

**FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO**

# **Assessing the effects of the operational conditions of a THP unit on the energy balance of a wastewater facility**

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Master in Bioengineering - branch of Biological Engineering

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November 22, 2020



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This work was developed in partnership with **Technische Universiteit Delft**, through the Erasmus+ Programme



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# Abstract

Thermal pretreatment of sludge can be used to enhance the digestability and biogas production of waste activated sludge and facilitate the dewatering process, in order to face excess waste activated sludge management problems. The objective of this work was to study the effects of thermal pretreatment temperature on the sludge processing energy balance, in regard to a wastewater treatment plant. For that, thermal treatment at different temperatures, 120°C, 160°C and 200°C, was performed on waste activated sludge, followed by a biochemical methane potential test (BMP) to assess biodegradability and methane production. After anaerobic digestion, a dewatering assay by press filter and CST measurements was performed. Finally, an energy balance regarding the implementation of a TH unit was produced.

For all tested temperatures, soluble chemical oxygen demand, total ammonia nitrogen and orthophosphate solubilisation increased with temperature and viscosity decreased for increasing temperatures. Methane volume enhancement was linked to sludge solubilisation, maximum methane production ( $238 \pm 32$  NmL CH<sub>4</sub>/gCOD) and biodegradability ( $68 \pm 9\%$ ) were obtained from samples treated at 160°C. The Gompertz modelling equation fitted well with the BMP results. Thermal treatment improved dewaterability and filterability for temperatures above 120°C but deteriorated below. Press filter dewatering was successful at increasing final solids concentrations.

Regarding the energy balance, a TH unit was self-sufficient for all treatment temperatures and provided extra energy for the plant. Pretreatment at 160°C was considered the best option as it improved methane production, dewatering and provided the biggest net balance out of all temperatures. However, untreated WAS processing seems to be more energetically favourable than installing a THP unit, which is in disagreement with literature findings.

**Keywords:** anaerobic digestion, sludge dewatering, energy balance, thermal hydrolysis



## Resumo

Actualmente, o aumento da produção de lamas ativadas de ETAR coloca problemas à gestão destes resíduos. O pré-tratamento térmico de lamas ativadas pode ser utilizado para melhorar a digestibilidade e a produção de biogás das mesmas, facilitando igualmente o seu processo de desidratação, a fim de reduzir a sua produção. Este trabalho teve como objectivo o estudo dos efeitos da temperatura do pré-tratamento térmico no balanço energético de uma estação de tratamento de águas residuais, noomeadamente no processamento das lamas ativadas. Para tal, foram realizados tratamentos térmicos a diferentes temperaturas, 120°C, 160°C e 200°C, em amostras de lamas ativadas, seguido de um teste do potencial bioquímico de metano (BMP) para avaliar a biodegradabilidade e a produção de metano das amostras termicamente tratadas. Após digestão anaeróbia, foi realizado um ensaio de desidratação por filtro de prensa e medições do tempo de retenção capilar (CST). Finalmente, foi elaborado um balanço energético relativo à implementação de uma unidade hidrólise térmica numa ETAR.

Para todas as temperaturas testadas, a solubilização da matéria orgânica solúvel (sCQO), do azoto amoniacal total e do ortofosfato aumentaram linearmente com a temperatura, enquanto a viscosidade diminuiu com o aumento da temperatura. O aumento do volume de metano está associado à solubilização da matéria orgânica e a produção máxima de metano ( $238 \pm 32$  NmL CH<sub>4</sub>/gCQO) e a biodegradabilidade ( $68 \pm 9\%$ ) foram obtidas para amostras tratadas a 160°C. A equação cinética de Gompertz ajustou-se bem aos resultados do BMP. O tratamento térmico melhorou a capacidade de desidratação e filtrabilidade de lamas termicamente tratadas para temperaturas superiores a 120°C, mas deteriorou para temperaturas inferiores. A desidratação mecânica por prensa permitiu o aumento da concentração de sólidos finais.

Relativamente ao balanço energético, a unidade TH mostrou-se auto-suficiente para todas as temperaturas de tratamento e permitiu fornecer energia extra para a ETAR. O pré-tratamento a 160°C é considerado a melhor opção, pois melhorou a produção de metano e desidratação das lamas, tendo obtido o balanço energético final mais positivo de entre as temperaturas testadas. No entanto, o processamento de lamas ativadas sem hidrólise térmica obteve o saldo energético mais elevado, o que parece estar em desacordo com a literatura mais recente.

**Keywords:** hidrólise térmica, digestão anaeróbia, desidratação de lamas, balanço energético



# Acknowledgements

This thesis was carried out at the Department of Water Management in the Faculty of Civil Engineering and Geosciences at TU Delft, through the Erasmus+ Programme. I would like to thank Professor Jules van Lier, for accepting my proposal to do an internship at the Water Lab and contributing with his expertise as my supervisor. Another big thank you to Professor Merle de Kreuk, who oversees the project I integrated. Your exceptional critical thinking and recommendations have helped me elevate my work and my academic standards.

I want to express my gratitude to my supervisor at FEUP, Professor Olga Nunes, who so kindly accepted to guide my work, especially in such a challenging way, with a student who was working abroad.

Some special words of gratitude to the following people, without whom I would not have been able to complete this research and without whom I would not have made it through my masters thesis!

Javier Pavez, my PhD tutor at TU Delft, for your valuable guidance throughout my work. You provided me with the tools and knowledge that I needed to organize my experimental design and successfully complete my dissertation. I hope to have made a positive contribution to your project and I wish you tremendous success in your career.

Maikon Kelbert, for the company and guidance during my lab experiments, for reassuring and guiding me throughout these months, thank you. Your companionship was crucial to make those long work days less lonely.

João Ferreira, for being an unexpected Portuguese friend at TU Delft and my beta proof reader. Your selfless support was an act of a true friend and my thesis was greatly improved with your input. Thank you.

To all my dutch friends that I had the pleasure to meet in my short stay in the Netherlands, thank you for bringing me along with you to enjoy this very atypical summer. I had the most fun learning about the dutch culture and experiencing it through all of you. Your company made my Erasmus+ experience so much more meaningful.

To my family, for your continuous support throughout my studies. I know it has taken long, but I am finally free! You have made all this possible, so thank you, as being able to pursue my academic dreams has been one of my greatest privileges and joys.

Finally, although a bit narcissistic, thank you Raquel (me)! For never giving up on your passions, for sticking to your aspirations, for your work ethic and your values. Everything you have ever wanted, you have worked for it, even at the cost of your own personal life sometimes. Your academic years are finally over and it is now time to tackle the real world. May you never waver in the face of challenges. Never forget what truly ignites your soul.

Raquel Tomé Gaspar



*“Water is the first principle of everything.”*

Thales of Miletus (c. 624 - 546 B.C.)



# Declaration

I declare, on my word of honour, that the information provided on this work is original and that all non-original contributions were duly referenced with identification of the source.

Raquel Tomé Gaspar, November 22, 2020



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# Abbreviations

|       |                                         |
|-------|-----------------------------------------|
| AD    | Anaerobic Digestion                     |
| ATP   | Adenosine Triphosphate                  |
| BMP   | Biochemical Methane Potential           |
| CST   | Capillary Suction Time                  |
| CSTR  | Continuous Stirred-Tank Reactor         |
| DNA   | Deoxyribonucleic Acid                   |
| DS    | Dry Solids                              |
| EBPR  | Enhanced Biological Phosphorus Removal  |
| MAD   | Mesophilic Anaerobic Digestion          |
| OP    | Ortho-phosphate                         |
| PAO   | Polyphosphate-Accumulating Organism     |
| PE    | Polyelectrolyte                         |
| PS    | Primary Sludge                          |
| RNA   | Ribonucleic Acid                        |
| SRT   | Solids Retention Time                   |
| TAN   | Total Ammonia Nitrogen                  |
| THP   | Thermal Hydrolysis Process              |
| TS    | Total Solids                            |
| tVOSC | total Volatile Organic Sulfur Compounds |
| VFA   | Volatile Fatty Acid                     |
| VS    | Volatile Solids                         |
| WAS   | Waste-Activated Sludge                  |
| WW    | Wastewater                              |
| WWTP  | Wastewater Treatment Plant              |



# Chapter 1

## Introduction

Water is easily taken for granted in countries with enhanced water infrastructures. Due to the current population growth, accelerated urbanization and economic development, the quantity of wastewater generated is increasing globally [79]. In the European Union (EU), the implementation of the Urban Waste Water Treatment Directive (91/271/EEC) ensures that EU citizens have access to quality drinking water and to healthy and clean water resources.

With the growing concern on water quality, wastewater treatment has seen an expanding growth across the world, both in developed countries where stricter legislation is applied and in developing countries, with the construction of new waste water treatment plants (WWTPs) [127].

The residue generated during the primary and the secondary wastewater treatment is generally called “sludge”, more specifically primary sludge and waste-activated sludge, respectively. From the various constituents removed during wastewater treatment, sludge is by far the largest in volume and the biggest by-product of wastewater treatment [39]. This increased production is related to the increasing widespread use of biological treatment in developed countries. Although sludge production varies greatly between countries in the European Union, the EU produced over 2.9 million tons of sludge just in 2017 [15] and this amount should increase as countries implement more and better wastewater treatment processes.

Sludge processing is costly. Sludge handling, transportation and disposal account for 30-40% of the capital costs and around 50-55% of the annual operation and maintenance costs of WWTPs [68, 86], becoming their biggest bottleneck [37]. In The Netherlands, after the year 2000, land-filling of dewatered sludge became forbidden, making incineration and co-incineration the standard sludge disposal method in the Dutch country [27]. This measure was implemented to ensure long-term soil quality protection, as produced sludge could not meet the stricter limit values for contaminants and heavy metals imposed for agricultural use of sewage sludge [65]. Transportation costs, incineration fees and the consumed energy are the main factors that justify high costs of sludge handling [66]. Therefore, a great effort has been put into minimizing sludge production and enhancing the quality of the biosolids, mainly by improving the anaerobic digestion process. An

efficient anaerobic digestion process produces fewer and dryer solids which reduces the handling costs of sludge [28]. Standard approaches to improve the anaerobic digestion process include the optimization of operational conditions, processing at a thermophilic temperature regime [40], co-digestion of mixed different materials and the pretreatment of input sludge, mainly by disintegration of waste-activated sludge [28].

A diverse number of techniques have been developed in recent years for the sludge pretreatment to improve subsequent digestion and final output quality [75]. These techniques focus on reducing solids and increasing the methanization of sludge by enhancing the rate and extent of hydrolysis of organic material, regarded as the rate-limiting step of anaerobic digestion [58]. The aim is to make the substrate more biodegradable, usually through cell-lysis processes or disintegration of sludge cells and flocs [55], that facilitate accessibility of the substrate to extracellular enzymes from the inoculum present within the digestors [28]. Positive results have been observed for mechanical, thermal, chemical and biological pretreatments [127, 75, 4] but thermal hydrolytic pretreatment has been shown to be an effective technique for achieving organic degradation, improved dewatering and higher methane yields [13, 99, 58].

The implementation of Thermal Hydrolysis Process (THP) in WWTPs shows interesting results in terms of dewaterability and reducing final digested solids. This process consists of heating up sludge to a set-temperature (90°C to 200°C) [20] under pressurized conditions and then flashing it. This creates a steam explosion that disrupts cell walls and the extracellular polymeric substances (EPS) that hold the sludge flocs together, improving the dewaterability by changing sludge structure while also improving digestability of biological sludge [72]. The increased solubility of organic compounds allows for higher digester loads and the higher digestibility promotes reduced digestion times during anaerobic digestion [58].

There is a consensus that the best treatment regime for THP is a treatment time of 30 minutes and a temperature between 160-180°C, since above 180°C recalcitrant compounds begin to form and hinder anaerobic digestion, while below the extent of biodegradability is not maximized [80]. These conditions allow for optimum biogas production and dewaterability improvement. However, few studies evaluate the influence of pretreatment on the WWTP energy balance upon variation of the operational conditions, in regards to not only biogas production, but also energy expenditure for pretreatment and dewatering.

This research focuses on the energy balance of a sludge handling process upon the introduction of a THP unit and the parameters that influence its performance. It is a relatively unexplored and unpublished area and the potential to make a contribution to knowledge is high. This work aims to develop a better system operation while ensuring both quality anaerobic digestion (AD) and the best possible dewaterability, minimising the cost as much as possible.

## 1.1 Knowledge Gap

A clear understanding of the influence of operational parameters in a thermal hydrolysis process unit on the energy balance of sludge processing in a wastewater treatment plant.

## 1.2 Main Objective

To understand the effect of temperature on thermal hydrolysis pretreatment of waste activated sludge on the downstream processing of sludge. Meaning, how it affects biogas production in relation to reaction time of anaerobic digestion and the dewatering process after AD, in final solids concentration and energy consumption. An overall energy balance pertaining to sludge processing will determine the operational conditions most efficient to the process and the WWTP energy considerations.

## 1.3 Research Questions and Methodology

Following up the main objective, it became necessary to structure the research design and propose smaller research questions that would allow to materialize this experimental work.

First, it was important to establish how does the pretreatment temperature influence the biodegradability and the biogas production of WAS during mesophilic anaerobic digestion. Also during anaerobic digestion, it was necessary to understand the release kinetics of ammonium and phosphorous of thermally treated sludge and if this nutrient release would influence biogas production and the extent of the anaerobic digestion. Subsequently, it was necessary to assess if thermally treated anaerobically digested sludge would influence the downstream sludge processing, specifically the dewatering process in terms of final solids concentration and energy expenditure. Finally, it was necessary to understand the energy considerations needed to integrate a thermal hydrolysis unit in a WWTP energy balance, and if a compromise between quality and economic feasibility could be reached with THP unit.

For that, the following research design was proposed in order to answer the research questions:

- A literature review on the main effects of the thermal pretreatment of WAS, in regards to biodegradability, dewaterability and nutrient release at different temperatures. Modelling considerations for energy balances and processing designs have also been studied;
- Experimental assessment of initial characteristics of WAS and subsequent thermal hydrolysis at different temperatures (120°C, 160°C and 200°C);
- Biomethane potential (BMP) tests of thermally treated sludge in mesophilic regime. Analysis of nutrients release during the BMP test run;
- Experimental dewatering analysis of sludge before and after anaerobic digestion by two methods: capillary suction time (CST) and press-filter;
- Energy modeling regarding the chosen WWTP layout. All relevant experimental data was used as input in the model.

## 1.4 Alterations regarding SARS-CoV-2 pandemic

The 2020 covid-19 pandemic has brought many challenges to our daily life and how we operate as a society. It is of common knowledge that all educational institutions closed down during the height of the pandemic, both in Portugal and in The Netherlands. In my personal case, the Technical University of Delft also closed down their facilities for more or less two months, starting late-March, time in which I returned to Portugal. This, of course, meant changes in my initial research proposal as it was uncertain if I was ever able to return to the Netherlands and how long that would take.

Luckily, I was able to return in late-May to develop my research. It is important to mention that right when I was about to begin my experiments in March, lockdown was enforced. This meant that, upon my arrival, I had to start my research from the beginning. On-campus work had to be done in shifts, which also meant considerable delays in my research scheduling. Regarding my initial proposal, the aim was to study both mesophilic and thermophilic regimes in anaerobic digestion with thermally treated sludge. Since my remaining exchange period was only of four months, I had a short period of time available to work and this meant I was only able to study the mesophilic regime. Each digestion BMP run takes around one month and 3 weeks to conclude, including preparation and analysis. Even though, through all difficulties and long hours, I was extremely fortunate to not have been severely affected by the pandemic, which allowed me to have a very memorable, enriching experience at the WaterLab.

## Chapter 2

# Thermal hydrolysis for wastewater treatment

Anaerobic digestion is an appropriate technique for the treatment of surplus sludge before final disposal and it is employed worldwide as the oldest and most important process for sludge stabilization [66]. The anaerobic digestion process is composed of four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis. For waste-activated sludge (WAS) degradation, the rate-limiting step is hydrolysis [10]. During the hydrolysis step, organic compounds, such as polysaccharides, proteins and fats are hydrolysed by extracellular enzymes to monomer or dimer compounds [69], which improve the biodegradability of sludge. Thermal hydrolysis pretreatment of sludge has been regarded as the most profitable and reliable technique to improve hydrolysis of particulate organic matter and biodegradability of sludge [19], as it breaks up the sludge matrix structure and decomposes large biopolymers into smaller molecules by applying high temperatures and pressures [72].

As previously mentioned, this treatment breaks down the extracellular polymeric substances (EPS) structure of sludge and disintegrates flocs, releasing the matrix-bound water [71]. As the trapped water intracellularly and in the matrix of the sludge is released, the sludge rheology changes considerably. A thermally treated sludge with a dry solids content of 12% appears as liquid and can be handled in a similar manner to raw sludge with 5–6% TS [54]. This means that higher loading volumes can be fed to the anaerobic digester, effectively increasing sludge processing capacity.

The use of thermal hydrolysis can have a positive effect on the energy balance of a WWTP due to the increase of biogas production, which can be used to fulfill the steam and electrical needs of the plant. It can also improve the quality of the biosolids produced after digestion. Both these factors positively affect the operational cost of the treatment plant [89]. The effects of thermal hydrolysis in sludge can be exploited to increase biogas production in anaerobic digestion, to improve dewaterability, to inactivate pathogens and to reduce the overall sludge production [58].

This chapter aims to elucidate the main literature findings that shed light on the operational conditions that allow for an efficient use of thermal hydrolysis as a pretreatment for anaerobic digestion.

## 2.1 Historical evolution of THP

Thermal treatment of sludge has a long track-record of good results and is a simple technology that has been gradually developing since mid-20<sup>th</sup> century.

The earliest example of THP can be traced back to the Porteous process in the 1940s, where it was exclusively used as a mean to improve the dewaterability of the sludge [47]. Raw mixed sludge (primary and activated sludge) was heated to 200°C and dewatered, reducing moisture to a 35-70% solids content without the use of chemicals. This allowed for a sterile product that would proceed to incineration, without being submitted to anaerobic digestion [94]. The Porteous process became the first example of a thermal hydrolysis concept to be installed worldwide. Today, almost all WWTPs built from 1938 to the seventies were closed down as the technology became obsolete and economically unfavorable. Main drawbacks included odour problems, corrosion and high strength liquors [16, 54].

In the late seventies, several researchers [99, 77, 43] tried to reintroduce thermal treatments for sludge minimisation at lower temperatures (100 – 175°C) in the pursuit of the optimum compromise between dewaterability and digestibility. This new wave of research ought to renew the use of thermal hydrolysis as a way to improve sludge minimisation and dewaterability, the biodegradability of biological sludges during anaerobic digestion, odour reduction and production of class A biosolids for land application [1]. Lower temperature processes were investigated [48] with most research concluding that the optimum temperature was about 170°C, particularly effective for the improvement of the anaerobic digestion of WAS [54].

As stricter regulations were being implemented during the 80's in Europe regarding nutrients removal of wastewater, new technologies based on hydrolysis emerged using acid, alkaline, heat and combinations between these for enhanced nutrient removal. The aim was to establish a standard collective physico-chemical approach to produce a sanitized product that could be used in land application [16]. In this context, projects such as the Hypro project, carried out under the EU Eureka programme in 1990, sought to use pre-precipitation coupled with thermal hydrolysis to produce a carbon source for biological denitrification of sludge. Precipitation with polymerized aluminium chloride would extract precipitates from effluent wastewater, that were then hydrolysed by THP and fed to the denitrification process, for an integrated nutrient removal process [45]. The majority of these new methods were unsuccessful at the time due to their high cost of operation.

More recently, the design of a new process successfully combined the thermal hydrolysis pretreatment with anaerobic digestion [16]. The Norwegian company Cambi built its first full-scale plant in Hamar, Norway, which has been operating since November, 1995. The Cambi treatment was built to minimise the amount of sludge and maximise the biogas production by up to 50% [17]. The digested and disinfected sludge can be a safer option for agricultural use,

adding another source of revenue to the WWTP [111]. Since Cambi, many other competitors, such as Veolia, who developed two main products, Bio Thelys™ [101] and EXELYS™ [102], and  $\text{teCH}_4^+$  [100] have emerged with similar technologies, proving that the thermal pretreatment of sludge has economic feasibility to be implemented as a lucrative industrial solution.

## 2.2 Literature review

Literature regarding THP for sludge processing is vast, specially regarding compositional and structural changes in sludge and its effects on the subsequent stabilization processing.

For the purpose of this work, it is crucial to understand the main changes regarding nutrient release, solubilization, rheology and dewatering that come with the thermal pretreatment of sludge, as they are the drivers of the economic rationale. This sub-chapter compiles the main literature on each of those subjects.

### 2.2.1 COD solubilization and biodegradability

Chemical oxygen demand is a measure of the oxygen required to oxidise all organic material present into water and carbon dioxide and thus a measure of the amount of organic material within a substance [66]. Results obtained for chemical oxygen demand (COD) solubilisation versus process temperature for a 30 min thermal pretreatment time are depicted in Figure 2.1. It can be observed that COD solubilisation increases almost linearly with temperature, showing higher percentages for temperatures above 140°C. This is true even for WAS with different characteristics, as demonstrated by Bougrier *et al.*, who compared the effect of thermal treatment on COD solubilisation of 5 different secondary sludge samples from urban and industrial effluents at different organic loads [13].

Regarding the contact time, it can have importance at lower temperatures (<100°C), but it has little impact at higher temperatures. This observation has been corroborated by several authors [107, 86, 5]. Ruffino *et al.* observed that the duration of the exposure had an equal relevance in determining the level of COD solubilisation, but the efficiency of the treatment in terms of soluble COD (sCOD) release decreased for durations longer than three hours [86]. Similar results were presented by Appels *et al.*, who analysed increasing exposure times for the same temperature. These researchers recorded that after 15 min. of treatment at 80°C, the soluble COD tripled compared to raw sludge, increasing up to 20 times after 60 min. comparatively to untreated sludge [5].

However, for higher temperatures, >100°C or >150°C, depending on the literature, the treatment time has little influence on improving COD solubilisation, as WAS strongly solubilises after 15 min of thermal treatment, maintaining a constant ratio until 30 min time, after which it becomes stagnant [107, 58].

Table 2.1 compiles some publications that aim to establish the range of THP conditions that would optimize biogas production and solubilisation as well as the removal of constituents. The

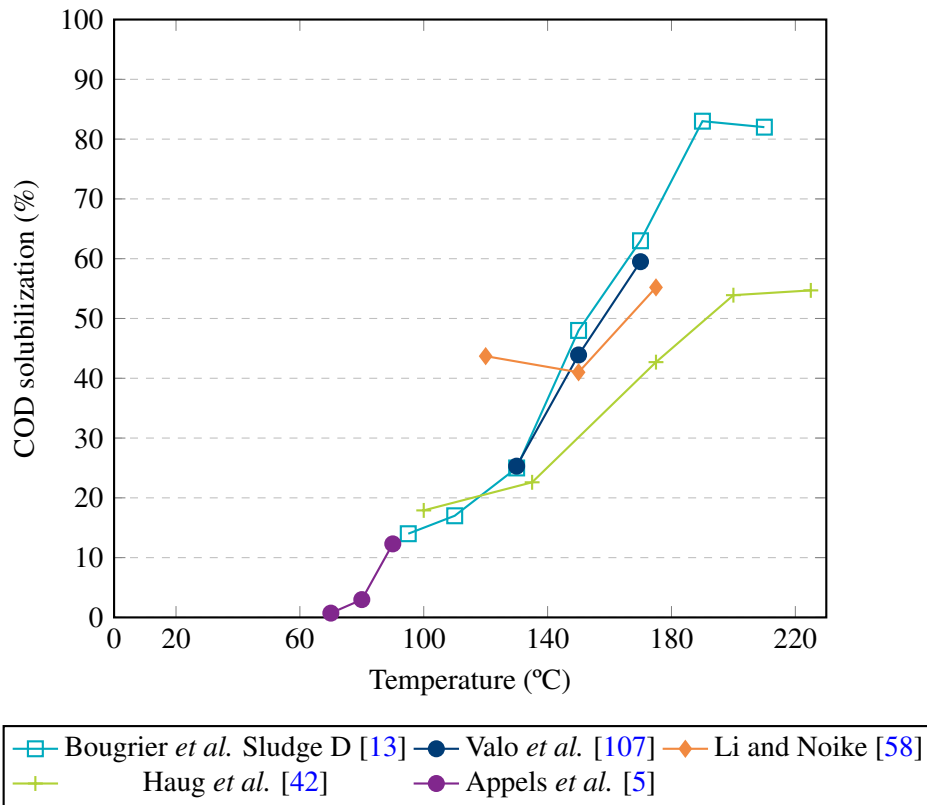


Figure 2.1: COD solubilisation as a function of temperature applied in the thermal treatment. Adapted from [13, 107, 58, 42, 5].

THP conditions shown in Table 2.1 produced the best results, although the studies usually tested for higher temperatures and time ranges.

By analysing Table 2.1, it is granted that the optimum temperature for a thermal pretreatment is around 165 – 175°C. This value is seen often throughout the literature as a compromise between solubilisation, biodegradability and dewaterability [54]. At this temperature, protein is strongly solubilised which is not always the case for lower temperatures (120-150°C). At lower temperatures, carbohydrates are more easily solubilised as they are mainly located on the exopolymers of sludge structure, whereas proteins tend to be found on the inside of cells [13].

For temperatures higher than 150°C, soluble reducing carbohydrates react at a higher rate with soluble proteins to form recalcitrant compounds through the Maillard reaction, as shown in Table 2.2. Although recalcitrant compounds reduce biodegradability, their formation so far seems inevitable. Common recalcitrant compounds found after thermal hydrolysis of sludge are melanoidins, responsible for the browning that occurs in sludge after it has been treated [30]. These organic compounds are difficult to degrade and can impose some toxicity to the inoculum, inhibiting anaerobic digestion [95]. Production of melanoidins is enhanced at increased temperatures, which indicates the Maillard reaction occurs in parallel with thermal hydrolysis of solids and the impacts of melanoidins formation must be balanced with the benefits associated with the improvement to solids reduction and biogas production [123].

Table 2.1: Literature review on impacts of thermal pretreatments on waste activated sludge anaerobic digestion

| Anaerobic digestion           |                    |             |         |       |                                                                                                         |                                                       |
|-------------------------------|--------------------|-------------|---------|-------|---------------------------------------------------------------------------------------------------------|-------------------------------------------------------|
| Reference                     | THP conditions     | Temperature | HRT (d) | Type  | Biogas production                                                                                       | Removal and solubilization                            |
| Wilson <i>et al.</i> [115]    | 150-170°C, 30 mins | 37          | 15-20   | batch | Specific production of 0.8 m <sup>3</sup> / kg fed(+35%)                                                | -                                                     |
| Valo <i>et al.</i> [107]      | 170°C, 60 mins     | 35          | 20      | CSTR  | Biogas yield of 142dm <sup>3</sup> CH <sub>4</sub> /kg COD fed (+61%)                                   | COD removal 70.7% (+61%)<br>TS removal 59.3% (+117%)  |
| Tanaka <i>et al.</i> [99]     | 180°C, 60 mins     | 37          | 8       | batch | Increase in biogas production by 1.9 times, compared to raw WAS                                         | Solubilization rate of VSS of 30% (+15%)              |
| Stuckey and McCarty [95]      | 175°C, 60 mins     | 35, 55      | 34      | batch | Bioconvertibility for mesophilic and thermophilic digestion of 61% and 51%, respectively (+13% and +9%) | -                                                     |
| Polanco <i>et al.</i> [37]    | 170°C, 30 mins     | 33          | 12      | CSRT  | Biogas production of 445L/kg VS fed. CH <sub>4</sub> increment of 55%                                   | VS removal of 45-60%                                  |
| Pinnekamp [77]                | 170°C, 45 mins     | 33          | 20      | batch | Gas yield increase by 74 % for WAS and 20-26% for primary sludge                                        | Maximum VS reduction (55%) at 220°C                   |
| Pérez-Elvira and Polanco [80] | 170°C, 30 mins     | -           | 17      | CSRT  | Biogas yield of 652 L/kg VS fed (+33%)                                                                  | 55% VS removal (+30%0)                                |
| Mottet <i>et al.</i> [69]     | 165°C, 30 mins     | 55          | 22      | batch | Biogas production of 215mL CH <sub>4</sub> /g CODin (+14% and +20% against control and 220°C)           | COD solubilization of 18%                             |
| Li and Noike [58]             | 175°C, 60 mins     | 35          | 1.5-10  | CSTR  | Methane production doubled from WAS with thermal pretreatment at 150°C and 175°C                        | Solubilization increases with increasing temperatures |
| Bougrier <i>et al.</i> [10]   | 170°C, 30 mins     | 35          | 24      | batch | CH <sub>4</sub> production of 333mL/g CODin (+76%)                                                      | COD solubilization between 45-50%                     |
| Bougrier <i>et al.</i> [11]   | 170°C, 30 mins     | 35          | 20      | CSTR  | CH <sub>4</sub> production of 256mL/g VSin (+51% against control)                                       | TS removal of 52% (+27%)<br>VS removal of 64% (+33%)  |

Table 2.2: Main remarks regarding the impacts of thermal pretreatments on waste activated sludge

| Reference                | Remarks                                                                                                                                         |
|--------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|
| Wilson et al. [115]      | Reduction of tVOSC, an indicator of biosolids odour, by 92% against 52% of MAD                                                                  |
| Valo et al. [107]        | For industrial applications, pretreatment at temperatures >170°C is more advantageous                                                           |
| Tanaka et al. [99]       | Low rate of solubilisation in combined WAS probably due to the complexity of organics (including refractory components)                         |
| Stuckey and McCarty [95] | For temperatures >175°C, bioconvertibility decreased sharply                                                                                    |
| Polanco et al. [37]      | For temperatures >170°C, there is a reduction in biodegradability due to the formation of recalcitrant compounds. Dewaterability becomes easier |
| Pinnekamp [77]           | For temperatures >180°C, biogas production decreases sharply due to the formation of melanoids                                                  |
| Mottet et al. [69]       | Formation of recalcitrant compounds at 220°C                                                                                                    |
| Li and Noike [58]        | Retention time for AD can be reduced 5 days. Pretreatment at 170°C is optimum for increasing both AD of WAS and methane production              |
| Bougrier et al. [10]     | Dewaterability was improved for temperatures above 150°C, but deteriorated for lower temperatures                                               |
| Bougrier et al. [11]     | Low difference in results from pretreatments at 150°C and 170°C. Cost of utilities is necessary to estimate the best option                     |

### 2.2.2 Influence of thermal hydrolysis on sludge rheology

The rheological properties of the sludge are a crucial aspect to take into consideration when designing efficient operating processes for wastewater treatment [33] as they affect the mixing of the medium, transport and mass exchanges between the solid, liquid and gaseous phases [93]. This will affect the design of tanks, digesters, pumps and transport lines, heat exchangers, sludge dewatering and biogas production units [36, 64].

Likewise, the rheology change in sludge attributed to thermal hydrolysis, is arguably the most prominent consequence of the treatment, as it aids with the downstream transport and dewatering [6]. Although literature can be found related to the rheological characterization of sludge [26, 34, 92], there is very little information regarding the changes in its properties when treated by thermal hydrolysis.

Sludge is widely accepted as a non-Newtonian shear thinning thixotropic fluid, behaving as a thixotropic colloidal suspension at high shear rates, but exhibiting a polymeric behaviour at low shear rates, with temperature dependency [33]. Thixotropic behaviour means that viscosity is time-dependent and shear thinning means that the viscosity decreases with the applied shear rate [87]. The flow behaviour of waste-activated sludge can be described by the Herschel-Bulkley model (Figure 2.2), with the equation:

$$\tau = \tau_H + K\dot{\gamma}^n \quad (2.1)$$

where  $\tau$  is the shear stress (Pas),  $\tau_H$  the Herschel-Bulkley yield stress (Pas),  $\dot{\gamma}$  the shear rate ( $s^{-1}$ ),  $K$  and  $n$  are flow consistency and flow behaviour index, respectively [64].

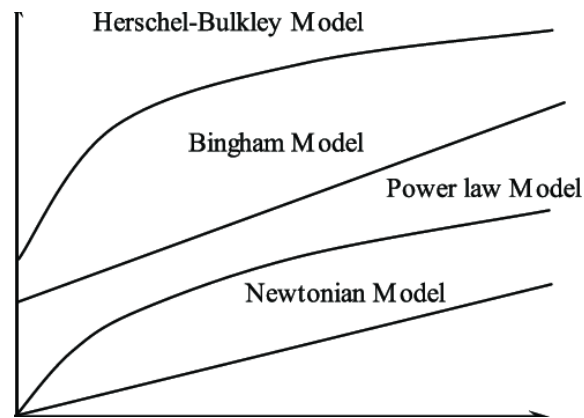


Figure 2.2: Rheological models.[67]

The rheological behaviour of sludge is fundamentally influenced by temperature, solids concentration and bound water content. Viscosity and yield stress are considered reliable rheological parameters for sludge characterization as they correlate well with the above parameters [33].

Other parameters, such as sludge density, particle size and size distribution, surface charge, settling rates, abrasiveness, particle friability, surface charge, liquid phase conductivity, pH, amongst others, play a role in influencing rheology, although the extent of that influence has yet to be examined properly [63]. Since sludge is such a complex material and there is no standardised method for rheometric measurements of sludge, analysing the extent of the influence of rheological properties on the operating conditions and scale up calculations of processing units can be quite difficult. So much so, that it makes it almost impossible to predict, in the present case, how the rheological behaviour will change after the thermal hydrolysis and if it will influence the AD process [64].

Temperature increase is the ruling mechanism of thermal hydrolysis and this is documented to reduce viscosity and yield stress [36, 33]. The dependence of these two parameters on temperature can be described by an Arrhenius' type equation, [33] as free water within the sludge moves more freely at higher temperatures. However, some authors [8] objected this modelling by showing that the rheological behaviour of sludge is irreversibly altered by thermal history since the initial yield stress decreased after cooling the heated sludge (for heating temperatures between 20°C-80°C) [35]. The higher the temperature of the preheat, the smaller the yield stress and higher the viscosity of the cooled-down sludge [8]. Irreversible changes in sludge structure [36], as a result of sludge flocs destruction, decrease particle-particle interactions which can significantly reduce the yield stress in a suspension [35]. This mainly because as most proteins denature with heat, they unfold and increase the water bound to their structure. This increases the hydrodynamic radius of the molecule which increases the viscosity of the solution. Furthermore, when sludge cools down, the kinetic energy barriers will prevent proteins to form in their native form, irreversibly maintaining their increased water-binding capacity [3].

Nonetheless, thermal treatment at higher temperatures ( $> 100^{\circ}\text{C}$ ) produces more notorious results. The rate of solubilisation and the denaturation of proteins increase in such a way that a drop in viscosity is achieved. *Bougrier et al* observed that the rheology curve for sludge treated at  $170^{\circ}\text{C}$  and  $190^{\circ}\text{C}$  became more linear, meaning sludge tend to behave more as Newtonian after thermal treatment [10]. *Urrea et al* found similar results, with reductions in apparent viscosity up to two orders of magnitude for temperatures between  $160^{\circ}\text{C}$  -  $200^{\circ}\text{C}$  and a transformation of sludge from a Bingham plastic to a Newtonian fluid at the end of the thermal treatment [106]. The viscosity of thermally treated sludge is always lower than untreated sludge for the same solids concentration [71].

Finally, the rheological behaviour of primary and secondary sludge are very distinct, and the ratio at which they are mixed for thermal treatment affects the final viscosity. Primary sludge is considered a suspension of flocculated matter, where particles are held together by van der Waals forces [64], whilst secondary sludge is composed of flocs of various sizes, which in themselves consist of microorganisms, such as single cells or filamentous bacteria, inorganic particles, organic debris and extracellular polymeric substances (EPS) [24]. The EPS forms a gel-matrix within the secondary sludge, as it retains large amounts of water, holding all the flocs together [71]. This makes secondary sludge much more viscous than primary sludge, and an important factor when studying the best approaches for thermal hydrolysis processing [6]. For the purpose of this work, only WAS was thermally treated, but the author considers important to refer that pretreatment of sludge can be applied to both primary sludge, activated sludge or a mix of both and the ratio at which these are mixed can also influence rheological behavior.

### 2.2.3 Influence of thermal hydrolysis on sludge dewaterability

It is a widespread consensus in the literature that thermal hydrolysis has a positive effect on sludge dewaterability, ever since it was first developed as a dewatering aid [42], only to be later used to improve anaerobic digestion [77, 99, 58]. Dewatering after anaerobic digestion can be done in various ways: through centrifugation, filter presses and sludge drying beds in order to achieve final cake solids of 25-35% total solids (TS) [66]. The dewatering step ensures that a wastewater facility produces compact stabilised sludge and saves on disposal costs.

WAS is known to be harder to dewater than primary sludge [16], and it has been long understood the reason is the extracellular polymeric substances (EPS) structure that forms a matrix with microorganisms, organic material and cell debris [70]. EPS stands for a designation used broadly for different classes of organic macromolecules such as polysaccharides, proteins, nucleic acids, lipids, and other compounds commonly found in the interstitial space of microbial aggregates like inorganic particles, multivalent cations and other particles [71]. The EPS relates to several physicochemical properties of sludge, such as surface charge, moisture content, compressibility, hydrophobicity and viscosity [59]. This matrix captures water, developing a gel-like consistency in sludge [72]. The production of EPS is a general property of microorganisms in natural environments [116]. EPS forms a three-dimensional, gel-like, highly hydrated [116] and often negatively charged biofilm matrix, [24] that secures microorganisms and particles, as if it formed a network

in the sludge. The mass of EPS and the water held within its structure can represent up to 80% of the mass of activated sludge [38]. In fact, simple sedimentation of activated sludge results in a settled layer with a solids content only of 1.5-4.0 wt%. With the addition of flocculants followed by mechanical dewatering, either by high speed centrifugation or using high pressure filtration processes, the sludge cake can reach 20-30 wt% solids content [91].

The nature of water in sludge and the EPS structure are tightly connected. According to *Kopp et al*, the type of bonding between the sludge particles and the water molecules establishes four different types of water: (i) free water, not bound to particles; (ii) interstitial water, bound by capillary forces between flocs and microorganisms; (iii) surface water, bound by adhesive forces and finally, (iv) intracellular water. The free water can be separated mechanically as it moves freely between flocs without being adsorbed, bound or influenced by capillary forces. Surface water is composed by several layers of water molecules bound by adsorptive and adhesive forces, covering the entire surface of the sludge. Water chemically bound to exopolymers is also considered part of the surface water. Intracellular water refers to the water in cells. Surface and intracellular water are often called bound water content [56].

The influence of EPS on dewatering has been investigated in various studies. *Houghton et al* aimed to establish the relationship between dewaterability and the amount of EPS found in sludge. For activated sludge samples, figure 2.3 illustrates the optimum level that allows for maximum dewaterability is around 35 mg EPS/g SS (suspended solids) [50]. CST refers to capillary suction time, a standard test used to determine the rate of water release from sludge, although it does not predict the extent of dewaterability in terms of final cake solids, a key parameter of interest for utilities [46].

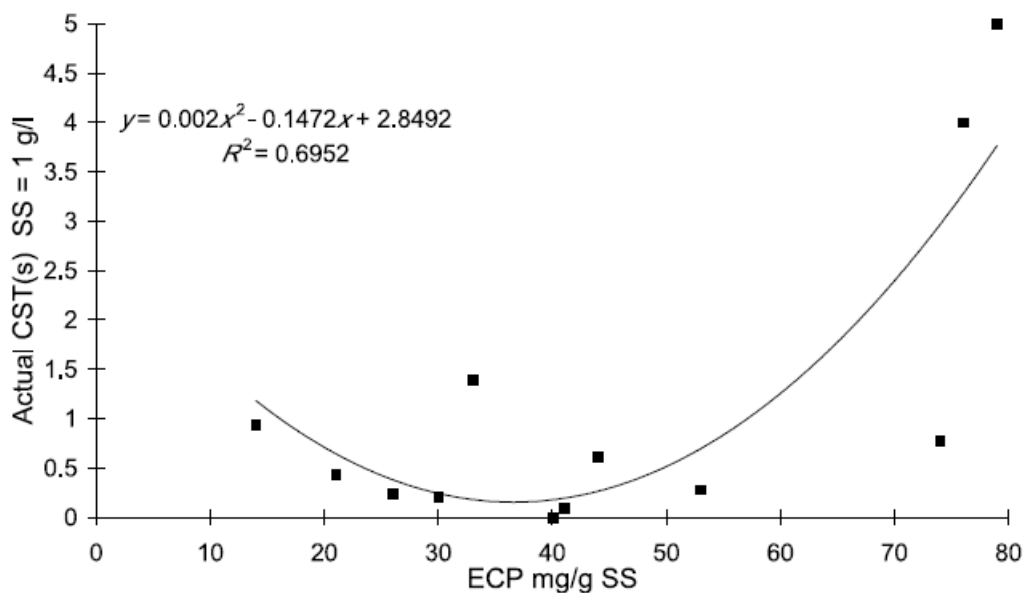


Figure 2.3: The relationship between the quantity of ECP ((microbial extracellular polymer, an analogous name for EPS) present and sludge dewaterability for activated sludge and CST, the rate of water release from the sludge [50].

Houghton also found that increasing levels of EPS (10 mg - 40 mg/g SS) aid in the sludge dewaterability by improving sludge flocculation [50]. This decreases the number of small particles in sludge [70], which has been previously shown to make sludge easier to dewater [53]. Nevertheless, the EPS water retaining capacity can be a hindrance after a certain level has been reached, as it counteracts the benefit of flocculation [50].

It becomes easy to understand that it is possible to increase the dewatering efficiency of activated sludge by degrading the EPS. Thermal pretreatment technologies improve dewaterability in two ways: (i) breaking the structure of proteins and polysaccharides which constitute almost 60% of WAS sludge EPS, thereby reducing its water content [71] and (ii) improving flocculation which reduces the amount of fine flocs [13].

Higgins reported that as the THP pretreatment temperature increased, the cake solids also increased with considerable differences going from about 27% TS cake at 130°C to 32% TS at 170°C, an 18.5% increase in cake solids, for a dewatering process performed after the thermally treated sludge was digested [46]. *Neyens et al* demonstrated that thermal hydrolysis at 120°C most effectively reduced the residual sludge and enhanced dewaterability, compared to the same treatment in acidic and alkaline conditions. The amount of total solids to be dewatered was reduced to 58% of the initial untreated amount and the TS content of the dewatered cake increased from 30% TS (initial untreated) to approximately 43% TS [72].

## 2.2.4 Nutrient release

During thermal treatment of WAS, several nutrients including phosphorus (P), nitrogen compounds (N), and some metal cations like  $Mg^{2+}$  and  $K^{+}$  are released in significant amounts, although the mechanisms regarding the release of these substances are not fully understood [119]. Most studies focus on the solubilisation of P, N and other organic compounds, but not on their specific release regarding the different fractions (organic, inorganic) especially after pretreatments such as thermal hydrolysis.

This section intends to summarize the mechanisms that explain the release of ammonia and phosphorous, two major nutrients. Their enhanced release by thermally treating sludge and possible consequences for anaerobic digestion are discussed.

### 2.2.4.1 Total ammoniacal nitrogen (TAN)

TAN exists in equilibrium in two ways: free ammonia (gaseous  $NH_3$ ) and ionised specie, ammonium ( $NH_4^{+}$ ). TAN refers to the sum of these two fractions. The relative concentration of each in TAN depends on the pH and temperature, with higher pH values and temperatures favouring the formation of free ammonia (FAN). Ammonia ( $NH_3$ ) is an essential nutrient for the growth of anaerobic microorganisms, but it can also act as an inhibitor at certain high concentrations. As previously stated, THP is a well-documented effective method for WAS solubilisation and improved anaerobic digestion. The release of N in the supernatant, with ammonium being the main nitrogen form ( $NH_4^{+}$ ) [22], has been shown to be correlated with sCOD concentration. [61]. Nitrogen is

usually found in microbial cells in raw sludge, mainly in EPS which can represent up to 50% of the dry weight of activated sludge [58]. The desintegration of aminoacids releases TAN, which usually happens for higher thermal treatment temperatures, as proteins are increasingly broken down at higher temperatures [13]. In fact, the  $\text{NH}_4^+ - \text{N}$  concentrations exhibited at 160 – 180°C reported a higher release rate compared to 120 – 140°C [119]. This means that the hydrolysis of macromolecules releases both sCOD and N rich molecules.

The subsequent anaerobic digestion fermentation of N-containing molecules releases ammoniacal nitrogen. Free ammonia nitrogen (FAN) has been suggested to be main cause of methanogenic microflora inhibition and its concentration is very sensitive towards changes in pH and temperature [83]. A wide range of inhibiting ammonia concentrations have been reported in the literature, including values from 1.5 to 5.7  $\text{NH}_3 - \text{N} \text{ g l}^{-1}$ , which could probably due to the differences in nature of substrates, inoculum, environmental conditions (temperature, pH) and acclimation periods [23].

#### 2.2.4.2 Phosphorous

Phosphorus (P) is a non-renewable resource [125] and an indispensable component of nucleic acids, both DNA (deoxyribonucleic acid) and RNA (ribonucleic acid), but also ATP (adenosine triphosphate), the primary energy-carrying molecule of all living organisms, making it vital to their growth [118]. It also has an important value in industry and agriculture, for which it is mainly used in fertilisers, detergents, animal feed and other chemicals [108]. However, currently known and economically exploitable phosphate reserves around the world are estimated to be depleted by 2100 [108], establishing the recovery and recycling of P as critical measures for a sustainable world. Most of the used P flows into wastewater gets accumulated in waste sludge during wastewater treatment [55]. Hence, P removal from wastewater and waste sludge has become relevant as it saves non-renewable phosphorus while preventing waterbodies eutrophication and contamination [2].

Phosphorous can be found in wastewater as inorganic phosphorous (Pi), which includes orthophosphates (OP), polyphosphates and iron or calcium phosphates [121] and as organically bound phosphorous (e.g. DNA) [44]. Orthophosphate represents the inorganic soluble fraction of P that is available to chemically or biologically react. Throughout the wastewater treatment, more than 90% of phosphorus in the influent is transferred to sludge [60] due to chemical P removal with flocculants (Fe- or Al-salts) [125] and enhanced biological phosphorus removal (EBPR) processes [118]. EBPR promotes the removal of P from wastewater without the need of chemical precipitants, by recirculating sludge through anaerobic and aerobic conditions cyclically. The microorganisms responsible for P removal are known as the polyphosphate accumulating organisms (PAOs), as phosphates are stored as long-chain polymers within these organisms [73].

Taking into consideration that direct reuse of WAS as P fertilizer in land is prohibited in The Netherlands, release of P from the sludge would be the first step of its recovery [59]. Releasing phosphate into the supernatant of sludge allows for its safe recovery as struvite or calcium phosphate by precipitation [118]. Struvite (magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ ) is

a crystalline solid with low solubility that functions as a slow releasing fertilizer, and this technology offers recovery efficiencies up to 80-90% [113, 74].

The efficiency of any removal strategy depends on the P species distribution in the WAS and pH, which can be largely affected by raw sewage quality, especially regarding metal contents and the operational conditions of the treatment process [59]. Phosphate precipitates such as ferric phosphate (Fe-P) and aluminum phosphate (Al-P) often mixed within the biosolids [125]. Therefore, an efficient way to release phosphate from sludge is required, for both biosolids and phosphate precipitates [125].

Anaerobic digestion is a proof method that can release organically bound P due to the destruction of organic matter, resulting in high P concentrations in the supernatant [121]. Additionally, waste-activated sludge that contains PAOs from EBPR processes used during the biological treatment are another source of P. Once these PAOs are exposed to the anaerobic conditions, the polyphosphate stored in the cells are hydrolysed to supply energy for the uptake of carbon sources (mainly volatile fatty acids, VFAs), thus being released to the supernatant as orthophosphates [73]. Released and soluble P as orthophosphate may bind with cations including  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Al^{3+}$  and  $Fe^{2+}$  and form P-precipitants as these cations are usually dosed excessively as flocculants [59]. The relationships between P fractions in WAS can be very complex, as P can have different sources which can hinder its recovery. The release mechanisms of phosphorous during anaerobic digestion are complex and involve a combination of actions of phosphate accumulating organisms (PAOs), hydrolysis of intracellular polyphosphate after cell lysis and processes of phosphate sorption-desorption [109, 60]. Phosphate dissolution and refixation occur simultaneously, which results in the transfer of phosphorus into solid phase as well [121].

Therefore, it is relevant to note that P release of sludge can be achieved by advanced treatment techniques. Thermal hydrolysis can be an interesting option, although little research has been carried out focusing on P release with sludge pretreatment [51, 82, 52, 55, 109]. Regarding thermal sludge pretreatment, *Xu et al.* found the maximum ortho-P release of about 90 mg/L (95% of total P) was observed at 50°C in 1 h [117]. Another low-temperature thermal treatment research by *Kim et al* found that T-P release was in the range of 11–16%, while Pi and poly-P were in the range of 7–10% and 3–7% at 50 – 80°C [55]. Both researches studied P release before anaerobic digestion.

Ahmad and Idris reported the largest amount of P released into the solution was about 48.9 mg/L at 170°C and that high temperatures improved the release of phosphorous [2]. *Liu et al.* found that a temperature of 170°C solubilised P to a small extent ( 47 mg/L, 5.0% of max T-P) for a treatment of 2h. They also concluded that pH adjustments appeared to be much more effective to solubilise P [59]. These studies only discuss P release from WAS by thermal treatment and do not incorporate the whole process of AD combined with pretreatment. *Dai et al.* observed a  $PO_4^{3-}$ -P concentration in sludge after THP (140°C) and AD increased from 13.86 to 30.62 mg/L, with contributions of 94% and 6% from THP and AD respectively, to the total  $PO_4^{3-}$ -P increase [62]. The P release of THP sludge after AD was not very significant, being consistent with the findings of *Han et al.* [41]. This can be due to several reasons. Struvite precipitation can occur for solutions with pH of 8-9 at high  $NH_4^+$ -N and  $PO_4^{3-}$ -P concentrations, both common in thermally

treated sludges [61]. The precipitation of P with heavy metals can also occur as high solid content sludges usually have higher concentrations of these metals [5]. Finally, acidogenic bacteria and methanogens need phosphorous for energy synthesis during AD.

## 2.3 Integration of THP in full-scale biological processes

This literature review has already established that THP is the most extensively used WAS pretreatment technology with various benefits such as increased organic loading rate, improved biodegradability and enhanced dewaterability [6]. However, one important drawback of this process is the production of recalcitrant compounds, that can potentially inhibit anaerobic digestion [124].

However, THP can also be used as an inter- or post-treatment for anaerobic digestion in several configurations. For the THP intertreatment, the anaerobic digester is fed a mixed raw sludge. After fermentation, the digestate is thermally hydrolysed and then digested in the second digester. This configuration allows for further biodegradability of the digestate and enhanced methane production at the expense of requiring a second digester and prolonging the hydraulic retention time (HRT). This configuration can also be adapted to feed the first digester only primary sludge and feed the second digester with the digestate from the first reactor and thermally hydrolysed WAS [21].

The conventional post-THP treatment configuration refers to a single-stage process for which a proportion of digested sludge is post-treated and recirculated to the digester, resulting in shortened SRT [98]. This configuration also allows for increased solids reduction and increased maximum cake solids [96]. *Yang et al.* reported that raw sludge co-digested with post-treated centrate at 160°C produced 11% more methane than thermally pretreated sludge at the same temperature, inferring that the organic matter assimilated for microbial metabolism and EPS generation during AD was hydrolysed during the post-treatment and contributed to the further improvement of biodegradability [120].

These findings show that an optimised anaerobic digestion with post-treatment could be a promising alternative to sludge treatment, although further research to fully assess the gains in methane production and dewaterability against the energetic load are still required.

The used configuration for this research is based on THP as a pretreatment, integrated in a full-scale wastewater treatment plant, as shown in 2.4. This configuration includes a struvite unit and an Partial nitrification-Anammox (PN/A) for nutrients removal, as nutrient in reject water can influence the subsequent treatment.

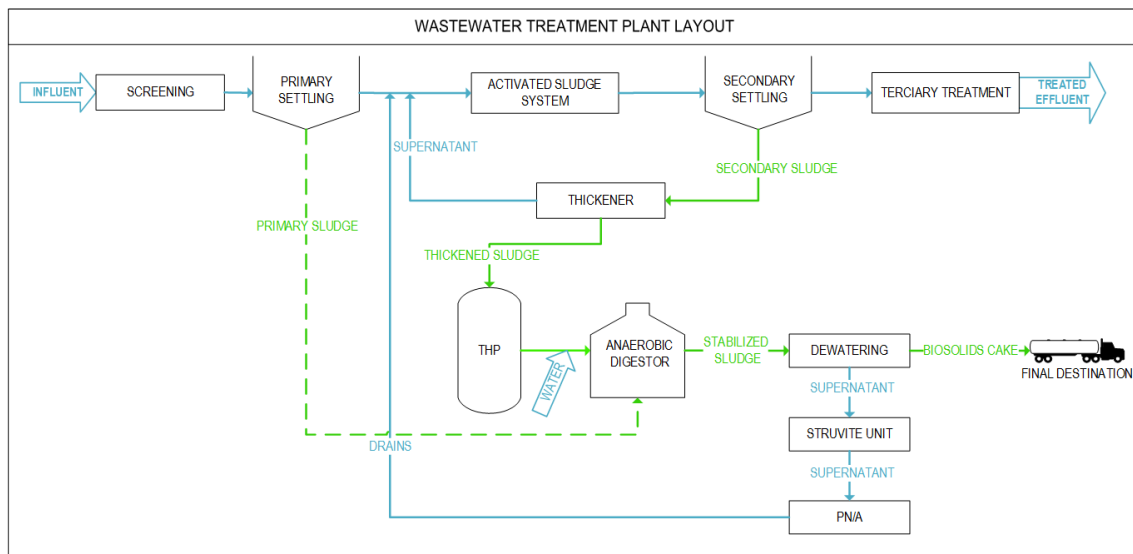


Figure 2.4: Integration of a thermal hydrolysis process within the WWTP. Adapted from [90]

### 2.3.1 Industrial solutions regarding THP

In regards to the inherent advantages, several kinds of full-scale THP operations have been commercialized worldwide. CambiTHP™ and Biothelys® are the two well established major brands in the industry. The first one offers solutions for pre-, intermediate- and post-treatment of sludge in regards to AD [17] and the latter only offers a configuration for pretreatment. Cambi has 54 reference plants worldwide, with a vast portfolio of various configurations and specifications portfolio, ranging from 200 to 135,000 ton DS/year. The main operating parameters for Cambi are temperature (150 – 165°C) and time (20–30 min) at 6 bar at a high solids inlet sludge (16-18% dry solids) [17]. As for Biothelys, temperature is set at 165°C for 30 min, at 9 bar. The Biothelys® TH process was originally developed by Veolia in the late 1990s. Biothelys® has only seven full-scale plants installed in Europe, according to their website, with throughputs that extend from 1000 to 32,000 ton DS/year [101].

ELIQUO Water & Energy, a Dutch founded company, provides a slightly different product, LysoTherm®, a continuous THP technology that uses tubular heat exchangers and thermal oil instead of steam or chemicals for the hydrolysis process. A regenerative water circuit provides approximately 90% of the heat demand, and since there is no steam generation this technology can have a positive impact on economic viability and environmental footprint of the plant [32]. Another Dutch company providing THP solutions is Sustec, which focuses on providing solutions for sludge treatment and resource recovery. Their TurboTec® technology is a continuous version of thermal hydrolysis (cTHP), treating organic material at a standard pressure of 4-6 bar and a temperature of 140 – 160°C, but higher temperatures (up to 180°C) can also be achieved. They have two full-scale installations in The Netherlands with a joint capacity of 20000 ton DS/year [14].

## Chapter 3

# Methodology and Materials

In the present chapter, the carried out methodology, used equipment and materials are presented. For a better description of the set-up and additional information, please refer to Appendix [A](#).

### 3.1 Waste-activated sludge samples

Waste-activated sludge and digestate samples were collected from Harnaschpolder WWTP, located in Den Hoorn, The Netherlands. This plant has a treatment capacity of 1.3 million population equivalents. Sampling was performed on several days: 12th June 2020 for WAS and digestate, and 20th August for WAS. WAS was sampled after centrifugation (so it was concentrated) and digestate was sampled from the mesophilic anaerobic reactors working with a mix of primary and secondary sludge. Harnaschpolder applies enhanced biological phosphorus removal processes in the activated sludge system so it is expected to find PAOs in the WAS of this treatment plant.

### 3.2 Thermal hydrolysis conditions

The thermal hydrolysis experiments were conducted using a high pressure/ high temperature (HP/HT) commercially available batch-type reactor produced by the Parr Instrument Company, USA (Parr – Series 4570 HP/HT reactor). This reactor produces steam-thermally treated sludge, which allows for a comparative performance with those used at full-scale installations.

The WAS was introduced in the reactor in a 700 mL stainless steel container at room temperature and three temperatures were chosen to carry out the treatment, 120°C, 160°C to 200°C, according to the performed test. Once the desired temperature was reached, treatments lasted for 30 minutes. Once finished, the vapor outlet was opened to allow for a quicker cooling and the samples were allowed to cool until 100°C. Below 100°C, the reactor was opened and the samples were left to cool at room temperature and refrigerated at 4°C until further analysis.

### 3.3 Biochemical methane potential (BMP) tests

#### 3.3.1 Experimental set-up

Biomethane potential tests were performed to determine kinetics and methane potentials of the different thermally treated WAS. The assays were carried out in an Automatic Methane Potential Test System (AMPTS®) II equipment (Bioprocess Control, Sweden) and performed in triplicates following a protocol by Holliger *et al.* [49]. Additional information pertaining the method can be found in Appendix A.2.1.

The culture medium volume was 300 mL with a inoculum to substrate ratio of 2 in terms of volatile solids (VS), placed in 500 mL glass bottles. The culture medium for each bottle can be found in Table A.1 from Appendix A.2.2. The incubation temperature was 35°C and reactors were stirred with stirrers from the AMPTs that connect to the isolation cap. The inoculum, WWTP mesophilic digestate (24.11 gVS/kg sludge), was pre-incubated for 7 days at 35°C to release all gas and allow to utilise any remaining substrate in the digestate sample. The four tested substrates were raw WAS and the three thermally treated sludge samples at different temperatures (120 °C, 160 °C and 200 °C). Endogenous methane production was also measured, considered the blank assay. A second set of reactors was run in parallel, also in triplicates, with 200 mL of working volume for N, P and COD monitoring, following the same standardized model. 1 mL samples were routinely taken from all assays and analysed for total N, orthophosphate and sCOD concentration.

The biodegradability of the substrates was estimated from the BMP value and the theoretical maximal methane yield of  $350 \text{ mL g}_{\text{COD}}^{-1}$  in standard temperature and pressure conditions, following the equation:

$$\text{Biodegradability}(\%) = 100 \times \frac{\text{BMP}(\text{mL}_{\text{CH}_4} \text{g}_{\text{COD}}^{-1})}{350(\text{mL}_{\text{CH}_4} \text{g}_{\text{COD}}^{-1})} \quad (3.1)$$

#### 3.3.2 Parameters determination

The experimental data was fitted to a nonlinear modified Gompertz equation (3.2) for an evaluation of the kinetic parameters [126].

$$B = A \exp \left[ -\exp \left( \frac{\mu_m e}{A} (\lambda - t) + 1 \right) \right] \quad (3.2)$$

For which, B: cumulative specific methane production ( $\text{mL}_{\text{CH}_4} \text{gVS}^{-1}$ ), A: maximum specific methane production potential ( $\text{mL}_{\text{CH}_4} \text{gVS}^{-1}$ ),  $\mu_m$ : maximum specific methane production rate ( $\text{mL}_{\text{CH}_4} \text{gVS}^{-1} \text{d}^{-1}$ ), e:  $\exp(1)$ ,  $\lambda$ : lag-phase (days), t: incubation time (days).

To fit the Gompertz equation to the average specific cumulative methane production curves, a nonlinear least-squares regression analysis was performed using the solver tool in MS Excel 2019. This method searches for values for A,  $\mu_m$ ,  $\lambda$  that minimise the sum of the squares of the differences between the predicted and the measured values [110]. The predicted values from the nonlinear regression analysis were plotted against the measured specific methane yields in order

to ascertain a visual fit. The correlation coefficient ( $R^2$ ) was calculated using the regression data analysis tool in MS Excel 2019.

### 3.4 Sample analysis

#### 3.4.1 Solids content essay

Total solids (TS) and volatile solids (VS) were measured according to the standard methods from American Public Health Association (APHA) [84]. Results for both TS and VS are expressed as a percentage of the raw sample and were made in triplicates.

Specific solubilisation can be estimated by dividing sCOD per VS, for each sample.

#### 3.4.2 COD and macronutrients concentration essays

Samples (1 mL) were centrifuged in a BioSan Microspin 12 centrifuge at 124000 g for 15 minutes. The supernatant was filtered with a 45  $\mu\text{m}$  syringe filter into 1.5 mL Eppendorf tubes and frozen at  $-21^\circ\text{C}$  until further analysis.

Analysis of the soluble fraction of COD, orthophosphate ( $\text{PO}_4^{3-}$ ) and TAN ( $\text{NH}_4\equiv\text{N}$ ) were performed directly in kits from Hach Lange Technologies (Germany) and measured in the DR3900 Laboratory Spectrophotometer (from the same company), following the manufacturer's instructions.

Kits used for sCOD,  $\text{PO}_4^{3-}$  and TAN were LCK314, LCK 350 and LCK 303, respectively.

#### 3.4.3 Rheology measurements

The rheology of thermally treated WAS was measured on a logarithmic scale, with increasing shear rate using an Anton Paar MCR 302 Rheometer (Anton Paar GmbH, Austria), which has two concentric cylinders (measuring cup C-CC27/SS/AIR and measure cylinder B-CC27 with 26.66 mm in diameter) as a rotational Couette geometry.

#### 3.4.4 Biogas composition analysis

Methane content of the biogas samples (1 mL) from day-30 of the BMP were analysed using a gas chromatograph 7890A (GC) system (Agilent Technologies, US) equipped with a flame ionization detector.

### 3.5 Dewaterability tests

#### 3.5.1 Capillary Suction Time (CST) Test

The capillary suction time (CST) test was used to determine the rate of water release from each of the examined sludges. The test was carried out using a Triton CST Timer, type 304M (Triton Electronics Ltd., Essex, UK) as per manufacturer's instructions, using CST paper, also from Triton

Electronics. The CST value for distilled water was measured and subtracted from the sample times to improve comparisons. CST measurements were carried out in triplicate.

### 3.5.2 Filter-press assays

The filter-press assay was used to measure the displacement caused by a constant pressure in a known mass sample, with a filter-press by Afmitech Friesland B.V., The Netherlands. Images of the setup can be found in appendix A.3.

A solution of  $2.5 \text{ g l}^{-1}$  of polyelectrolyte (PE) was prepared from a stock concentrated polymer solution and let to stabilize over a magnetic stirrer for one hour. The necessary polymer concentration was estimated by an initial assay with three different doses: 15, 20 and 25 g PE/kg TS, being visually assessed the strength of the floc (the denser and bigger the better) and the cleanliness of the permeate (the less suspended particles the better). After choosing the specific concentration (25 g PE/kg TS), the amount of sludge and polymer required to obtain a 100 g suspension was calculated by the following equations for which both TS and  $C_{PE}$  come in g PE/L.

$$m_{sludge}(kg) = \frac{0.1}{1 + \left(\frac{TS \times C_{PE}}{2500}\right)} \quad (3.3)$$

$$m_{PE}(kg) = 0.1 - m_{sludge} \quad (3.4)$$

The compressor was set up to the desired pressure and the timer to 999 seconds. The timer started counting as soon as the desired pressure is achieved and once it reaches the stipulated time, it stops the dewatering process by releasing the shaft. The compression cell was assembled according to A.6 in appendix A.3.2 and placed in the press-filter, aligned with the piston. The displacement was measured after the target pressured has been reached. Each assay was tested two times, i.e., two runs of 999 seconds. Subsequently, the cell was disassembled and samples from the cake layer were analysed in triplicates for TS. The supernatant was relatively clear; if it contained too much solids, the amount of dosed polymer was not adequate.

## 3.6 Overall energy balance

The energy balance scenario modelled in this work is represented by Figure 3.1, which is only in regard to the processes that can be influenced by the addition of a THP unit in sludge handling processes. Experimental and theoretical energy values were calculated for one tonne of raw sludge, considered as one cubic meter of sludge.

Methane production of the anaerobic digestion was extrapolated from laboratory trials to a full-scale operation has been achieved considering the same biogas productions from BMP tests. Energy production from biogas was modelled considering the use of combined heat and power system (CHP) at 90% efficiency, for a lower heating value of methane of  $50 \text{ MJ/m}^3$ . The energy balance included both electric and thermal energy (exhaust gases and hot water) in the final net balance equation.

Energy values for dewatering were considered from the experimental technique, fulfilled by a press-filter, although in full-scale several dewatering units can be used. The final biosolids are then sent to their final destination, which does not affect the energy balance of WWTP.

Power consumption for the rest of the processes, i.e., steam consumption of THP unit [85], THP unit energy demand [18, 19], and anaerobic digestion energy demand [66, 7, 88] have been determined theoretically considering literature values, and empirical information regarding real full-scale processes at Harnaschpolder [90]. Following thermal hydrolysis, no heat exchanging system was modelled, since hot sludge is diluted with cool water to around 10 % TS before entering the anaerobic digester, which will enable a reduction in temperature. Additional detailed information is provided in each subsection.

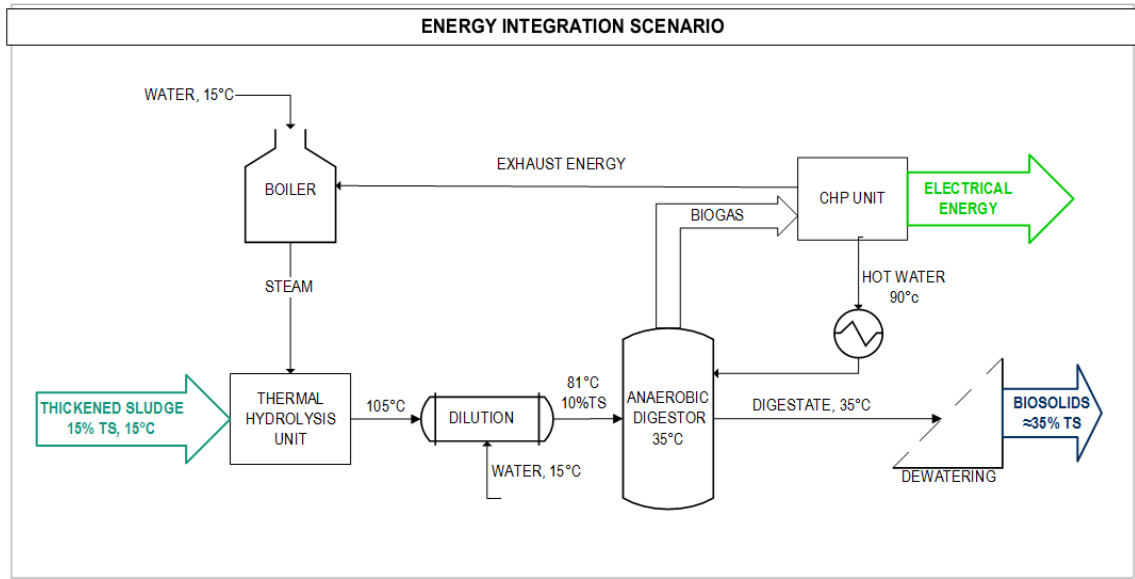


Figure 3.1: Energy Integration Scenario.

### 3.6.1 Steam consumption for the thermal hydrolysis process

The thermal hydrolysis process can be analysed using a black box approach (Figure 3.2), for which the steam consumption, assuming direct heating by injection of steam, can be calculated using the following equations [85]:

$$X = (T_o - T_i) \frac{C_{p,H_2O} - TS \cdot (C_{p,H_2O} - C_{p,s})}{H_{steam} - T_o \cdot C_{p,H_2O}} \quad (3.5)$$

$$\frac{X}{TS} = (T_o - T_i) \frac{C_{p,H_2O} - TS \cdot (C_{p,H_2O} - C_{p,s})}{TS \cdot H_{steam} - T_o \cdot C_{p,H_2O}} \quad (3.6)$$

Where:

$X$  : specific steam consumption (ton steam/ton wet sludge)

$\frac{X}{TS}$  : specific steam consumption for dry solids (ton steam/ton dry solids)

$T_o$  : temperature of hot hydrolysed sludge after pressure flash (°C)

$T_i$  : temperature of influent sludge (°C)

$TS$  : total solids of influent sludge in percentage (%)

$C_{p,H_2O}$  : specific heat of water and  $C_{p,s}$  : specific heat of solids

$H_{steam}$  : enthalpy of steam fed to the THP system (kJ/kg)

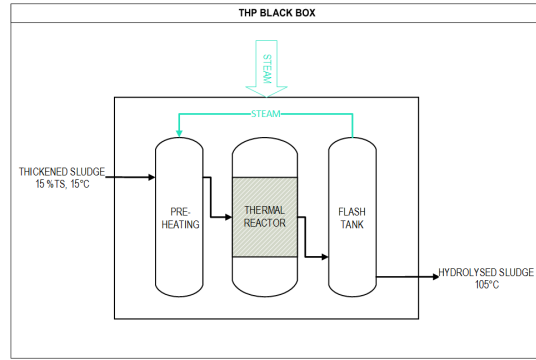


Figure 3.2: Black Box Approach

The recovery of heat from the flash vapours (saturated steam at 105°C) to the pre-heating stage of the substrate allow considerable savings in the steam consumption, leading to energy savings in the boiler.

### 3.6.2 THP energy demand

An empirical equation by Cano *et al.* was used to assess the energy pre-treatment requirements that considers a biogas boiler with an overall efficiency of 90%:

$$E_{THP} = 0.34c \quad (3.7)$$

Where energy ( $E_{THP}$ ) comes in kWh/m<sup>3</sup> sludge and  $c$  is the sludge concentration fed into the system in terms of volatile solids, in kg/m<sup>3</sup> sludge.

### 3.6.3 Heat demand of the AD unit

An approach to model the energy demand of the AD unit is to focus on the heat necessary to maintain a desired digestion temperature. The amount of heat required for anaerobic digestion can be simplified as the amount of energy required to heat sludge ( $Q_h$ ) and the amount of heat needed to cover the losses of energy to the environment from the tanks ( $Q_l$ ). Heat produced by biomass metabolism was neglected. It can be expressed as the following equation:

$$Q_{AD} = Q_h + Q_l \quad (3.8)$$

Since hot sludge needs to be cooled down after THP, an efficient approach is using cold water to dilute the sludge to 10% TS, ensuring there is no need to heat up sludge, thus  $Q_h = 0$ . Heat losses for the digestion tank,  $Q_l$ , assuming a closed tank with no evaporation and negligible heat losses from radiation, can be expressed as the following equation:

$$Q_l = UA(T_{AD} - T_{amb}) \quad (3.9)$$

where  $A$  is the heat transfer area (m<sup>2</sup>),  $T_{amb}$  is the ambient temperature (°C) and  $U$  is the overall heat transfer coefficient of the digester tank (W m<sup>-2</sup> K), defined by Equation 3.10. The  $U$  can be represented in terms of its partial thermal resistances, both conductive and convective (Equation

3.11).

$$\frac{1}{U} = \sum R \quad (3.10)$$

$$\frac{1}{U} = \frac{1}{h_e} + \sum \frac{x_i}{K_i} + \frac{1}{h_i} \quad (3.11)$$

For which  $h_e$  and  $h_i$  are the exterior and interior convection heat transfer coefficient ( $\text{W}^2 \text{m}^{-1}$ ),  $x_i$  the thickness of the element  $i$  (m) and  $K_i$  the thermal conductivity of the element  $i$  ( $\text{W m}^{-1} \text{°C}$ ). Values used for these calculations can be found in Table 3.1 [88, 104, 105]. The AD digester was considered to have a diameter of 64 m and a height of 8.2 m, with a working volume of 30920  $\text{m}^3$ , as to mimic the full-scale sizing of Harnaspolder [90]. Since no information regarding the construction materials of the anaerobic digester were provided, a general digester was modelled for which the walls and base were made of reinforced concrete 30 cm thick, with a 8 cm polyurethane isolation, covered in stainless steel (1 cm). The roof consisted of a layer of isolation, covered externally with stainless steel (same thickness as for the walls) [88].

Table 3.1: Thermal characteristics of the materials modeled for the digester.

| Material                  | $h_e$ (W.m2.C) | K (W/m.C) | $x_i$ (m) | $h_i$ (W.m2.C) |
|---------------------------|----------------|-----------|-----------|----------------|
| Air                       | 25,32          | -         | -         | -              |
| Stainless steel, Type 347 | -              | 16        | 0,01      | -              |
| Polyurethane              | -              | 0,023     | 0,08      | -              |
| Reinforced concrete       | -              | 1,7       | 0,3       | -              |
| Digestate                 | -              | -         | -         | 50             |

### 3.6.4 Energy from biogas production and CHP integration

The energy potential,  $E(\text{kJ kg}^{-1})$ , from biogas [19] can be expressed as the amount of methane produced  $B(\text{kg})$ , multiplied by the lower heating value of methane,  $H_v = 50 \text{MJ kg}^{-1}$  [78]:

$$E_{Gas} = BH_v \quad (3.12)$$

For this energy integration scenario, a combined heat and power system (CHP) plant was considered to cover the heat demand of the AD process and a portion of the electrical demand of the WWTP [57]. Efficiency of the CHP unit was based on the lower heating value (LHV) of methane [31]. According to typical value of commercial biogas engines, 10% of the biogas energy ( $E$ ) is lost as inefficient heat [18] and, and from the remaining, 35% is converted into electric energy (EE) and 65% into thermal energy (30% in exhaust gases (EG) and 35% in hot water (HW)). These can be expressed as [19]:

$$E_{gas} = EE + EG + HW + 0.1EB \quad (3.13)$$

$$EE = 0.35(0.9E) \quad (3.14)$$

$$EG = 0.3(0.9E) \quad (3.15)$$

$$HW = 0.35(0.9E) \quad (3.16)$$

### 3.6.5 Dewatering energy demand

The energy demand for the press-filter can be measured through the displacement of the sample, taking into account the pressure used, by the simple equation of work done by a constant force:

$$W = Fd \cos(\theta) \quad (3.17)$$

$$F = AP \quad (3.18)$$

where  $W$  (J),  $F$  (N), the displacement,  $d$  (m), and  $\cos(\theta)$  equals one, as the force is in the direction of motion. The force can be calculated by 3.18, multiplying the area,  $A$  (m), by the pressure,  $P$  ( $\text{Nm}^{-2}$ ).

### 3.6.6 Overall energy equation

The global energy equation can be expressed as:

$$E_{net} = E_{gas} - E_{THP} - Q_D - W \quad (3.19)$$

## 3.7 Statistical analysis

One-way ANOVA at a 95% significance ( $p\text{-value} < 0.05$ ) was applied to determine statistical significance between independent results, followed by a pairwise Tukey HSD test to establish pair-wise differences.

## Chapter 4

### Results

#### 4.1 Effects of pretreatment on characteristics and solubilisation of waste activated sludge

Results of the effects of pretreatment at different temperatures on the properties of WAS are shown in Table 4.1.

Table 4.1: Initial sludge assessment after THP with WAS as control sample. For TS and VS samples, n=3. For sCOD,  $\text{PO}_4^{3-}\text{-P}$  and TAN of WAS and 160°C, n=3. For sCOD,  $\text{PO}_4^{3-}\text{-P}$  and TAN of 120°C and  $\text{PO}_4^{3-}\text{-P}$  of 200°C, n=1. For sCOD and TAN of 200°C, n=2.

| sample                             | WAS           | 120°C       | 160°C          | 200°C          |
|------------------------------------|---------------|-------------|----------------|----------------|
| TS (g/kg)                          | 58.15 ±0.02   | 51.86 ±1.47 | 47.14 ±1.61    | 36.09 ±0.02    |
| VS (g/kg)                          | 45.40 ±0.08   | 41.68 ±2.15 | 36.95 ±1.63    | 27.58 ±0.08    |
| VS/TS                              | 0.79          | 0.80        | 0.78           | 0.76           |
| sCOD (mg/L)                        | 1117.2 ±199.5 | 12820.0     | 20113.0 ±422.0 | 29750.0 ±778.0 |
| sCOD/VS                            | 16.5          | 307.6       | 544.3          | 1078.7         |
| $\text{PO}_4^{3-}\text{-P}$ (mg/L) | 401.1 ±31.3   | 628.0       | 1125.3 ±18.5   | 1504.0         |
| TAN (mg/L)                         | 143.2 ±29.2   | 120.6       | 241.3 ±17.0    | 797.5 ±17.7    |

According to the principle of mass conservation, total solids in the reactor should not change throughout the thermal treatment. Decreases in TS, like the ones seen in table 4.1 indicate a loss of mass or a dilution in the system. This could be attributed to a partial condensation of steam in the sludge or some solids might have been stuck on the sides of the reactor. The same decrease rate is found for volatile solids (VS), which further supported this hypothesis. Several authors have reported similar findings, including *Taboada-Santos et al.* who reported a dilution factor of 1.3 in thermally treated sludge [97]. The VS:TS ratio remained somewhat constant throughout all treatment temperatures.

Analysing soluble sCOD, there is an effective increase all throughout the tested temperatures, as shown in Table 4.1. Figure 4.1 shows the increase of sCOD:VS ratio with temperature. The increase in organic content with temperature increase indicates that insoluble polymers were broken down into soluble particulates that could be transferred into the liquid phase, thus increasing

sCOD. This behaviour was observed for all tested sludges, as expected according to previous literature findings [58].

Analysing the results of orthophosphate (O-P) in table 4.1, an increase is also observed, associated with the increasing temperatures. The enhancement in  $\text{PO}_4^{3-}$  seems to be higher than previous reported findings. This could be because the WAS that is produced at Harnaschpolder has high load in polyphosphate accumulating organisms (PAOs), which release polyphosphate once they burst during thermal hydrolysis. Thermal treatment seems very effective at releasing this P-fraction.

However,  $\text{NH}_4^+-\text{N}$  concentrations at 160°C - 200°C exhibited a relatively higher increase compared to 120 – 160°C, although not enough independent measurements were performed in order to do an ANOVA and assess if this increase is significant. Similar results have been reported by [114, 119]. However, it can still be inferred that for temperatures higher than 160°C there was protein degradation alongside solubilisation, and that up to 160°C the proteins were mostly solubilised instead of being degraded, or the primary structure remained intact. The substantial release of ammonium may pose complications in the upcoming anaerobic digestion, especially for sludge treated at 200°C, as high concentrations can inhibit methanogenic activity.

Thermal treatment also affected the sludge rheology. Waste activated sludge is considered a non-Newtonian fluid, meaning the shear stress ( $\tau$ ) is not linearly related to the shear rate ( $\dot{\gamma}$ ), as shown in Fig. 4.2. All samples exhibited a non-Newtonian behaviour. As observed, the behaviour of all samples changed with increasing shear rates.

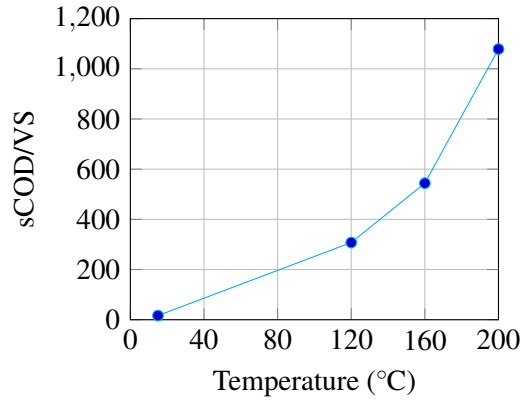


Figure 4.1: sCOD/VS for each thermally treated sample. Activated sludge was considered to be at 15°C.

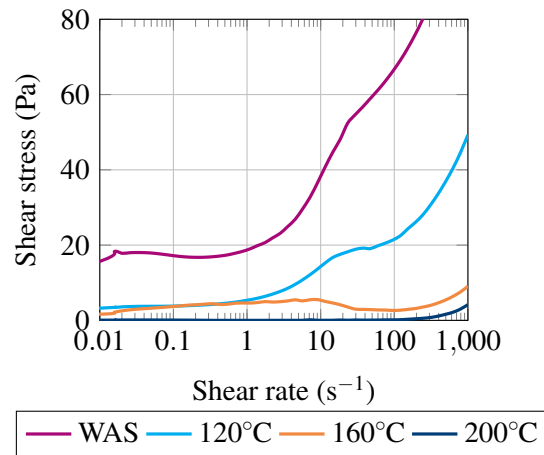


Figure 4.2: Shear stress variation with shear rate for treated and untreated sludge samples, n=3.

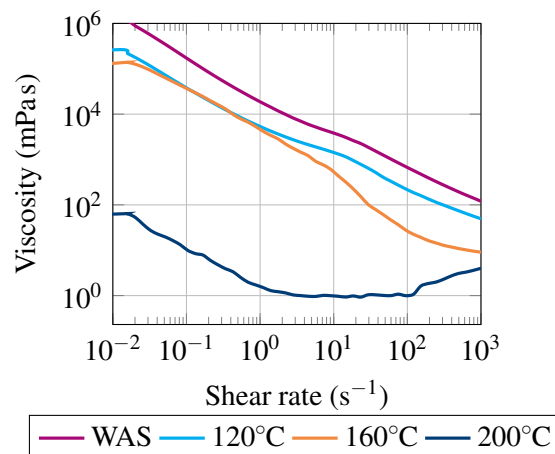


Figure 4.3: Viscosity variation with shear rate for treated and untreated sludge samples, n=3.

Figure 4.3 shows that apparent viscosity ( $\tau/\dot{\gamma}$ ), for a given shear rate, decreased with thermal treatments. Apparent viscosity is not affected by the shear rate in Newtonian fluids [29], which would produce a viscosity per shear rate graph with a constant, flat line. The shear-thinning behaviour is observed throughout all samples, as viscosity decreases for increasing shear rates, which means thermally treated sludge still maintained some of its initial rheological behaviour. However, samples with a 200°C treatment had the lowest viscosity and it could be considered constant for shear rates between 0 and 100  $s^{-1}$ , meaning that they behaved very similarly to a Newtonian fluid [29] in this range. The apparent viscosity of WAS was the highest and it decreased with increasing temperatures, which was expected, as thermal treatment has been reported to decrease the viscosity of sludge samples [87].

For increasing treatment temperatures, there is a decrease in apparent viscosity, which means treated sludge will flow more easily. This means that thermal treatment changes the sludge structure and releases the bounding water throughout all treatments. The thermally treated sludge samples became more Newtonian for increasingly higher temperatures, more evident for treatment temperatures of 200°C, also reported by *Urrea et al.* [106]. Thus, pretreated sludge should be easier to pump and to mix. This less dissipative flow is a result of the reduction in the amount and size of the particles and polymers, decreasing the interactions between them, which allows for the sludge to behave more like a homogeneous liquid [106]. It has been proven that the use of thermal hydrolysis improves the fluidity of the sludge, facilitating its subsequent handling in operations of pumping and transport [87, 36].

## 4.2 Effects of pretreatment on BMP tests

The aim of thermal hydrolysis is to improve the anaerobic digestion of sludge with increased methane yields, and improve dewatering by producing dryer, more compact biosolids. Therefore, batch anaerobic digestion tests were carried out in order to choose the best treatment temperature in terms of  $CH_4$  production. Figure 4.4 presents specific methane production per gram of COD in the substrate after 30 days. For that, the endogenous production of the inoculum was subtracted to the methane production of all pretreatments. The colored area for each plot represents the standard deviation of measurements. Cumulative methane production graphs of the raw data can be found in Appendix A.2. All pretreatments allowed a final methane production equal or higher than for untreated sludge (WAS). Decreasing methane production in the graphs indicate that the BMP run has ended and that the blank methane production was higher than the specific sample. Table 4.2 presents the maximum methane production, methane content and biodegradability percentage at the end of the BMP run for each sample. Figure 4.5 presents the methane production rates per day for all samples throughout the 30 days.

Analysing figure 4.4, it is observed that WAS reached the maximum methane production around day 21, samples treated at 120°C reached the peak around day 13, 160°C at day 11, and 200°C around day 29. These values were reached a few days before the end of the BMP run (Table 4.2).

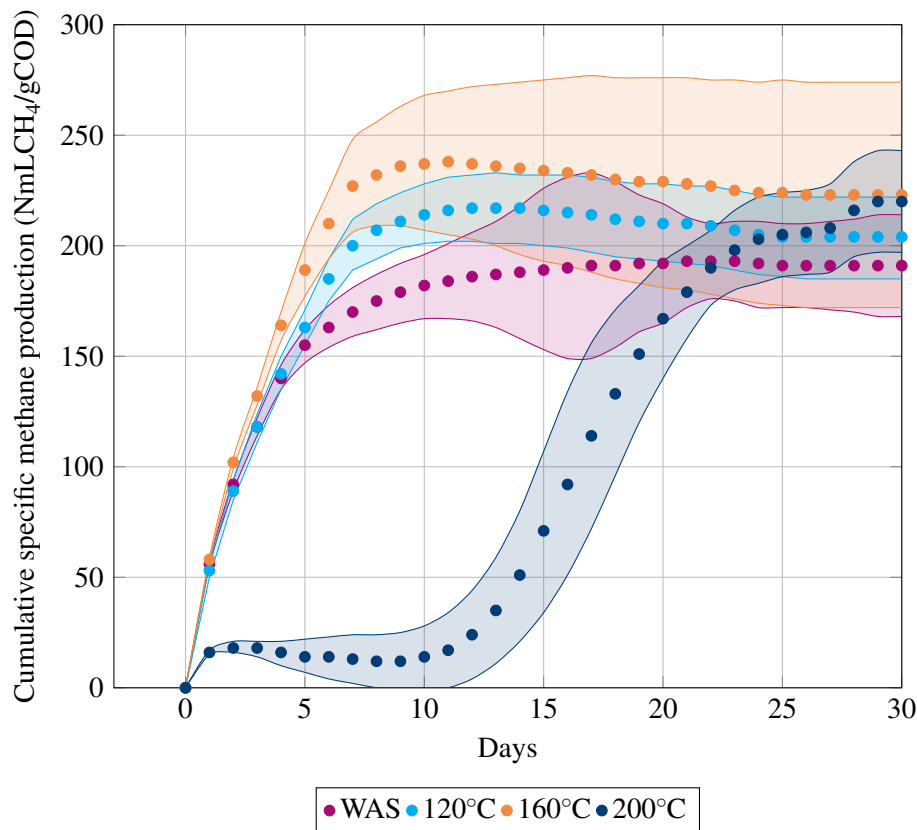


Figure 4.4: Methane production profile from the BMP test of thermal pre-treated sludge at various pretreatment times. Endogenous methane production by a blank test has been subtracted to the real values. For all samples,  $n=3$ .

There was a decrease in methane production in the 200°C samples around days 8-9, which indicated an inhibition in the anaerobic inoculum metabolism that is also supported by the long lag-phase and consequent rapid increase in methane production. The inhibition could either be due to the high  $\text{NH}_4^+-\text{N}$  concentrations or refractory compounds produced during the thermal treatment. Usually, aromatic low-weight structures are inhibitory, such as furfural and 5-hydroxymethylfurfural (5-HMF), but can be degraded over time [103]. The inoculum might also not have been adapted to the ammonium concentration, as inoculum from the sampling WWTP (Harnaspolder) works around 0.8 g  $\text{NH}_4^+-\text{N}/\text{L}$  and the BMPs were dosed with concentrations around 1.2-1.5g  $\text{NH}_4^+-\text{N}/\text{L}$ . The lag-phase could indicate both acclimatization of the inoculum to higher ammonium concentrations and a reduction in the concentration of refractory compounds, that have been degraded in the meantime.

One possible future research topic could be to carry out a continuous mesophilic digestion in order to understand if the lag-phase would persist or not with an adapted inoculum (to the ammonium). In acclimated sludges, the lag-phases tend to be shorter. The rapid increase that follows the lag-phase indicates that the inoculum did have the capacity to degrade the organic material, producing methane out of it.

Table 4.2: Maximum methane production, methane content and biodegradability percentage, at the end day of the BMP test. For all samples except the end day, n=3.

| sample                                                     | WAS         | 120°C       | 160°C       | 200°C       |
|------------------------------------------------------------|-------------|-------------|-------------|-------------|
| Max CH <sub>4</sub> production (NmL CH <sub>4</sub> /gCOD) | 193 ±21     | 217 ±15     | 238 ±32     | 220 ±23     |
| CH <sub>4</sub> content in biogas (%)                      | 78.48 ±1.32 | 76.10 ±1.94 | 79.95 ±2.92 | 80.31 ±2.51 |
| Biodegradability (%)                                       | 55 ±6       | 62 ±4       | 68 ±9       | 67 ±7       |
| BMP end (day)                                              | 21          | 17          | 16          | 30          |

Analysing Table 4.2, max methane production was the highest for samples treated at 160°C, although all hydrolysed sludges increased their methane production comparatively to WAS, more specifically, max methane production increased 12.4 %, 23.3% and 14.0% for samples treated at 120°C, 160°C and 200°C, respectively. One-way ANOVA of the max methane production suggested that the treatments were not significantly different (p-value = 0.0576 > 0.05) at achieving max methane values. However, a Tukey HSD Test showed a significant difference between max methane production for WAS and samples treated at 160°C (p-value = 0.04489 < 0.05), which indicates that thermal treatment at this temperature effectively increased methane production compared to untreated WAS.

Although there seems to be no difference between WAS and thermally treated sludge regards to methane production (except at 160°C when analysed by the Tukey test), samples with hydrolysed sludge had shorter reaction times which indicates that at full-scale, anaerobic digestion of thermally treated sludge might impose shorter SRTs. In a batch reactor, this means lesser energy costs as AD finishes in a shorter time or more frequent loading rates. Concerning the BMP run duration, both 120°C and 160°C halved the duration of their runs compared to raw untreated sludge (WAS), while the sample treated at the highest temperature took the longest. This indicates that the thermal treatment is effective at reducing reaction times while maintaining similar biogas productions. In practical terms, the application of a THP could decrease the digester times by half, allowing to process double the amount of sludge for the same energy that would be needed to maintain a anaerobic digester fed only with raw WAS.

Figure 4.5 presents the methane production rates throughout the BMP run. For WAS, 120°C and 160°C samples, the production rates follow a similar pattern, as microorganisms metabolise the readily available substrate. Around day 10 there seems to be a stabilisation of the production rates which might indicate a change in substrate. Samples treated at 200°C exhibit a lag-phase that coincides with the lag-phase of Figure 4.4, with a maximum rate of approximately 50 NmL CH<sub>4</sub> around day 17.

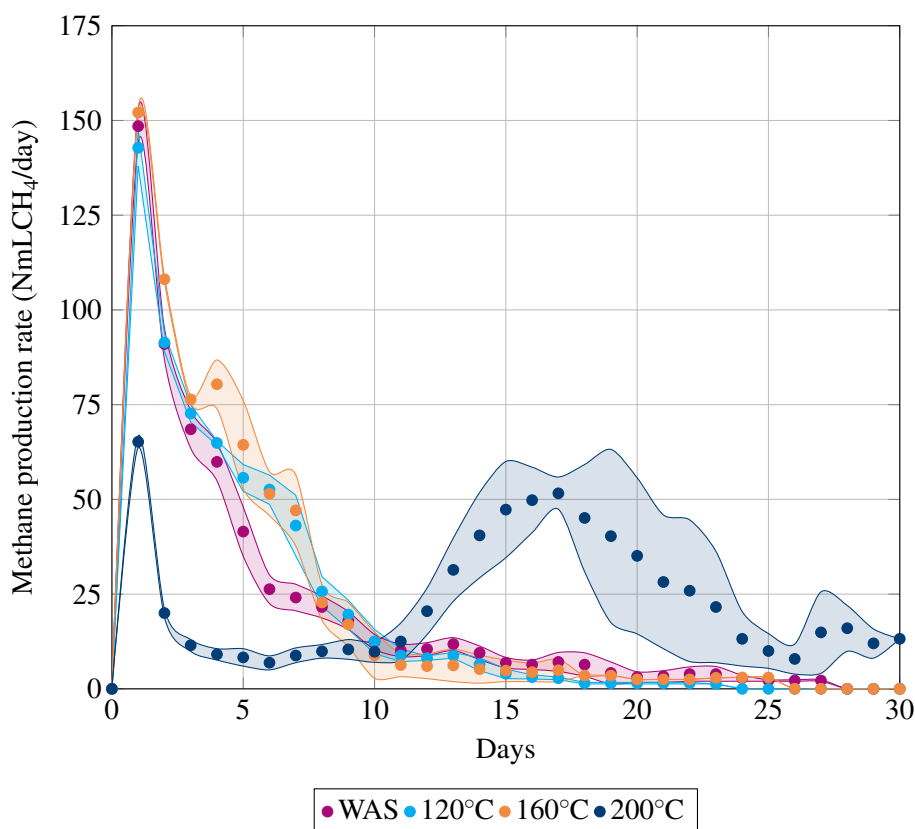


Figure 4.5: Methane production rates per day from the BMP test of thermal pre-treated sludge at various pretreatment times. For all samples,  $n=3$ .

The difference in methane production rates led to the conclusion that two types of organic matter constituted the sludge samples: one fraction corresponded to readily accessible organic matter like monomers and dimers compounds, whereas the second fraction was more slowly fermented. This behaviour could be confirmed by the COD evolution plot (Fig. 4.7), that showed sharp decreases for the same days that methane production was high.

Nevertheless, all pretreatment conditions had a positive effect by increasing the biogas production. These results were assessed further by means of kinetic parameters estimation from the Gompertz model fitting with the experimental data.

Figure 4.6 (a) shows the Gompertz model fit (dashed line) with the experimental data for activated raw sludge (WAS) and pre-treated sludge from each temperature assay, and Figure 4.6 (b) shows the fit between the model predicted data and the experimental data. In general, there is an overall agreement between all the Gompertz model and the experimental data. For both fittings, the values for the average experimental methane production were used. Table 4.3 presents the parameters obtained in the optimisation process.

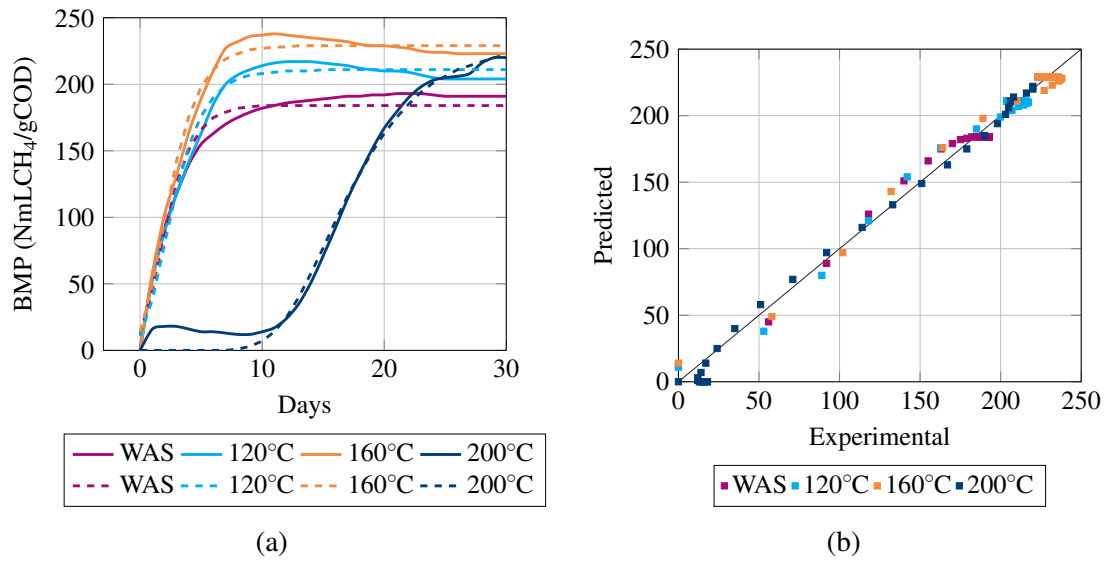


Figure 4.6: **(a)** Gompertz model fit with methane production of anaerobic test using thermally pretreated sludge and non-treated WAS as substrates. Full lines correspond to experimental data, and dashed lines to predictive model. **(b)** Fitting between predicted and experimental data for BMP methane production.

Table 4.3: BMP kinetic parameters from Gompertz equation modelling.

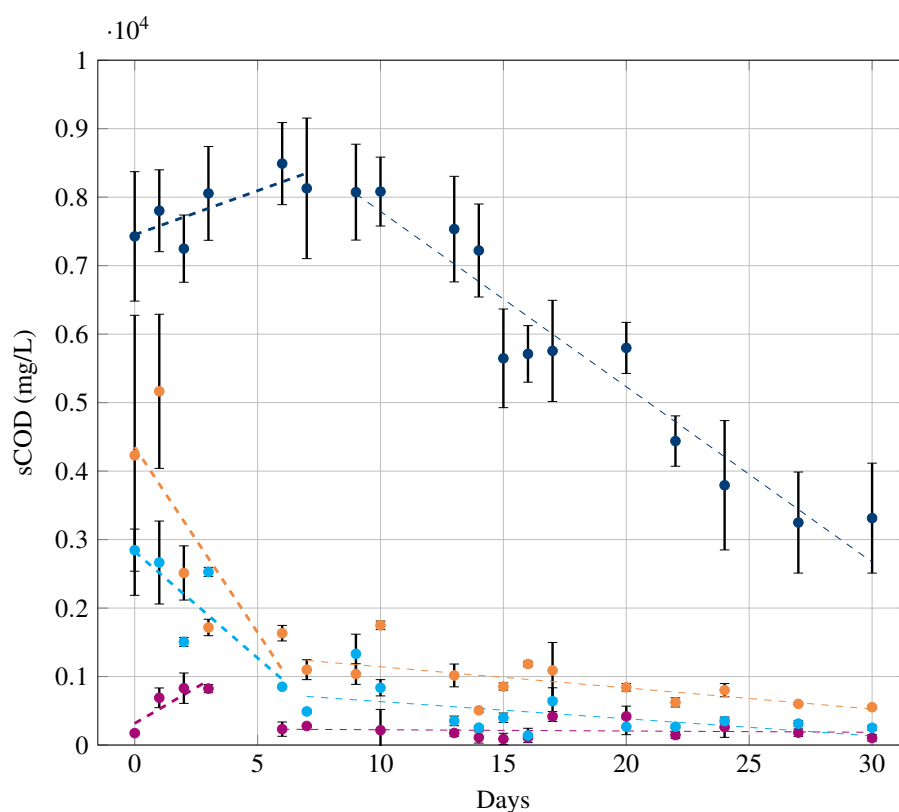
| sample    | WAS   | 120°C | 160°C | 200°C |
|-----------|-------|-------|-------|-------|
| A         | 184   | 211   | 229   | 229   |
| $\mu_m$   | 44    | 44    | 50    | 20    |
| $\lambda$ | 0     | 0     | 0     | 11    |
| $R^2$     | 97.54 | 98.31 | 98.45 | 99.8  |

The model predicts very well during the exponential production phase for WAS and the samples treated at 120°C and 160°C. Experimental data showed higher maximum methane production for samples treated at 160°C than the model (238 mLCH<sub>4</sub>/gCOD, compared to 229 mLCH<sub>4</sub>/gCOD). The model underestimated the max methane production rates, but successfully estimated the lag-phase for samples with sludge treated at 200°C.

However, some discrepancy was observed at later digestion stages, but a very good fitting was obtained overall by analysing the  $R^2$  values in Table 4.3. At the later digestion stages, methane production for all samples except 200°C decreases as the blank produces more methane than the samples. This is due to the fact that the inoculum has consumed most of the substrate that was more available due to thermal hydrolysis. The decrease in substrate and biogas production indicated that the anaerobic digestion has reached its final stage and that the BMP run should be stopped. Since all runs were kept working for 30 days, it is expected that the model might not predict as well at the later stages.

### 4.3 Nutrient release

In order to assess sCOD evolution throughout the BMP run, as well as orthophosphate and total ammonium nitrogen (TAN) release profiles, daily samples were taken from the BMP flasks and analysed. Results for sCOD evolution in relation to elapsed time are plotted in Figure 4.7, and results for TAN and  $\text{PO}_4^{3-}$  are shown in Figures 4.8 and 4.9, respectively. First-order kinetic equations were fitted for all nutrient release graphs. In regard to sCOD release evolution, two different release equations were plotted for each sample.



|                                   |                                      |                                     |                                      |
|-----------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| ● WAS                             | ● 120°C                              | ● 160°C                             | ● 200°C                              |
| --- $y = 209.05 \cdot x + 315.97$ | --- $y = -310.56 \cdot x + 2,824.62$ | --- $y = -541.5 \cdot x + 4,351.27$ | --- $y = 128.56 \cdot x + 7,451.3$   |
| --- $y = -1.83 \cdot x + 241.56$  | --- $y = -25.04 \cdot x + 884.63$    | --- $y = -30.84 \cdot x + 1,451$    | --- $y = -255.95 \cdot x + 10,351.1$ |

Figure 4.7: sCOD evolution throughout the 30-day BMP run. First order kinetics equations were fitted to the sCOD concentration that distinguish two different release rates. For all samples,  $n=3$ .

COD is regarded as an important parameter of organic compounds concentration, and sCOD reflects the concentration of the soluble organic fraction [124]. Regarding sCOD evolution, all samples showed a general decrease in concentration, as expected. For the 200°C sample, up until day 10 there was a slight increase in sCOD concentration before a sharp decrease. This increase might have been due to the production of volatile fatty acids (VFAs), an intermediate product of anaerobic digestion, as methanogens are most likely inhibited. This might support the hypothesis that refractory compounds were being degraded by the anaerobic communities

until their concentration no longer inhibits methanogenic activity, which happened around day 10, when methane production picked up (Figure 4.4). Methane production would necessarily mean consumption of the available VFAs. This behaviour of increasing sCOD was also seen in WAS, but only for the first 4 days. This can be an indication of the hydrolysis process taking place in the sample; as the inoculum degraded insoluble matter into soluble molecules, sCOD necessary increased if it was not being consumed as fast as it was being produced.

For the 120°C and 160°C samples, the kinetics equations indicated two different release rates for sCOD that could infer that there are two different substrates, one initially more easily metabolised, mostly due to the thermal treatment and another more complex, with a lower metabolisation rate (seen as a lower slope in the equations) that probably suffered some hydrolysis by the inoculum.

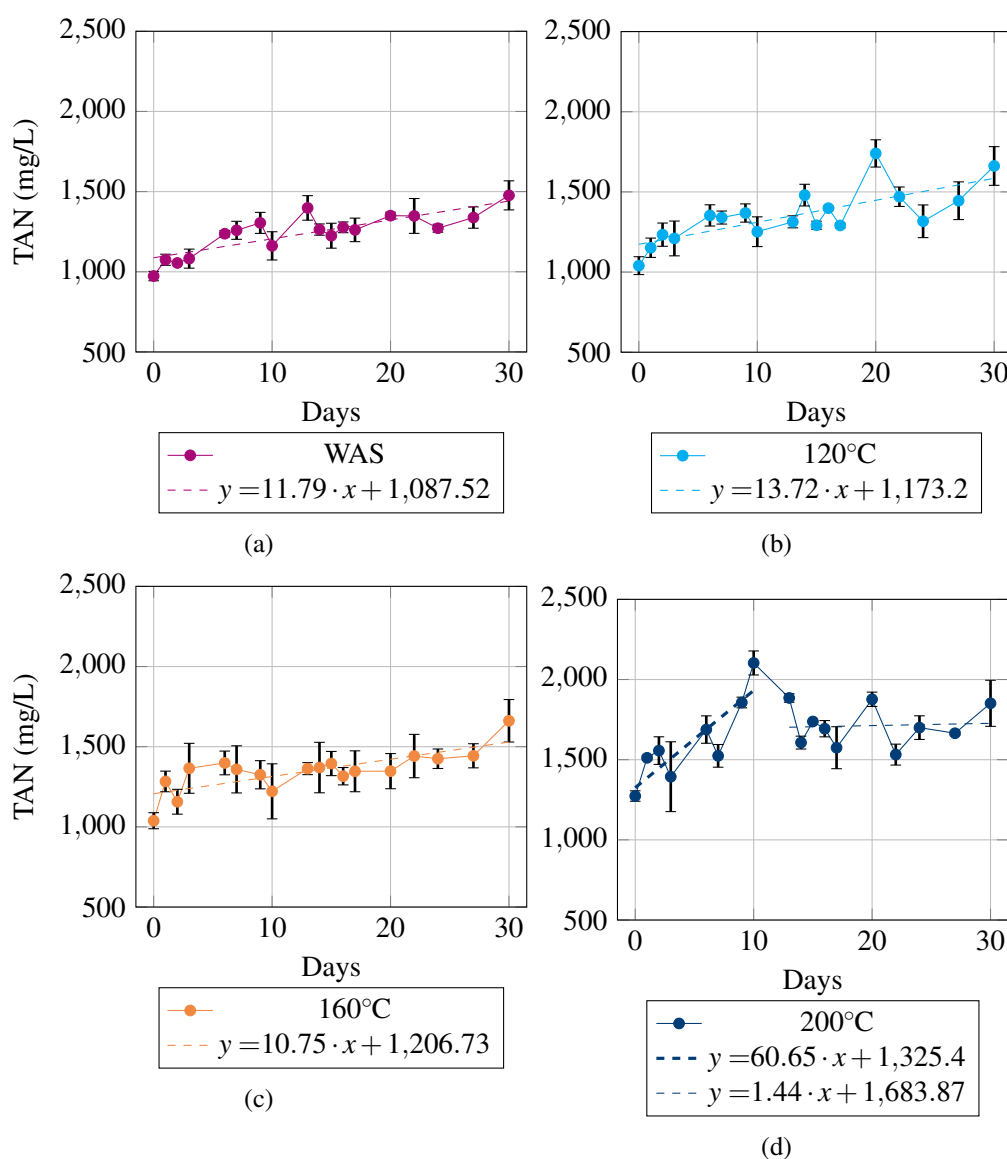


Figure 4.8: TAN evolution throughout the 30-day BMP run. First order kinetics equations were fitted to each TAN release profile. Sample (d) showed two different release patterns that were fitted separately. For all samples,  $n=3$ .

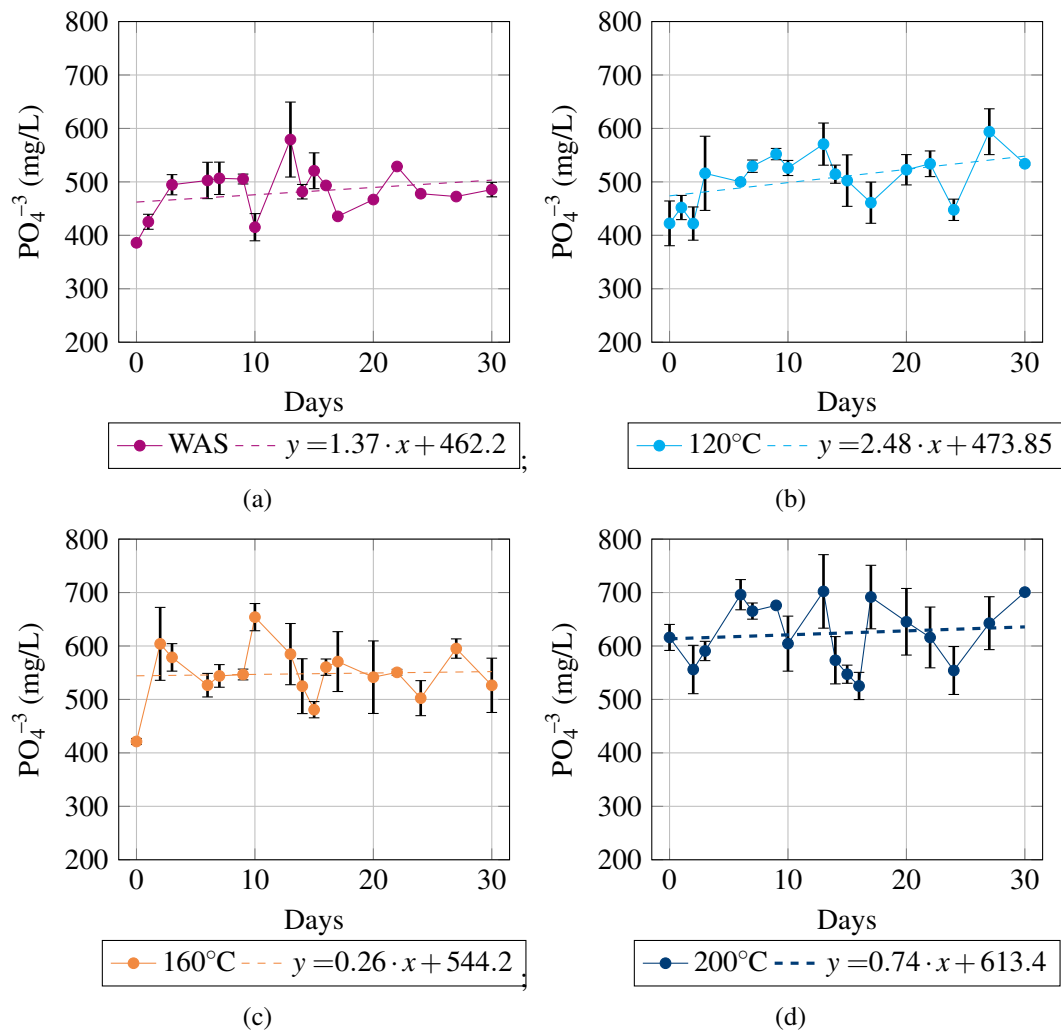


Figure 4.9:  $\text{PO}_4^{3-}$  evolution throughout the 30-day BMP run. First order kinetics equations were fitted to each  $\text{PO}_4^{3-}$  release profile. For all samples,  $n=3$ .

With the biodegradation of organics in WAS, nitrogen and phosphorus compounds were released to the liquid phase. To assess if these macronutrients influence mesophilic digestion, total ammonium nitrogen (Figure 4.8) and orthophosphate (Figure 4.9) were measured throughout the BMP run.

Analysing Figure 4.8, a steady increase of TAN can be seen in all samples. For increasing thermal treatment temperatures, the final TAN concentration also increases. Protein solubilisation increased the concentration of easily metabolised amino acids that once degraded release TAN. First order kinetic release equations also showed an increasing release rate throughout the run, although for samples with sludge treated at 200°C two different release behaviours were distinguished. Final TAN concentration for WAS was 1476,67 mg/L, 1661,67 mg/L for both 120°C and 160°C and finally, 1851,67 mg/L for 200°C. At higher temperatures, there was an increase in ammonium in the first 10 days for the 200°C sample run. The timing of this phase corresponded to the methane production lag-phase, which indicated that there is an effective TAN release, either

by further hydrolysis of residual polymers or the degradation of inhibitory refractory compounds, which was happening alongside VFA formation.

There is a decrease in TAN after the 10 day mark for the 200°C, and the concentration at the end of the BMP is lower than the concentration at the release peak. There is effective decrease in soluble TAN, most likely due to the formation of struvite, as there is also a decrease in soluble orthophosphate for the same time period (Figure 4.9, graph (d)). Methanogenesis increases the pH and can lead to struvite precipitation if at a range of pH= 8-9 and in the presence of high  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  [62]. As previously mentioned, struvite (magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is a crystalline solid that precipitates commonly in thermally treated sludges with pH of 8-9 at high  $\text{NH}_4^+-\text{N}$  and  $\text{PO}_4^{3-}-\text{P}$  concentrations [61].

Unfortunately, pH measurements were not performed, so there is no clue on the extension of ionization of N-molecules. Although both forms are inhibitory, free ammonium nitrogen has been suggested to be the main inhibitor due to its high permeability to cell membranes [83], although the performed test does not distinguish from either forms.

Analysing 4.9, there seems to be no trend associated with OP release for all samples, but rather a more erratic release behaviour throughout the BMP run, thus only one first order kinetic equation was plotted for each sample. These equations have a very low slope, mainly because initial and final OP concentrations do not vary much. This can be an indication to the complex interactions that OP had with available molecules, as it could have been constantly shifting between soluble available to complexated form. Fluctuations in pH due to VFA formation might also help to explain the oscillatory behaviour of OP. It could also indicate experimental errors, as very small volumes of samples (4  $\mu\text{L}$ ) were pipetted in the kits used to measure this compound. Still, there was an increase in soluble OP from the 1st day of digestion comparatively to the last. WAS OP increased 25.8 %, from 386.0 to 485.6 mg/L; samples from sludge treated at 120°C went from 422.4 to 533.9 mg/L, an increase of also 25.8%. For the 160°C samples, initial  $\text{PO}_4^{3-}-\text{P}$  concentration was 421.3 and by the end of the BMP run was at 526.4 mg/L; and for 200°C treated sludge, the initial OP concentration was 616.0 mg/L and final 700.8 mg/L which means an  $\text{PO}_4^{3-}$  release increased during AD of 24.9 % and 13.8 %, respectively. Final OP concentrations during AD for all samples were relatively similar except for samples at 200°C which exhibited a significant higher value (Tukey's HSD test p-value < 0.01 for all pairs with sludge treated at 200°C).

These results indicate that thermal treatment might have some influence on the final orthophosphate concentration, as a result of the hydrolysis degradation of organic compounds, but has no apparent effect on the extension of this release during anaerobic digestion for thermal treatment temperatures up to 160°C.

At 200°C, the starting OP concentration is already higher than the final concentrations for all other samples, which indicates once again, the extent of degradation that treatment at this temperature imposes. However, release of OP during AD is not significantly different between all samples (ANOVA p-value = 0.5795 > 0.05). However, for samples with sludge treated at 200°C there was a sharp decrease of OP concentration observed around day 10, which coincides with

TAN depletion and further supports the hypothesis that there is some struvite formation happening during anaerobic digestion. The subsequent orthophosphate increase can indicate that the PAOs keep releasing  $\text{PO}_4^{3-}\text{-P}$ , as result of their own anaerobic metabolism. These two processes are most likely happening simultaneously which might also explain the erratic behavior of OP release throughout the BMP run.

In this work, only orthophosphate was measured, it would have been interesting to have measured total P, as to indicate how and if thermally treated sludge had an influence on OP release during anaerobic digestion. Total P measurements could aid in understanding the extent of the transformation of the OP fraction. To the best of the author's knowledge, OP was released during AD as a result of organic matter degradation and PAOs metabolism. Precipitation was also seen in samples after centrifugation (not shown) which is expected as OP reacts very easily with cations to form precipitates.

Since total P was not measured throughout this thermal hydrolysis process and AD, we cannot assess directly the extent of P solubilisation during digestion. However, these results seem to indicate that thermal hydrolysis facilitates the solubilisation of organic P to orthophosphate. The results imply that P solubilisation via its degradation would have occurred during the AD process; whereas the pH condition or the simultaneously released metal cations (e.g.,  $\text{Fe}^{2+}$ ) probably induced the precipitation of the freed orthophosphate [59].

## 4.4 Dewatering

### 4.4.1 Characteristics of thermally treated sludge

The CST of the sludge samples was used to evaluate the sludge initial filterability. Tests were carried out with and without polyelectrolite, which works as a dewatering polymer, as to mimic common practices in full-scale. As shown in Fig. 4.10, the CST of the sludge increased from 304 s to 1387 s as the thermal treatment temperature increased from 20°C (considered for raw WAS) to 120°C, and then decreased to 114.5 s and finally 14.9 s in treatment temperatures of 160°C and 200°C, respectively. These results show that different treatment temperatures have different effects on the sludge dewaterability, and that there is an extreme where the poorest dewaterability was achieved, at around 120°C. Thus, for temperatures below this threshold filterability of sludge was deteriorated.

These results were similar to those obtained by *Liu et al.*, who found an peak value at 135°C [59] in the relationship between temperature and the sludge dewaterability, and *Bougrier et al.* who observed a threshold of 130°C [13]. Although each sample has a different TS concentration, which ultimately affects the CST values, these same values were normalized with TS concentrations from each sample and the same behaviour was observed.

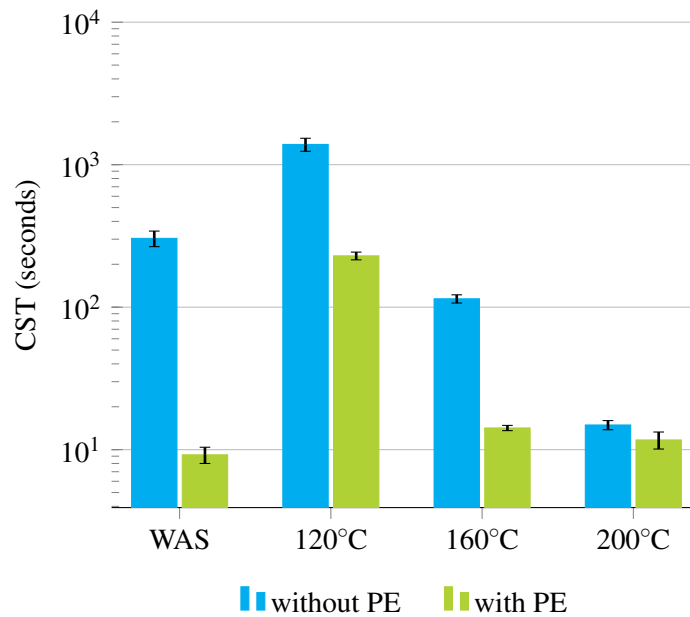


Figure 4.10: CST values for the initial hydrolysed sludge prior to anaerobic digestion, with and without addition of polyelectrolyte (PE). WAS is used as a comparison and it had not been treated thermally. For all samples,  $n=3$ .

This could be due to the sludge solubilisation and the increase in small particles, despite particle size not being the only parameter having an impact on CST [11]. *Chu et al.* also reported an increase in CST, which they hypothesized as the increase in bound water linked to the particles surface. As the particles diameters are lower, the surface of contact is higher, as well as the quantity of bound water [25]. Possible, the matrix structure of sludge is not fully destroyed which, in addition to the reduction of particle size, hinders the release of water from sludge.

Still, CST measurements for samples treated at 160°C or higher showed that the sludge became more fluid and could release more water, becoming easier to dewater. This effectively shows a change in sludge structure, corroborating the rheology results found in section 4.1: the decomposition of biopolymers increases the release of bound water, effectively decreasing the viscosity of sludge for increasing thermal treatment temperatures. Thermally treated sludge is therefore easier to pump. Similar results were found by *Yu et al.* that proposed the decrease of viscosity for thermally treated sludge could be due to the release of bound water, which must have been to such extent that it overcame the negative effect of electrostatic repulsive force among flocs, resulting in a improvement of dewaterability [122].

For the CST measurements with the addition of polymer, the results follow the same trend as observed for samples without PE. All filterability results are within the same range (9.2 s, 14.2 s and 11.7 s respectively), which indicates the dosed amount of polymer was enough to dewater the samples accordingly, reaching the same CST plateau. For the 120°C sample, the dosed PE does not seem to be sufficient to allow for such an extensive dewatering as for the previous samples but it still reduced the original CST value by a factor of 10. The results of CST with PE for the 120°C

samples help to corroborate the hypothesis that at this temperature there is an increasing amount of smaller particles that are still trapped in the sludge structure.

#### 4.4.2 Characteristics of mesophilic digestate, post BMP

Since the final goal of this work is to develop an energy model regarding the effects of THP on sludge processing, it becomes imperative to analyse the anaerobic digestate after digestion, as to follow the normal flow of a WWTP process. Filterability results were performed on the digestate and the CST results can be found in Figure 4.11a. Additional information can be found in Appendix A.3.1.

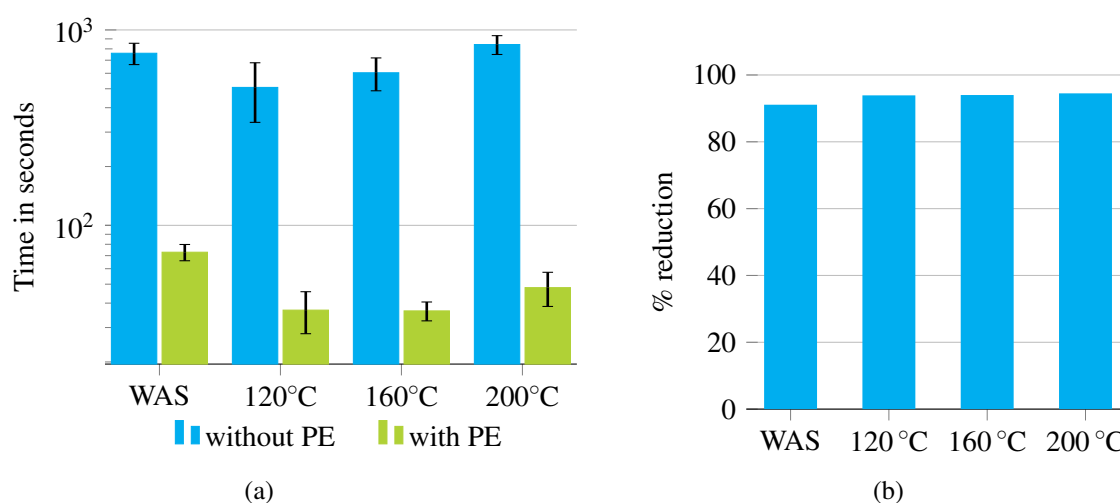


Figure 4.11: Capillary suction time results for BMP samples after anaerobic digestion. (a) CST values obtained with and without adding PE. For samples without PE,  $n=6$ . For samples with PE,  $n=3$ . (b) CST reduction in percentage for digestate samples with PE.

CST values were similar between all samples (see Appendix A.3.1 for detailed information), and the highest value was 878.95 s, corresponding to the 200°C, followed by WAS with a CST of 814.75 s. The 120°C and 160°C samples were lower and had very similar results, both close to 600 s. However, ANOVA analysis suggested that the one or more pairs of treatments were significantly different ( $p\text{-value} = 1.5 \times 10^{-5} < 0.05$ ), for which the Tukey's HSD test was applied to each of the 6 pairs to pinpoint which of them exhibited statistically significant differences. The Tukey's HSD test proposed the CST value of WAS was significantly different of those from 120°C, and CST values from 200°C were significantly different from samples with sludge treated at 120°C and 160°C. This last result can be due to the non-biodegradable compounds left after AD that might keep some structure by bonding with each other. These compounds are generally found at a greater concentration for sludge thermally treated at higher temperatures, such as 200°C.

Moreover, for the CST tests with added polymer, Figure 4.11b presents the percentage of CST reduction with polymer at 35 gPE/L. All samples suffered a reduction of over 90%, and were significantly different between each other ( $p\text{-value} = 0.0012$  for ANOVA). The Tukey HSD test

established the CST value with polymer for WAS was statistically different from all treated samples, but CST values were not different between treatment temperatures.

Figure A.7a (in Appendix) shows the mixture of sludge and polymer at 35 gPE/L. Results show that polymer demand increases during digestion, which has also been reported by *Kopp et al.*. A possible explanation for this result is the further release of EPS [56]. *Houghton et al.* established a relationship between the quantity of EPS present and digested sludge dewaterability, in which the increase in EPS would also increase CST, although the validity of his equations is yet to be confirmed with further investigation [50].

The results obtained in this work showed the addition of an electrolyte significantly aids dewatering, although at the expense of an extra additional material. Since sludge drying is an energy intensive process, dewatering, i.e., removing water without evaporation, becomes an important process to reduce water content in sludge before final disposition. Sludge conditioning prior to dewatering with a polymeric solution is very common, and, according to this work, advised but with an additional cost of polymer and a higher mass of final solid waste, which should be subjected to a cost/benefit analysis.

#### 4.4.3 Press filter dewatering for post-AD processing

In this work, a filter press was used for mechanical dewatering of anaerobically treated sludge although several alternatives are available in the industry. Results in Figure 4.12 show the total displacement for each pressure with different colors for the specific displacement of each 999 s round. Detailed results can be found in Appendix A.5.

The most evident result seen is that one round of 999 s was enough to filtrate all the samples, including anaerobically digested WAS, as the displacement regarding the second round was not significant. This result is more evident in the 160°C and 200°C samples. For these two treatment samples, total displacement was somewhat constant throughout all pressure, which indicates that a lower filtering pressure can be used to achieve the same biosolids concentration, hence allowing for energy savings. In the 120°C sample, the displacement at 4 bar is more than double at the higher pressures, indicating that at this thermal treatment, dewatering is more difficult and extra energy is needed to reach a high solids concentration.

However, displacement halves at 5 and 6 bar pressures, indicating that a 5 bar pressure would be enough to dewater the sludge. Energy calculations are needed to assess whether it is more energetically efficient to dewater at 4 bar or at 5 bar, since both increased displacements and pressures account for more energy expenditure. Finally, results for WAS are contradictory, since the biggest displacement was found at 6 bar, although the solids concentration remained stable from pressures at 5 bar to 6 bar. The displacement diminished from 4 bar to 5 bar, with an increasing solids concentration which is an expected behaviour but increased for 6 bar pressure. This could be an indication of wrongful execution of the dewatering protocol.

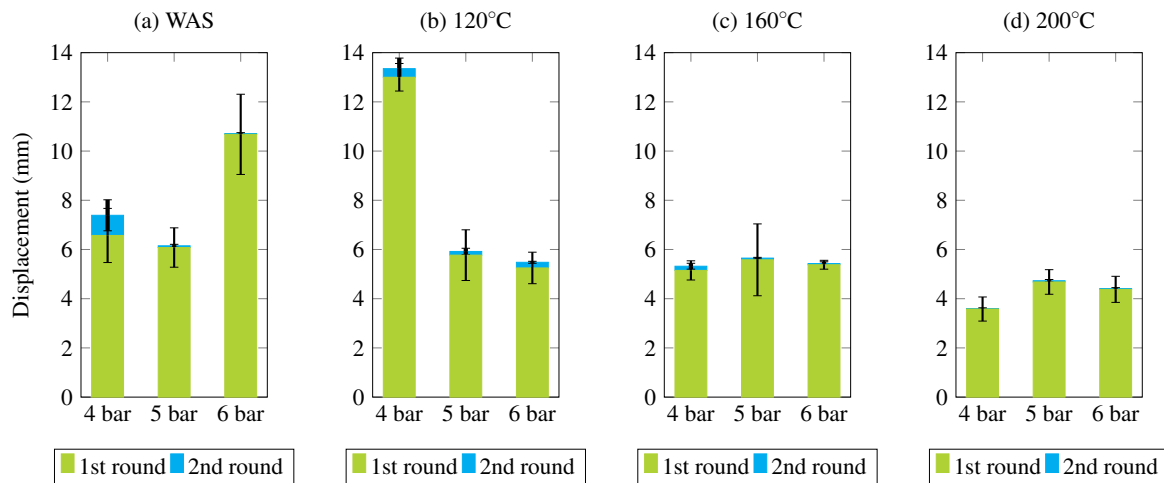


Figure 4.12: Filter-press results measured in displacement for three different pressures. For pressures 4 and 5 bar,  $n=3$  and for pressure 6 bar,  $n=2$ .

In short, these results complement the CST measurements, indicating that thermally treated sludge at 120°C seems to be the most difficult to dewater, and for increasing treatment temperatures, total displacement reduces. Sludge at 200°C is the easiest to dewater, which had been previously reported by [42, 70, 10, 12].

Cake solids achieved after dewatering are found in Figure 4.13. After pressing the samples, a solid disk-shaped cake was achieved (see Appendix A.7b (b) for a representative image). Total solids measurements were taken in triplicate from all these disks and final total solids concentrations can be found in Appendix A.4.

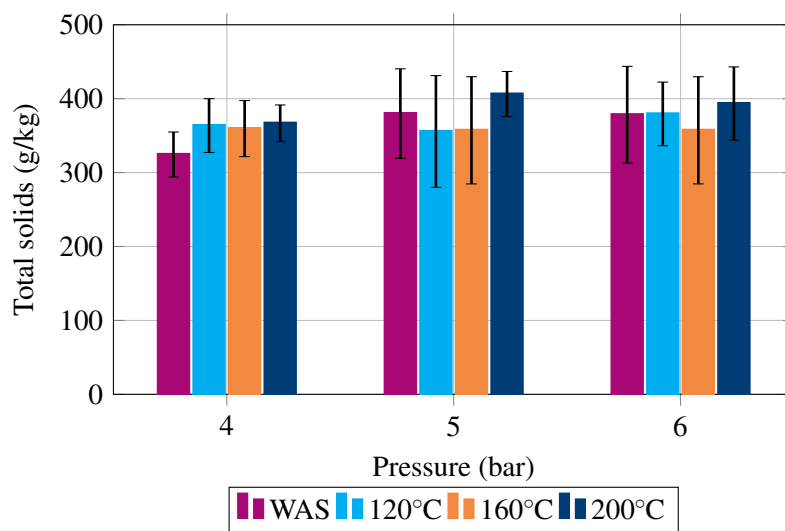


Figure 4.13: Total solids after press filter dewatering, for BMP samples with polymer. For each pressure,  $n=6$ .

Except for the 160°C samples that remained constant, all samples achieved a maximum value for total solids at 5 bar: WAS achieved a value of 379.84 gTS/kg, 120°C samples dried to 388.59

gTS/kg and sludge thermally treated at 200°C reached 406.25 gTS/kg. An increase in total solids for increasing pressures would be expected, as the more pressure is applied, the more efficient is the dewatering process. However, there is a decrease in TS for the WAS and 200°C temperature, most likely due to a loss of solids in the supernatant of the press filter. The polymer concentration might not have been adjusted to these samples and some solids would not aggregate, flowing with the supernatant to be discarded.

ANOVA statistical analysis of the final solids concentration for each pressure showed that at 5 and 6 bar, there is no significant difference between samples (p-values = 0.2947 and p-value=0.6641 > 0.05, respectively). However, for 4 bar pressure, final solids concentrations are statistically significant (p-value = 0.0352 < 0.05 for one-way ANOVA) and the Tukey HSD test showed that WAS and 200°C samples showed statistically significant difference. These results support previous results that indicate that pressures superior to 4 bar are sufficient to dewater all samples with no distinction between treatments, i.e., the alterations to physical properties that might have induced by thermal treatment are not sufficiently prominent to alter dewatering at higher pressures.

## 4.5 Energetic integration of a thermal hydrolysis unit in a WWTP

In this section, an energetic balance of the thermal hydrolysis within the WWTP at three different temperatures was performed and compared with the conventional scenario: no THP and anaerobic digestion of raw sludge. Figure 4.14 represents overall energy balance regarding thermal pretreatment of sludge at 160°C and subsequent stabilisation and handling; Table 4.4 summarizes the values for all pretreatment temperatures.

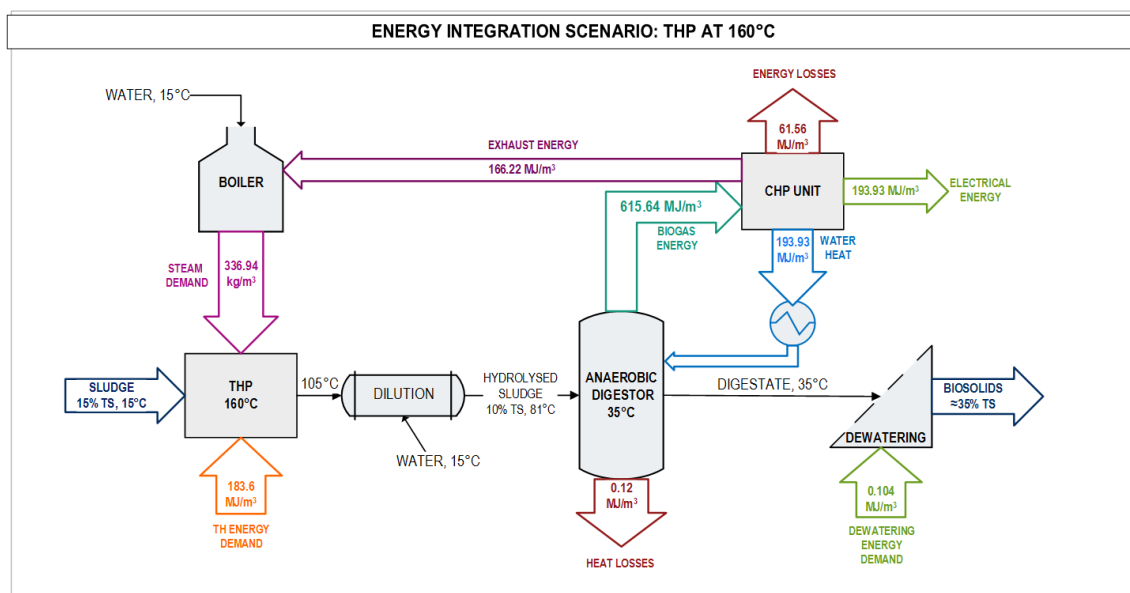


Figure 4.14: Energy Integration Scenario for THP at 160°C

The implementation of a TH unit, if energetically integrated, seems to be self-sufficient by having a positive net balance for all temperatures, which means it provides more energy to the WWTP than it uses. A first glance analysis shows the highest net positive balance for anaerobic digestion of WAS with no thermal treatment. However, the energy balance does not take into consideration the reaction time nor the disposal costs of the biosolids. An increasing reaction time implies more heating demand to maintain the digester working and less turnover of the inlet sludge.

Table 4.4: Overall energy balance of sludge processing with thermal pretreatment at different temperatures.

| Contributions                           | WAS          | 120°C        | 160°C        | 200°C        |
|-----------------------------------------|--------------|--------------|--------------|--------------|
| TH steam demand (kg/m <sup>3</sup> )    | -            | 320.1        | 336.9        | 365.2        |
| TH energy demand (MJ/m <sup>3</sup> )   | -            | 183.6        | 183.6        | 183.6        |
| AD heat losses (MJ/m <sup>3</sup> )     | 0.12         | 0.12         | 0.12         | 0.12         |
| Energy from biogas (MJ/m <sup>3</sup> ) | 553.87       | 578.13       | 615.64       | 609.58       |
| Electric Energy                         | 174.47       | 182.11       | 193.93       | 192.02       |
| Exhaust Gases                           | 149.54       | 156.10       | 166.22       | 164.59       |
| Hot Water                               | 174.47       | 182.11       | 193.93       | 192.02       |
| CHP losses (MJ/m <sup>3</sup> )         | 55.39        | 57.81        | 61.56        | 60.96        |
| Dewatering energy (MJ/m <sup>3</sup> )  | 0.143        | 0.144        | 0.104        | 0.072        |
| BMP run time (days)                     | 21           | 17           | 16           | 30           |
| <b>Net balance (MJ/m<sup>3</sup>)</b>   | <b>498.2</b> | <b>336.5</b> | <b>370.3</b> | <b>364.8</b> |

Analysing the energy regarding the THP unit, the most advantageous configuration seems to be for sludge treated at 160°C, since it produced more energy from the biogas, which therefore, implied a higher net balance. However, as previously shown, the methane production is not significantly different between all thermally treated samples and since that is the main driver for any change in the net balance, it can be assumed there is no significant change between thermally treated samples in regard to the net balance. This is mainly because the implication used for the THP unit energy demand only takes into consideration the concentration of inlet sludge, a parameter regarded in literature as the driver for energy demand, which was standard for all scenarios at 15% TS [19]. It should be noted that the hydrolysis temperature and working pressure of the THP unit will also play a significant role in the energy demand, as well as the degree of integration regarding the CHP unit. The THP energy demand can also be expressed as 51 kWh/m<sup>3</sup>, which is a common unit in literature. For standardisation purposes, all energy values in the model are shown in MJ/m<sup>3</sup> of sludge.

The literature provides several reference values for the energy demand of the TH unit with different degrees of integration. Values regarding full-scale installations, with total integration with a CHP range from 10.2 kWh/m<sup>3</sup> for 8.5% TS [112] to 5.0 kWh/m<sup>3</sup> for 14 % TS [81]; theoretical values tend to overestimate, with Perez-Elvira *et al.* estimating 14.0 kWh/m<sup>3</sup> for 3%

TS [76], 15.2 kWh/m<sup>3</sup> for 8% TS [80] and 18.5 kWh/m<sup>3</sup> for 13% TS [81]. Cano *et al.* proposes an energy demand for thermal treatment of sludge of 10-15 kWh/m<sup>3</sup>, in which all heat requirements are satisfied by the exhaust gases from CHP and electrical requirements [19]. Since this approach already absorbs the contributions of the electrical energy in the TH unit energy demand, some information would be lost namely the energy the TH unit would spend, even if the electrical energy produced from the biogas was to be added as an input. Comparison of these results with the one obtained for this model indicates an over-estimation, however, the empirical equation used to calculate the TH energy demand does not integrate the CHP unit. Instead it includes a boiler at 90% efficiency which logically increases the energy value. However, it was considered that all biogas was to be fed to a CHP unit. A CHP allows for an efficient way to produce electricity, but also heat, in the form of high grade heat as steam at 400°C (considering exhaust gases), and a low grade heat as a liquid stream (water usually at 70-90°C) [19]. The CHP system considered uses a gas engine, as most of the full-scale installations for energy recovery are of this kind. Gas engines also have higher electric yield than that of turbines.[80]

Since the approach for the energy demand of THP does not differentiate between treatment temperatures, the specific steam demand for the thermal hydrolysis was estimated. Results shown in Table 4.4 are relative to a THP unit that operates with flash steam integration. Steam demand increased with increasing treatment temperature, which is expected, although the values are quite similar to one another. A more in depth analysis regarding steam demand is presented in the next section.

As for dewatering, the energy demand for sludge treatment at 200°C is exactly half the energy needed for raw sludge, 0.072 (MJ/m<sup>3</sup>) compared to 0.144 (MJ/m<sup>3</sup>). This fraction of the energy is not very expressive in the net balance, but the associated costs with subsequent disposal might be, considering the amount of biosolids produced. Unfortunately, analysis of final solids quantity was not included in the experimental research.

Taking into account all these considerations, if a THP unit were to be implemented in a WWTP, it would be more energetically interesting for thermal treatments at 160°C. Yet, the results obtained suggested that no THP unit and just the AD of WAS is even more energetically sustainable although this rationale does not take into account digestion reaction time and the effect that this would have on sludge turnout in the WWTP. Literature supports the idea that a THP unit improves methane production, although results obtained in this work were not significantly different. Finally, the THP unit seems to be self-sufficient and provide extra electric energy for the WWTP, while improving dewatering.

#### 4.5.1 Steam requirements of the TH process

Due to the fact that modelling the energy demand of the TH unit can be a very challenging procedure, an easier and more reliable alternative is to compare it in terms of the specific steam consumption. To assess the influence of treatment temperature, the steam demand for the thermal hydrolysis pretreatment was calculated for all experimental temperatures, with and without the

steam integration from the flash set, as described in the blackbox approach. The results are found in 4.5.

Analysing Table 4.5, two major conclusions can be drawn: increasing treatment temperature increases steam demand for the same %TS in the raw WAS and the integration of the released steam from the flash cooling can reduce the overall steam demand by almost 70%, and this value increases with the increase in the reaction temperature. If the flash steam is reused, then a thermal treatment at 160°C or 200°C uses almost as much steam as a lower pretreatment. Considering that higher pretreatment temperatures improve biogas production during AD, then a TH unit can be viable if it efficiently integrates all heat sources.

Analysis of the equations 3.5 and 3.6 (see Chapter 3) shows the actual hydrolysis temperature has no impact on the steam consumption of the process. In fact, the steam released during the flashing process is recycled to efficiently pre-heat the raw, cold sludge. The steam demand becomes directly proportional to the temperature difference between the hydrolysed sludge (after flashing) and the raw sludge. Usual post-flashing temperatures vary between 103°C to 107°C, as long as the pre-heating is operated at atmospheric pressure.

Table 4.5: Steam demand for TH process.

| sample                                  | 120°C  |        | 160°C  |        | 200°C   |        |
|-----------------------------------------|--------|--------|--------|--------|---------|--------|
| Flash integration                       | no     | yes    | no     | yes    | no      | yes    |
| Steam demand (kg/m <sup>3</sup> sludge) | 394.78 | 320.14 | 685.48 | 336.94 | 1230.17 | 365.25 |
| % reduction                             | 18.9   |        | 50.8   |        | 68.5    |        |

The steam demand for the TH unit can be determined as the energy required to heat up sludge from the inlet temperature to the desired outlet conditions and by the need to make up for any energy losses. In order to minimise steam consumption, some parameters can be manipulated regarding the 'black box': sludge inlet concentration and sludge inlet temperature. As mentioned before and regarded in literature as a paramount factor, sludge inlet concentration has a direct relation with heat needs, as higher sludge concentrations require less water to be heated up [18]. Sludge inlet temperature also affects steam consumption, as less energy is required to reach the set temperature, although this approach is very seldomly taken into consideration at full-scale installations.

Most commercially available solutions operate under atmospheric conditions during the pre-heating of sludge, at which the pretreatment temperature is relatively low, that of 80°C which is a low threshold for steam recovery. Some new second-generation thermal hydrolysis technologies, such as tH4+ by teCH4+, preheat and flash at higher pressures with the use of a thermocompressor, allowing the recovery of 100% of the process vapors, while further increasing the steam explosion of sludge [100].

### 4.5.2 Energy demand for dewatering

The energy demand for dewatering was calculated based on the experimental work and results can be observed in Table 4.6 and Figure ???. The lowest value for each temperature was used in the overall energy balance. Analysis of the dewatering energy corroborates the results found for sludge filterability, and the general indication from literature. For higher pretreatment temperatures, dewatering is improved. For all samples except for 120°C, the lowest energy demand was found at 4 bar, even though the best dewatering capacity, i.e., higher solids content after dewatering was found to be at the pressure of 5 bar. For 160°C and 200°C, dewatering energy is considerably lower than that for untreated sludge or sludge treated at 120°C. An economic evaluation regarding incineration costs versus dewatering costs would be required to assess which pressure would benefit the WWTP management the most.

Table 4.6: Dewatering energy demand for a press filter operating at different pressures. Values calculated from the average displacement for each sample.

| Energy for dewatering (kJ/m <sup>3</sup> sludge) |        |        |        |        |
|--------------------------------------------------|--------|--------|--------|--------|
| pressure (bar)                                   | WAS    | 120°C  | 160°C  | 200°C  |
| 4                                                | 143.14 | 260.65 | 104.01 | 71.91  |
| 5                                                | 149.11 | 144.48 | 138.08 | 118.10 |
| 6                                                | 311.31 | 160.49 | 159.24 | 131.83 |

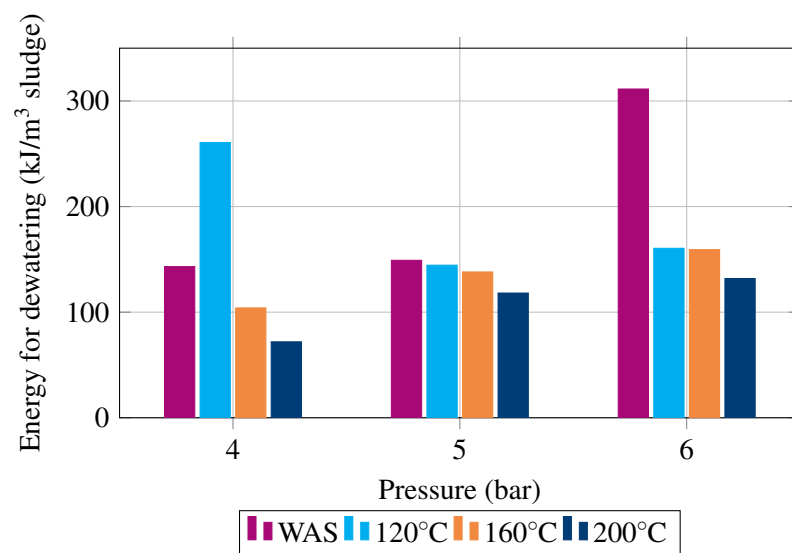


Figure 4.15: Dewatering energy demand for a press filter operating at different pressures.

ANOVA analysis of the energy requirements for each pressure suggested that the dewatering pressures are not significantly different for the level of significance ( $p\text{-value} = 0.5073 > 0.05$ ). This result proposes that the driver for choosing a dewatering pressure is not the energy it uses, but rather the final solids concentration, as those influence disposal costs.



## Chapter 5

# Conclusions and recommendations

### 5.1 Main conclusions

This research aimed to identify the effects of temperature of thermal hydrolysis unit as pretreatment on the overall energy balance of a wastewater treatment plant. The main conclusions from this research are:

Increasing the temperature of thermal pretreatment had a positive effect on COD solubilisation; TAN and orthophosphate also had their solubilisation improved for increasing temperatures as a result of organic matter break-down, mainly proteins, and PAOs disintegration, respectively. The sludge rheology was also changed with thermal pretreatment, with sludge viscosity diminishing for higher temperatures.

Regarding the BPM tests, thermally treated samples had a higher specific methane production and, therefore, a higher biodegradability. Samples treated at 160°C were the most biodegradable (68%) with the highest maximum methane production of 238 NmLCH<sub>4</sub>/gCOD. ANOVA analysis indicated that there were no significant differences between methane production at different temperatures but Tukey HSD analysis suggested statistically significant difference between WAS and sludge treated at 160°C. Although higher temperatures induced a higher solubilisation, they also seemed to enhance the formation of recalcitrant compounds that can inhibit the anaerobic metabolism and the extent of biodegradability, and should require further downstream processing on the reject water. This was further supported by the reaction time for the BMP runs that was the longest for samples at 200°C - 30 days, almost double the time it took samples treated at 120°C and 160°C to finish digestion, 17 and 16 days respectively. The Gompertz model showed a good fit for the methane production curves with  $R^2$  values higher than 0.95 for all samples.

Orthophosphate and TAN release kinetics seemed to have no effect on methane production. Both macronutrients increased during AD, supporting the statement that anaerobic digestion of thermally treated sludge may enhance N and P release. Results also suggested struvite formation for samples treated at 200°C.

The thermal treatment also improved dewatering for temperatures above 160°C, making samples more filterable and easier to compress. At 120°C, dewatering and filterability were more

difficult comparatively to raw WAS. This might be due to a decrease in particle size, which increased surface area for interaction and an incomplete sludge EPS destruction which provided a structure for water to bind. A pressure of 4 bar was sufficient to dewater all samples, except for 120°C which required a pressure of 5 bar. Final solids concentration increased with dewatering pressures, reaching an optimum value for all samples at 5 bar. At this pressure, all samples reached a total concentration of 350 gTS/kg or higher.

Finally, an energy balance model was produced in with the energy demand for the THP unit and subsequent sludge handling processes. Results indicated that for a THP unit, thermal treatment at 160°C was the more energetically efficient, although all treatment temperatures produced surplus energy that could be integrated in the energy demand of the WWTP. Thermal pre-treatment at 160°C also allowed for an increased biodegradability, a higher methane production, an improved dewaterability and reduced digester reaction times. Nonetheless, the integration of a THP unit was, according to this work, self-sufficient energy wise for all treatment temperatures. However, overall net energy comparison showed that just anaerobic digestion of WAS was the scenario that produced more surplus energy, which seems to contradict literature finds.

## 5.2 Recommendations for future work

The current research allowed the understanding of the effects of thermal pretreatment of sludge on the subsequent sludge processing units. However, several issues were observed to be missing in literature during the development of this research and recommendations are made for further research on the studied phenomena.

It would be interesting to measure the different N fractions, total P and pH during anaerobic digestion to understand the extent of the interactions between the fractions throughout digestion and if thermal hydrolysis of sludge alters the extent of the solubilisation of these macronutrients. This is important for further nutrient removal in the dewatering supernatant.

To complete the initial goals, and further develop the knowledge on the effects of thermal hydrolysis on biogas production in anaerobic digestion, it would be advised to perform a BMP test in thermophilic regime.

Regarding the lag-phase reported for sludge treated at 200°C, studying the methane production with ammonium release in a continuous mesophilic reactor could help to understand if the lag-phase was due to the production of recalcitrant compounds or TAN inhibition.

As for the energy demand for the THP unit, it would be important to develop a more specific model that would take into consideration all the parameters indicated as not included, such as sludge concentration, steam integration inside the THP unit, several degrees of CHP integration, pumps, tubing and losses to the system. Finally, an economic assessment and sensitivity analysis to understand which option is indeed the most economically efficient, either 160°C or 200°C and how changes in sludge concentrations into the THP unit affects the whole process, as it is considered the main driver for TH costs.

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## Appendix A

# Additional information regarding methodology and results

### A.1 THP Setup



Figure A.1: THP Setup: Includes a temperature PDI controller, a heat isolated chamber and a insert where the samples are placed within.

## A.2 Biochemical methane potential test (BMP)

### A.2.1 Automatic Methane Potential Test System (AMPTS) II

The Automatic Methane Potential Test System (AMPTS) II is an analytical instrument for conducting real-time BMP and anaerobic biodegradability assays, having sampling, analysis, recording and report generation fully integrated and automated. A multi-channel analyser consisting of 15 parallel reactors and the same number of gas flow meters (flow cells) attached to a data acquisition system, allows for the real-time investigation of a high number of samples.

The instrument setup can be divided into three units that are simplified by A, B and C unit. In unit A, the sample incubation unit, can host up to 15 vials containing small amounts of a sample with anaerobic inoculum that are incubated at a desired temperature. The media in each vial is mixed by a slow rotating agitator that inserts in the isolating rubber cap of the bottle.

Biogas is then continuously produced and directed by a tubing system to unit B, the CO<sub>2</sub>-absorbing unit, where each the biogas produced in each vial passes through an individual vial containing an alkaline solution. This alkaline solution retains several acid gas fractions, such CO<sub>2</sub> and H<sub>2</sub>S, by chemical interaction with NaOH, only allowing CH<sub>4</sub> to pass through to the biomethane Gas Volume Measuring Device (unit C). A pH indicator is added into each vial for controlling the acid binding capacity of the solution.

In the Gas Volume Measuring Device (unit C), the volume of CH<sub>4</sub> gas released from unit B is measured using a wet gas flow measuring device with a multi-flow cell arrangement. This measuring device works according to the principle of liquid displacement buoyancy and can monitor ultra low gas flows; a digital pulse is generated when a defined volume of gas flows through the device. An integrated embedded data acquisition system is used to record, display and analyze the results [9].



Figure A.2: BMP setup. The sample incubation unit (unit A) and the CO<sub>2</sub>-absorbing unit (unit B) are shown in the forefront. On top of the working bench, unit C is also slightly displayed.

### A.2.1.1 Sampling

The isolation rubber cap has three inserts, shown in Figure A.3, one for the rotator, the second for a biogas escape and a third one that reaches the bottom of the bottle for sampling. A small tube was attached to this insert on the rubber cap. The tubing was secured with a clamp to maintain anaerobic conditions. For sampling, a syringe was first attached to the tubing, then the clamp is released and the syringe pulled to remove the desired amount of sample. Before detaching the syringe from the tube, the clamp was closed to prevent any contamination thus ensuring a correct sampling.



Figure A.3: Cap of a test bottle with 3 inserts: the rotator, the tubing for CH<sub>4</sub> measurement and the sampling point with a red clamp to ensure anaerobic conditions.

### A.2.2 BMP composition per bottle

Table A.1: BMP culture medium

| Name                                                    |           | Blank        | Positive     | WAS          | 120°C        | 160°C        | 200°C        |
|---------------------------------------------------------|-----------|--------------|--------------|--------------|--------------|--------------|--------------|
| <b>Constituent</b>                                      | Unit      |              |              |              |              |              |              |
| Reaction Volume                                         | mL        | 300          | 300          | 300          | 300          | 300          | 300          |
| Inoculum/Substrate ratio                                | gVS/gVS   | 2            | 2            | 2            | 2            | 2            | 2            |
| Inoculum concentration <sup>1</sup> (gVS/kg sludge)     | gVS/kg    | 24.11        | 24.11        | 24.11        | 24.11        | 24.11        | 24.11        |
| Substrate concentration <sup>2</sup> (gVS/kg substrate) | gVS/kg    | -            | 40           | 67.86        | 41.68        | 36.95        | 27.58        |
| Final substrate concentration in the medium             | gVS/L     | 10           | 10           | 10           | 10           | 10           | 10           |
| Aproximate biodegradability of substrate (%)            | %         | 0            | 99           | 30           | 30           | 30           | 30           |
| Substrate approx COD/VS ratio                           | gCOD/gVS  | 0            | 1            | 1.42         | 1.42         | 1.42         | 1.42         |
| <b>Constituent to be added per bottle</b>               | Unit      |              |              |              |              |              |              |
| Substrate volume                                        | mL        | 0.0          | 75.0         | 44.2         | 72.0         | 81.2         | 108.8        |
| Inoculum volume                                         | mL        | 248.9        | 248.9        | 248.9        | 248.9        | 248.9        | 248.9        |
| Carbonate Buffer(100 g/L) volume                        | mL        | 3.0          | 3.0          | 3.0          | 3.0          | 3.0          | 3.0          |
| Macronutrients volume                                   | mL        | 1.8          | 1.8          | 1.8          | 1.8          | 1.8          | 1.8          |
| Micronutrients volume                                   | mL        | 0.2          | 0.2          | 0.2          | 0.2          | 0.2          | 0.2          |
| Demi Water volume                                       | mL        | 46.2         | 0            | 2.0          | 0            | 0            | 0            |
| <b>TOTAL</b>                                            | <b>mL</b> | <b>300.0</b> | <b>328.8</b> | <b>300.0</b> | <b>325.8</b> | <b>335.0</b> | <b>362.6</b> |

### A.2.3 Cumulative methane production

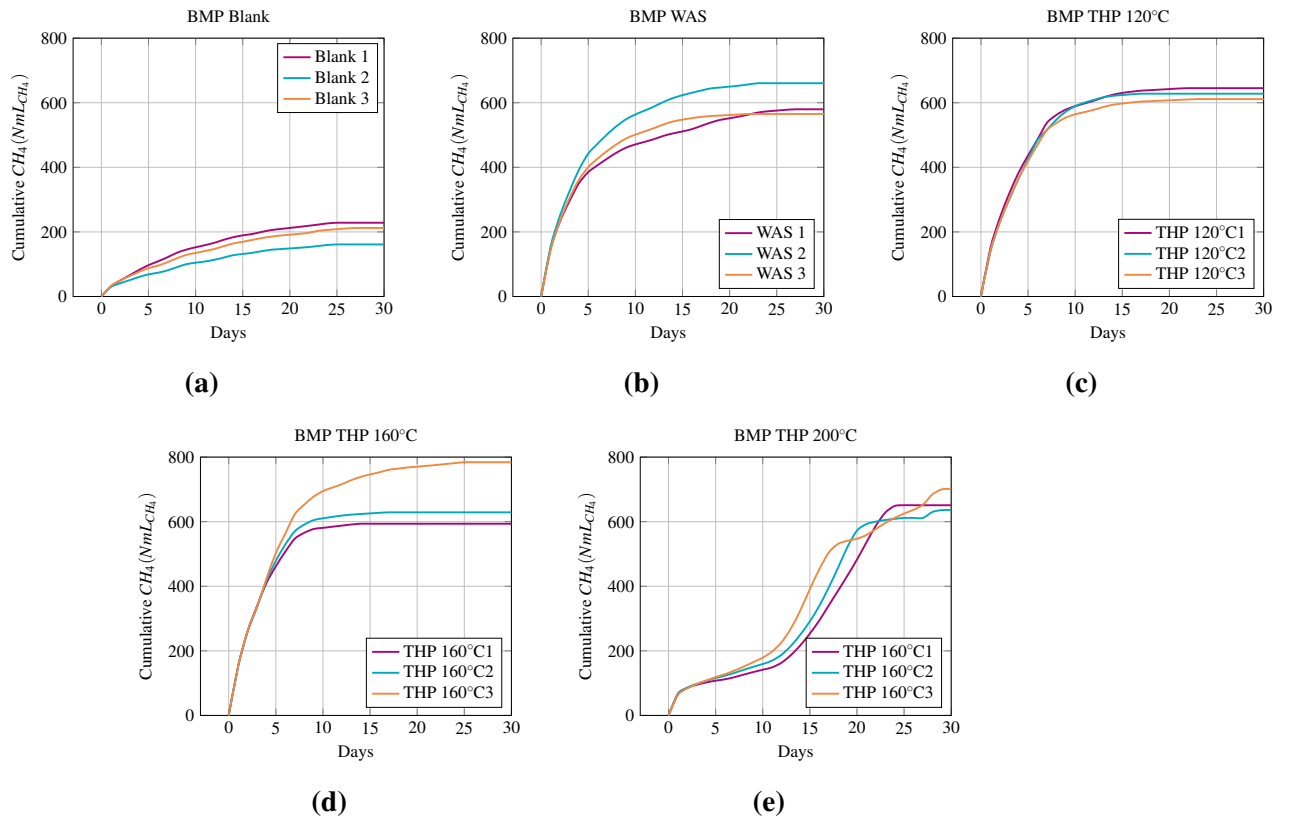


Figure A.4: Cumulative methane production, without subtracting endogenous production (blank).  
 (a) Blank (b) WAS (c) THP at 120°C (d) THP at 160°C (e) THP at 200°C

## A.3 Dewaterability tests

### A.3.1 CST

Table A.2: Capillary suction time results for thermally treated sludge, with and without the addition of a dewatering polymer, polyethylene (PE). For each sample,  $n=3$ .

| CST(s)       | without PE(s)      | with PE(s)       |
|--------------|--------------------|------------------|
| <b>WAS</b>   | $1384.1 \pm 145.7$ | $229.2 \pm 14.3$ |
| <b>120°C</b> | $114.5 \pm 7.6$    | $14.2 \pm 0.6$   |
| <b>160°C</b> | $14.9 \pm 1.1$     | $11.7 \pm 1.6$   |
| <b>200°C</b> | $304.0 \pm 38.1$   | $9.2 \pm 1.2$    |

Table A.3: Capillary suction time results for BMP samples after anaerobic digestion, with (n=3) and without (n=6) the addition of a dewatering polymer, polyethylene (PE). Results in seconds with percentage of reduction.

| CST(s)       | without PE(s)       | with PE(s)       | reduction(%) |
|--------------|---------------------|------------------|--------------|
| <b>WAS</b>   | 814.75 $\pm$ 57.76  | 72.87 $\pm$ 6.97 | 91.1         |
| <b>120°C</b> | 606.98 $\pm$ 107.80 | 36.83 $\pm$ 8.93 | 93.9         |
| <b>160°C</b> | 603.67 $\pm$ 115.46 | 36.50 $\pm$ 4.04 | 94.0         |
| <b>200°C</b> | 878.95 $\pm$ 74.47  | 48.00 $\pm$ 9.53 | 94.5         |

### A.3.2 Press-filter

#### A.3.2.1 Setup

The press-filter operated exclusively manually. The target pressure would be regulated with a ROSCA, and the speed at which the pressure was applied could also be adjusted manually. The counter would only begin once the target pressure was reached as it pressed on the cell. That meant that some dewatering would already be taken place before the timer set off. The FP cell would be assembled as shown in Figure A.6, from left to right. Between the cell components 3 filters were placed on each side of the sample: one coarse and 2 fine mesh circles.



Figure A.5: Press filter Setup: Includes a manual lever that allows for faster or slower pressure



Figure A.6: FP cell setup



(a) Dewatering mixture with digestate and polymer.



(b) Solids layer after pressing.

Figure A.7: Dewatering mixture (sludge plus polymer) immediately before pressing (a), and after, as a cake layer (b).

## A.3.2.2 Results

Table A.4: Filter-Press results for total displacement in relation with total solids (TS). For total displacement, n=3 and for TS, n=9.

| <i>pressure</i> | <b>4 bar</b>         |                  | <b>5 bar</b>         |                  | <b>6 bar</b>         |                  |
|-----------------|----------------------|------------------|----------------------|------------------|----------------------|------------------|
| <i>sample</i>   | <i>displac. (mm)</i> | <i>TS (g/kg)</i> | <i>displac. (mm)</i> | <i>TS (g/kg)</i> | <i>displac. (mm)</i> | <i>TS (g/kg)</i> |
| <b>WAS</b>      | 7.38 ±1.33           | 324.49 ±30.44    | 6.15 ±0.80           | 379.84 ±30.44    | 10.70 ±1.70          | 378.31 ±26.91    |
| <b>120°C</b>    | 13.35 ±1.00          | 363.58 ±36.39    | 5.92 ±0.92           | 388.59 ±75.62    | 5.48 ±0.60           | 379.36 ±43.00    |
| <b>160°C</b>    | 5.32 ±0.51           | 359.50 ±37.87    | 5.65 ±1.43           | 357.16 ±72.51    | 5.43 ±0.25           | 404.19 ±42.56    |
| <b>200°C</b>    | 3.60 ±0.48           | 366.81 ±24.74    | 4.73 ±0.48           | 406.25 ±30.59    | 4.40 ±0.49           | 393.38 ±49.56    |

Table A.5: Displacement results in regards to two rounds per essay.

(a) Displacement in two times at 4 bar, n=3.

| <b>4 bar</b>  |                        |                        |                   |
|---------------|------------------------|------------------------|-------------------|
| <i>sample</i> | <i>displac. 1 (mm)</i> | <i>displac. 2 (mm)</i> | <i>total (mm)</i> |
| <b>WAS</b>    | 6.57 ±1.10             | 0.82 ±0.63             | 7.38 ±1.33        |
| <b>120°C</b>  | 13.00 ±0.56            | 0.35 ±0.43             | 13.35 ±1.00       |
| <b>160°C</b>  | 5.15 ±0.39             | 0.17 ±0.12             | 5.32 ±0.51        |
| <b>200°C</b>  | 3.58 ±0.49             | 0.02 ±0.03             | 3.60 ±0.48        |

(b) Displacement in two times at 5 bar, n=3.

| <b>5 bar</b>  |                        |                        |                   |
|---------------|------------------------|------------------------|-------------------|
| <i>sample</i> | <i>displac. 1 (mm)</i> | <i>displac. 2 (mm)</i> | <i>total (mm)</i> |
| <b>WAS</b>    | 6.08 ±0.80             | 0.07 ±0.06             | 6.15 ±0.80        |
| <b>120°C</b>  | 5.77 ±1.03             | 0.15 ±0.13             | 5.92 ±0.92        |
| <b>160°C</b>  | 5.58 ±1.46             | 0.07 ±0.03             | 5.65 ±1.43        |
| <b>200°C</b>  | 4.68 ±0.50             | 0.05 ±0.05             | 4.73 ±0.48        |

(c) Displacement in two times at 6 bar, n=2.

| <b>6 bar</b>  |                        |                        |                   |
|---------------|------------------------|------------------------|-------------------|
| <i>sample</i> | <i>displac. 1 (mm)</i> | <i>displac. 2 (mm)</i> | <i>total (mm)</i> |
| <b>WAS</b>    | 10.68 ±1.73            | 0.03 ±0.04             | 10.70 ±1.70       |
| <b>120°C</b>  | 5.25 ±0.64             | 0.23 ±0.04             | 5.48 ±0.60        |
| <b>160°C</b>  | 5.38 ±0.18             | 0.05 ±0.07             | 5.43 ±0.25        |
| <b>200°C</b>  | 4.38 ±0.53             | 0.03 ±0.04             | 4.40 ±0.49        |