayr (2014).

#### 4.4.6 Biogas volume and composition

The produced biogas volume was determined by the water displacement method. The biogas collected to aluminum bags was pressed to water filled cylinder and the volume of the

gas was read from the graduation in the cylinder. The contents of methane and carbon dioxide in biogas were determined with a Geotech GA2000 portable gas analyser equipped with infrared and electrochemical detector.

## 5 RESULTS AND DISCUSSION

### 5.1 Biowaste and feedstock characteristics

The characteristics of the biowaste sample (BIO) and two feedstock samples used in biogas batch experiments (FEED1 and FEED2) were determined. Even though the BIO sample was not used in the experiments, the data is still presented to make comparisons.

Table 3. Characteristics of biowaste samples and feedstocks used in the batch experiments and their standard deviations.

	BIO	FEED1	FEED2
TS (%)	32.1 ± 0.7	12.8 ± 0.3	12.4 ± 0.6
VS (%)	23.6 ± 0.3	7.9 ± 0.1	7.5 ± 0.2
VS/TS-ratio (%)	73.7 ± 0.8	61.3 ± 1.3	61.1 ± 3.1
TKN (g/kg)	6.2 ± 0.3	7.0 ± 0.1	6.4 ± 0.1
TAN (mg/kg)	375 ± 7	3349 ± 60	3568 ± 90

BIO had higher total and volatile solids content compared with FEED1 and FEED2. The nitrogen levels in the samples varied between 6.2–7.0 g/l. Compared with BIO both the feedstock samples had a greater amount of ammoniacal nitrogen and lower VS/TS-ratio (Table 3).

The characteristics of the feedstock samples (FEED1 and FEED2) were similar even though the samples have been collected at different times. This indicates that there was not so much seasonal variation in these samples, but on the other hand not all the possible analyses were done. Feedstock samples could still differ in respect of some other parameter. BIO sample differed from feedstock samples, because the sample type is different. BIO was a biowaste sample while the feedstock samples were digestate taken straight from the biogas reactor. The feedstock samples have been subjected to anaerobic degradation and therefore they differ especially regarding the total and volatile solids. This explains also the high TAN values in the feedstock samples, because when the organic nitrogen in biowaste is anaerobically degraded it transforms to ammoniacal form. The TAN concentration in the feedstock samples varies around 3500 mg/kg, which exceeds the limit for ammonia



inhibition according to Rajagopal et al. (2013). Based on this it can be estimated that ammonia inhibition occurs when using these feedstocks in biogas experiments.

Previously in HSY Kombi-project the characteristics of the organic fraction of municipal solid waste coming to the Ämmässuo waste treatment center were studied. For the total municipal biowaste the TS-value was 28.7 %, VS-value 25.5 %, VS/TS-ratio 89% and TKN 6.7 g/kg for fresh matter, and the TAN values were not reported (Mönkäre et al. 2015). The BIO sample assayed in this study had overall similar values, but also some variation existed. TS-value was slightly higher while VS-value was lower. As a result, the overall VS/TS-ratio was lower and this could result from seasonal changes in biowaste composition. In their report Mönkäre et al. (2015) also pointed that biowaste composition may vary depending on the sampling date. The TKN-levels in both assays were in similar range.

## 5.2 Process water characteristics

The characteristics of the process water were determined and the values were compared with the previous measurements made in HSY Kombi-project.

Table 4. Characteristics of the process water (sampled in May 2016) and their standard deviations.

Parameter and unit	Value
pH	8,3
Conductivity (mS/cm)	42,2
COD (g/l)	4.6 ± 0.4
TKN (g/l)	8.4 ± 0.4
TAN (g/l)	5.6 ± 0.3

The process water had a slightly alkaline pH and high COD content. The amount of nitrogen was high and a large part from this was in ammoniacal form. The conductivity of the water was high (Table 4).

The process water characteristics were sampled in HSY Kombi-report by Mönkäre et al. (2015) before the anaerobic digestion plant was in operation. The TKN level in their report was 1100 mg/l, which was much lower value than the result obtained in this study (8400 mg/l). TAN value was not reported in the Kombi-report. A major part of the nitrogen was in ammoniacal form, which suggests that the nitrogen containing matter has been subjected to degradation. According to these results, the introduction of anaerobic digestion has had

significant affects to the nitrogen levels of the process water and also the Kombi-report (Mönkäre et al. 2015) noted that the operation of the plant might affect its composition. There also could be seasonal variation in the characteristics of the process water and more analyses should be applied in different dates to find out the changes and the average composition of the process water. In any case, the highly grown nitrogen levels of the process water are critical information and they should be considered carefully for example from the nutrient recovery point of view. It is worth to consider, that could the application of biochar in the anaerobic digestion process improve the nutrient (especially nitrogen) recovery regarding the process water.

### 5.3 The ability of biochars to adsorb ammonium ions

The ammonium adsorption capacities and ammonium removal percentages for the biochar samples and zeolite were calculated from the results of the shake experiments.

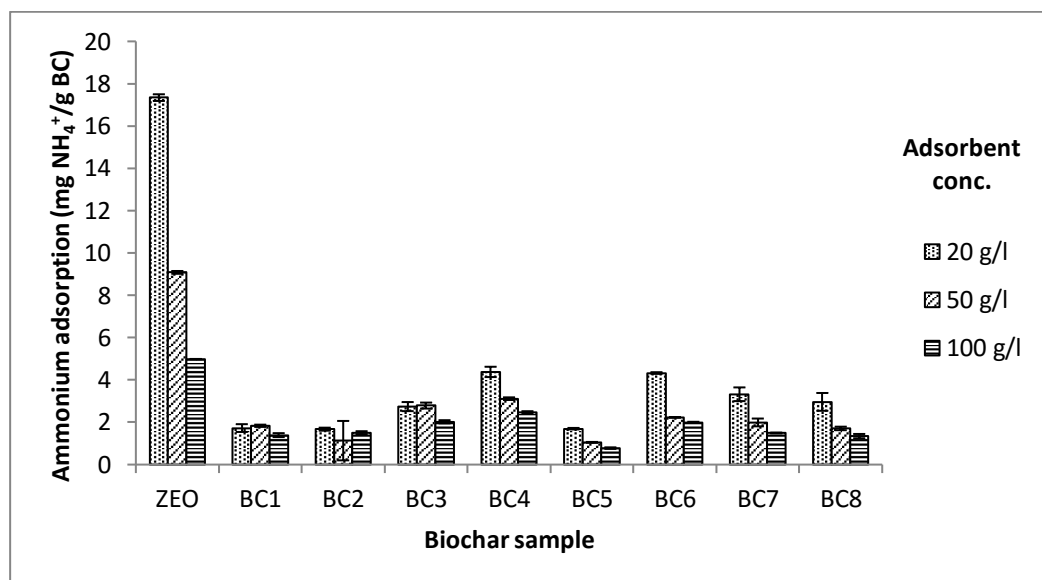


Fig. 5. Ammonium adsorption biochar samples and for the zeolite. Three biochar concentrations and control with no biochar addition was sampled.

The adsorption capacity values for zeolite were 5.0–17.3 mg/g depending on the zeolite concentration. For the biochars the values were 0.8–4.4 mg/g depending on the biochar and concentration. The highest adsorption capacities in biochars were in BC4 (2.5–4.4 mg/g) and in BC6 (2.0–4.3 mg/g) while the lowest values were in BC2 (1.5–1.7 mg/g) and in BC5 (0.8–1.7 mg/g). Other biochars had adsorption values in between these two ends. Zeolite possessed higher capability to adsorb ammonium ions from aqueous solution compared with the biochars (Fig. 5).

Table 5. Biochar and zeolite ammonium removal percentages. All data are means from duplicate samples and standard deviations were below 2 %.

Sample concentration (g/l)	Ammonium removal percentage (%)								
	ZEO	BC1	BC2	BC3	BC4	BC5	BC6	BC7	BC8
20	63.4	6.1	5.9	9.5	15.1	6.1	15.6	11.9	10.7
50	82.9	16.1	17.9	24.0	26.8	9.4	20.0	17.9	15.4
100	91.0	24.5	26.5	34.8	42.6	14.0	35.8	26.8	24.2

With the lowest zeolite concentration (20 g/l) was possible to remove 63.4 % ammonium from the solution while with biochars the removal rate was 5.9–15.6 %. With the highest dose the removal rates were 91.0 % with zeolite and 14.0–42.6 % with biochars. Ammonium removal percentage was the highest in the samples with the highest adsorption capacity and as expected zeolite had the highest removal rate. In all the samples, the removal rate showed an increasing trend (Table 5).

The results showed that biochars could adsorb ammonium ions from the solution but compared to a well-known ammonium adsorbent zeolite the adsorption was lower. Zeolites are aluminosilicate minerals and they are proven to have high cation exchange capacity, ion adsorption, and high  $\text{NH}_4^+$ -selective properties (Kithome et al. 1998). The capability of zeolite to adsorb ammonium ions was experimentally confirmed in this study. Because ammonium is a positively charged ion it can be assumed that good adsorbent needs to possess ion (especially cation) exchange capability. The ion exchange capability in biochars results from their negatively charged surface groups, especially oxygen and hydrogen containing functional groups, which are formed during the thermal decomposition of biochar feedstock (Ahmad et al. 2014). Hale et al. (2013) studied the ammonium adsorption of biochars made from cacao shell and corn cob biochars and they also suggested that binding is based on via electrostatic exchange with other cationic species on the surface of the biochar. Compared with zeolites the cation exchange in biochars was lower but nevertheless some kind of adsorption and ion exchange properties exist, since all the biochars were capable to remove ammonium ions from the solution. Some biochars (BC4 and BC6) had better adsorption capacity than others.

According to Ahmad et al. (2014) the feedstock and manufacturing have a significant role in biochar characteristics. In this study, the most of the biochars were pyrolytic and made from wood materials, but pyrolytic biochar made from food production residues (BC6) and hydrochar made from anaerobically digested sewage sludge (BC8) was included. Com-

pared to others the adsorption of BC8 did not differ very much, so it can be estimated that in this case the manufacturing type did not have very big effect. On the other hand, only one hydrochar was sampled, so therefore no further conclusions can be made. According to Gai et al. (2014) biochars made in lower temperatures (250-400 °C) has been found suitable to produce biochars for removing inorganic and polar contaminants. In their study a decrease in ammonium adsorption was found when the pyrolysis temperature (400, 500, 600 and 700 °C) was increased (2014). All the sampled biochars were manufactured in relatively low temperatures. In any case variation in the biochar adsorption capacities exists and probably this results from differences in manufacturing parameters, temperatures and feedstock materials.

As it can be seen from this study, differences between biochar ammonium adsorption capacities exist. Sarkhot et al. (2013) obtained the ammonium adsorption values of 5.3 mg/g, which is in the similar range than in this study. Zhu et al. (2012) noted even lower adsorption, but on the other hand the initial ammonium concentrations in their study was lower. Also biochars with high ammonium adsorption capacities exist. The biochar adsorbed amounts were lower in comparison with the results obtained by Kizito et al. (2015), where the maximum adsorbed amount was 54.84 mg/g. This value is even higher than the adsorption capacity of zeolite in this study. This suggests that biochars with relatively high ammonium adsorption capacities exists. If the benefits of adsorption in anaerobic digestion were considered, a high adsorption capacity could be a positive thing. This could limit the ammonia inhibition by capturing the excess ammonium and preventing the conversion of ammonium to more toxic ammonia. The benefits of well-known ammonium adsorbent zeolite in anaerobic digestion have been scientifically proven (Montalvo et al. 2012) especially with high ammonium loads (Tada et al. 2015), so biochars with good ammonium adsorption capacities could have similar positive effects. In this study, it was shown that not all the biochars are as effective adsorbents as zeolites, but at least all the sampled biochars could remove some amounts of ammonium ions from the solution. It can be assumed that they at least have the possible ability to act as ion exchangers for ammonium removal and balance the ammonium levels in the anaerobic digester. However, it was also pointed out, that ammonium adsorption capacity can vary depending on the biochar, and biochars with high adsorption values exist. If the manufacturing of biochars is optimized in a way that ammonium adsorption is maximized, better effects could occur.

The differences between the biochar ability to adsorb ammonium ions can depend on other reasons than the biochar itself and manufacturing. According to Kizito et al. (2015) increase in initial ammonium concentration, the temperature, biochar particle size, contact time, and pH affects to the adsorption. In this study different conditions were not applied, but by optimizing the conditions biochars could have acted as better adsorbents. For example, the temperature and pH could have been adjusted to match mesophilic conditions and in these conditions the adsorption could have been higher. Also the biochar dosage affects the adsorption and in this study the adsorption shows a decreasing trend when the dosage of biochar is increasing. This can be explained by the increasing available adsorption sites while the total ammonium concentration remains the same (Zhu et al. 2012).

In HSY partial flow digestion the digestate is composted alongside the coarse fraction of biowaste and bulking materials and during the composting a certain amount of process water drains to the waste water collection system (Mönkäre et al. 2015). As mentioned before, the introduction of the anaerobic digestion plant has possibly increased the nitrogen levels in the process water significantly, and especially the TAN levels are high. Regarding to this, the biochar ammonium adsorption could serve as a nutrient recovery method. Kizito et al. (2015) suggests that biochars has the potential to adsorb ammonium from pig-gery manure and thus they can act as nutrient filters before discharging the effluents into waste water collection. Biochar applied to the anaerobic digestion or composting process could have similar effects by capturing the ammonium from the digestate and process water, prevent the ammonia volatilization and reducing the nutrient loss to the process water. The HSY Kombi-report (Mönkäre et al. 2015) suggests with some assumptions that 5000 m<sup>3</sup>/a of process water is used in the irrigation of composts (50 % of this evaporates or stays in the final compost and 50 % ends to the leachate). The average amount of process water directed to the WWTP in 2011–2014 was 3019 m<sup>3</sup>/a (Mönkäre et al. 2015). Based on these results biochar could increase the restraint of nitrogen compounds in solid stage digestate and prevent the leaching of them into process water, which is ultimately directed to the WWTP.

#### **5.4 Biochar nutrient release**

From all the biochars the releasing DOC and DTN were measured with 24 h shake experiments in MilliQ-water. One biochar concentration (100 g/l) was used.

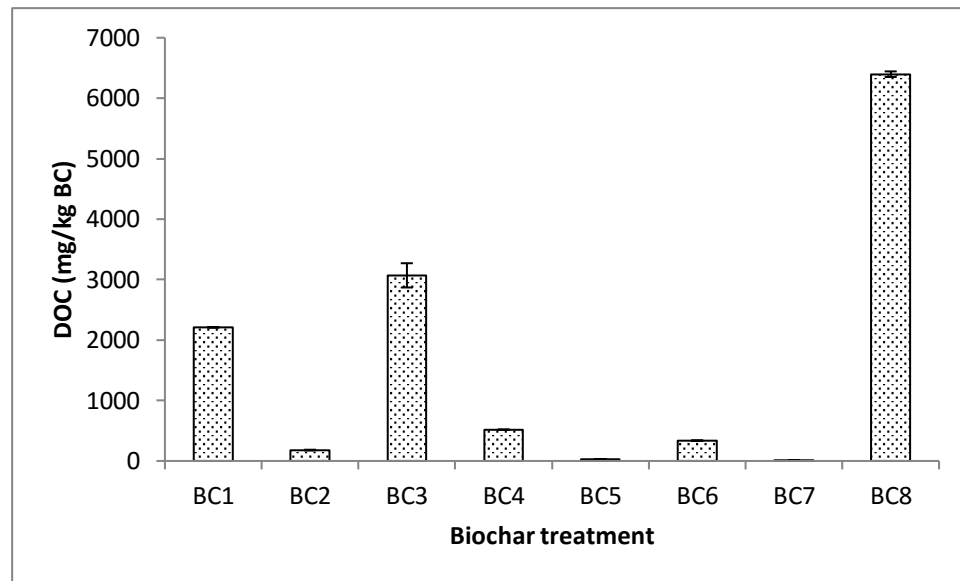


Fig. 6. DOC (mg/kg BC) measured from biochar leachate in 24-hour horizontal shake experiment in Milli-Q water.

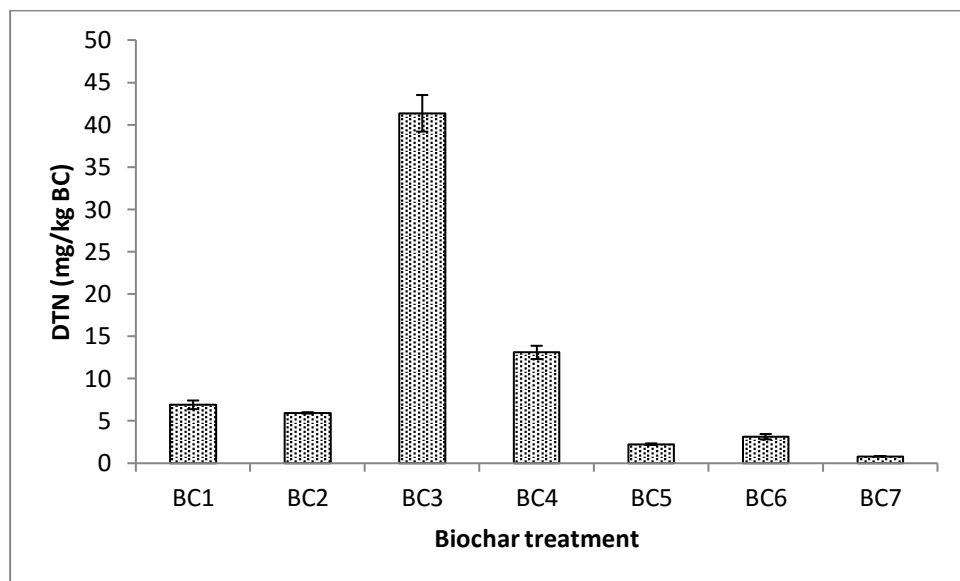


Fig. 7. DTN (mg/kg BC) measured from biochar leachate in 24-hour horizontal shake experiment in Milli-Q water. BC8 was excluded from the graph because the value was very high compared to other samples ( $2705 \pm 26$  mg/l).

The DOC release in biochars was between 8.9–6397 mg/kg, so a lot of variation existed between the samples. BC8 had the highest DOC value while BC5 and BC7 had the lowest values. The same kind of trend of variation applied also regarding to DTN and the values were in the range of 0.83–2705 mg/kg. BC8 had very high DTN value (2705 mg/kg), while in other biochars this value was in between 0.83–41.3 mg/kg. Similarly than in DOC, BC5 and BC7 had the lowest values in DTN also (Fig. 6, Fig. 7).

The results showed that all the biochars released both DOC and DTN but in very different amounts. In general the DOC release was higher in comparison with the DTN, which probably results from the composition of biochars. The dominant element in biochars is carbon, and therefore the amounts of released DOC are higher. Interestingly, BC8 released significantly more DTN than other biochars and also the DOC value was the highest. BC8 was the only HTC treated biochar so according to this it is possible to speculate, that does HTC treatment provide biochars releasing more nutrients compared with the pyrolytic biochars. The biochar nutrient release into the liquid phase has not been studied very well, but few studies on this issue exist. Compared with the experiments made by Mukherjee & Zimmerman (2013) the results obtained in this study are similar. A lot of variation existed between the samples and some biochars can release significantly more DOC than others.

The differences in the nutrient release can relate to biochar feedstocks or manufacturing methods. Mukherjee & Zimmerman (2013) suggested that biochars made in lower temperatures release more nutrients, which supports the observations in this study. BC3 (320 °C) and BC4 (420 °C) biochars are made from the same feedstock by the same manufacturer and BC3 released more DOC and DTN than BC4. The highest DOC and DTN value in this study was observed in BC8 (210 °C), which is hydrochar made from anaerobically digested sewage sludge. Chan & Xu (2009) also noted that the nutrient composition and availability depend highly on the used feedstock and pyrolysis condition. The feedstock in BC8 may serve as a good leachate source especially regarding the nitrogen release, since the anaerobically treated digestate is rich in nitrogen (Tambone et al. 2010).

The benefits of biochar nutrient release for anaerobic digestion have not been studied specifically, but there could be similar good effects than in biochar used as soil fertilizer. According to Lehmann et al. (2011), biochars can release useful nutrients to the soil and biochars are known to be extremely variable in nutrient composition (Chan & Xu 2009). If the biochars release useful nutrients in soil, the same kind of approach could also work in the anaerobic digestion environment. Additionally, if the releasing material is easily degradable, it could have some positive effects on the methane production. In any case, it must be considered that the amount of biochar compared to the feedstock is low and therefore the amounts of nutrient release may not have that significant effect on the bigger picture. On the other hand, the high DOC and DTN values could also propose the easier degradation, which could affect positively the methane production.

## 5.5 Biogas batch experiments with biochar treatments

5.5.1 The effects of pyrolytic biochar on dry anaerobic digestion of nitrogen rich feedstock  
 The first biogas experiment was made with pyrolytic biochar (BC5). Two different biochar treatments (3 % and 6 % of biochar compared with the fresh weight) were applied and a control treatment was included. The volume and the composition of the biogas were determined and the characteristics of the digestate after the experiment were studied. The treatments were done in duplicates, except the BC 6 % was tested only with one reactor due to the technical problems. At the beginning of the experiment the gas siphon of another BC 6 % reactor was blocked and too much pressure occurred inside and therefore it needed to be discarded. The VS in the methane yields does not include the biochar, since it is considered as an additive material that does not itself contribute to the methane yield.

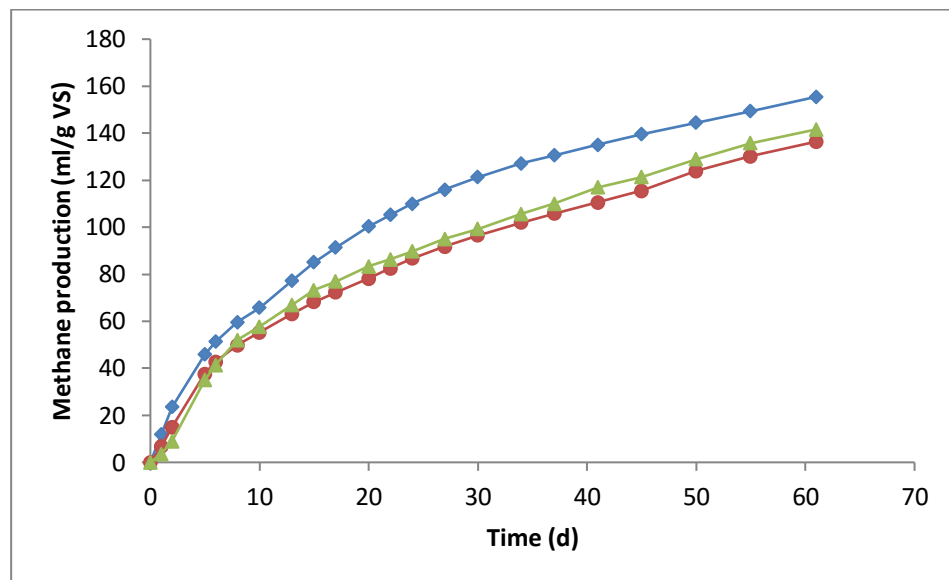


Fig. 8. Cumulative methane production in batch experiments. All data are means from 2 reactors except BC 6 % from single reactor. ◆ = CTRL, ● = BC 3 %, and ▲ = BC 6 %.

The cumulative methane production was 155 ml/g VS in CTRL, 136 ml/g VS in BC 3 %, and 142 ml/g VS in BC 6 %. CTRL had higher methane production compared with the biochar treated groups (BC 3 % and BC 6 %). Methane production was higher throughout the whole experiment. Between the biochar treated groups, the methane production was similar in the beginning but over the whole experiment it seems that BC 6 % group had slightly better methane production. (Fig. 8).



Table 6. Digestate characteristics, methane yields, and average methane contents for each treatment.

	CTRL	BC 3 %	BC 6%
pH	8.22 ± 0.03	8.23 ± 0.07	8.25
TS (%)	10.58 ± 0.07	13.36 ± 0.04	15.74 ± 0.06
VS (%)	5.78 ± 0.02	8.57 ± 0.04	11.02 ± 0.04
Methane yield (ml/g VS)	155 ± 6	136 ± 20	142
Average methane content (%)	63.4 ± 0.2	61.6 ± 0.8	61.5
TKN (g/kg)	7.5 ± 0.1	7.8 ± 0.2	8.3 ± 0.2
TAN (g/kg)	5.0 ± 0.02	4.5 ± 0.2	4.4 ± 0.2
VFAs (mg/l)	44.6 ± 1.4	39.8 ± 1.4	42.7

TS and VS on BC 3 % and BC 6 % groups were higher due to additional biochar in the digestate. The average methane content in CTRL was also slightly better while between BC 3% and BC 6% it is quite similar. VFA amounts in all the reactors were low and in the similar range at the end of the experiment. The nitrogen levels in the reactors after the experiments were in the same range but also minor variation existed. The greatest TKN levels were in biochar treated groups but on the other hand, the TAN levels in biochar treated groups were lower than in CTRL group (Table 6).

The results from this experiment suggest that the pyrolytic biochar did not affect the biogas production. The overall cumulative methane production in biochar treated reactors was lower in comparison to the control reactors but on the other hand the values are quite close to each other and fall within the range of standard deviation. BC 6 % was tested only with one reactor and therefore the standard deviation was not possible to measure. The cumulative methane productions were lower compared to the methane potentials of municipal solid waste, which are 215–482 ml/g VS according to Ward et al. (2008). The reason for this could be that the feedstock samples have been taken straight from a biogas reactor and they have already degraded and produced biogas for a while. As mentioned previously the nitrogen levels of the feedstock are high in comparison with the ammonia inhibition values presented by Rajagopal et al. (2013) already in the beginning (Table 3) and therefore it is likely that ammonia inhibition occurs and affects the biogas yields. It is not possible to analyze the differences between the groups statistically since the number of replicate samples is insufficient for studying the normality of the data or to use non-parametric tests. In any case, these experiments provide useful data when assessing the possible effects of biochar in anaerobic digestion under dry conditions, but to get reliable scientific results, further experiments with more replicates and statistical analyses should be done.

The addition of pyrolytic biochar to anaerobic digestion has had positive effects in previous studies but also evidence for limited effects exists, as noted by Mumme et al. (2014). Therefore, the issue is not completely clear. Any clear explanation for the lower methane production in biochar treatments in this study was not found. For some reason the biochar could cause minor inhibition in the process, or the result could also be due to the uncertainty in the experiments. Mumme et al. (2014) found out that in some cases the biochar containing fermentations with strong ammonia inhibition followed the trend toward more serious inhibition, which is similar to the result obtained in this study. The amount of biochar added in BC 6 % was similar in comparison with Mumme et al. (2014). Compared to other available studies (Cai et al. 2016, Lü et al. 2016, Luo et al. 2015) the effect on the methane production has at least been positive, even though it has not increased significantly. It is suggested that biochar shortens the methanogenic lag phase, enhances the methane production rate, and enhances the production and degradation of intermediate and volatile fatty acids (Cai et al. 2016, Lü et al. 2016, Luo et al. 2015). In this experiment, the lag phase did not exist since the feedstock was active and produced biogas straight from the beginning, and therefore the effects on the lag phase could not be seen. If the biochar would have been applied to a situation where fresh feedstock would start to degrade in the presence of inoculum, the possible effects could have been more noticeable. VFA levels in the end of the experiment were low and in similar range and these are probably due to complete degradation, since the experiment was kept on over 60 days. The effects on VFAs could have been better observed in continuous reactors.

BC5 used in this experiment possessed the lowest ammonium adsorption capacity from the biochar samples and therefore was not the best option when considering the possible mitigation of ammonia inhibition. Biochars with higher adsorption capacities could have performed better. On the other hand Lu et al. (2016) suggests that the alleviation of ammonia inhibition by biochars is more based on biochemical than physiochemical reasons, because the ammonium adsorption capacities in biochars are limited. According to their results, biochar enriches micro-organism cultures (Lü et al. 2016). Cai et al. (2016) also found out that there were no significant differences in nitrogen levels between control and biochar treatments, which would suggest that biochar does not affect the degradation of proteins and do not adsorb significant amounts of ammonium. The available research related to the ability of biochars to mitigate ammonia inhibition is somewhat contradictory and this could result from the different characteristics of the biochars. Porous biochars could work

better in enriching micro-organism cultures whereas biochars with higher ammonium adsorption capacities could stabilize the ammonium levels. Additionally all the available studies related to biochars and anaerobic digestion are made in wet conditions while this study simulated dry conditions. The mass transfer between the feedstock, biochar, and micro-organisms is probably more difficult in dry conditions and this can affect the results. More attention should be focused in optimal conditions in the reactor. According to these results, it can be assumed that at least in this case the pyrolytic biochar did not increase the methane production in the anaerobic digestion of nitrogen rich feedstock in dry conditions.

### 5.5.2 Effects of hydrochar on dry anaerobic digestion of nitrogen rich feedstock and increased TAN concentrations

The second biogas experiment was made with hydrochar (BC8). In this case just one hydrochar concentration (4.5 % of biochar compared with the fresh weight) was used. Biochar was applied to normal feedstock and to feedstock with increased ammonium concentration. Control treatments were included and all the treatments were sampled in duplicates. Again the VS in the methane yields does not include the hydrochar.

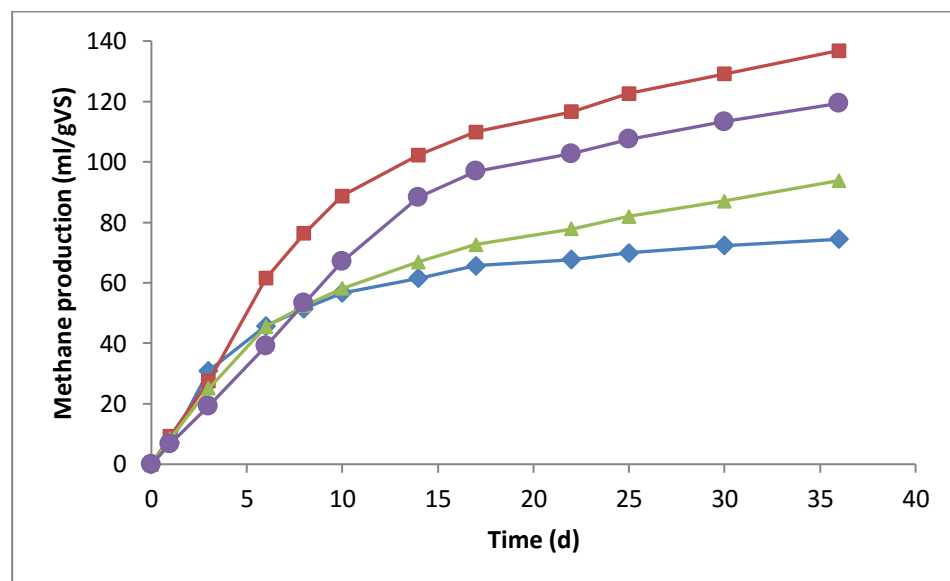


Fig. 9. Cumulative methane production in batch experiments with HTC biochar. All data are means from 2 reactors.  $\blacklozenge$  = NH<sub>4</sub><sup>+</sup> CTRL,  $\blacktriangle$  = NH<sub>4</sub><sup>+</sup> HTC,  $\bullet$  = CTRL, and  $\blacksquare$  = HTC.

The cumulative methane production was 74 ml/g VS in NH<sub>4</sub><sup>+</sup> CTRL, 99 ml/g VS in NH<sub>4</sub><sup>+</sup> HTC, 122 ml/g VS in CTRL, and 132 ml/g VS in HTC. The methane yields were lower in treatments with additional TAN. Both hydrochar groups had better methane production compared with their controls. Compared with the average methane yields hydrochar in-

creased the methane production by 26 % in additional TAN treatments and by 15 % in treatments without additional TAN. The standard deviation was higher in  $\text{NH}_4^+$  CTRL group compared with the others (Fig. 9).

Table 7. Digestate characteristics, methane yields, and average methane contents for each treatment. N.A. stands for not analyzed.

	CTRL	HTC	$\text{NH}_4^+$ CTRL	$\text{NH}_4^+$ HTC
pH	$8.23 \pm 0.03$	$8.27 \pm 0.07$	$8.41 \pm 0.01$	$8.41 \pm 0.04$
TS (%)	$9.0 \pm 0.2$	$11.6 \pm 0.1$	$8.55 \pm 0.03$	$11.24 \pm 0.04$
VS (%)	$5.3 \pm 0.2$	$6.37 \pm 0.07$	$5.04 \pm 0.01$	$6.31 \pm 0.09$
Methane yield (ml/g VS)	$119 \pm 7$	$137 \pm 9$	$74 \pm 23$	$94 \pm 3$
Average methane content (%)	$57.4 \pm 0.1$	$59.5 \pm 1.1$	$47.6 \pm 0.7$	$55.1 \pm 1$
TKN (g/kg)	$7.15 \pm 0.04$	$7.6 \pm 0.2$	$9.6 \pm 0.3$	$10.0 \pm 0.2$
TAN (g/kg)	$4.2 \pm 0.2$	$4.22 \pm 0.05$	$6.3 \pm 0.4$	$6.59 \pm 0.05$
VFAs (mg/l)	N.A.	N.A.	N.A.	N.A.

Again the TS and VS on hydrochar treated groups were higher due to additional biochar in the digestate. The average methane content was higher in the both HTC biochar treated groups compared to their controls. Between additional TAN treatments there was greater difference in methane content ( $47.6$  in  $\text{NH}_4^+$  CTRL and  $55.1$  in  $\text{NH}_4^+$  HTC) compared with treatments with no additional TAN ( $57.4$  and  $59.5$  respectively). Nitrogen levels were higher in additional TAN treatments (Table 7).

The results suggest that hydrochar had better effects on anaerobic digestion compared with the pyrolytic biochar. Feedstock TAN concentrations were originally high and additional TAN in the reactors caused inhibition and a clear decrease in the biogas production, as expected. Hydrochar improved the methane production in both treatments (with and without additional TAN) and it seems that the benefits were better with higher TAN concentrations. On the other hand, the same limitations as in experiments with pyrolytic biochar apply also in this case. Statistical analyses cannot be done and the standard deviation in  $\text{NH}_4^+$  CTRL group was high. Therefore, the results must be interpreted with high caution. In any case the preliminary data from these experiments shows promising results and further research should be done to solve the question.

The effects of hydrochar on anaerobic digestion have not yet been researched that much. The only article found was by Mumme et al. (2014) where both pyrolytic biochar and hydrochar effects on anaerobic digestion was studied. They found out that hydrochar increased the biogas production while pyrolytic biochar did not have a clear effect (Mumme

et al. 2014). Hydrochar increased methane production in low TAN concentrations (1626 mg/kg) 31 % and in high concentrations (6626 mg/kg) 21 % (Mumme et al. 2014). In this study similar results were obtained regarding to additional TAN treatments, since the increase was 26 % with initial TAN concentration of 6568 mg/kg (3568 mg/kg + additional TAN). Interestingly with lower TAN concentrations (3568 mg/kg) the increase in methane production was lower (15 %) as opposed to the observations by Mumme et al. (2014). This could suggest that hydrochar mitigates strong ammonia inhibition even better than mid-high inhibition but again the limitations of the study must be considered. Comparing pyrolytic biochar (BC5) and hydrochar (BC8) used in these biogas experiments, hydrochar showed better ability to adsorb ammonium ions. The ammonium adsorption capacity in both the biochars is still relatively low, so the good effects can also result from other mechanisms. Mumme et al. (2014) studied the effects of biochar on the anaerobic microflora and found out that both pyrolytic biochar and hydrochar increased the bacterial numbers slightly or moderately but compared with zeolite reactors the numbers were lower. The benefits can also result from biochar ability to offer good environments for microorganisms. The applied hydrochar amount was 4.5 % compared to the fresh weight, which is slightly lower than the amount applied by Mumme et al. (2014). This suggests that even with this kind of amount it is possible to increase the methane production. To minimize the biochar production costs, it would be useful to find the lowest dose that has positive effects.

Mumme et al. (2014) suggested that the ability of hydrochar to enhance methane production in anaerobic digester could result mainly from the larger fraction of anaerobically degradable carbon. According to their study, the hydrochar possessed a labile fraction of 10.4 % while for pyrolytic biochar this was 0.4 % (Mumme et al. 2014). Based on this the hydrochar could act as better additional feedstock in the reactor and, which could explain why methane production was promoted only with hydrochar. Mumme et al. (2014) estimated that their hydrochar made from anaerobically treated wheat straw digestate had a methane yield of 19 ml/g VS. The value is relatively low, but on the other hand the feedstock has already been subjected to the biogas production. The higher degradability of hydrochars has also noted by Bai et al. (2013) and they suggest that hydrochar is readily biodegradable while pyrolytic biochar was more stable and that pyrolytic biochar had one order of magnitude slower degradation compared with hydrochar. Considering the anaerobic digestion, it may not be desirable if the increase in the yields results mainly from the

biochar degradation. On the other hand only about 10 % of the hydrochar is subjected to degradation (Mumme et al. 2014), so there still exist quite a large fraction that can benefit the process in other ways.

These results suggest that hydrochar had better effects on the anaerobic digestion compared to the pyrolytic biochar, but the mechanism still remains unclear. Hydrochar had better ammonium adsorption capacity compared with the pyrolytic biochar used in this study but on the other hand, the adsorption is still limited. The literature suggests that hydrochar could degrade faster and act as an additional feedstock in the reactor, which could be the reason for the increased methane production. Further studies are needed to solve mechanism and confirm the results. When considering the HSY partial flow digestion, it should also be studied what kind of biochar is the best for both anaerobic digestion and composting. Mäkinen (2016) studied the effects of pyrolytic biochars on composting and found positive results, while in this study the hydrochars acted better than pyrolytic biochars in anaerobic digestion.

### 5.6 Hydrochar from anaerobically digested sewage sludge

VTT provided the yields and elemental compositions of the hydrochar they manufactured. The hydrochar was made from anaerobically digested sewage sludge in the temperature of 210 °C with a residence time of 3 hours.

Table 8. Hydrochar (BC8) yields from HTC treatment.

Feedstock TS (%)	Hydrochar yields	
	From total weight (%)	From TS (%)
13	11	82

Table 9. Elemental compositions of the feedstock and hydrochar (BC8).

	C (%)	H (%)	O (%)	S (%)	N (%)	Ash measured (%)
Feedstock	27.6	3.8	34.4	0.8	3.3	46.3
Hydrochar	23.8	2.9	26.4	2.6	1.9	58.8

The TS of the original feedstock (anaerobically digested sewage sludge) was 13 %. The ultimate hydrochar yield was 11 % from the total feedstock weight, which stands for 82 % from the original feedstock TS. The rest was a liquid yield, which was separated from the product by centrifuging and drying. Both the feedstock and hydrochar have high ash contents (46.3 and 58.8 %). Carbon and oxygen are the main elements of the feedstock (27.6 and 34.4) and the hydrochar (23.8 and 26.4 %) (Tables 8 and 9).

The initial ash content in the feedstock is quite high and this results as high ash content in the product. In addition, the carbon content in the feedstock was relatively low and therefore the hydrochar is not very rich in it either. In other hydrochars produced from anaerobically digested sludge the feedstocks and products have similar characteristics (Berge et al. 2011, Kim et al. 2014). It seems that the hydrochars produced from anaerobically digested biomasses possess lower carbon and higher ash contents compared with the hydrochars produced from other feedstocks. This can result from the lower initial organic material in them, because they have a least to some degree degraded in anaerobic digestion. On the other hand Mumme et al. (2011) managed to produce hydrochar from anaerobically digested maize silage with relatively good carbon content, so certain optimization potential can be assumed if optimal manufacturing parameters are found.

### 5.7 Biochar PAH-analysis

The sum of 15 PAHs was sampled from the biochars. Also two PAH guideline values are presented in order to make comparisons.

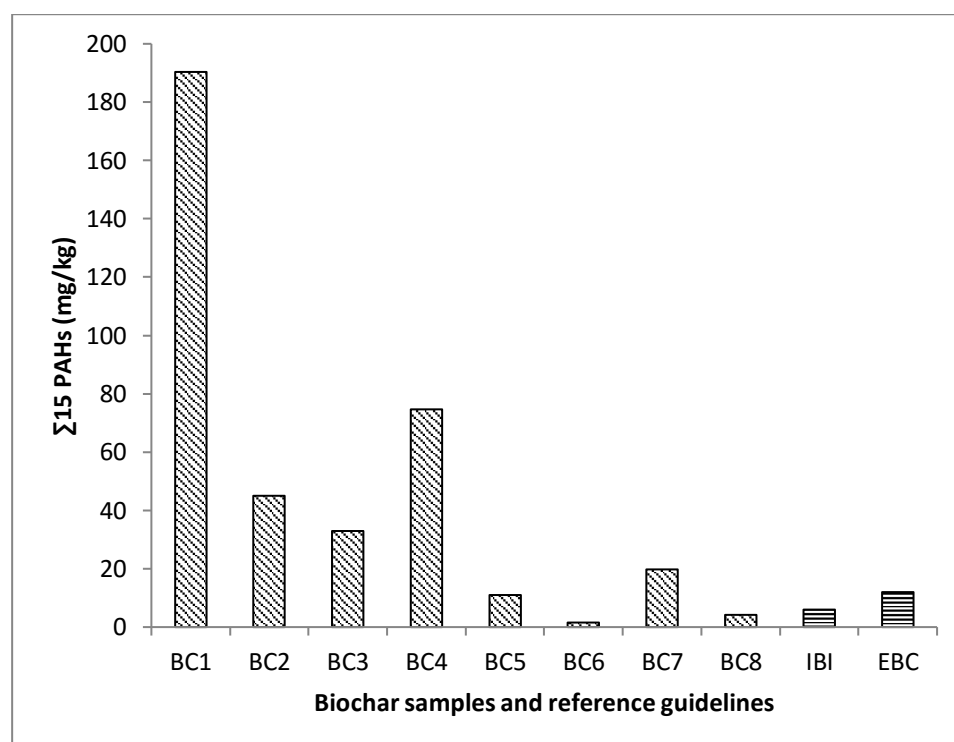


Fig. 10. The sum of 15 PAHs in biochar samples and two biochar PAH guideline values. IBI stands for International Biochar Initiative and EBC for European Biochar Certificate.

The sum of 15 PAHs was analyzed from all the biochar samples. The PAH concentration varied in the range of 1.6–190 mg/kg. In recent years, IBI has published standards for the

biochar definition and characteristics and they suggest the PAH guideline value of 6 mg/kg for biochars (IBI 2012). In addition, EBC has published its own voluntary certificates and their value is 12 mg/kg for a basic grade biochar (EBC 2016). BC 1 had by far the highest PAH content (190 mg/kg) and BC4 had quite a high value (75 mg/kg) too. Some samples had mid-high values and additionally biochar samples with low amounts of PAHs existed. BC6 had only 1.6 mg/kg and BC8 4.3 mg/kg PAHs (Fig. 10).

BC6 and BC8 were the only biochars that underbid both IBI and EBC biochar guideline values for PAHs. In BC5, the value was higher than the IBI guideline but lower than the EBC guideline. All the other biochar samples exceeded both guideline values. High PAH values in biochars are not unusual and in the literature the amounts vary greatly. Hale et al. (2012) studied PAHs in 50 different biochars and the amounts varied between 0.07–45 mg/kg. Also significantly larger values exist. In a study conducted by Schimmelpfennig and Glaser (2012) the average concentrations in five biochars samples were in the range of 3.9–2945 mg/kg. The results obtained from literature are in accordance with these results.

If the digestate is composted and the remaining biochar is expected to serve as soil amendment, the PAH values probably need to be under the legislative guidelines (2007/2014, 86/278/ETY). On the other hand, the ultimate PAH-values in the digestate may still remain under the guidelines, since the amount of originally added biochar is minor in comparison with the amount of the feedstock in anaerobic digestion. However, the possibility of a procedure like this should be legally examined, since the dilution of the contaminant may be prohibited. Attention on the PAH content of biochars should be focused, since due to increased production it is possible that legislative values are set to guide their production in the future. PAHs are the most important contaminants in biochars, so probably these are among the firsts on the target list. According to current voluntary certificates and standards these values would be relatively low in comparison with some high PAH values in biochars. So far the production of biochars is not controlled or certified.

## **6 CONCLUSIONS**

The results of this study showed that pyrolytic biochar did not have a significant effect on anaerobic digestion, while hydrochar seemed to work better. Hydrochar increased the me-



thane yields in both normal and ammonium increased feedstock. The ammonium adsorption capacities of the biochars were limited and therefore it is possible that the good effects were based on other mechanisms. Literature suggests that hydrochar has higher biodegradability compared with pyrolytic biochar and therefore it could act as additional feedstock in the digester, and this could explain the better results. There is also evidence, that hydrochar could support the growth of anaerobic micro-organisms. The applied hydrochar dose was 4.5 % compared with the feedstock fresh weight and with this kind of dosage differences in the methane production were observed. Due to the biochar production costs, it would be beneficial, that good effects could be seen with as small biochar amount as possible. On the other hand, the limitations of these experiments must be considered carefully. Statistical analyses were not done and therefore the results must be interpreted with a high caution.

It was also shown that the characteristics of biochars vary depending on the feedstock and manufacturing methods and therefore the optimization of biochars could be beneficial when considering their use in anaerobic digestion. Ammonium adsorption capacities in the sampled biochars were relatively low, but in the literature higher values exist. Studies of zeolite addition to anaerobic digestion have proved that high ammonium adsorption capacity is beneficial in mitigating ammonia inhibition with high TAN concentration. If the adsorption capacity of biochars is maximized by optimizing feedstocks and manufacturing, they could act as cost-effective adsorbents in anaerobic digestion. Additionally, the adsorption of ammonium could retain the nutrients in the digestate and process water preventing the nutrient loss to the WWTP. High PAH-levels in some biochars showed that focus on the possible contaminants must also be considered, if the produced digestate is utilized as soil amendment. There already exist guideline values for PAHs in biochars and additionally the Finnish legislation for contaminated soils or PAHs in composts can limit the use of biochars.

Hydrochar production from sewage sludge digestate could be a potential sludge management method if the hydrochar value can be increased in anaerobic digestion and composting. Previous studies showed, that the use of biochar in composting has good effects. This study carefully suggests that the use of hydrochar could be beneficial in anaerobic digestion, but due to the statistical limitations the results must be interpreted with caution. Further experiments with more replicates and statistical analyses should be done to ensure the observations and get scientifically reliable results. Future studies should focus on finding

the biochar associated mechanisms that enhance the methane production. The biodegradability of hydrochars in anaerobic conditions could be studied with standard BMP tests. The finding of biochar with high ammonium adsorption could be continued by sampling more biochars. Also the smallest biochar dose with effects on the methane production would be critical information in order to minimize the production costs. When considering the HSY partial flow digestion, it would be essential that the biochar would suit both anaerobic digestion and composting. Therefore, attention should also be focused on the production of a suitable biochar for both processes.

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## APPENDICES

Appendix 1. The values of biochar ammonium adsorption capacities.

Sample concentration (g/l)	Ammonium adsorption capacity (mg NH <sub>4</sub> <sup>+</sup> /g BC)								
	ZEO	BC1	BC2	BC3	BC4	BC5	BC6	BC7	BC8
20	17.3 ± 0.2	1.7 ± 0.2	1.7 ± 0.1	2.7 ± 0.2	4.4 ± 0.2	1.7 ± 0.1	4.3 ± 0.1	3.3 ± 0.3	3.0 ± 0.4
50	9.1 ± 0.1	1.8 ± 0.1	1.1 ± 0.1	2.8 ± 0.1	3.1 ± 0.1	1.0 ± 0.1	2.2 ± 0.1	2.0 ± 0.2	1.7 ± 0.1
100	5.0 ± 0.1	1.4 ± 1	1.5 ± 0.1	2.0 ± 0.1	2.5 ± 0.1	0.8 ± 0.1	2.0 ± 0.1	1.5 ± 0.1	1.3 ± 0.1



Appendix 2. The values of nutrient release (DOC and DTN) from biochars.

Sample	DOC (mg/kg)	DTN (mg/kg)
BC1	2209.4 ± 4.3	6.9 ± 0.5
BC2	180.2 ± 5.7	5.95 ± 0.08
BC3	3070.0 ± 200.5	41.3 ± 2.2
BC4	517.5 ± 1.5	13.1 ± 0.8
BC5	30.8 ± 0.3	2.3 ± 0.1
BC6	337.0 ± 4.4	3.1 ± 0.3
BC7	8.9 ± 2.9	0.83 ± 0.02
BC8	6397.3 ± 46.3	2705.3 ± 26.1

Appendix 3. The values and composition of 15 PAHs in biochars.

PAH-compound	PAH-amount (mg/kg)							
	BC1	BC2	BC3	BC4	BC5	BC6	BC7	BC8
Naphthalene	66,09	13,70	2,97	25,11	7,71	0,58	10,16	0,13
2-Methylnaphthalene	49,23	3,26	3,35	10,75	1,19	0,10	0,72	0,11
1-Methylnaphthalene	24,05	1,77	2,34	5,56	0,44	0,10	0,50	0,30
Acenaphthalne	2,63	0,00	0,00	1,22	0,03	0,00	0,67	0,00
Acenaphthene	2,54	1,29	1,32	1,30	0,17	0,09	0,09	0,31
Fluorene	11,23	1,80	2,14	2,02	0,20	0,44	0,00	0,36
Phenathrene	9,94	3,00	2,00	3,23	0,74	0,13	3,72	1,42
Anthracene	4,16	3,51	2,02	2,27	0,12	0,05	0,94	0,00
Fluoranthene	2,38	1,83	1,86	1,98	0,13	0,03	0,90	0,64
Pyrene	2,63	1,90	1,96	2,07	0,15	0,02	0,84	0,57
Benz[a]anthracene	4,04	4,79	4,79	4,78	0,04	0,01	0,39	0,11
Chrysene	3,17	3,72	3,74	3,77	0,06	0,01	0,46	0,13
Benz[b]fluoranthene	4,63	0,00	0,00	5,78	0,04	0,01	0,16	0,13
Benz[k]fluoranthene	3,56	4,41	4,44	0,00	0,01	0,01	0,12	0,00
Benz[a]pyrene	0,00	0,00	0,00	4,91	0,02	0,00	0,08	0,07
SUM	190,28	44,99	32,93	74,74	11,05	1,58	19,75	4,29