Conventional and Advanced Thermal Hydrolysis in Sewage Sludge Pre-treatment

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Abstract

The thermal hydrolysis process (THP), a method that employs heat (at temperatures surpassing those of autoclaves, reaching up to 200 ℃) and pressure (reaching up to 25 bar) in the absence of oxygen, holds promise as a technology for pre-treating sludge before anaerobic digestion (AD) to enhance biogas production. Operating at elevated temperatures, THP also offers sludge disinfection for safe utilisation as fertiliser and improves sludge dewaterability. However, the requirement for high reaction temperatures presents drawbacks to the technology. At temperatures exceeding 150 ℃, the colour of the sludge darkens. This dark brown hue could impede the UV disinfection phase of wastewater treatment when the post-dewatering digestate wastewater is reintroduced into the wastewater stream. Furthermore, the harsh reaction conditions of THP not only lead to high energy consumption but also increase the formation of ammonia nitrogen and refractory compounds in the treated sludge. These compounds act as inhibitors of methanogenesis, significantly impacting methane production in anaerobic digestion processes.

Advanced thermal hydrolysis (ATHP), an oxidative thermal hydrolysis process, has been introduced to overcome the challenges of THP. By incorporating Fenton's peroxidation, ATHP can be operated under milder conditions. This approach helps alleviate energy consumption, mitigate the impact on sludge colour, and minimise the production of refractory dissolved organic substances.

In this study, a mixture comprising 55 % primary sludge and 45 % waste activated sludge from the Mangere Wastewater treatment plant in Auckland, New Zealand was used. For THP treatment, 600 mL of sewage sludge was fed into the reactor in each batch. The sludge was subjected to temperatures of 145, 160, 175, and 190 ℃, with varying processing times ranging from 5 to 30 min prior to anaerobic digestion. The vessel was pressurised with 6 bar of nitrogen (N_2) *gas. The working pressure varied from 10.2 to 14.1 bar, depending on the set temperature. The influence of a sudden decompression (flash phase) on sludge solubilisation was also examined to elucidate the solubilisation mechanism.*

The research findings indicate hydrolysis constitutes the primary solubilisation process (accounting for approximately 76 % to 87 % of sludge solubilisation). However, the contribution of sudden decompression through flashing from working pressure to atmospheric *pressure at the end of the process is substantial (ranging from 24 % to 13 %, depending on the treatment conditions).*

THP treatment at 190 °C for 10 min resulted in the highest degree of sludge solubilisation, approximately 45%, while the maximum biogas yield (around 389 mL biogas/g VS added) was achieved with sludge treated at 145 °C for 30 min. Operating THP at a lower temperature of 145 °C can minimise the release of ammonia nitrogen (NH_3*-N) and reduce the colour of the sludge significantly.*

For the ATHP experiments, the sludge mixture was treated at 100, 115, 130, and 145 °C, with a processing time varied from 5 to 30 min and oxygen pressure from 10 to 30 bar before AD. The highest biogas production (439.6 mL biogas/g VS added) was observed in the sludge treated at 145 °C for 15 min with an oxygen pressure of 20 bar. Conversely, ATHP treatment at 145 °C for 30 min with an oxygen pressure of 30 bar yielded a higher degree of solubilisation (25 %) in the treated sludge.

The results demonstrated that under ATHP conditions of 145 °C for 15 min with an oxygen pressure of 20 bar, there was no increase in NH_3*-N or refractory compounds that could inhibit methanogenesis. Furthermore, ATHP led to a 13% increase in biogas yield with a shorter reaction time compared to THP.*

Dedication

Gửi cho bà ngoại của con, người đã ở bên con lúc tuổi thơ, người đã động viên con trong những thành công hay thất bại của cuộc đời. Chúc bà của con an giấc!

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Phuong Linh Ngo

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Glossary

AD	Anaerobic digestion
ATHP	Advanced thermal hydrolysis process
BOD	Biological oxygen demand
COD	Chemical oxygen demand
FPS	fermented primary sludge
pCOD	particulate chemical oxygen demand
PS	Primary sludge
SBRS	Sludge from sequencing batch reactors
sCOD	Soluble chemical oxygen demand
SS%	Solubilisation degree
tCOD	Total chemical oxygen demand
THP	Thermal hydrolysis process
TRL	Technology readiness level
TS	Total solids
VFAs	Volatile fatty acids
VS	Volatile solids
WAS	waste activated sludge
WWTPs	Wastewater treatment plants

Publications

Peer-reviewed journal articles

Ngo, Udugama, Gernaey, Young, & Baroutian. (2021). Mechanisms, status, and challenges of thermal hydrolysis and advanced thermal hydrolysis processes in sewage sludge treatment. *Chemosphere, 281*, 130890. https://doi.org/10.1016/j.chemosphere.2021.130890

Ngo, Young, Brian, & Baroutian. (2023). New insight into thermal hydrolysis of sewage sludge from solubilisation analysis. *Chemosphere*, 139456. https://doi.org/10.1016/j.chemosphere.2023.139456

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Chapter 1

Introduction

Sewage sludge disposal is one of the biggest challenges that wastewater treatment plants (WWTPs) are facing because of energy costs, environmental pollution, and hazardous contaminants. Its management consumes 40 – 50 % operational cost of WWTPs [1].

Different methods for managing sludge have been developed, including composting, landfilling, anaerobic digestion (AD), pyrolysis, and incineration. Among these, AD is commonly used because of its various benefits, such as low environmental impact, minimal solid residue, and high bioenergy production [2]. However, AD technology does exhibit certain limitations in sewage sludge digestion, attributed to its low hydrolysis rate, resulting in massive volume requirements, low biogas production rates, and a low methane content [3, 4]. Consequently, many pre-treatment technologies have been developed to enhance AD performance, for instance, thermal hydrolysis [5], alkaline pre-treatment [6], ultrasonic pre-treatment [7], and application of enzymes [8].

Among the developed pre-treatment processes, thermal hydrolysis process (THP) has been gaining interest from scientific communities and industry, with a remarkable rise in the number of full-scale systems in WWTPs worldwide [9]. Since 1995, there have been over 70 Cambi THP installations across 20 countries worldwide [10]. The technology in sewage sludge treatment involves reactions carried out at elevated temperatures (above autoclave temperature, up to 200 °C) and pressure (up to 25 bar) in the absence of oxidants [11-14]. During THP, the sterilisation of sludge, the disintegration of sludge flocs, and the rupture of cooked cell membranes occur due to high temperature and pressure conditions [5, 15]. As a consequence, THP brings in advantages in terms of sludge pre-treatment, including increasing solubilisation to enhance anaerobic biogas production [5, 12, 16, 17], which is the most crucial benefit of the method, providing disinfection for the sludge to safely used as fertiliser [18], and improving dewaterability of the sludge [5, 12, 16]. The technology also provides a significantly smaller volume of anaerobic digester due to shortening digestion time [19]. So far, the consensus for the operating conditions of the technology is from 170 °C to 175 °C for 30 min under the equilibrium pressure corresponding to saturated steam within the reactor [9].

Nevertheless, some problems with the THP still require solution, including high energy consumption, formation of AD inhibitory compounds, and UV disinfection absorption for treating wastewater from post-dewatering AD sludge. Therefore, the technology is still subject to a copious degree of research despite its 29 years of commercialisation. Modified THPs, such as the advanced thermal hydrolysis process (ATHP), have been investigated recently.

Advanced thermal hydrolysis process utilises a combination of THP and Fenton's peroxidation [14]. In contrast to THP, this process employs the synergistic effect of oxidation factors such as H_2O_2 without adding any catalyst under less severe temperature and pressure [14, 20]. Therefore, the formation of refractory materials could be eliminated, and a considerable amount of energy can be saved by operating at a lower temperature [9]. Though decreasing temperature will reduce the solubility of the sludge, the presence of H_2O_2, in turn, increases the soluble chemical oxygen demand (sCOD) [9]. A 175 % increase in the disintegration degree of sludge at 99 °C compared to THP experiments at 165 °C was shown, demonstrating the effectiveness of the process [20]. Methane production is also enhanced through ATHP, wherein ATHP conducted at 115 °C for 5 min under 1 bar has been shown to produce the same amount of methane compared to THP being run at 170°C for 30 min under 8 bar [9]. However, it should also be noted that high concentrations of H_2O_2 could inhibit subsequent AD [9].

Whilst there have been a significant number of studies of THP, many inconsistent findings have been reported due to the lack of a conventional apparatus or a standardised protocol for running THP experiments at a laboratory scale [21]. For example, it is still unclear whether a prolonged reaction time is necessary [22] or not [9]. Furthermore, there are diverse perspectives regarding the optimal THP conditions for sewage sludge pre-treatment to eliminate inhibitors for the following AD. Currently, information about the influence of interacting factors is sparse. The current focus within literature surrounds investigating time or temperature individually, however, the question remains open as to what the ideal combination of these conditions is, in order to optimise biogas production and reduce sludge colour.

ATHP is a new technology which currently has insufficient information for pilot development and commercialisation. Thus, the technology needs more research in terms of the optimal oxidation dosage and the extent to which the presence of oxidation compounds impacts the methanogenesis bacteria.

Moreover, an extensive fundamental understanding of the reactions involved in THP and ATHP still needs to be well documented. Additionally, previous studies have yet to attempt to compare

THP to ATHP, analyse the technology readiness of ATHP, or adequately understand the reactions involved in the process.

The aim of this research is to develop a detailed fundamental understanding of the solubilisation mechanism of THP and ATHP for sewage sludge, and to optimise the process for maximum biogas production. This information plays a central role in the reactor design and process scale-up. These are very important for process development when a sound knowledge and understanding of the reaction mechanism and engineering skills for obtaining a satisfactory performance of the process are required.

1.1 Hypothesis

A comprehensive understanding of the solubilisation mechanism of THP can provide a better reaction condition to reduce the colour of treated sludge and the energy cost while enhancing biogas production. ATHP will be an alternative method to overcome the disadvantages of THP.

1.2 Research Objectives and Scope

To investigate the hypothesis of this study, the following objectives were developed:

- **To characterise the sewage sludge from WWTP**
  Sewage sludge varies from WWTPs due to the differences in the community's social economy and, more importantly, the differences between sewage collecting systems. This research project employed sewage sludge sourced from the Mangere WWTP in Auckland, New Zealand. The sludge composition at this facility comprises a blend of 55% primary sludge and 45% waste activated sludge.

- **To perform a comprehensive literature review on mechanism, status, and challenges of THP and ATHP in sewage sludge treatment**

  A comprehensive understanding of the mechanisms in THP and ATHP is not adequately covered in previous studies. Additionally, a systematic assessment of the current status and obstacles of these technologies is lacking. This study presents a thorough review of the mechanisms, current status, and challenges of both THP and ATHP. Furthermore, this study examines the technological readiness of ATHP and offers practical insights for their future applications.

- **To understand the sludge solubilisation mechanism and the impact of THP operating conditions on solubilisation of sludge**

  The solubilisation degree represents the biodegradability of the sludge. Hence, comprehending the mechanisms behind sludge solubilisation in THP holds the key to process optimisation or modification. This study assesses the solubilisation mechanisms in THP, while also evaluating the combined impact of time and temperature on sludge solubilization through a severity factor.

- **To investigate the effect of THP on AD performance and optimise biogas production**

  THP was operated at 145 ℃ to 190 ℃ for the period up to 30 min under pressure varied from 10.2 to 14.1 bar (depending on the set temperature) to analyse the formation of refractory compounds, ammonia nitrogen and volatile fatty acids (VFAs) which influence AD performances significantly. The optimum THP conditions to maximise biogas production and minimise colour and ammonia production is discussed.

- **To investigate the effect of ATHP on AD performance and the role of oxygen**

  The impact of ATHP on solubilising sludge has been confirmed. Also, the incorporation of oxidative chemicals significantly minimises the processing temperature of ATHP; however, the chemical residues in the treated sludge should not be disregarded. As it was observed that hydrothermal deconstruction happens during THP in the presence of any oxygen, this study opted for oxygen as a substitute for H_2O_2 in ATHP. Since oxygen will not persist in the sludge after treatment, the influence of residual oxidation chemicals on methanogenesis will be eliminated. Tested temperatures ranged from 100 ℃ to 145 ℃ for durations up to 30 min, with oxygen pressure of 10, 20 and 30 bar.

1.3 Thesis Structure

This thesis consists of a total of six (6) chapters and incorporates a set of scientific articles that have been published or are in the process of submission to journals indexed by International Scientific Indexing (ISI). While there might be some minor overlap of content between chapters, particularly within the Introduction and Experimental sections. Nevertheless, the outcomes presented in each chapter are distinct and together contribute to the fulfilment of the project goals. A summary of the chapters in this thesis is outlined as follows.

Chapter 1: Introduction

This chapter contains the background information on THP and ATHP, and defines the processes, the knowledge gaps, the hypothesis, and the objectives of this research project. The scope and explanation of each phase of the study is also discussed.

Chapter 2: Mechanisms, status, and challenges of THP and ATHP processes in sewage sludge treatment

This chapter details the mechanisms happening during THP and ATHP, including the free radical, solubilisation, Maillard reaction, and viscosity reduction mechanisms. This chapter also analyses the current technical challenges of THP and evaluates the technology readiness level for ATHP.

Chapter 3: New insight into thermal hydrolysis of sewage sludge from solubilisation analysis

This chapter evaluates the influence of sudden decompression, reaction time, and temperature on sludge solubilisation to understand the mechanism. The primary mechanism of sludge solubilisation and the main influence factors are highlighted. The changes in volatile fatty acids in different THP conditions are also analysed.

Chapter 4: Thermal hydrolysis of primary sludge and waste activated sludge mixture: biogas production and formation of inhibitors

This chapter explores the formation of inhibitory compounds affecting methanogenesis in treated sludge under various tested THP conditions. The biogas production of the treated sludge under different conditions is analysed and compared to comprehend the influencing factors. The optimal THP condition that yields the highest biogas production for the mixture of primary sludge and waste activated sludge is determined.

Chapter 5: A novel strategy for integration of oxidation within advanced thermal hydrolysis of sludge

This chapter assesses the effect of O_2 on sludge solubilisation. From this experimental work, the interplay among time, temperature, and O_2 in the formation of NH_3-N and VFAs within the treated sludge during ATHP was elucidated. The enhancement of biogas yield in comparison to THP and the identified optimal condition for ATHP are also highlighted.

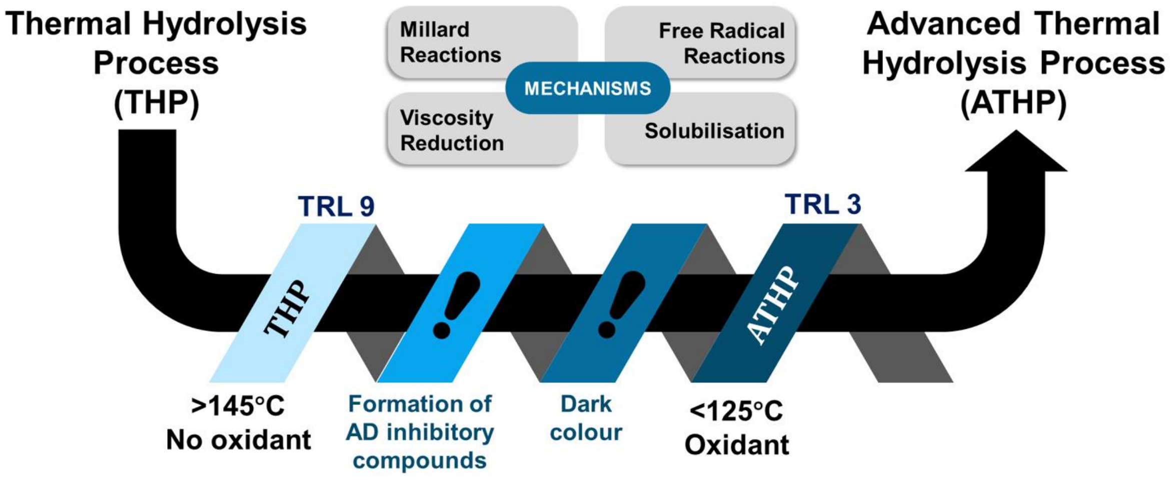
Chapter 6: Concluding remarks

This chapter outlines the main findings from conducting this research. Recommendations for future work are also offered.

Supplementary data that were used within or produced during this study are presented in the Appendix.

Chapter 2

Mechanisms, status, and challenges of THP and ATHP processes in sewage sludge treatment



Thermal hydrolysis is a promising technology for sludge pre-treatment prior to AD to enhance biogas production. However, the technology is facing two main problems; the dark colour of sludge can affect UV disinfection and the formation of methanogenesis inhibitors such as ammonia nitrogen and refractory compounds have a significant impact on methane production in anaerobic digestion processes. ATHP, which is an oxidative THP, has been introduced to overcome these challenges. This chapter provides a comprehensive review of the mechanisms and reactions which occur during THP and ATHP. Technical and implementation challenges of both technologies are discussed.

The content of this chapter has been published, details in the footnote. The theme has been modified to improve the flow and readability of the thesis.

Ngo, Udugama, Gernaey, Young, & Baroutian. (2021). Mechanisms, status, and challenges of thermal hydrolysis and advanced thermal hydrolysis processes in sewage sludge treatment. *Chemosphere, 281*, 130890. https://doi.org/10.1016/j.chemosphere.2021.130890

2.1 Introduction

Current wastewater treatment practice is transforming a wastewater pollution problem into a sludge problem. Sludge treatment represents a huge cost for the treatment plants. The sludge disposal is also challenging because of hazardous contaminants and environmental pollution. Different sludge management methods including composting, landfilling, anaerobic digestion, pyrolysis, and incineration have been developed to solve these challenges. Out of these technologies, AD is commonly used due to its various benefits, such as low environmental impact, low cost, minimum solid residue, and high bioenergy production [2]. However, with a low hydrolysis rate, AD technology has elicited a variety of limitations, for instance, the requirement for large digesters and inadequate rates of methane-deficient biogas production [3, 4, 23]. Consequently, many pre-treatment technologies have been developed to enhance AD performance, namely thermal hydrolysis [5], alkaline pre-treatment [6], ultrasonic pre-treatment [7], and application of enzymes [8].

Among the developed pre-treatment processes, thermal hydrolysis process has been gaining interest from the scientific community and industry for more than 20 years, with a remarkable rise in the number of full-scale THPs in wastewater treatment plants worldwide [9]. Nevertheless, there are still some problems with the technology that require solutions, including the high energy consumption, formation of AD inhibitory compounds, and UV disinfection absorption for treating the wastewater from post-dewatering AD sludge. Therefore, the technology is still subject to a copious degree of research despite its 29 years of commercialisation. Modified THPs, such as ATHP, have also been investigated in recent years.

Whilst there are a significant number of studies of THP, many inconsistent findings have been reported due to the lack of a conventional apparatus or a standardised protocol for running THP experiments at lab-scale [21]. For example, it is still not clear whether a long reaction time is necessary [22] or not [9]. Moreover, an extensive fundamental understanding of the reactions involved in THP is still not well documented by prior research. There is also a lack of a systematic review regarding the current status and challenges of the technology. There are some useful review articles on different aspects of THP (Table 2-1), however, no work has attempted to compare THP to ATHP, analyse the technology readiness of ATHP, or properly understand the reactions involved within the process. To this end, this paper provides a comprehensive review of the mechanisms, status, and challenges of the THP and ATHP, alongside a discussion of the technology readiness associated with each technology to provide a practical view for future application. These overviews can act as a fundamental background for the further evolution of the technology.

Table 2-1. Reviews on sludge pre-treatment using THP (published within the last two decades)

Reference	Review highlights	Areas where further work is required
[21]	Influencing factors on biogas yield, mass and energy balance, and dewaterability improvement	The influence of pre-heating and cooling, and the importance of flash tank in THP
[24]	Advances and disadvantages of THP a as sludge AD pre-treatment method, and solutions to overcome THP limitations	The influence of sludge characterisation and pre-heating and cooling in THP
[25]	Reaction temperatures from 140-200°C cause negligible differences in methane production. However, temperatures above 160°C significantly enhance dewaterability of the sludge	The impact of sludge characterisation and reaction time on enhancing methane production
[26]	THP reaction pathways and mass transfer	Influencing factors of THP
[27]	THP enhances biogas production of AD and the process is net energy positive. THP should be used only for waste activated sludge	Technical challenges and formation of potential inhibitors of biogas production
[28]	An increase in methane production at different pre-treatment conditions	THP pre-heating and cooling time, and working pressure
[29]	Dewaterability enhancement for sludge	Viscosity reduction and technical aspects of THP

2.2 Thermal hydrolysis process

Thermal hydrolysis in sewage sludge treatment involves reactions carried out at elevated temperatures (above autoclave temperature, up to 200°C) and pressure (up to 25 bar) in the absence of oxidants [11-13]. The technology was initially applied to enhancing the sludge dewatering process [5, 30] before being used as one of the most effective pre-treatment methods to enhance biogas production for anaerobic digestion.

During THP, the sterilisation of sludge, the disintegration of sludge flocs, and the rupture of cooked cell membranes occur due to high temperature and pressure [5, 15]. Consequently, THP of sewage sludge has numerous advantages in terms of sludge pre-treatment such as enhancing dewaterability of the sludge [5, 12, 16, 19], providing disinfection for the sludge to be safely used as fertiliser [18], and the paramount benefit of the process, increasing solubilisation of the sludge to enhance anaerobic biogas production [5, 12, 16, 17]. The technology also allows for an anaerobic digester with significantly smaller volume due to shortened digestion time. Thus, the THP has been gaining interest in not only research but also commercial applications, both in batch and continuous operations [18].

Table 2-2 shows the previous investigations on anaerobic biodegradability enhancement and inhibition by THP at different conditions. In general, almost all authors concluded that the THP has a significant positive effect on biogas production from WWTP sludge. The enhancement could reach up to 75% in comparison to AD without THP pre-treatment [12] or be as low as only 30% [31]. This noticeable variation in biogas production from previous studies may be caused by variations in sludge composition and operating conditions of the THP.

The significant differences in the sludge composition from different WWTPs can be the result from differences in the social economy of the community, and more importantly the differences between sewage collecting systems. The inflow of municipal WWTPs may come only from domestic wastewater with separate discharge systems, or it may contain other kinds of sewage from industry, stormwater, and landfill leachate if combined or intercepted discharge systems are applied [32]. Another source that influences influent composition to the treatment plant is infiltration. The sewers leak, and in case the groundwater table is very high, there is a net inflow of water into the sewer, diluting the sewage. On the other hand, if the groundwater table is low (summer conditions, dry conditions), sewage might leak from the sewer into the underground. This may explain the variation in the results in Table 2-2 despite the studies all using mainly waste activated sludge (WAS) or primary sludge (PS) of municipal WWTP. Therefore, in order to understand the change in THP operating conditions for each kind of sludge, the sludge subjected to THP research needs to be comprehensively characterised. Further research may need to focus on whether the differences in the composition of sewage sludge is a significant influencing factor in THP research and application.

Table 2-2. Impact of THP conditions on anaerobic digestion of sludge and formation of inhibitory compounds

Sludge			THP conditions			Anaerobic digestion enhancement		Inhibitory compounds formed		Reference
Type	tCOD (g/L)	VS (%)	T (°C)	Pressure (bar)	Reaction time (min)	Increase in sludge solubilisation (%)	Increase in biogas production (%)	Increase in ammonia nitrogen (%)	Sludge colour (PtCo)	
WAS	46.1	68.4	100	-*	30	12.9	14	23.4	-	[5]
			135	-	30	17.5	43	34.0	-	
			175	-	30	37.6	58	63.8	-	
			175	-	120	43.3	-	110.6	-	
	20.6	73.4	115	01	05	19.7	13.5	9.4	-	[9]
			135	1.1	05	22.4	22.5	6.1	-	
			170	7.1	05	39.3	50.0	27.9	-	
			170	7.3	15	41.8	51.5	47.2	-	
			170	7.9	25	47.2	63.5	53.7	-	
			170	8.2	35	46.4	50.0	48.1	-	
	-	-	180	21	30	-	75	100	-	[12]
	100	78.3	140	-	30	31.87**	-	-	3837	[16]
			145	-	30	40.31**	-	-	7500	
			150	-	30	40.00**	-	-	7300	
			155	-	30	46.41**	-	-	9600	
			160	-	30	44.00**	-	-	11500	
			165	-	30	50.33**	-	-	12677	
	13.0	76.3	120	-	30	35.8	45.3	-	-	[22]
	15.0	77.4	150	-	30	33.1	58.3	-	-	
	15.9	76.5	175	-	30	47.3	61.7	-	-	
	-	-	165	06	20	-	40	-	-	[31]
	-	70.0	100	01	30	-	30	121	-	
	95.1	79.8	130	-	30	20.6	17.1	<1	-	[33]
			140	-	30	23.4	17.4	<1	-	
			150	-	30	29.3	21.0	<1	-	
			160	-	30	35.5	18.9	<1	-	
			170	-	30	41.5	27.1	<1	-	
PS +WAS	49.6	70.0	175	-	30	-	14	-	-	[5]
	-	-	180	21	30	-	20	-	-	[12]

(tCOD: Total chemical oxygen demand; WAS: Waste activated sludge; PS: Primary sludge; VS: volatile solid was measure in percentage of total solid; *: information not available; **: sludge solubilisation (%))

The main factors which influence how THP improves the methane yield of sewage sludge include processing time, total pressure, and temperature. Among them, temperature is the most significant parameter. Many researchers argue that a slight change in temperature can result in a significant difference in enhancing the biodegradable characteristics of the sludge [5, 9, 16, 17, 22, 34]. For instance, Li and Noike [22] provided a result that the biogas production increased 20 % when the reaction temperature rose from 120 °C to 150 °C. However, the optimal temperature for pre-treatment of sludge varies in many studies. In terms of WAS, Dwyer *et al.* [16] reported that the most effective THP pre-treatment temperature is 145 °C, whereas Haug *et al.* [5] concluded 175 °C, and Park *et al.* [35] confirmed 186 °C. In contrast, all Cambi®THP, Bio Thelys™, and Exelys™ processes, which are commercial THPs, operate at 165 °C. The fact that these results are contradictory implies that other factors should also be taken into account, such as the forming of refractory compounds, time needed for heating the sludge to the setting temperature, and for cooling before going into the AD digester. For example, Abelleira-Pereira *et al.* [9] and Whitlock *et al.* [36] stated that the flash phase, when a sudden depressurisation occurs, is the most essential phase of THP sludge pre-treatment. They also highlighted that the involvement of the flash phase is more important than the reaction time. When the pressure is released suddenly, a shear force is applied to the cooked cells, which then leads to an increase in the solubilisation of the sludge [15].

The second influencing factor that was considered is reaction time. It is well understood that longer reaction time increases the solubility of compounds. For example, Aboulfoth *et al.* [37] found that the solubilisation improves with a reaction time up to 4 hours. However, a higher degree of solubilisation does not necessarily lead to a higher rate of biogas production. Higher solubilisation degree achieved by longer reaction time may contain more soluble refractory materials and inner compounds, which will inhibit the AD process. Haug *et al.* [5] reported that THP reaction time does not increase biomethane production beyond the first 60 min, whereas the disintegration degree of sludge is double at 120 min compared to the level at 60 min. Correspondingly, Penaud *et al.* [17] stated that the optimal reaction time is 30 to 60 min. On the other hand, Abelleira-Pereira *et al.* [9] proved that there is no significant change in biogas production for THP times between 5 and 30 min. Furthermore, Neyens and Baeyens [29] suggested that increasing the reaction time from 10 to 30 min has little influence on the result. Despite these results, the optimal reaction time proposed by many researchers is still 30 min Table 2-2). These findings have been subsequently reciprocated within the industry, as the sludge pre-treatment reaction time for the Cambi®THP and Exelys™ processes is currently 30 min. This is also the optimal time that Li and Noike [22] highlighted. Although the technology is applied in many other fields, including food processing, the reaction time for pre-treatment of sewage sludge needs further research with the goal of increasing digestibility.

Similarly, there are insufficient results regarding the influence of pressure on the pre-treatment. While the shear force created by sudden depressurisation is crucial to cell rupture, which in turn increases the solubilisation of the sludge [9], there is inadequate information regarding the impact of pressure. For most of the studies, as well as the commercial Cambi®THP, the pressure applied for THP is around 6 to 9 bar. However, THP of sludge can be operated at pressure as high as 21 bar [12].

2.3 Advanced thermal hydrolysis process

To mitigate problems, such as UV disinfection absorption created by the dark colour of the effluent arising from the elevated temperature of the THP, an ATHP was developed. This is a novel sludge pre-treatment process which utilises a combination of THP and Fenton's peroxidation [14]. In contrast to THP, this process employs the synergistic effect of oxidation factors such as H_2O_2 without the addition of any catalyst under less severe temperature and pressure [20]. Therefore, the formation of refractory materials could be eliminated, and a considerable amount of energy can be saved with a lower operating temperature [9]. Though decreasing temperature will reduce the solubility of the sludge, the presence of H_2O_2 in turn increases sCOD [9]. A 175 % increase in disintegration degree of sludge at 99 °C in comparison to THP experiments at 165 °C was shown, demonstrating the effectiveness of the process [20]. Methane production is also enhanced through ATHP, wherein ATHP conducted at 115 °C for 5 min has been shown to produce the same amount of methane compared to THP being run at 170°C for 30 min [9]. However, it should also be noted that high concentrations of H_2O_2 could inhibit the subsequent AD [9, 14]. Similarly, Takashima and Tanaka [38] reported that despite the increase in sCOD induced by adding H_2O_2, methane production is decreased. Therefore, the technology needs further research to become a potential method for sewage sludge pre-treatment.

2.4 Fundamental mechanisms

During THP and ATHP of sludge, many physical and chemical transformations and reactions occur. The main changes in sludge include i) degradation of the gel structure and release of linked water in the sludge enhancing the dewaterability of the sludge after treatment [30]; ii) formation of VFAs which enhance biogas production in the downstream anaerobic digestion; and iii) formation of coloured compounds and refractory organic materials which conversely inhibit the biomethane production [16, 21]. These phenomena are driven by four main mechanisms: free radical formation, solubilisation, melanoidins formation, and viscosity reduction.

2.4.1 Free radical mechanism

The impact of THP and ATHP on enhancing hydrolysis of organic material has been confirmed [26, 39]. During the process, free radicals, which are known as reactive species for rapidly decomposing organic compounds into VFAs and other short chain molecules, are created. The process of forming free radicals has three distinct stages, including initiation, propagation, and termination [40].

The initiation stage is defined as the degradation of compounds to produce radicals, leading to a remarkable increase in the total number of free radicals. In THP, high temperature and a lack of oxygen cause the degradation of organic material into hydrogen ($H^{\cdot}$) and alkyl radicals ($R^{\cdot}$), generally known as the initiation stage (Eq. 1) [26]. This reaction proliferates three subsequent reactions (Eqs. 2-4) of the propagation stage to produce highly reactive hydroxyl radicals ($^{\cdot}OH$) (Eq. 2), alkyl radicals ($R^{\cdot}$), (Eq. 3) [26] and $R_2N^{\cdot}$ radicals (Eq. 4) [41]. The propagation stage occurs as a result of reactions between free radicals [40]. During the propagation stage, the level of free radicals remains constant due to the balance between formation and degradation reactions [26].

$$\mathrm{RH} \overset{\Delta}{\rightarrow} \mathrm{R}^{\cdot} + \mathrm{H}^{\cdot} \tag{1}$$

$$\mathrm{H}^{\cdot} + \mathrm{H_2O} \rightarrow \mathrm{HO}^{\cdot} + \mathrm{H_2} \tag{2}$$

$$\mathrm{RH} + \mathrm{HO}^{\cdot} \rightarrow \mathrm{R}^{\cdot} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{R_2NH} + \mathrm{HO}^{\cdot} \rightarrow \mathrm{R_2N}^{\cdot} + \mathrm{H_2O} \tag{4}$$

In the final stage (termination), free radicals react together to produce short-chain alcohols (Eqs. 5 & 6) and carboxylic acids (Eq. 8) such as formic, acetic, and butyric acid [42], which are known as the "intermediate" products of the THP pre-treatment. Figure 2-1 shows the amount of VFAs produced by THP.

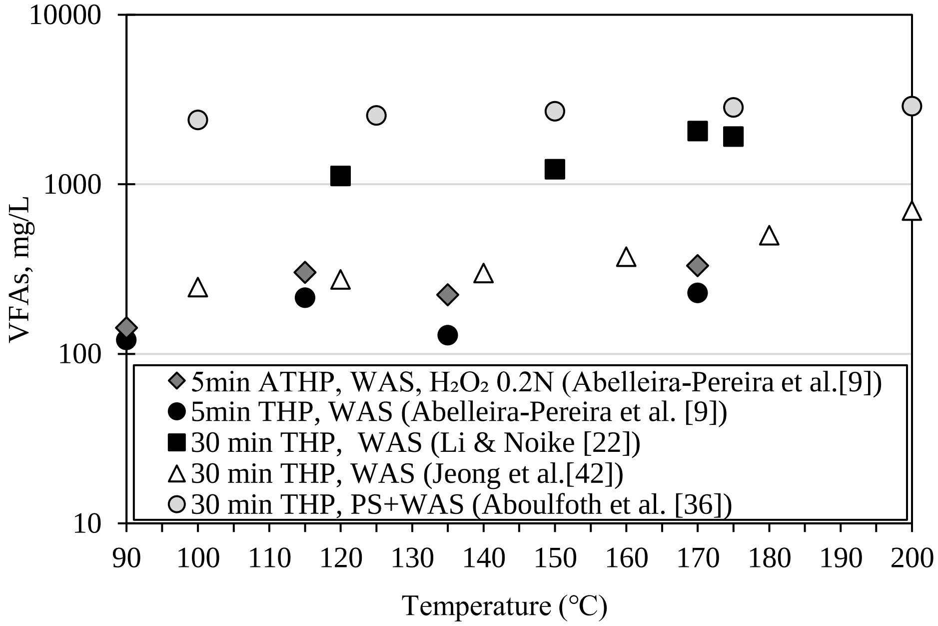


Figure 2-1. Final concentrations of VFAs formed from THP and ATHP of sludge [9, 22, 37, 43]

These VFAs play a key role in producing biomethane in the subsequent AD. The persistent compounds in the termination stage can also be created through intramolecular rearrangement, as can be seen in Eq. 7 [41]. Another primary product of THP is ammonia shown as ammonium ions in solution in Eq. 6, which is an inhibitor in the following AD stage, particularly when used for sludge pre-treatment. Jeong *et al.* [43] suggested that a total ammonia nitrogen concentration higher than 1.7 g/L can negatively affect the performance of AD [43]. As sewage sludge contains a high amount of protein, the concentration of ammonia nitrogen in the output of THP needs to be considered. For example, Yan *et al.* [34] reported a significant increase in NH_4^+-N from 21 mg/L to 200.9 mg/L when sludge was subjected to THP at 100°C. They also indicated that more ammonia nitrogen can be produced at higher THP temperatures.

$$R^{\cdot} + HO^{\cdot} \rightarrow ROH \tag{5}$$

$$R_2N^{\cdot} + 3H_2O \rightarrow NH_4^{+} + 2ROH + \frac{1}{2}O_2 \tag{6}$$

$$\mathrm{RC^{\cdot}OHR' \rightarrow HRCOR'} \tag{7}$$

$$\mathrm{R^{\cdot} + 2HO^{\cdot} \rightarrow R'COOH + 2H_2} \tag{8}$$

In ATHP, where oxygen species such as H_2O_2 or ozone are present, additional sequential reactions can occur by oxygen. There are four more reactions in the first stage (initiation) besides Eq. 1 depending on the applied oxidative compound. If H_2O_2 is used, the first additional reaction is the degradation of H_2O_2 to create hydroxyl radicals (Eq. 9) [41]. H_2O_2 can also be degraded into oxygen and water (Eq. 10) [44]. Oxygen attacks one of the weak bonds between carbon and hydrogen in the organic compounds to produce hydroperoxyl (Eq. 11) [44]. Also, organic compounds can be degraded by H_2O_2 at a very early stage to create alkyl and hydroxyl radicals (Eq. 12) [45].

$$\mathrm{H_2O_2 \rightarrow 2HO^{\cdot}} \tag{9}$$

$$\mathrm{H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2} \tag{10}$$

$$\mathrm{RH + O_2 \rightarrow R^{\cdot} + HOO^{\cdot}} \tag{11}$$

$$\mathrm{RH + H_2O_2 \rightarrow R^{\cdot} + HO^{\cdot} + H_2O} \tag{12}$$

In the propagation stage of ATHP, there are more additional reactions (Eqs. 13-18) to the Eqs. 2-4 occurring in the THP. Consequently, many other radicals such as organic peroxyl radical ($ROO^{\cdot}$) are produced during ATHP (Eq. 14) [46]. The reactions shown in Eqs. 9, 10 and 12 can also occur in the propagation stage if the reaction shown in Eq. 18 takes place.

$$\mathrm{H^{\cdot} + O_2 \rightarrow HOO^{\cdot}} \tag{13}$$

$$\mathrm{R^{\cdot} + O_2 \rightarrow ROO^{\cdot}} \tag{14}$$

$$\mathrm{RH + ROO^{\cdot} \rightarrow R^{\cdot} + ROOH} \tag{15}$$

$$\mathrm{ROO^{\cdot} \rightarrow R'^{\cdot} + CO_2} \tag{16}$$

$$\mathrm{ROOH \rightarrow RO^{\cdot} + HO^{\cdot}} \tag{17}$$

$$\mathrm{RH + HOO^{\cdot} \rightarrow R^{\cdot} + H_2O_2} \tag{18}$$

In the termination stage, there are no other reactions in ATHP besides equations (5), (6), (7), and (8). However, because of the presence of hydroxyl radicals, one of the most robust oxidation species (2.1 times stronger than chlorine), at a very early stage of the reaction, the degradation of the parent compound should occur more rapidly as compared to THP [44]. For example, in Figure 2-1, the amount of VFAs produced from ATHP is greater than for THP at similar temperatures and sludge compositions. The other benefit of ATHP, according to current work on the process, is that the required temperature is considerably lower than THP [9]; and thus, it can eliminate the production of refractory compounds and save energy. However, the process requires additional research to gain a comprehensive understanding due to the currently inadequate information available related to the process.

2.4.2 Solubilisation mechanism

The transition of particulate chemical oxygen demand (pCOD) into sCOD as a result of elevated temperature and pressure, called solubilisation, is another primary mechanism involved in the THP of sludge. During the biological nutrient removal stage of the wastewater treatment process, the micro-organisms grow by consuming nutrients in the liquid phase to form a biological floc before settling into a solid phase at the clarifier unit. When nutrients remain in the form of microbial cells, they are protected by the cell wall. As a consequence, WAS is not degradable and exists in the insoluble phase. Other solid materials in sewage sludge include fibers, hairs, and coarse particles generated from chemical precipitation and sedimentation during primary treatment methods, and these should also be considered.

Hydrolysis is one of the vital solubilisation mechanisms of the process. During THP or ATHP, the energy from applied heat increases the reactivity of water significantly, which in turn helps water to destroy the chemical bonds in complex molecules to produce simpler compounds (Eq. 19) [47, 48].

$$\mathrm{A-B\ +\ H_2O \overset{\Delta}{\rightarrow} A-H\ +\ B-OH} \qquad (19)$$

The mechanism also happens to non-biodegradable extracellular polymeric substances like the membrane of the cell, which catalyses cellular rupturing and increases the solubilisation of sludge [37]. Additionally, a sudden release in pressure at the final stage of the THP, the flash phase, produces a shear force to disrupt the cell and subsequently leads to an improvement in the disintegration of sludge [9]. The significant improvement in solubilisation of sludge by using THP has been well established. Hiraoka *et al.* [49] concluded that the solubilisation of sludge increases when the temperature is above 90 °C. Aboulfoth *et al.* [37] reported that the disintegration degree of sludge after THP pre-treatment at 100 °C is between 10 % to 20 % depending on the reaction time and the solid content in the sludge. Additionally, when the reaction temperature rose to 175°C, the disintegration degree increased to values upwards of 58.51 % [22]. Consequently, THP is a promising method to enhance the solubilisation of WAS and biomethane production.

2.4.3 Maillard reaction mechanism

One major drawback of using THP for sludge pre-treatment is the formation of coloured and recalcitrant dissolved compounds when the temperature elevates. These brown soluble polymers not only absorb UV effectively, hence leading to the failure of UV disinfection in the presence of such compounds [9], but they also reduce the biomethane production and increase the effluent nitrogen generation of the subsequent anaerobic digestion [16].

The Maillard reaction has been well documented as the dominant process responsible for the production of these refractory materials and the dark colour of effluent sludge after THP pre-treatment [16, 50, 51]. Specifically, the Maillard reaction is the non-enzymatic browning reaction between carbonyl groups and amino compounds such as amino acids, peptides, and proteins [52]. At temperatures below 140 °C, low molecular weight compounds (usually less than 70 kDa) such as amadori compounds are formed via polymerisation of low molecular weight amino acids and carbohydrates [53]. At higher temperatures, the Maillard reaction can also form larger molecular weight compounds (more than 100kDa), causing dark colours within the sludge (Figure 2-2). Melanoidins, which are the final products of the Maillard reaction, are an example of these larger compounds [54, 55]. Depending on the temperature and the presence of amino acids and sugar compounds, one or both of the mechanisms can occur (Figure 2-2) [16]. The starting temperature for forming melanoidins is 140 °C, when the solubility of sugars and proteins is enhanced [21, 56]. Dwyer *et al.* [16] demonstrated that when the THP temperature rose from 140 °C to 165 °C, the colour of the sludge increased significantly from 3837 PtCo/L up to 12677 PtCo/L. The measured molecular weight of the melanoidins in waste activated sludge was more than 10 kDa and accounted for more than 80% of the total colour of the THP pre-treated sludge [6, 16]. In addition, when the temperature reaches 160 °C, another non-enzymatic browning reaction known as caramelisation occurs, which will promote further darkening of the sludge [21, 57]. Different to Maillard reaction, caramelisation is the pyrolysis of sugar without the involvement of protein [21].

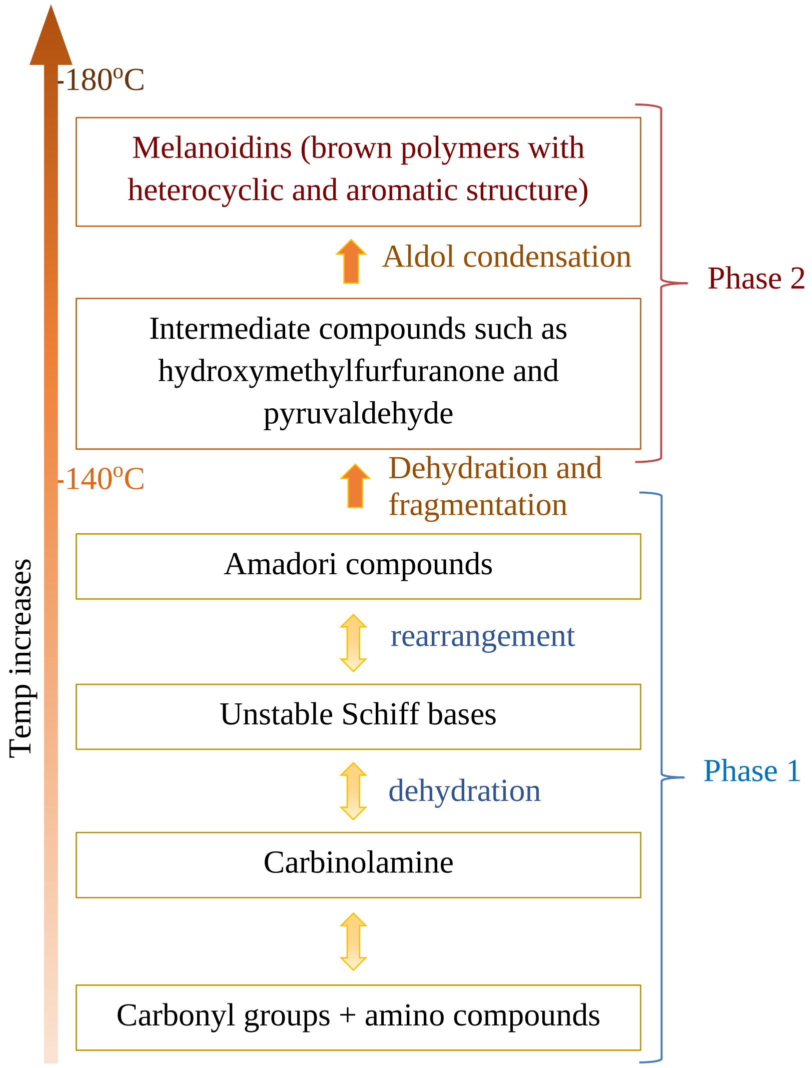


Figure 2-2. Maillard reaction mechanisms in THP

(Data from Dwyer *et al.* [16], Hofmann [54], Hodge *et al.* [55])

Maillard reaction products are considered toxic and constraining to anaerobic microorganisms [51]. It has been proposed that the antimicrobial capabilities of melanoidins such as binding metals [58], inactivating enzymes [59], and cross-linking proteins [60] are the mechanisms of inhibition. Marounek *et al.* [61] suggested that no VFA production could be collected from melanoidins during anaerobic digestion by rumen microorganisms. Additionally, Penaud *et al.* [51] argued that the biodegradability of the effluent could be enhanced two-fold if the dark colour compounds were removed. Thus, there is a need for an in-depth investigation into THP sludge pre-treatment to eliminate formation of coloured and refractory compounds.

In contrast, ATHP operates at a significantly lower temperature than THP, below 140 °C [9], and it is speculated that no melanoidins will be produced at this temperature [16]. However, the observed biogas production from the process was unstable and not higher than that of THP [9]. H_2O_2 is highlighted as an inhibitor of AD [9]. Thus, further studies need to focus on optimising the dosage of oxidants to prevent inhibition of the AD afterward.

2.4.4 Viscosity reduction mechanism

In sewage sludge treatment, the higher viscosity the sludge has, the more difficult steps such as mixing, dewatering, and solubilising become; and the process needs to overcome these factors which in turn leads to lower biomethane production of the AD and an increased energy cost for the whole system [43, 62].

Higgins *et al.* [63], when investigating the enhancement of dewaterability of sludge due to viscosity reduction after pre-treating by THP, observed a considerable increase in dewatering sludge from 27 % solid at 130 °C to 32% solid at 170 °C. Additionally, a lower viscosity of the sludge means that the liquid phase dominates and so a greater percentage of volatile solids (VS) can be fed into the digester which also enhances biogas production and minimises the volume of the digester [6].

In most of the previous studies, THP had a great influence on the viscosity reduction of the WAS. Carrère *et al.* [28] highlighted that at temperatures above 150 °C, THP could release linked water by breaking the gel structure of the cells within the sludge, in turn increasing the solubilisation and reducing the viscosity of the WAS. This finding was also confirmed by Whitlock *et al.* [36], Liu *et al.* [6] and Bougrier *et al.* [64]. It was reported that at 100 °C, THP can reduce the viscosity of WAS significantly from 110 mPa.s to 80 mPa.s [64], or from 5000 – 10000 mPa.s to 300 – 1000 mPa.s through THP pre-treatment at 175 °C [6]. Similarly, Jeong *et al.* [43] reported that at 140°C, the viscosity of the sludge dropped from 3000 mPa.s to 250 mPa.s for a 7 % WAS solution. Hii *et al.* [65] argued that the reduction in viscosity of treated sludge linearly relates to the increasing treatment temperature. Additionally, the impact of thermal treatment on the viscosity of the sludge not only depends on temperature, but is also influenced by the reaction time and sludge concentration [62]. However, Hii *et al.* [62] suggested that at reaction temperatures higher than 140 °C, the modification of sludge viscosity is less time-dependent than at lower reaction temperatures.

The ATHP has a substantial impact on enhancing the solubility of sludge, which is supposed to provide a significant influence on the viscosity. However, current knowledge about the effect of the process on the viscosity of the sludge is limited. Therefore, further investigation is required in order for the effect to be fully understood.

2.5 Technical Challenges

2.5.1 Formation of ammonia nitrogen

Ammonia nitrogen is well known as one of the inhibitory compounds which suppress methanogenesis. If the concentration of NH_4^+-N in the digester is higher than 1.5 g NH_4^+-N/L, the performance of AD starts to be negatively impacted [34]. Nakakubo *et al.* [66] discovered that at an ammonia concentration of 4.6 g NH_4^+-N/L, the biomethane yield in the AD process can drop by 50%.

By using THP, a significant increase in ammonia nitrogen content can be observed. During the free radical formation stage of THP, nitrogen from proteins and other organic materials is released as NH_4^+-N (Eq. 6). This is particularly significant with WAS as it contains a high concentration of proteins in the bacterial cells. Depending on the sludge type and composition, the total nitrogen content in the sludge can be varied. For example, Jeong *et al.* [43] concluded that the total nitrogen from raw WAS from South Korea is significantly high, at around 4350 mg/L, whereas Abelleira-Pereira *et al.* [9] showed that the amount of total nitrogen in WAS from a WWTP in Valladolid, Spain, is four times lower, at about 1467 mg/L. However, nitrogen content in WAS is the highest of all organic waste. Liu *et al.* [6] confirmed that the concentration of crude protein in WAS is around 68.68 g/kg, which is two times higher than in kitchen waste and five time higher than in vegetable and fruit residue in their test.

The amount of ammonia nitrogen in the WAS after THP pre-treatment can increase by up to 100 % or more [12]. Table 2-3 shows that after pre-treatment at 175 °C the NH_4^+-N present in the sludge can increase by 54 % [9] or up to 64 % [5]. In contrast, by using ATHP with the presence of H_2O_2 and at mild temperatures (115 °C), the amount of NH_4^+-N in the sludge slightly declines (Table 2-3). The decrease of ammonia nitrogen after using ATHP pre-treatment could be explained by ammonia escaping in the gas phase more rapidly than it is produced [34].

However, there is inadequate research on ATHP so far; thus, future work should be conducted to determine the mechanism behind this effect.

Additionally, using appropriate inoculum for AD can be another solution for high ammonia concentration sludge. Oosterhuis *et al.* [31] determined that there was no inhibitory impact on the methane yield by using inoculum from an AD at a full-scale THP which contained bacteria adapted for ammonia nitrogen. Hence, further research on inoculum should also be conducted.

Table 2-3. Increase in NH_4^+-N content after THP of WAS

Pre-treatment conditions	N-NH_4 input (mg/L)	N-NH_4 output (mg/L)	Reference
THP 175 ℃, 30 min	470	770	[5]
THP 170 ℃, 25 min	198	304	[9]
ATHP 115 ℃, 5 min	177	122	[9]
THP 100 ℃, 30 min	21	201	[34]

2.5.2 Formation of refractory colour compounds

Currently, the overwhelming consensus is that the optimal operating temperature for THP is from 165 ℃ to 180 ℃ [29]. As a result, most of the commercial THPs (Cambi®THP, Exelys™, Bio Thelys™, and LysoTherm®) are set up at 165 ℃, which theoretically should result in the production of melanoidins – dark brown resistant compounds [21, 56]. Such refractory compounds bring in three main problems for WWTPs: the inhibition of methane production, an increase in effluent nitrogen of the subsequent AD, and the failure of UV disinfection [9, 16]. These recalcitrant dissolved compounds cannot be digested by AD, and are additionally toxic for methanogenic bacteria, leading to inefficient degradation reactions. Therefore, a high fraction of nitrogen and chemical oxygen demand (COD) will remain unchanged in the effluent, and will henceforth be returned to the wastewater inflow which may result in an overload of the wastewater system [16]. The production of melanoidins during THP pre-treatment can increase the colour of the sludge remarkably from 3837 PtCo/L up to 12677 PtCo/L [16]. These colour compounds can also lead to the failure of UV disinfection [9]. This issue may then have a negative impact on the natural water ecosystem. Thus, the complications arising from colour are a critical issue that must be resolved in the future.

In contrast, due to the application of a milder temperature, it is clear that no melanoidins will be produced during ATHP. Therefore, in terms of eliminating refractory compounds, ATHP is a potential alternative method which needs to be considered. Besides reducing reaction temperature, short reaction time can be considered as another solution for THP to minimise the formation of colour compounds.

2.5.3 Solubilisation of inert compounds

The solubilisation of inert compounds that are inherent in the sludge before treatment is another considerable challenge of THP. As the solubilisation of organic materials increases when the treatment temperature is elevated, many inert compounds such as hairs, fibres, and bacterial cell walls in sewage sludge can be solubilised into the liquid phase [67]. Phothilangka *et al.* [12] reported that the concentration of soluble inert compounds rose significantly from 0.9 $kgCOD/m^3$ to 5.7 $kgCOD/m^3$. These soluble inert compounds are then recirculated into the mainstream wastewater after dewatering the sludge. Similar to the forming of refractory compounds, solubilisation of inert compounds has a significant effect on the quality of effluent wastewater streams. It is noted that the recirculated liquid from the sludge pre-treated by THP can contribute 10 mg/L COD to the effluent wastewater due to the increase in soluble inert compounds [12]. This, in tandem with the COD already present, lowers the ratio of biological oxygen demand (BOD) to COD, thereby significantly reduces the treatment capacity of the wastewater treatment system. Thus, this issue may endanger the natural water ecosystem due to an increase in COD and nitrogen quantity in the WWTP discharge if this problem is not solved.

There is as yet insufficient information regarding the capacity of ATHP to solubilise inert compounds. A high level of the solubilisation of inert compounds could be expected due to the significant enhancement of sCOD from the process. However, more research needs to be conducted to more clearly understand the mechanism of ATHP.

2.6 Technology Readiness Level

In order to employ THP or ATHP, a comprehensive understanding of the technology readiness level (TRL) of these processes is vital. The concept of TRL was first used by NASA to rate the readiness of space technology developments related to space missions and then in the general aerospace engineering industry [68]. The primary benefit of using a TRL scale is it allows for multiple technologies at different stages of development to be rated for their "mission readiness" in an unbiased manner. This concept of TRL has since been employed in other areas of engineering to assess the readiness of technologies for full-scale commercial implementation. In the domain of resource recovery and hydrothermal processing, this TRL concept has been applied to rate multiple competing technologies in different applications [69-72].

The TRL of a technology for a given application is rated on a scale of 1-9, and for practical application, it can be segmented into 3 main categories. For technologies that are only tested in a laboratory scale, a TRL level between 1-3 can be allocated [69]. For Technologies that have been tested at a pilot scale, under conditions (feedstock, temperature, and time) that are similar to industrial realities, a TRL level between 4-6 can be allocated. For Technologies that are tested in full-scale implementation (often the first small yet commercial-scale plant) a TRL level between 7-9 can be allocated. These TRL bands can be further narrowed down into a specific TRL number by considering the progress made in technical knowhow, number of applications, and understanding of the fundamental mechanisms [69]. In general, progressing from one TRL level to another TRL level becomes exponentially more difficult in terms of resources required [69].

2.6.1 Thermal hydrolysis process

The Thermal hydrolysis process has been applied widely in industry for more than 20 years, with a significant rise in the number of full-scale systems in WWTPs worldwide [9]. Five companies have successfully commercialised THP for sludge pre-treatment: Cambi, Veolia Water, Haarsley, Sustec, and Eliquo Water (Table 2-4). Cambi leads in THP installation with the most installed THP plants worldwide (more than 40 THP plants since 1995). Cambi provides the combination of THP (Cambi®THP) and AD in a reliable, stackable, and stable system [73]. Cambi®THP is a batch process which has three main units, including a pulper, reactors, and a flash tank (Figure 2-3). The system is designed for three reactor sizes including 2 m^3 (B2), 6 m^3 (B6), and 12 m^3 (B12). The Cambi®THP reactor operates at 165 °C and 6 to 6.5 bar for 20 to 30 min per batch.

Table 2-4. THP installations [74-78]

Installations	Capacity (tonne dry sludge/ year)	Feedstock	Disposal method	THP type
CAMBI™:				
Blue Plains, USA	150,000	PS + WAS	Land application	B12
Gaoantun, China	146,000	PS + WAS	Land application	B12
Gaobeidian, China	99,645	PS + WAS	Land application	B12
Huaifang, China	65,700	PS + WAS	Land application	B12
Xiaohongmen, China	65,700	PS + WAS	Land application	B12
Crossness, UK	62,000	PS + WAS	Land application	B12
Ringsend, Ireland	56,000	PS + SBRS[1]	Land application	B12
Riverside, UK	40,000	WAS	Land application	B12
Howdon, UK	40,000	Mixed sludge	Drying	B12
Beckton, UK	36,500	PS + WAS	Land application	B12
Mapocho, Chile	36,000	WAS	Landfill	B12
Cardiff, UK	35,000	SBRS	Land application	B12
Qinghe II, China	32,850	PS + WAS	Land application	B12
Tilburg, The Netherlands	28,600	WAS	Incineration	B12
Seafield, Scotland	27,000	PS + WAS	Land application	B6
Vilnius, Lithuania	23,000	Mixed sludge	Drying	B12
Cotton Valley, UK	22,240	PS + WAS	Land application	B12
Vigo-Lagares, Spain	22,000	PS + WAS	Land application	B6
Nigg Bay, Scotland	22,000	PS + WAS	Land application	B12
Whitlingham, UK	20,000	PS + WAS	Land application	B12
Jurong, Singapore	19,000	WAS	Incineration	B6
Psyttalia, Greece	15,500	WAS	Incineration	B6
Romerike, Norway	15,000	Biowaste	Land application	B12
VEOLIA:				
Esholt, UK	32,800	WAS	-	Bio Thelys™
Oxford, UK	26,000	WAS	-	Bio Thelys™
Marquette-Lez- Lille, France	22.000	PS + WAS	-	Exelys™

Monza, Italy	15,800	-	-	Bio Thelys™
Ljubljana, Slovenia	14,600	PS + WAS	Land application	Exelys™
Versailles, France	8,300	-	-	Exelys™
Billund, Denmark	3,300	-	-	Exelys™
Le Pertuiset, France	2,000	-	-	Bio Thelys™
Tergnier, France	1,600	PS + WAS	-	Bio Thelys™
Saumur, France	1,600	-	-	Bio Thelys™
Château-Gontier, France	1,000	-	-	Bio Thelys™
Bonneuil-en-France	300	-	-	Exelys™
HAARSLEY:				
Grevesmuhlen, Germany	3,500	PS + WAS	-	HCHS
Lancut, Poland	1,500	PS + WAS	-	HCHS
SUSTEC:				
Apeldoorn, Netherland	13,000	WAS	-	TurboTec®
Venlo, Netherland	7,000	WAS	-	TurboTec®
ELIQUO WATER:				
Amersfoort, Netherland	12,000	-	-	LysoTherm®
Lingen, Germany	1,200	-	-	LysoTherm®

[1] SBRS: sludge from sequencing batch reactors

Veolia Water provides two THP technologies, Exelys™ (continuous) and Bio Thelys™ (batch). The configurations of both systems are shown in Figure 2-3. Both processes run at 165 °C and 9 bar for a retention time of around 30 min. The Exelys™ is the first industrially commercialised continuous THP. It consists of a plug flow reactor operating at 165 °C and 9 bar pressure. In contrast, Bio Thelys™ consists of a feed tank, a mixer, two batch reactors working in parallel, and a buffer tank. According to Abu-Orf and Goss [18], the continuous Exelys™ process possesses a slightly enhanced solubilisation of COD compared to the batch Bio Thelys™ system. So far, the company has implemented seven Bio Thelys™ and four Exelys™ in Europe (Table 2-4).

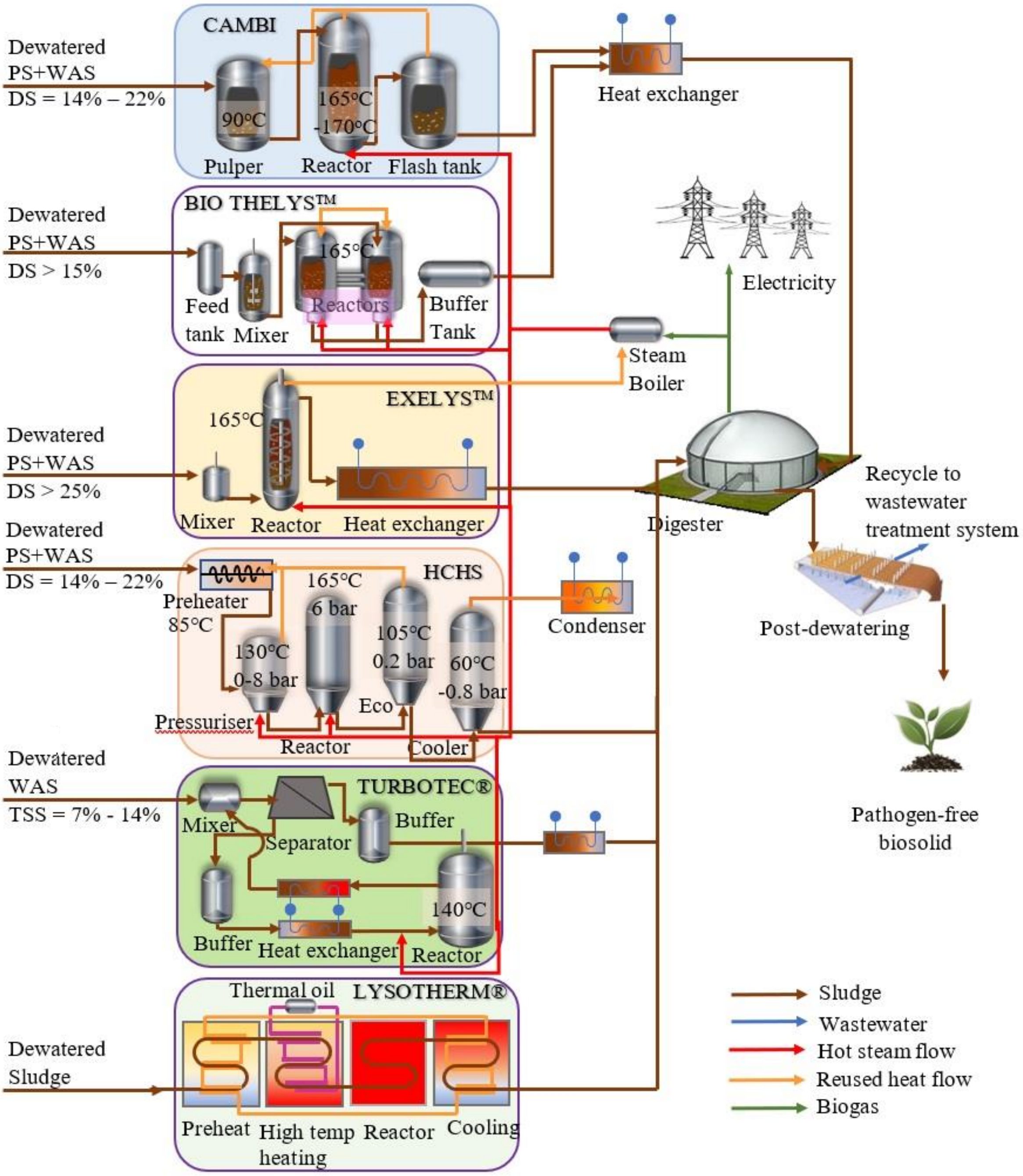


Figure 2-3. Schematic of commercial THPs
(Data from Abu-Orf and Goss [18], Cambi [74], Haarslev [76], Eliquo [77], Williams and Burrowes [78], Veolia [79], Panter *et al.* [80]).

The newest THP vendors are Haarsley, Sustec, and Eliquo Water. These three companies utilise continuous THP technology (Figure 2-3). While HCHS of Haarsley and TurboTec® of Sustec use a direct heating system (hot steam) [81], LysoTherm® of Eliquo Water uses an indirect heating method (thermal oil). Each company has successfully installed two THP plants so far (Table 2-4). Among these commercial THP systems, only TurboTec® is designed for secondary sludge. However, Williams and Burrowes [78] suggested that TurboTec® can also work well with a mixed PS and WAS. The technology also provides a unique way to enhance energy efficiency by using a mixer to blend cold feed sludge with 105 °C recirculated hydrolysed sludge to heat the cold raw sludge and cool down the pre-treated sludge. TurboTec® then takes advantage of the difference in viscosity of the sludge before and after pre-treatment to separate the sludges (Figure 2-3).

Evidently, THP technology for the application of WWTP pre-treatment can easily be awarded a TRL of 9. This is because multiple commercial entities employ competing THP based processes as commercial-scale operations.

2.6.2 Advanced thermal hydrolysis process

Currently, ATHP is only conducted at a lab-scale and further investigation is required regarding the improvement in biomethane production as well as the formation of inhibitory compounds. Although the technology has been hailed as a viable and effective alternative for THP for sludge pre-treatment [38, 39, 82], there is an inadequate understanding of the operating conditions of the method to see it propagated throughout the industrial field as yet.

In comparison to THP, ATHP is still in its infancy, with some promising lab-scale demonstrations available. At the same time, the process fundamentals of ATHP are understood. Considering these two facts, a TRL level of 3 (the highest possible for lab-scale demonstration) can be awarded to the ATHP process.

2.6.3 Implications

As mentioned previously, THP is the only commercial-scale process currently available while ATHP has only been tested at lab-scale. This means both significant time and economic resources need to be diverted to transition the lab-scale ATHP process into a commercial-scale solution, to realise any benefits of ATHP and compete with the THP.

However, there is a potential economic advantage in commercialising ATHP as the process promises improvements at a plant-wide level. From a plant-wide perspective, studies have reported net savings of 140 €/t of dissolved solids being treated [20]. However, at a unit operation level, ATHP operates at reduced temperature and pressure but requires H_2O_2 addition which means the gains at a unit operation level might not be significant or even negative.

Abelleira-Pereira *et al.* [9] estimated the additional cost of H_2O_2 addition for ATHP to range from 7.53 - 15.22 US$/m³ of raw sludge (based on the 2014 price of H_2O_2, which was 0.20 to 0.60 USD per liter) while the economic benefits of reduced heating demand are unlikely to outweigh the cost of H_2O_2 addition.

From a practical point of view, it can also be stated that the ATHP concept will be more economically and environmentally valuable for plants that are struggling with UV disinfection and to meet effluent specifications. It should be also noted that the more stringent effluent specifications are, the higher the economic incentive to develop the ATHP to a commercial scale.

From process operations and design points of view, both the THP and ATHP processes are remarkably similar. Hence some of the know-how gained in the development of the THP process can be transferred into ATHP development reducing the costs and timeline for commercialisation.

This process similarity also allows for initial commercial application of the ATHP process to be carried out as a retrofit/conversion of an existing THP into an ATHP as some of the key equipment used in both the processes would be the same. Wastewater treatment facilities, where the ATHP process will be located, are quite open to these types of retrofit projects.

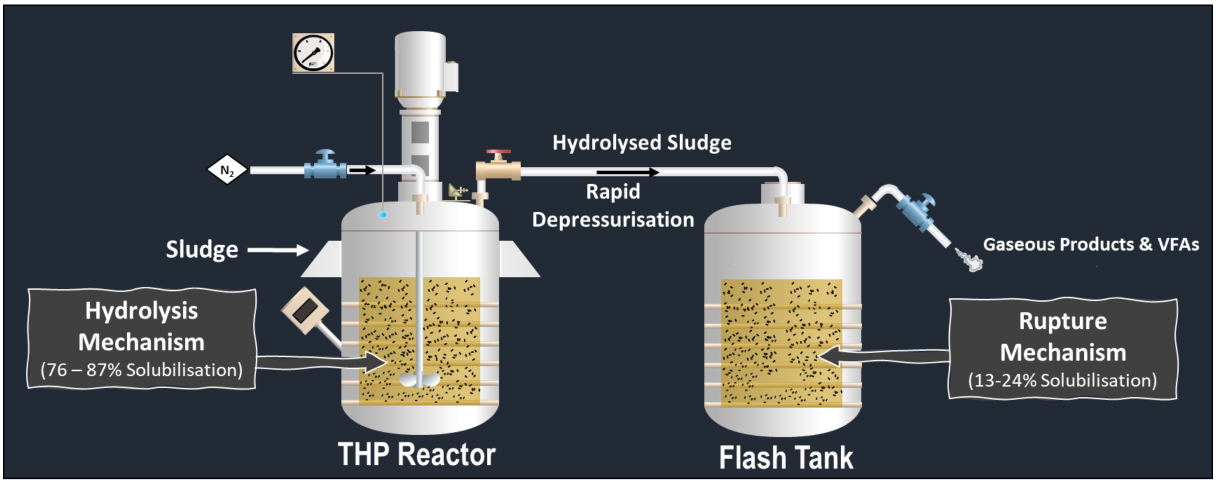
2.7 Summary of Chapter and Conclusions

The thermal hydrolysis process is an effective and reliable sludge pre-treatment technology for AD, which has been successfully applied in industry for more than 20 years. Many advantages of the technology in terms of sludge pre-treatment have been reported and include enhancing dewatering, enabling higher loading rate, and improving the quality and quantity of the biogas. However, the technology can still be much improved if free radical formation can be enhanced at a lower temperature to reduce formation of inhibitors such as melanoidins and ammonia nitrogen. The significant difference between biogas production results reported in various studies highlights a crucial need to implement an in-depth investigation into the mechanisms, and each influencing factor of THP in terms of pre-treating WWTP sludge. Furthermore, ATHP could be a promising alternative technology that can overcome the current problems of THP, however, the technology needs more research in terms of the optimal oxidation dosage and the extent to which the presence of oxidation chemicals impacts the methanogenesis bacteria.

Overall, this chapter provides a comprehensive overview of the main mechanisms that happened during THP and ATHP, which will be the foundation for modifying the technology. The detailed investigation of the solubilisation mechanism and the formation of inhibitory compounds is discussed in the next chapter.

Chapter 3

New insight into thermal hydrolysis of sewage sludge from solubilisation analysis



The previous chapter reviewed the main mechanisms that happened during THP. In this experimental study, these mechanisms will be investigated deeply to provide a better understanding of the process. This chapter evaluates the influence of flashing, reaction time, and temperature to comprehend these mechanisms. It was found that while hydrolysis is the primary process (accounting for approximately 76 – 87 % of sludge solubilisation), the sudden decompression via flashing at the end of the process contributes a significant percentage (around 24 – 13 % depending on the treatment conditions) to the solubilisation of the treated sludge.

The content of this chapter has been published, details in the footnote. The theme has been modified to improve the flow and readability of the thesis.

Ngo, Young, Brian, & Baroutian. (2023). New insight into thermal hydrolysis of sewage sludge from solubilisation analysis. Chemosphere, 139456. https://doi.org/10.1016/j.chemosphere.2023.139456

3.1 Introduction

The thermal hydrolysis process has emerged as a potential method for pre-treating sewage sludge prior to anaerobic digestion (AD) over the last 20 years [83]. The advantages THP offers are significant. Thermal hydrolysis improves the dewaterability of the sludge [5, 12, 16], turns sludge into pathogen free biosolid [18], and reduces the volume of an anaerobic digester considerably via enhancing the biodegradable level of sludge [19]. More importantly, implementing THP to pre-treat the sludge helps enhance biogas production from 245 L/kg VS added to 443 L/kg VS added due to the significant improvement in the solubilisation degree of the sludge [5].

Thermal hydrolysis involves the application of high temperatures (above autoclave temperature up to 200°C) and pressure (up to 25 bar) in the absence of oxidants [13]. There are four stages during THP, including heating, reacting, depressurising and cooling. On a commercial scale, depressurising at the end of THP can be conducted using a flash tank or a heat exchanger and steam recovery. For example, Cambi® THP, designed by Cambi company, uses the flash tank to depressurise at the end of the process [18]. By contrast, EXELYS™, designed by Veolia, applies a heat exchanger and steam recovery system [18]. When a flash tank is included in THP, a fast release of sludge from high pressure to ambient conditions will create a shear force to rupture microbial cells [83]. However, the involvement of a flash tank will increase the capital cost for the process. Therefore, there is a need to evaluate if the installation of a flash tank is worth it.

With the presence of a flash tank, the solubilisation mechanism of sewage sludge using THP is based on two main processes, hydrolysis and flashing [83]. Hydrolysis happens when the temperature increases above the autoclave temperature. The energy applied will enhance the reactivity of water significantly to break the chemical bonds in complex molecules to create simpler compounds (Eq. 20) [48].

$$\mathrm{A-B\ +\ H_2O \overset{\Delta}{\rightarrow} A-H\ +\ B-OH} \tag{20}$$

Sewage sludge contains a high number of microbial cells from waste activated sludge (WAS) [24]. Hydrolysis of non-biodegradable extracellular polymeric materials like the cell membrane also occurs to cause cellular rupturing under elevated temperatures [37]. This can increase the solubilisation of sludge significantly [83]. Additionally, in the final flash phase of THP, when sludge is flashed out from the reactor to the flash tank, the shear force produced from the sudden pressure drop can break the cell membrane and subsequently leads to an improvement in the solubilisation degree of sludge [9]. As a result, the significant enhancement in the disintegration of sewage sludge by employing THP has been well established (Table 3-1). Depending on processing conditions and sludge type, sludge disintegration can be increased from 32 % to 58 % (Table 3-1).

Table 3-1. Key literature on the effects of THP on sludge solubilisation

Reference	**Sludge type**	**Temp. (°C)**	**Time (min)**			**Flash**	**Solubilisation degree**
			Heating	**Processing**	**Cooling**		
[3]	WAS	135	35	30	30-40	-	34 %
		190	50	30	30-40	-	46.3 %
[5]	WAS	175	20	120	15	-	50 %
[22]	WAS	170	-	60	-	-	49 %
		175	-	30	-	-	55 %
[35]	Mixture of food waste and sewage sludge (1:1)	140	-	30	-	-	45 %
		160	-	30	-	-	43 %
		180	-	30	-	-	51 %
[84]	WAS*	170	25-60	30	-	-	49-57 %
		150	25-60	30	-	-	33 %
[85]	Sewage sludge	180	-	76	-	-	29.7 %
[86]	WAS	150	-	30	-	Yes	37 %
		180	-	5	-	Yes	39 %
		180	-	30	-	Yes	39 %
[87]	FPS** + WAS (1:1)	160	~93	30	~180	No	46 %
		160	~93	60	~180	No	41 %
		180	~113	30	~180	No	38 %
		180	~113	60	~180	No	39 %
	WAS	160	~93	30	~180	No	45 %
		160	~93	60	~180	No	49 %
		180	~113	30	~180	No	58 %
		180	~113	60	~180	No	55 %

-: information not available; *: waste activated sludge; **: fermented primary sludge

The optimum THP temperature range to enhance anaerobic sludge digestion was reported to be from 160 ℃ to 180 ℃ [5, 64, 87] and has been applied successfully in the industry. All Cambi®THP, Bio Thelys™, and Exelys™ processes run at 160 – 165 ℃ for 30 min [83]. Notwithstanding, these extreme reaction conditions result in some critical problems that require solutions, such as the formation of inhibitory substances for AD and the requirement of high energy input [83]. Primarily, the dark colour of post-dewatering AD sludge would fail the UV disinfection phase of wastewater treatment [16]. Thus, THP continues to be researched, even though the technology has been commercialised for over 20 years [83]. To overcome these problems, two process adjustment methods have been recommended. While Dwyer *et al.* [16] suggested lowering the reacting temperature to 145 ℃, Dohányos *et al.* [88] recommended rapid thermal treatment for only 60 sec at 170 ℃. However, the impact of time and temperature on solubilisation is complex. To understand whether lowering reaction temperature or shortening processing time would be effective in maximising biogas production, reducing the dark colour of treated sludge, and optimising the energy consumption for THP, an in-depth understanding of the solubilisation mechanisms is required.

Whilst there are numerous studies of THP for sewage sludge, the solubilisation mechanism has not yet been fully investigated for pre-treatment sewage sludge. In addition, despite the flash phase being claimed as a vital phase to enhance the solubilisation of the sludge, there is a scarcity of information on to what extent the flash phase contributes to solubilise the sludge.

This chapter focuses on the contribution of the flash phase to the solubilisation mechanism and what is the dominant mechanism to disintegrate the sewage sludge when flash depressurisation is employed after THP. This chapter also analyses the influence of processing time and temperature on the solubilisation degree of sewage via the combination parameter of time and temperature (severity factor).

3.2 Materials and methods

3.2.1 Materials

Sewage sludge was picked up from the Mangere Wastewater treatment plant in Auckland, New Zealand and was used in this study. The sludge was a mixture of primary sludge (55 %) and waste-activated sludge (WAS) (45 %) obtained from the feeding tank prior to anaerobic digestion. The sludge was preserved at -4 °C and was thawed at 4 °C in the refrigerator a day before use. The main characteristics of the sludge are pH of 5.78 ± 0.01, total solids (TS) of 68.5 ± 0.2 g/L, volatile solids (VS) of 54 ± 0.2 g/L, total COD (tCOD) of 145.8 ± 3.1 g/L, soluble COD (sCOD) of 12.7 ± 0.3 g/L, total nitrogen (TN) of 2.8 ± 0.01 g/L, ammonia nitrogen (NH_3-N) of 0.295 ± 0.004 g/L.

Certified calibration standard gas mixtures of oxygen, carbon dioxide, carbon monoxide, and nitrogen for gas chromatography and pure nitrogen gas for reactor pressurisation were purchased from BOC Ltd. (Auckland, New Zealand). Test kits for chemical oxygen demand were acquired from Hach Pacific (Auckland, New Zealand). Sigma-Aldrich chromatographic grade organic acids were applied as reference standards for calibrating the VFAs. The acids used for calibration were acetic acid, propionic acid, butyric acid, and valeric acid.

3.2.2 Thermal hydrolysis

Thermal hydrolysis of sludge was conducted using a 1 L autoclave reactor (Amar Equipment Ltd., Mumbai, India) equipped with a 1 L flash tank (Figure 3-1). To understand to what extent the rapid depressurisation phase is involved in solubilising the sludge, THP experiments were carried out at 145, 160, 175 and 190 °C for 30 min. These conditions correspond to conditions of commercial THP processes of Eliquo Water, Cambi, Haug *et al.* [5], and Park *et al.* [35], respectively. In each run, 600 mL of sewage sludge was fed into the reactor. The vessel was subsequently pressurised with 6 bar of N_2 gas. The working pressure varied from 10.2 to 14.1 bar, depending on the set temperature. The impeller motor was set up to stir at 300 rpm. At the end of each run, 300 mL of the sludge was flashed in the flash tank to determine the impact of the rupture mechanism. The flash tank was at atmospheric pressure. The temperature of the sludge dropped significantly to 70 - 80 °C after being flashed into the flash tank. The resulting solid-liquid slurry was collected from the reactor vessel and the flash tank for TS, VS, tCOD, sCOD, and VFAs analyses. All experiments were run in triplicate.

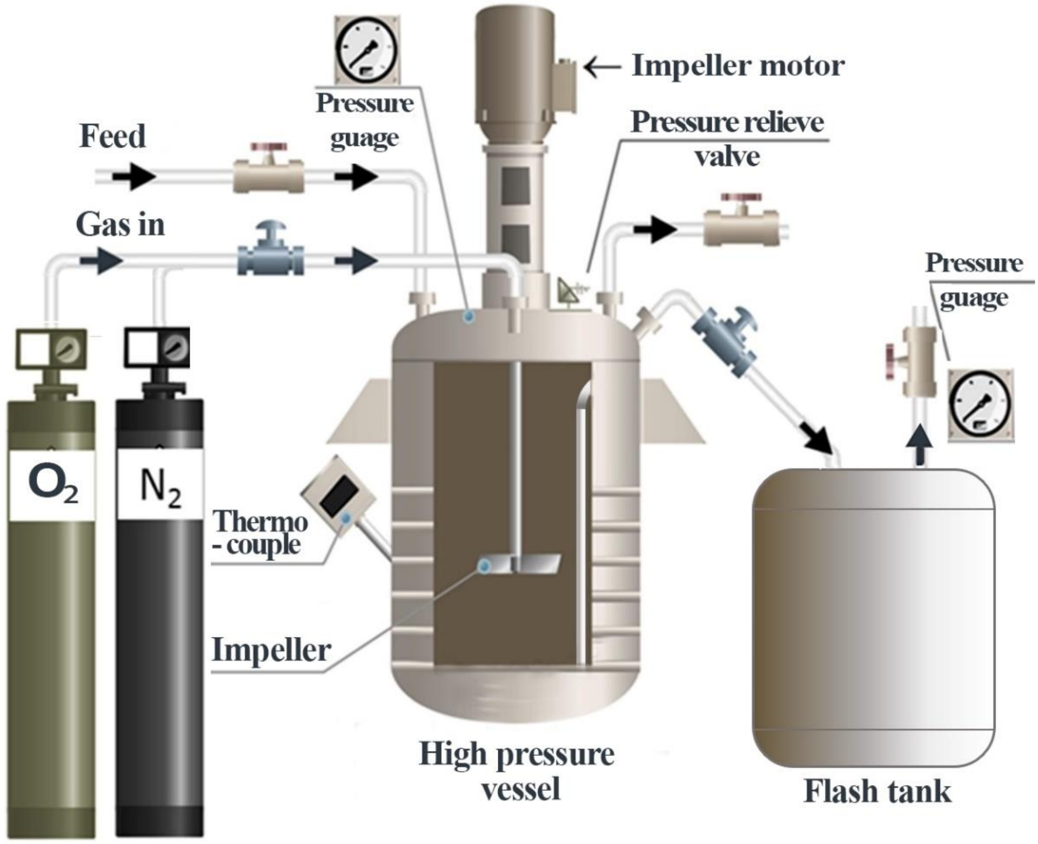


Figure 3-1. Experiment set up for thermal hydrolysis

To study the impact of hydrolysis temperature and time on sludge solubilisation, three additional reaction times (5, 10, and 20 min) were tested at four temperatures (145, 160, 175, and 190 °C). The reaction time was calculated starting from when the inside of the reactor reached the desired temperature. Heating time (the time needed to heat up to the desired internal temperature) was around 15 to 20 min. At the completion of each run, all the sludge was flashed in the flash tank. The sludge was taken out for analysis. All conditions were run in triplicate.

3.2.3 Analyses

The TS and VS analyses were carried out according to Standard Methods 2540D and 2540E of The American Public Health Association (APHA, 2014). The tCOD and sCOD content were assessed with a high-range COD test kit (20 - 1500 mg/L) from Hach and evaluated by a Hach DR3900 spectrophotometer.

Volatile fatty acids, including acetic acid, propionic acid, butyric acid, and valeric acid, were detected using a Shimadzu QP2010 Plus gas chromatograph (Kyoto, Japan) with flame ionisation detection (GC-FID). The column used in the instrument is a nitroterephthalic-acid-modified polyethylene glycol (PEG) column (DB-FFAP, 30.0 m × 0.53 mm × 0.5 µm, Agilent Technologies, US). The carrier gas was helium. The column was first heated to 40 °C and maintained temperature for 2 min after sample injection. Henceforth a temperature ramp-up at a rate of 10 °C/min to 180 °C and kept at 180 °C for 26 min. Peak identification of VFAs was obtained by calibrating reference standard solutions to sample peak retention times.

The off-gas composition was analysed using an SRI GC (8610c) 2010 gas chromatograph (Torrance, California, USA) equipped with thermal conductivity (TCD) (for hydrogen and oxygen) and flame ionisation (FID) detection (for carbon monoxide and carbon dioxide). The gas samples were vented out of the reactor vessel (at the end of THP and before the sludge was flashed to the flash tank) and injected into a Hayesep D Pre-column (length 0.5 m) and subsequently the Hayesep D Column (length 2 m). The experiment used helium as a carrier gas. The Hayesep D Column was first warmed up to 50 °C and held at said temperature for 1 min. Following this, the temperature of the column was elevated to 90 °C at 10 °C/min and remained at 90 °C for 3 min. To finish off, the column was heated to 270 °C at a rate of 30 °C min. By calibrating reference standard gas to sample peak retention times, carbon dioxide peak identification was achieved. The off-gas sampling caused a 1 bar pressure drop in the reactor.

3.2.4 Solubilisation degree

In this study, solubilisation was measured based on the transition of particulate chemical oxygen demand (pCOD) into soluble chemical oxygen demand (sCOD). The influences of hydrolysis and rupture on sewage sludge solubilisation were determined by calculating the solubilisation degree (SD%) using Eq. (21) [22]:

$$\mathrm{SD\%} = \frac{\mathrm{sCOD}}{\mathrm{tCOD}} \times 100\% \tag{21}$$

3.2.5 Severity factor

To estimate the influence of different treatment conditions during THP, the reaction time and temperature have been combined into a single parameter under the name “reaction ordinate” (R_o) [89]. The R_o helps to combine the data in complicated reaction systems and to eliminate challenges in data comparison when processing is carried out using various equipment/reactor scales under various reaction circumstances [90, 91]. The reaction ordinate parameter is determined as per Eq. (22) [89]:

$$R_{\mathrm{o}} = t \exp\left(\frac{T_{\mathrm{r}} - T_{\mathrm{b}}}{14.75}\right) \tag{22}$$

where t is the THP treatment time (min), T_{r} is the reaction temperature (°C), and T_{b} is the base temperature (°C) at which the solubilisation mechanism will occur. In this study, the base temperature was selected as 100 °C because when the temperature exceeds this, the impact of THP on the solubilisation of the sludge was recorded [49, 83].

The severity factor (SF), which has been used to represent the severity of THP [92], is defined as per Eq. (23):

$$\mathrm{SF} = \log_{10} R_{\mathrm{o}} \tag{23}$$

Previous modelling studies of THP of biomass and lignocellulosic materials have utilised the severity factor [91-94]. The SF is also reminiscent of other parameters employed for oil and gas or pulp and paper processes [90, 95]. In this study, the used material is sewage sludge, one kind of biomass which is appropriate to apply the severity factor.

3.2.6 Statistical analysis

A two-factor ANOVA was used to analyse the experimental data obtained from different treatment temperatures and with or without flash depressurisation. The p-value of each factor was applied to interpret the impact of temperature and flash depressurisation on the solubilisation of sludge. Main effects were contemplated significant if $p \leq 0.05$, and interaction was contemplated significant if $p \leq 0.01$.

3.3 Results and discussion

3.3.1 Effect of flash depressurisation

3.3.1.1 COD solubilisation

Figure 3-2a shows that the solubilisation degree of the sludge produced by THP with a flash phase at all four treatment temperatures is significantly higher than by THP without flash depressurisation. The contribution of the sudden depressurisation on SD% of the sludge at 145 °C was 24 % compared to when the flash phase was absent (Figure 3-2b). The percentages were 22 %, 16 %, and 13 % as the treatment temperature rose to 160 °C, 175 °C, and 190 °C, respectively (Figure 3-2b). This result indicates the considerable influence of the flash phase in solubilising the sludge. Similarly, Abelleira-Pereira *et al.* [9] noted that a longer THP time does not influence methane production enhancement as significantly as the involvement of flash depressurisation.

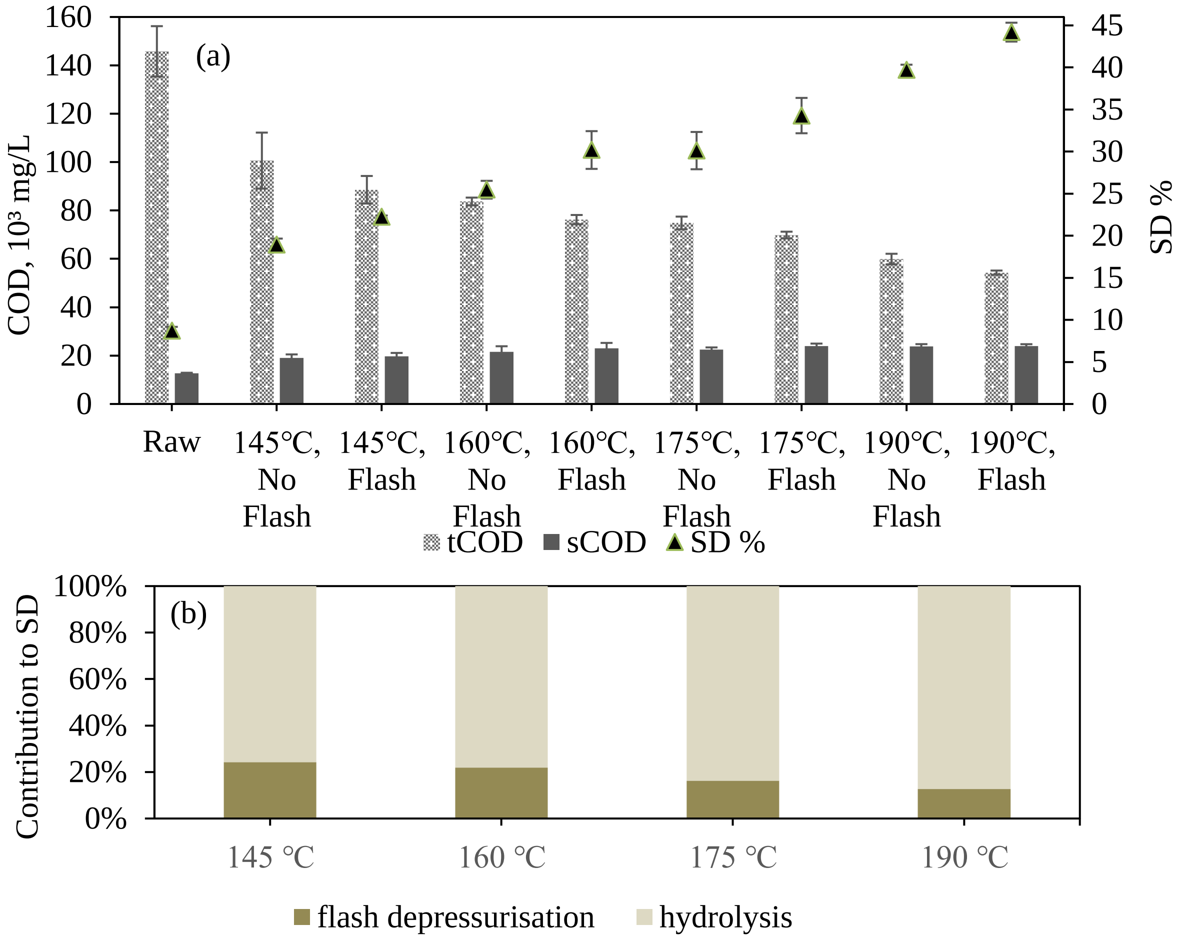


Figure 3-2. (a) The difference in sludge solubilisation degree by using a flash phase; (b) The contribution of flash depressurisation and hydrolysis in solubilising sludge at four different temperatures

Additionally, the result shows the contribution of flash depressurisation reduced at higher reaction temperatures from 24 % at 145 °C to 13 % at 190 °C (Figure 3-2b). However, the ANOVA analysis shows no interaction between temperature and flash (for tCOD, $p = 0.47$; for sCOD, $p = 0.79$) (Table 3-2, Table 3-3). This indicates that the influence of the flash phase on cell lysis is statistically independent of the THP temperature at four testing temperatures. The decreasing contribution of flash depressurisation to solubilisation as temperature increases is due to the higher treatment temperatures hydrolysing more cell membranes [37].

Table 3-2. Two-way ANOVA of effect of temperature and sudden decompression on tCOD of treated sludge

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
Temperature	83.48	7.7E-13	3.01
Flash	19.47	0.0001	4.26
Interaction	0.87	0.47	3.01

Table 3-3. Two-way ANOVA of effect of temperature and sudden decompression on sCOD of treated sludge

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
Temperature	14.17	1.6E-05	3.01
Flash	3.31	0.08	4.26
Interaction	0.35	0.79	3.01

Interestingly, comparing THP with flashing and without flashing at four reaction temperatures, Figure 3-2a reveals a decrease in tCOD when the flash phase was applied by 12,050 mg/L, 7,500 mg/L, 5,000 mg/L and 5,625 mg/L at 145 °C, 160 °C, 175 °C and 190 °C, respectively. The *p*-value is 0.001 (Table 3-2), proving the decrease in tCOD by flashing is significant. Theoretically, the reduction in tCOD is supposed to transform to sCOD due to cell rupture by sudden depressurisation. However, the amount of sCOD did not increase but remained similar regardless of whether the flash phase is present (Figure 3-2a), which indicates a loss in sCOD during flashing as otherwise the increased solubilisation should increase the sCOD quantity. This loss of sCOD during the flash phase can be attributed to the escape of some volatile compounds into the gas phase at high temperatures and rapid depressurisation. For example, the boiling point of acetic acid is 117.9 °C which is significantly lower than the working temperature of THP. As a result, when applying a flash phase at the end of THP, the loss of soluble compounds should be considered.

3.3.1.2 Solid solubilisation

Figure 3-3a reveals a significant reduction of TS by 15,750 mg/L, and the percentage of VS increased from 78 % to 87 % when THP at 145 °C was applied (Figure 3-3b). With flashing after THP at 145 °C, the TS decreased further by 1,100 mg/L, making a total of 16,850 mg/L of TS reduction (Figure 3-3a). This further reduction resulted from the solubilisation by flash depressurisation. Notwithstanding, the amount of volatile solid was not higher when flash was employed at all treatment temperatures, which discloses a VS loss during the flash phase.

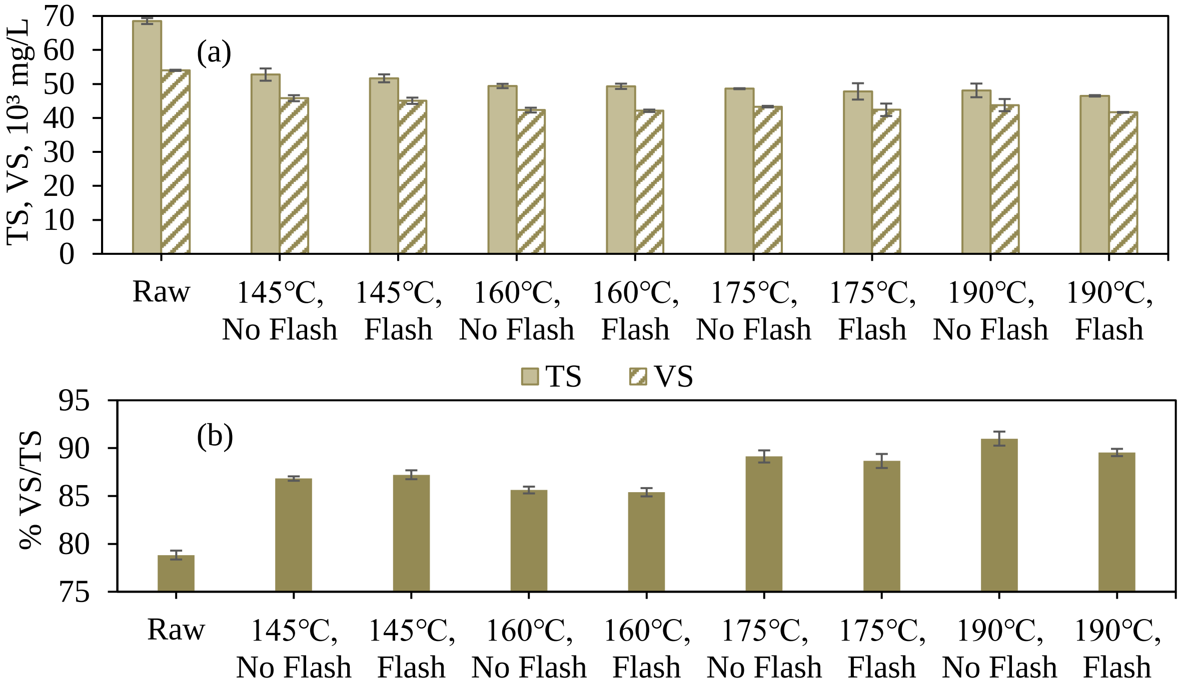


Figure 3-3. Changes in TS and VS (a) and VS/TS ratio (b) by THP at different temperatures with and without flash depressurisation

3.3.1.3 Changes in volatile fatty acids

After being treated by thermal hydrolysis, the concentration of VFAs increased from 2,010 mg/L to 2,814 mg/L with THP at 145 °C, and no flashing (Figure 3-4). This result agrees with Aboulfoth *et al.* [37], which reported an increase in VFAs from 2,000 mg/L to 2,700 mg/L after using THP at 150 °C.

Additionally, at the reaction temperature of 145 °C, subsequent flashing did not change the amount of VFAs significantly, whereas higher treated temperatures showed a loss in VFAs. For example, with THP at 160 °C, there was a loss of 650 mg/L of acetic acid and 36 mg/L of propionic acid when the flash depressurisation was applied (Figure 3-4). Due to the low boiling temperature of acetic acid (117.9 °C), there would be a significant loss of acetic acid when the sludge was flashed from high pressure to the ambient atmospheric pressure at temperatures higher than 117.9 °C. As short-chain VFAs are essential to producing biogas, the loss in VFAs during the flash phase should be considered when applying THP with a flash phase before anaerobic digestion. Consequently, the outlet gas from flash tanks is designed to return to the digesters in the Cambi system [74].

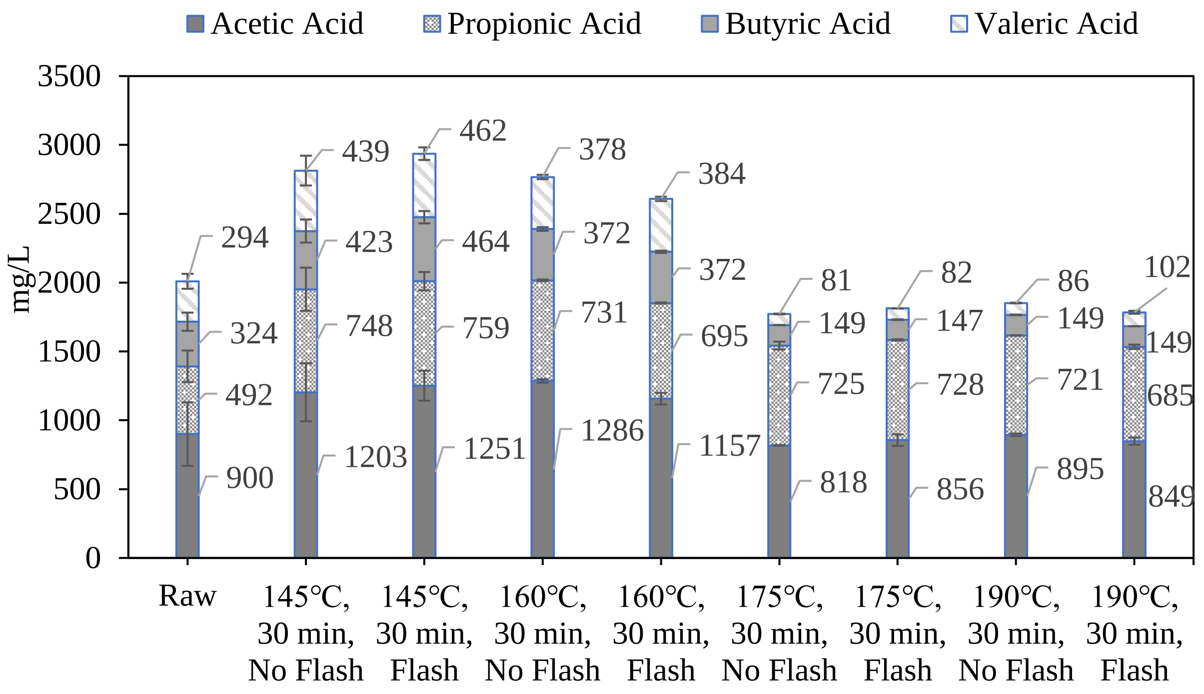


Figure 3-4. Volatile fatty acids contained in the sludge after THP with and without flash depressurisation

The amount of VFAs reduced significantly, by 995 mg/L, when the treatment temperature elevated from 160 °C to 175 °C, without flash. There was a remarkable drop in the concentration of valeric acid and butyric acid by 297 mg/L (78 %) and 223 mg/L (60 %), respectively (Figure 3-4). Interestingly, there was no significant difference in the amount of VFAs in the sludge between THP at 175 °C and 190 °C. This demonstrates that THP at 160 °C and 30 min is a threshold whereby a massive degradation of VFAs happens. This result is consistent with the conclusion from Gál *et al.* [96] that the significant decomposition temperature range of the pure organic acids is from 185 °C. Volatile fatty acids are important for biogas production in anaerobic digestion. Thereby this threshold should be considered when the enhancement of biogas production is one of the primary purposes of THP.

3.3.2 Hydrothermal deconstruction occurred during thermal hydrolysis

During THP pre-treatment, a significant drop in tCOD was observed. As can be seen in Figure 3-2a, this loss of tCOD was mainly due to the increase in temperature and not due to flash depressurisation. A large amount of tCOD was reduced during THP at 145 °C without flash depressurisation by 31 % (Figure 3-2a). The loss of tCOD rose only 8 % more with flash depressurisation at the end to make a 39 % tCOD decrease in total. Additionally, at a higher reaction temperature (190 °C) and without flash depressurisation, the loss of tCOD increased almost double to 59 % (from 145.8 to 59.9 g/L) (Figure 3-2a). When flash depressurisation was applied, there was only 3 % more loss in tCOD, indicating a loss of volatile organics due to depressurisation as mentioned in 3.3.1.3 but not as significant as the loss due to degradation/deconstruction. More importantly, Figure 3-5 shows a reduction of almost half of the oxygen concentration in the headspace of the reactor (from 821 mg/L to 452 mg/L). In contrast, a considerable amount of CO_2 (213 mg/L) was detected in the off-gas when THP at 190 °C was applied, proving that wet oxidation occurred during the treatment.

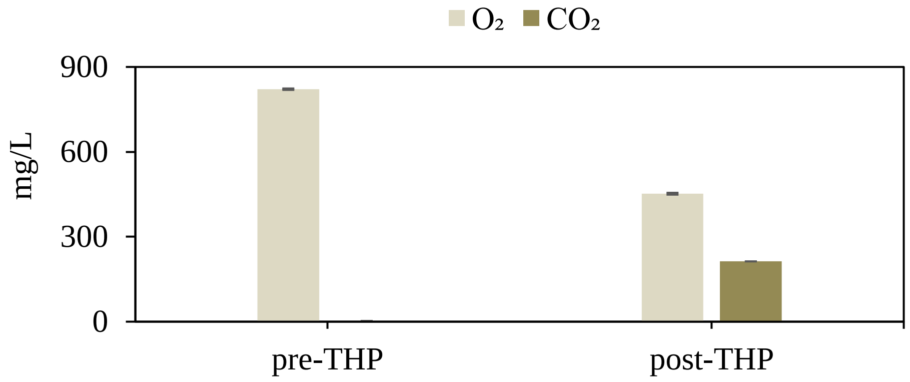


Figure 3-5. Oxygen and carbon dioxide concentration in the headspace of the reactor before and after THP at 190 °C, 30 min

Hydrothermal deconstruction (wet oxidation) can happen from 150 °C and 20 bar [42, 97-99]. With the presence of oxygen at high temperatures, free radicals such as hydroxyl ($HO^\cdot$) and hydroperoxyl ($HOO^\cdot$) will be formed. These free radicals can solubilise the insoluble organics, convert hydrolysis products into simpler compounds such as organic acids and alcohols, or completely oxidise short-chain organics to CO_2, N_2, water and residual ash [100]. Although the reactor was pressurised by nitrogen, there was air in the headspace of the vessel and the dissolved air in the sludge at the beginning, which was the right condition for wet oxidation to occur. Based on the significant loss in tCOD when THP was applied without flash depressurisation and a considerable amount of CO_2 in the off-gas, it can be concluded that hydrothermal deconstruction occurred during THP. This oxidative deconstruction mechanism should be considered in commercial scale THP units. The availability of air/oxygen in the commercial THP unit via a steam injection could also lead to this oxidative degradation.

3.3.3 Effects of time and temperature on thermal hydrolysis with flash depressurisation

Figure 3-6a shows the COD solubilisation of sewage sludge as a function of the severity factor (SF, Log *R*o) when a flash depressurisation is employed. In general, when the severity factor of THP is elevated, the hydrolysis reaction will be promoted to hydrolyse large water-insoluble polymeric compounds such as fibres, carbohydrates, and proteins into soluble monomers [91]. Consequently, increasing the severity factor results in an increase in the solubilisation degree of the sludge. However, as shown in Figure 3-6a, the highest SD%, 45 %, was achieved for SF 3.65 and 3.95. With SF above 3.95, THP gave a lower SD% (44 %). This result indicates that the degradation of COD started outweighing solubilisation at SF 3.95.

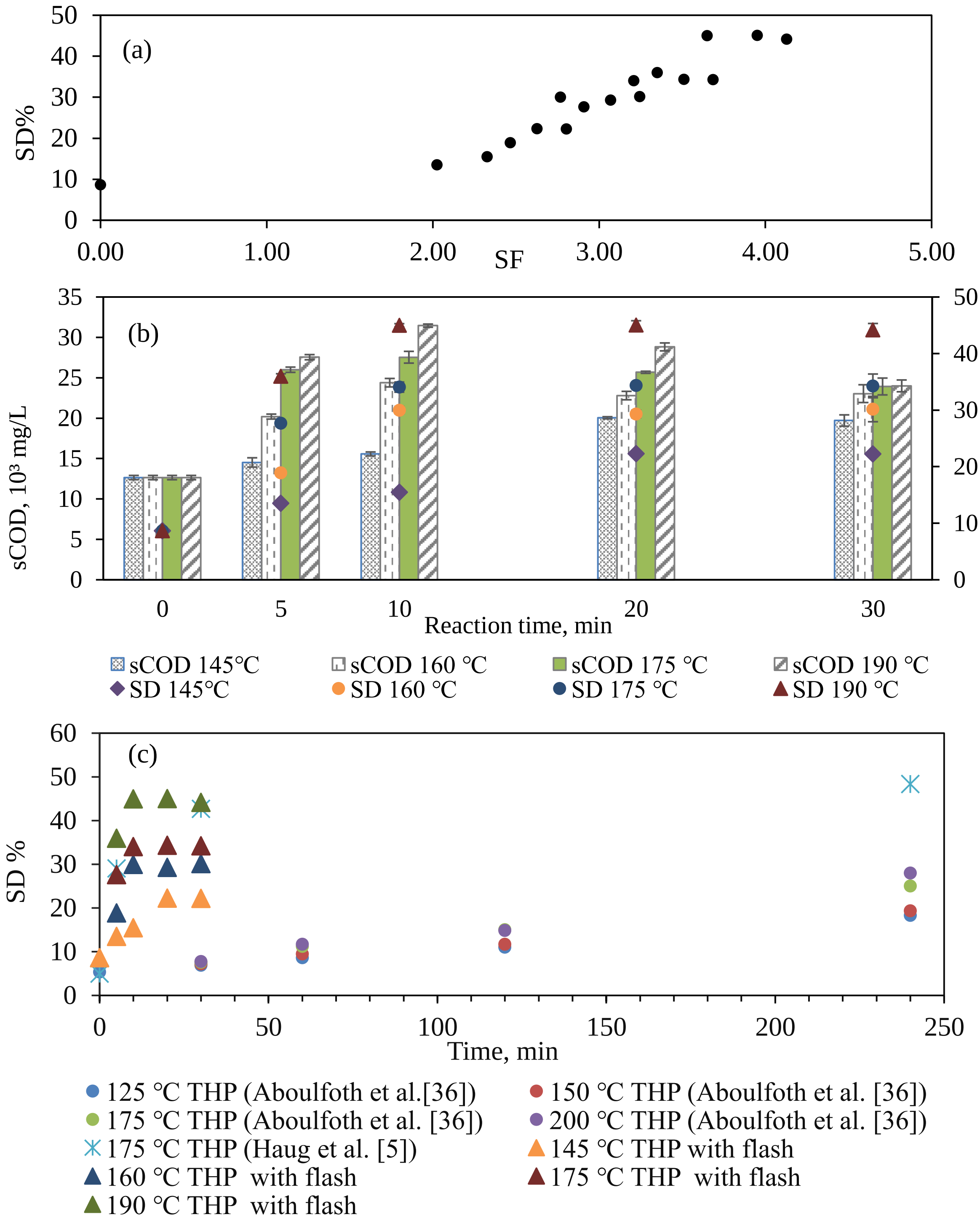


Figure 3-6. (a) The influence of severity factor on COD solubilisation; (b) The impact of THP on the solubilisation degree of the sludge by reacting time and temperature; (c) The solubilisation degree of the sludge after being treated by THP with flashing, compared with the results from literature which applied THP without flashing

3.3.3.1 The impact of temperature

Temperature plays an important role in solubilising the COD in the sludge. For any reaction time, a higher temperature always provides a higher solubilisation degree for the output. In this study, with the flash phase applied at the end of THP, data in Figure 3-6b still shows that the concentration of sCOD and SD% is always higher when the treatment temperature is greater for any treatment duration. Only at 30 min processing time, there was no significant difference in sCOD of the sludge between 175 °C and 190 °C. However, the SD% of the sludge after being treated at 175 °C in 30 min was significantly lower than that at 190 °C. This result agrees with other previous studies. For example, Bougrier *et al.* [64] found that sCOD rises linearly with treatment temperature for all different sludge samples when the reaction temperature is below 200 °C. Considering this, we can conclude that temperature significantly influences the solubilisation of sewage sludge during THP, whether the flash phase is used or not.

3.3.3.2 The impact of time

Contrary to temperature, time influences sCOD differently when applying flash depressurisation. Without flash depressurisation, the solubilisation of the sludge improves linearly with a reaction time of up to 4 hours [37]. However, we can see a different path in this study when flash depressurisation was employed. As can be seen in Figure 3-6b, for reaction conditions from 160 °C and above, the sCOD increases significantly during the first 10 min and reaches the highest amount of 24,400 mg/L, 27,500 mg/L, and 31,456 mg/L at 160 °C, 175 °C, and 190 °C, respectively. Following this, the amount of sCOD started to decrease, signifying the beginning of the COD degradation process. However, the solubilisation degree of sludge remained constant at all reacting temperatures from 160 °C to 190 °C, indicating that the two opposing factors influencing the solubilisation degree, degradation and solubilisation, are equal and cancel each other out.

The reaction occurred similarly but slower for the mild condition of 145 °C. The level of sCOD reached the highest amount after 20 min to 20,050 mg/L (Figure 3-6b) and then declined, showing that the degradation process occurred after 20 min of reaction time.

When THP with a flash depressurisation was used for pre-treating the sludge prior to anaerobic digestion to enhance methane production, Abelleira-Pereira *et al.* [9] argued that treatment times between 5 and 30 min cannot make any significant change in biogas production. If we look more deeply at the results in Figure 3-6b, we can see that a 5 min treatment time provided the highest amount of sCOD, but a 10 min treatment resulted in the highest solubilisation, which brought the sludge to the most biodegradable condition. Also, treatment at 190 °C for 10 min gave the highest SD% (45 %), which could be the best conditions to enhance biogas production. Similarly, Bougrier *et al.* [64] suggested THP up to 190 °C prior to anaerobic digestion to enhance biogas production. Also, Park *et al.* [35] concluded that the optimum temperature for sludge pre-treatment by THP is 186 ℃.

However, other factors should be considered, such as the formation of refractory compounds, inhibitory compounds, and colour, because in some cases higher solubilisation degree does not necessarily lead to an enhancement in biogas production [83].

The hydrolysis reaction starts when the temperature reaches 100 °C [49]. As treatment time has a significant impact at a very early stage (10 min), the heating time will play an important role as it takes time to reach the reaction temperature (Table 3-1). In contrast, considering this, Dohányos *et al.* [88] suggested a rapid thermal treatment for only 60 sec at 170 ℃, as heating time would influence the solubilisation of sewage sludge. Also, it is important to note that achieving such rapid heating industrially could be challenging because of thermal mass and heat transfer issues.

3.3.4 Solubilisation mechanism

Although the flash phase contributes considerably to solubilising sewage sludge, as discussed earlier in section 3.3.1.1, hydrolysis is still the main solubilisation mechanism, contributing to more than 74% of the solubilisation degree of the treated sludge under all four tested conditions (Figure 3-2b). Additionally, the total solids reduced considerably, by 15750 mg/L, when THP at 145 ℃ was applied without a flash phase (Figure 3-3a). When the reaction temperature increased to 160 ℃, the TS reduced by a further 3350 mg/L. In contrast, the addition of a flash phase only made an 1100 mg/L difference in TS solubilisation at THP 145 ℃ and 100 mg/L at THP 160 ℃. Due to these, time and temperature must always be the two main parameters to modify THP whether a flash phase is applied or not.

Studies have shown a linear increase in SD% of the sewage sludge with reaction time when THP was applied without a flash depressurisation [37], whereas, with a flash depressurisation results from Figure 3-6b, the reaction time only makes a difference in the first 10 min. This can be explained by the rupture of cells during flash depressurisation. Without the flash depressurisation, hydrolysis is the only process that solubilises the sludge, and it takes a long time for the cell membrane to break down via hydrolysis (Figure 3-6c). This is why Aboulfoth *et al.* [37] found an increase in solubilisation over periods of 4 h. By contrast, in this study, the maximum level of sCOD and the highest solubilisation degree were achieved after 10 min at any tested treatment temperature (Figure 3-6b). These observations are supported by theory, wherein a sudden release of pressure creates a shear force to break the cell membrane and subsequently leads to cell lysis [9]. Considering the impact of time when flashing is applied, THP with a flash should not require longer than 10 min reaction time to achieve the highest solubilisation degree of sewage sludge.

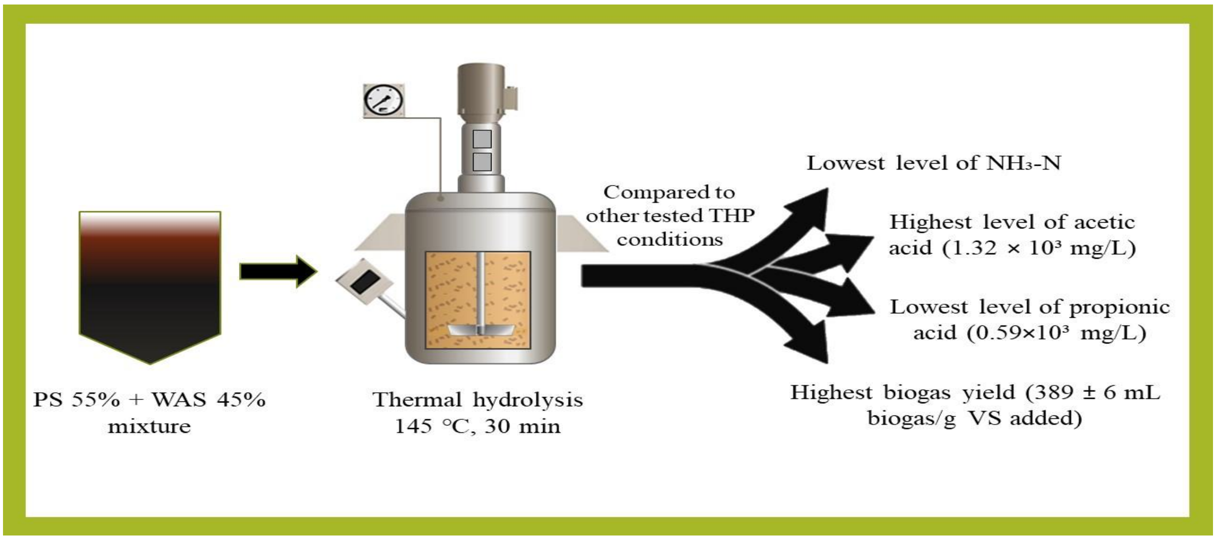
3.4 Summary of chapter and conclusions

This chapter evaluated the influence of flashing, reaction time, and temperature to understand the mechanism. In this study, THP at 190 °C with 10 min and 20 min reaction times with flash depressurisation provided the highest SD% of the sludge (45 %). However, to minimise the energy consumption and the darkening colour of the sludge, the reaction time should be around 10 min. There are two main solubilisation processes when THP is followed by flash depressurisation. Hydrolysis is the primary solubilisation mechanism which contributes to approximately 76 to 87 % of the increase in SD% of the sludge. However, flash depressurisation contributes considerably, from 13 % up to 24 % of the rise in SD%. Also, with flash depressurisation, THP can achieve the required solubilisation level in a shorter reaction time, within 10 min, which in turn can help reduce the dark colour of the sludge and the formation of inhibitory compounds for anaerobic digestion afterwards. A degradation/deconstruction reaction by the occurrence of wet oxidation should also be considered when air or oxygen is available in the THP reactor. In this study, hydrothermal deconstruction was responsible for 7 % of the tCOD loss.

The following chapter investigates the formation of inhibitory compounds, such as melanoidins (via colour of the treated sludge) and ammonia nitrogen during THP and its relationship with biogas yield.

Chapter 4

Thermal hydrolysis of PS and WAS mixture: biogas production and formation of inhibitors



Chapter 3 analysed the solubilisation mechanism in the treated sludge under different THP conditions. The results indicated that THP at 190 ℃ for 10 min and 20 min yielded the highest SD% for the treated sludge. This chapter delves into the biogas production and the formation of compounds inhibiting methanogenesis in the sludge under each pre-treatment condition. For the tested sludge in this study, THP at 145 ℃ for 30 min proved to be the condition that provided the highest biogas yield (389 mL biogas/g VS added). Thermal hydrolysis at 145 ℃ did not increase the ammonia nitrogen concentration in the sludge and resulted in the highest amount of acetic acid (1.32 × 10^3 mg/L).

The content of this chapter has been published, details in the footnote. The theme has been modified to improve the flow and readability of the thesis.

Ngo, Young, Brian, & Baroutian. (2023). Thermal hydrolysis of primary sludge and waste activated sludge mixture: Biogas production and formation of inhibitors. *Journal of Cleaner Production*, *428*, 139354. https://doi.org/10.1016/j.jclepro.2023.139354

4.1 Introduction

Sewage sludge management poses substantial issues in WWTPs. It constitutes approximately 50 % of the operating expenditure costs of WWTP facilities, including the cost of infrastructure (digestor, land costs, and storage facilities), energy costs, and the cost of disposal [10]. In European countries, landfilling costs range from 138 €/t to 281 €/t [10]. The disposal of sewage sludge is also challenging due to hazardous contaminants, odour pollution, and the generation of polluting leachate [83, 101].

Anaerobic digestion is one of the most viable methods for sewage sludge treatment because of the many advantages of the technology in minimising solid residue, lowering the capital and operational cost, lowering the environmental impact, and providing bioenergy production [2]. Nevertheless, AD application has numerous limitations because of a low hydrolysis rate of sewage sludge. Particularly for waste-activated sludge (WAS), where most organic matter is enclosed in microbial cell membranes, a long retention time is necessary [102]. The typical retention time of conventional AD systems is around 20 to 30 days to obtain a 30 to 50 % degradation efficiency of the dry solids of WAS [82]. This low hydrolysis rate requires large digesters and provides inadequate methane production rates [3, 4].

Many thermal, chemical, mechanical, and biological pre-treatment technologies have been employed to improve sewage sludge disintegration and biogas generation [28]. Among them, thermal hydrolysis pre-treatment has been proposed as an efficacious method for accelerating the hydrolysis of sewage sludge [5]. During THP, high temperatures lead to the hydrolysis of organic substances into smaller and more soluble molecules, making sewage sludge more suitable for biodegradation [103]. Additionally, for THP processes which have flash decompression, such as Cambi® THP, a commercial technology, a sudden depressurisation together with hydrolysis creates a shear force which helps to break down the cell membrane and enhance the solubilisation degree of the sludge more efficiently [83]. THP also makes the sludge become a more homogenised solution [43]. Consequently, employing THP as a pre-treatment method for sewage sludge before AD can shorten retention time, minimise sludge mass, and enhance methane production [3].

However, the current THP technology still shows some limitations. There is a high energy demand for producing hot steam to elevate the temperature and pressure in the reactor to reach the required conditions. For instance, the Cambi process needs to run at 165 °C, 6.5 bar for 30 min [104]. More importantly, the energy produced from biogas is not sufficient enough to meet this high energy demand of THP, resulting in the requirement of additional support fuel [104]. Consequently, optimising the process to increase the biogas yield and alleviate energy use is desirable [105].

The target of THP is to increase the solubilisation of the sludge, which in turn leads to an increment in biogas production. Nevertheless, a high solubilisation degree does not always produce a high biogas yield [83]. After being treated at high temperatures, the sludge's colour increases significantly due to the forming of refractory compounds such as melanoidins [16]. These refractory compounds were reported as inhibitors to anaerobic microorganisms, leading to reduced biomethane yield [21].

The thermal hydrolysis process also produces a significant amount of ammonia nitrogen in the sludge. The concentration of NH_4^+-N increased ten times from 21 mg/L to 200.9 mg/L when sludge was pre-treated by using THP at 100 °C [34]. Although ammonia is a crucial element for AD because it is involved in protein synthesis and neutralisation of the acidic conditions created by the metabolic activity of acidifying bacteria, it can be an inhibitor for AD by poisoning methanogenic bacteria at high concentrations [106]. A reduction in biogas yield was revealed when the concentration of NH_4^+-N was above 200 mg/L [107].

A number of studies have investigated optimising THP conditions to increase biogas production and reduce energy consumption [34, 35, 84]. However, little is known about the influence of inhibitors derived from each THP condition on biogas production. This chapter provides a comprehensive analysis of the effect of THP on the colour of the sludge, representing the formation of melanoidins and the influence of the technology on producing ammonia, which are the two inhibitors of methanogenic bacteria. Also, this chapter analyses the correlation between volatile fatty acids and biogas production to provide a detailed understanding of which pre-treatment condition should be applied.

4.2 Materials and methods

4.2.1 Materials

Sewage sludge in this study was collected from the Mangere Wastewater treatment plant in Auckland, New Zealand. The sludge was feed sludge to anaerobic digestors at the wastewater treatment plant, consisting of 55 % PS and 45 % WAS. Upon receipt, the sludge was stored in a laboratory freezer at -4 °C. A day before usage, the sludge was thawed out at 4 °C in the refrigerator. The main characteristics of the sludge are presented in Table 4-1.

Pure nitrogen gas from BOC Ltd. (New Zealand) was used for reactor pressurisation. Hach Pacific (New Zealand) high-range chemical oxygen demand test kits were used for COD analysis. Hach Pacific (New Zealand) high-range nitrogen ammonia reagent test kits were applied for NH_3-N. Sigma-Aldrich (New Zealand) chromatographic grade acetic acid, propionic acid, butyric acid, and valeric acid were employed as reference standards for the calibration of VFAs. In this study, the inoculum for anaerobic digestion was recycled digestate from the digestors at the Mangere Wastewater treatment plant.

Table 4-1. Sludge characteristics

Parameter	Value	Units
pH	5.78 ± 0.01	_
Total Solids (TS)	68.5 ± 0.2	g/L
Volatile Solids (VS) Content	54 ± 0.2	g/L
Total COD (tCOD)	145.8 ± 3.1	g/L
Soluble COD (sCOD)	12.7 ± 0.3	g/L
Total Nitrogen (TN)	2.8 ± 0.01	g/L
Ammonia Nitrogen (NH_3-N)	0.291 ± 0.004	g/L

4.2.2 Thermal hydrolysis

The thermal hydrolysis of sludge was performed using a 1 L autoclave reactor (Amar Equipment Ltd, India) equipped with a flash tank (Figure 3-1).

The temperature conditions for THP were chosen based on the conditions of commercial THP processes and from literature. The experiments were conducted at four reaction temperatures of 145 °C (based on Eliquo Water THP), 160 °C (based on Cambi THP), 175 °C (based on Haug *et al.* [5]), and 190 °C (based on Park *et al.* [35]) for 5, 10, 20 and 30 min. The reaction time was measured from when the interior temperature of the reactor reached the set condition. It took around 15 to 20 min to achieve the desired internal temperatures. The reactor received 300 mL of sewage sludge for each run before being pressurised by 6 bar of N_2 gas. The operating pressure ranged from 10.2 to 14.1 bar, depending on the chosen temperature. The impeller mixing speed was set to stir at 300 rpm. The sludge was flashed into the flash tank at the end of each run. The sludge was removed for anaerobic digestion and analysis. All conditions were run in triplicate.

4.2.3 Anaerobic digestion

The batch anaerobic digestion in this study was retrieved from the water displacement method described by Rasapoor *et al.* [108]. The system comprises three sub-units: (1) a 100 mL anaerobic digestion bottle, (2) a 1000 mL water displacement bottle, and (3) a 500 mL water collection bottle (Figure 4-1). Tygon E-3603 flexible tubing was used to connect the units. To prevent gas leakages, rubber washers were situated between the cap and gas outlet port of digestion bottles and water displacement bottles. The digesters seeded with the inoculum with the ratio of substrate to inoculum (S/I) was 0.5 (volatile solids (VS) basis) based on the optimal range from Haider *et al.* [109]. After filling with 80 mL of substrate and inoculum, digestion bottles were flushed with nitrogen gas for 5 min to establish the anaerobic condition [110]. Thereafter, the caps were fastened immediately. All samples were then incubated under mesophilic conditions (35 ± 1 °C) for 21 days [107]. The biogas produced inside the 100 mL digester generates pressure to push water in the water displacement bottle to the collection bottle. The biogas yield was measured by weighing the water in the 500 mL water collection bottle daily. All experiments were performed in triplicate. There were three digesters for only inoculum with no substrate to analyse the biogas produced from the inoculum.

Figure 4-1. Experimental setup for anaerobic digestion

The biogas generation from the substrate was calculated using equation (24) adopted from Rasapoor et al. (2016):

$$Y_{\mathrm{t}} = (V_{\mathrm{t}} - Y_{\mathrm{i,t}}.m_{\mathrm{i}})/m_{\mathrm{s}} \quad (24)$$

In which, Y_t is the cumulative biogas (mL biogas/g VS added) generated by the substrate at the time t; V_t is the volume (mL) of cumulative biogas measured at the time t; $Y_{i,t}$ is the cumulative biogas (mL biogas/g VS added) generated by the inoculum at the time t; m_i is the mass of VS of inoculum added (g); and m_s is the mass of added VS of substrate (g) to the digester.

4.2.4 Analyses

The total solids and volatile solids analysis methods were from Standard Methods 2540D and 2540E of The American Public Health Association [111]. High-range COD test kits (20 - 1500 mg/L) from Hach (method 8000) were used to evaluate tCOD and sCOD. The true colour of the sample was measured by a Hach DR3900 spectrophotometer using the Platinum-Cobalt method (method 8025). Similarly, nitrogen-ammonia (NH_3-N) content was evaluated by a Salicylate method (method 10031) from Hach. A high-range test nitrogen ammonia reagent set was used for this method.

The concentration of VFAs in the sludge was assessed by using a Shimadzu QP2010 Plus gas chromatograph (Japan) equipped with flame ionisation detection (GC-FID). The column employed in the GC is a nitroterephthalic-acid-modified polyethylene glycol (PEG) column (DB-FFAP, 30.0 m × 0.53 mm × 0.5 μm, Agilent Technologies, US). Helium was the carrier gas for the instrument. Initially, the column was heated to 40 °C and was kept at 40 °C for 2 min after sample injection. The temperature of the column was then heated up to 180 °C at a rate of 10 °C/min and this temperature was maintained for 26 min. The VFAs analysed were acetic acid, propionic acid, butyric acid, and valeric acid. The concentration was determined by calibrating reference standard solutions to sample peak retention times.

4.2.5 Solubilisation degree

Solubilisation degree (SD%) in this study is the ratio between soluble chemical oxygen demand (sCOD) and total chemical oxygen demand (tCOD). It was used to determine the influence of THP on the solubilisation of sewage sludge. Solubilisation degree was calculated by using Eq. (25) [22]:

$$\mathrm{SD\%} = \frac{\mathrm{sCOD}}{\mathrm{tCOD}} 100\% \quad (25)$$

4.2.6 Statistical analysis

The experimental data from various THP pre-treatment conditions were analysed using a two-factor ANOVA analysis. The *p*-value of each factor was applied to interpret the effect of temperature and time of THP conditions on producing NH_3-N. The effect was considered significant if $p \leq 0.05$.

4.3 Results and discussion

4.3.1 Solubilisation degree and biogas production

4.3.1.1 Solubilisation degree

Sludge flocs and microbial cells are disrupted by THP, thus increasing the solubilisation degree of the sludge. Figure 4-2a displays the significant increase in the solubilisation degree of the sludge after THP treatment. After 5 min processing time, the SD% of sewage sludge increased by half from 8.7 % to 13.2 % at 145 ℃ and by more than four times to 36 % at 190℃. Figure 4-2a also shows a linear rise in the SD% of sludge with the temperature at any reaction time. This result is consistent with many previous studies. For example, Bougrier *et al.* [64] argued COD solubilisation grew correlatedly with the elevation of pre-treatment temperature from 90 ℃ to 210 ℃. Similarly, Toutian *et al.* [33] reported the SD% level of sewage sludge rose linearly from 20.6 % to 41.5 % when the temperature elevated from 130 ℃ to 170 ℃ at 30 min pre-treatment time.

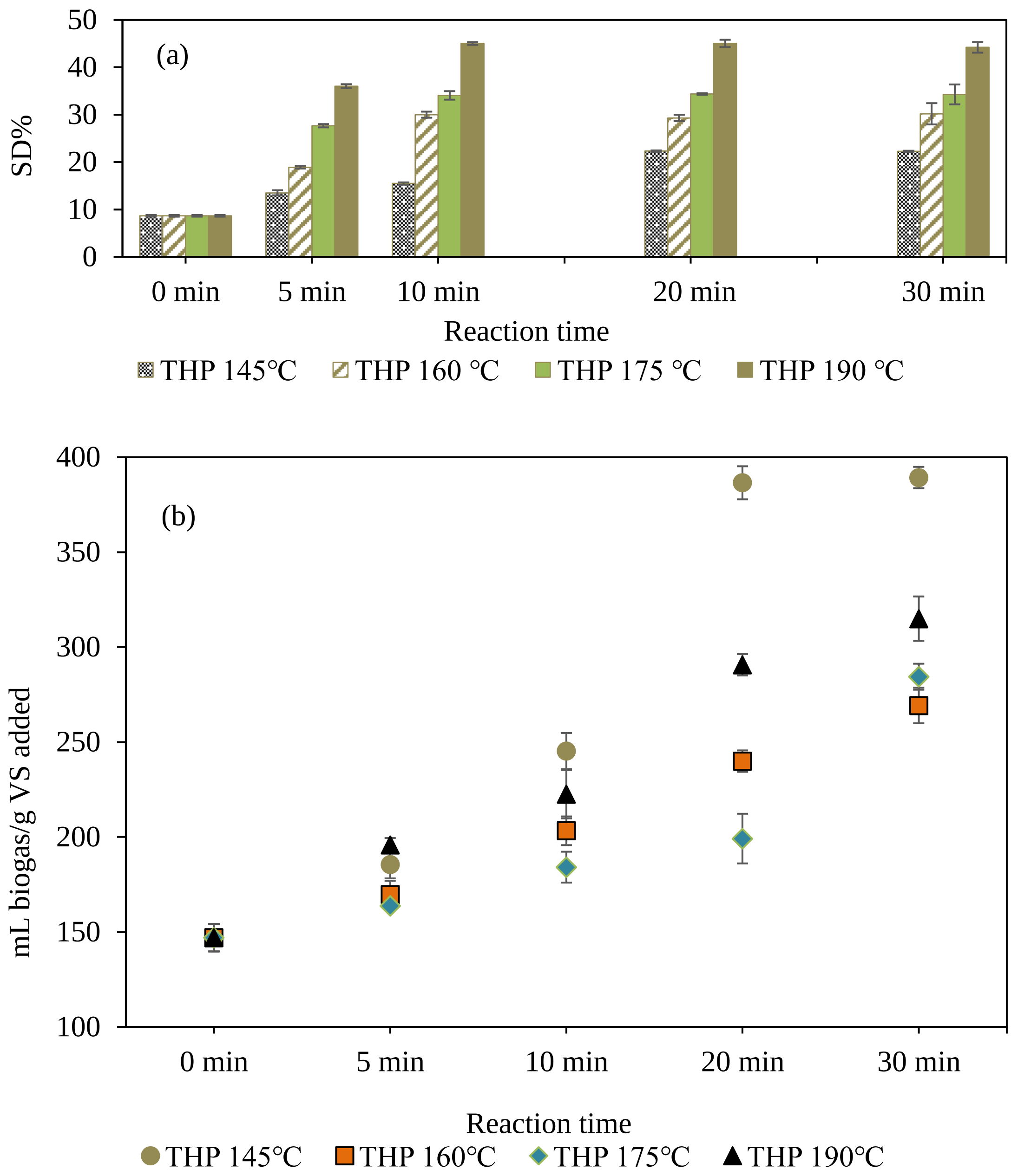


Figure 4-2. (a) Solubilisation degree of sewage sludge at different THP pre-treatment conditions; (b) Biogas production of sewage sludge with different THP pre-treatment conditions

The highest solubilisation of the sludge in this study was 45 % at 190 °C after 10 min processing time. When the retention time was longer than 10 min, the SD% level of sewage sludge remained constant at all reacting temperatures (Figure 4-2a). In the case of THP at 145 °C, the SD% level reached the highest percentage of around 22.3 % at 20 min then remained at the same level at 30 min which is a similar pattern to more severe pre-treatment temperatures. The highest level of SD% being reached over a longer time indicates the hydrolysis process was slower for the mild condition of 145 °C (Figure 4-2a).

4.3.1.2 Biogas production

Figure 4-2b shows that the longer the pre-treatment time, the higher the biogas production. With THP at 160 °C, 175 °C and 190 °C, the highest biogas yields of each reacting temperature were obtained after 30 min pre-treatment. This result is parallel to previous studies such as Haug *et al.* [5], Bougrier *et al.* [84], and Kim *et al.* [112] (Table 4-2). They all found that the longer reaction time, up to 30 min, could maximise the biogas yield.

Table 4-2. Biogas production from sewage sludge after using THP pre-treatment

Reference	Sludge Type	Pre-treatment condition	AD enhancement
[5]	WAS	175 °C, 30 min	CH_4 increased from 115 to 186 mL/g COD_{in} – 62 % increase
[22]	WAS	175 °C, 60 min	Biogas production increased from 108 to 216 mL/g COD_{in} – 100 % increase
[35]	Sewage sludge	186 °C, 105 min	CH_4 production increased from around 139 to 200.5 mL/g VS_{in} –44 % increase
[84]	WAS	175 °C, 30 min	CH_4 production increased from 145 to 256 mL/g VS_{in} – 51 % increase
[112]	WAS	210 °C, 30 min	Biogas production increased from 293 to 411 mL/g VS_{in} – 51 % increase
[113]	60 % WAS + 40 % PS	121 °C, 60 min	Biogas production increased from 350 to 420 mL/g VSS_{in} – 20 % increase

Figure 4-2b also shows that for 5 min processing time, the sludge treated by THP at 190 °C was the most biodegradable, with 196 biogas/g VS added - the biogas yield. However, from 10 min of reacting time, THP at 145 °C yielded the greatest biogas production compared to other pre-treatment temperatures. Interestingly, THP at 190 °C was the pre-treatment condition that brought the highest solubilisation degree for the sludge but was not the condition providing the highest amount of biogas yield.

Figure 4-2b reveals that the highest increase in biogas production (387 to 389 mL biogas/g VS added) was provided by THP at 145 °C for 20 and 30 min pre-treatment time. The biogas production of pre-treated sludge at 145 °C, 20 min is double that of THP at 190 °C, 10 min, which is the pre-treatment condition providing the highest SD%. The result reveals higher solubilisation degree does not always create more biogas production because a high reacting temperature will cause an increase in methanogenic inhibitors in the sludge. Higher SD% achieved by higher reaction temperatures may solubilise more refractory compounds and release more NH_3-N, which can inhibit methanogenic growth and activity, reducing biogas production. Mottet *et al.* [114] reported that refractory compounds such as amadori compounds and melanoidins were obtained at severe pre-treatment temperatures. Amadori compounds are formed from the polymerisation of low molecular weight amino acids and carbohydrates when the temperature is elevated to close to 140 °C [53]. When the processing temperature increases above 140 °C, melanoidin formation starts, generating dark colours within the sludge.

Additionally, thermal hydrolysis was reported to increase the levels of ammonia nitrogen in sludge, which can inhibit methanogenic growth and activity; hence, the biogas production decrease. Jeong *et al.* [43] reported that THP at 220 °C increased NH_4^+-N from 228 mg/L to 1,804 mg/L. The following sections will discuss the influence of possible inhibiting factors created by THP on biogas production.

4.3.2 The colour of the sludge after thermal hydrolysis

As can be seen in Figure 4-3, high pre-treatment temperature and long reaction time caused the darkening of the sludge colour. The more severe the pre-treatment temperature, the darker the sludge will be. After 5 min of processing time, with THP at 145 °C, the colour of the sludge was minimal. However, the colour of sewage sludge increased from 1710 PtCo to 2525 PtCo, 4235 PtCo and 5795 PtCo when the treatment temperature rose to 160, 175 and 190 °C, respectively. Using THP at 190 °C for 30 min darkened the colour of the sludge almost six times from 1710 PtCo to 9945 PtCo. Similarly, Dwyer *et al.* [16] reported that by increasing the temperature of THP from 145 to 160 °C, the colour of sewage sludge increased three times (from 3837 to 11500 PtCo). The result of this study shows that the rate of browning associated with the Maillard reaction increased linearly over the temperature range studied.

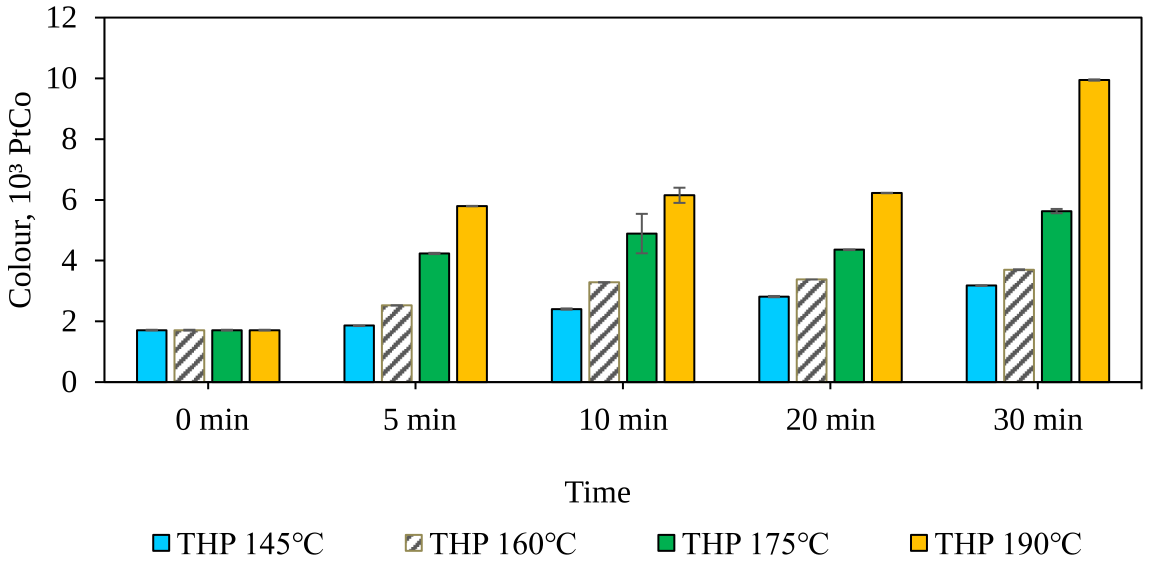


Figure 4-3. Changes in sewage sludge colour after THP pre-treatment

The colour of sludge pre-treated by THP for 190 °C, 30 min (9945 PtCo) was three times darker than by THP for 145 °C, 20 min (2815 PtCo) or by THP for 145 °C, 30 min (3180 PtCo) (Figure 4-3). When the processing temperature is elevated above 150 °C, Maillard reactions will start [83]. The darker colour of sludge formed during the THP above 150 °C is due to the formation of melanoidins. Melanoidins have been proven to inhibit AD and lower biogas production [16]. Ergo, pre-treated sludge at THP 190 °C for 30 min had the highest solubilisation degree (45 %) (section 4.3.1.1) but achieved a lower biogas yield (315 mL biogas/g VS added) compared to THP for 145 °C, 20 min (biogas yield: 387 mL biogas/g VS added) or THP for 145 °C, 30 min (biogas yield: 389 mL biogas/g VS added). Correspondingly, Dwyer *et al.* [16] and Penaud *et al.* [17] concluded that although THP at 165 °C offered a higher solubilisation degree in sludge, the biodegradability of sludge showed little change between 140 and 165 °C.

Furthermore, the browning colour of sludge due to the formation of melanoidins can cause the failure of UV disinfection [16]. Melanoidins are refractory compounds that cannot be treated during AD or wastewater treatment. When the water from the digestate of treated sludge is recycled to the wastewater treatment system to be treated before discharging, the dark colour of the sludge will absorb UV at the UV disinfection stage and cause a decrease in UV transmission for the final effluent. Thereby, Dwyer *et al.* [16] concluded that THP for 145 °C, 30 min should be chosen for pre-treating sewage sludge.

However, in this study, the condition that brought in the highest biogas yield for sludge is by THP for 145 °C, 30 min, which could provide a biogas production rate at 389 mL biogas/ g VS added. The biogas production rate increased by 45 % compared to the pre-treated sludge by THP for 160 °C, 30 min. The highest biogas production achieved at a low THP treatment temperature at 145 °C in this study can be explained by the sludge used. Differentiating from Dwyer *et al.* [16] who used only WAS, a mixed sludge of (55 % PS and 45 % WAS) was used in this study. Due to containing 55 % of PS, the sludge already possesses a good level of biodegradability with a VS/TS ratio of 79 % which indicates more straightforward hydrolysis and a lower treatment temperature requirement. By this, it can be concluded that the optimum condition of THP for mixed sludge of primary sludge and waste-activated sludge is 145 °C, 30 min.

4.3.3 Ammonia (NH_3-N) in the sludge after thermal hydrolysis

Ammonia is crucial for anaerobic digestion due to its role in protein synthesis and neutralising the acidic conditions from acidifying bacteria activities [106]. Nevertheless, a high concentration of NH_3-N can poison methanogenic bacteria, which in turn reduces biogas production [115]. Siles *et al.* [116] found that 620 mg/L of free ammonia in synthetic wastewater could inhibit 100 % methane production. The optimum ammonia concentration for microbial growth in AD ranges from 50 to 200 mg/L [106, 107].

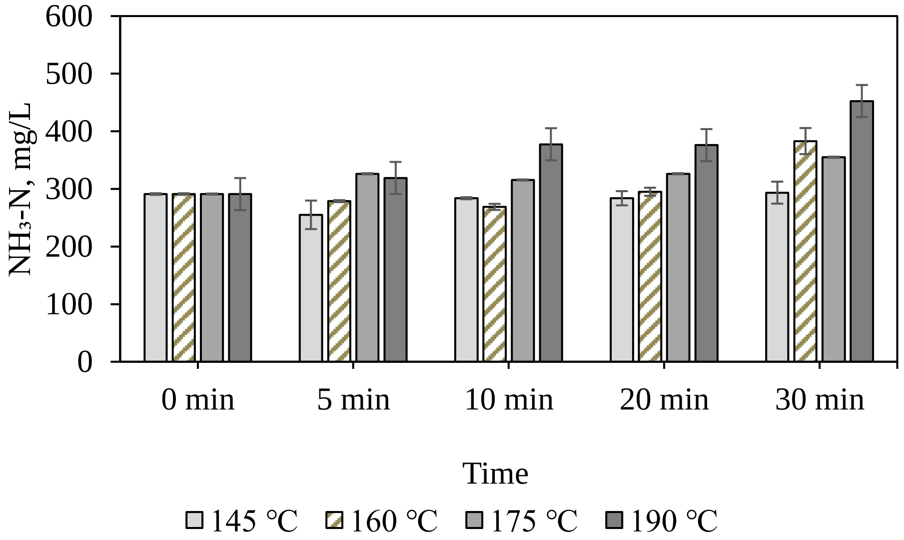


Figure 4-4. NH_3-N concentration in sewage sludge after being pre-treated at different THP conditions

Figure 4-4 shows the increase of ammonia nitrogen in sewage sludge after being treated at severe temperatures of 175 and 190 °C. The rise in NH_3-N concentration started when sludge was treated at 175 °C after 5 min processing time from 291 to 326 mg/L (12.4 %). After a longer reaction time, the increase is more significant ($p < 0.01$). After 30 min THP processing time, the concentration of NH_3-N in sludge at 160, 175, and 190 °C was 383, 385, and 453 mg/L, respectively (Figure 4-4). This corresponds to the lower biogas yield of pre-treated sludge at these conditions discussed previously.

However, Figure 4-4 shows no increase of NH_3-N concentration in sludge when THP at 145 °C was applied. For temperatures lower than 150 °C, the main solubilisation of THP is for carbohydrates, not proteins [64], which can explain why there is no increase in NH_3-N concentration at 145 °C. Carbohydrates are found mainly in the exopolymers of the sludge structure (the membrane), whereas proteins are primarily found inside cells [64]. As such, for "low" temperatures like 145 °C, only exopolymers were affected, leading to the solubilisation of carbohydrates. When treated at a higher temperature, cell walls lysis occurred, which in turn increased the solubilisation of protein and released ammonia from the degradation of the protein [64].

4.3.4 VFAs concentration in the sludge after thermal hydrolysis

Volatile fatty acids are important for methanogenesis in the anaerobic digestion process. Nevertheless, high amounts of VFAs, especially butyric acid and propionic acid, can cause adverse effects on methanogenesis [117]. Mamimin *et al.* [118] reported that a concentration of butyric acid more than 8 g/L could inhibit the methane production process. Similarly, a high amount of propionic acid typically results in no methane production due to the failure of methanogenesis. Derimelk and Yenigun [119] concluded that the threshold of propionic acid that would inhibit methanogenic archaea growth is 0.95 g/L. Keeping the concentration of propionic acid below 0.5 g/L, its negative impact on methanogenesis can be prevented [118].

In this study, the THP conditions that provided the highest biogas yield was at 145 °C, 20 and 30 min, with the biogas production being 387 and 389 mL biogas/ g VS added, respectively. This was followed by THP at 190 °C for 30 min with 315 mg biogas/ g VS added (Figure 4-2b). Figure 4-5 shows the highest concentration of acetic acid (1.32×10^3 mg/L) was obtained at 145 °C temperature and 30 min processing time. The acetic acid in sludge treated at 145 °C and 20 min was also high, with a value around 1.18 ×10³ mg/L. As acetic acid is the substance that will convert to methane during methanogenesis, the highest concentration of acetic acid in the sludge treated at 145 °C and 30 min, corresponds to this condition producing the most significant increase in biogas production.

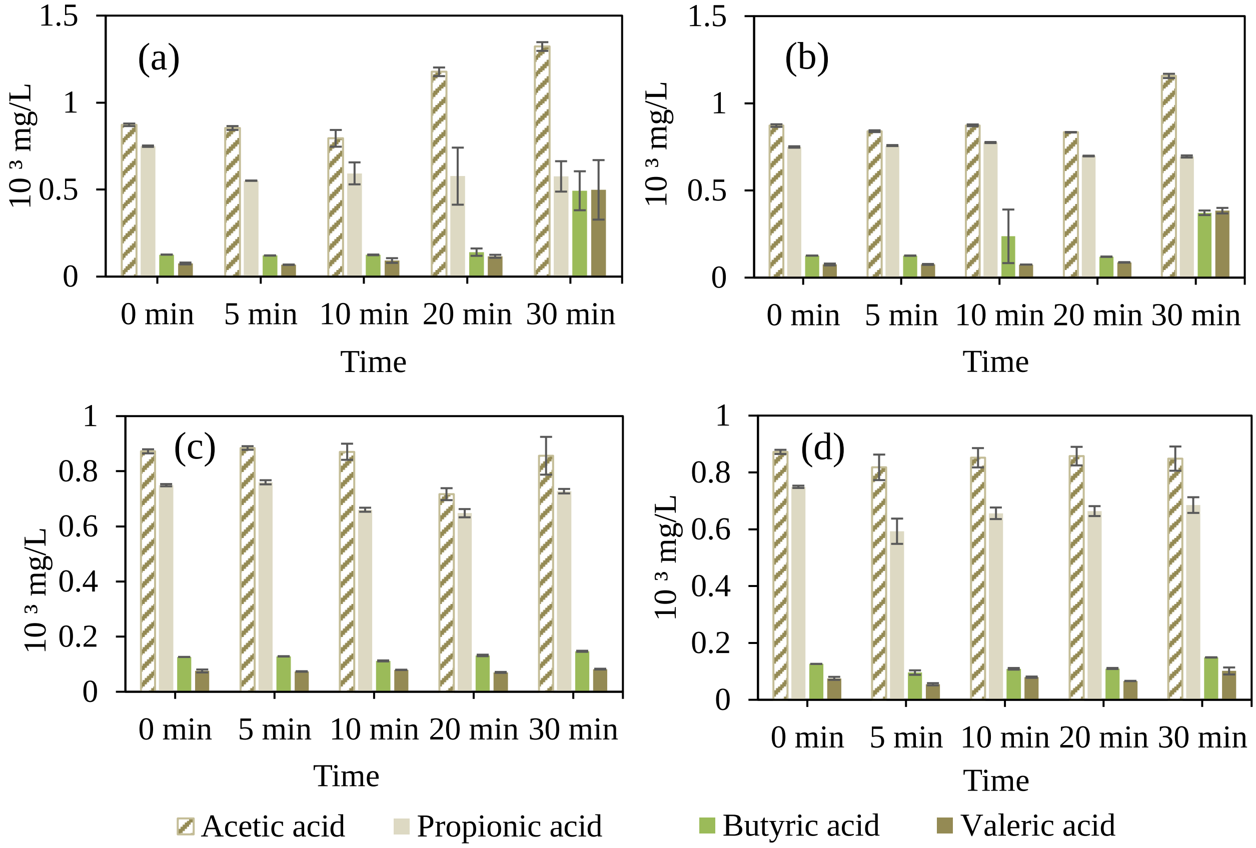


Figure 4-5. VFAs of sludge after being treated at different THP conditions: (a) at 145 °C; (b) at 160 °C; (c) at 175 °C; and (d) at 190 °C

Figure 4-5 also shows a low propionic acid concentration at THP 145 °C for 30 min, at around 0.58 ×10³ mg/L, which did not create any inhibition condition for methanogenesis. Mamimin *et al.* [118] argued that propionic acid quantities exceeding 0.5 g/L will negatively influence methanogenesis. Here, the level of propionic acid in the sludge treated at higher temperatures was around 0.68 to 0.76 ×10³ mg/L, which can inhibit the methanogenesis process. This result also explains the low biogas production for THP at 190 °C and 10 min, where the SD% was the highest level compared to other treatment conditions.

4.4 Summary of chapter and conclusions

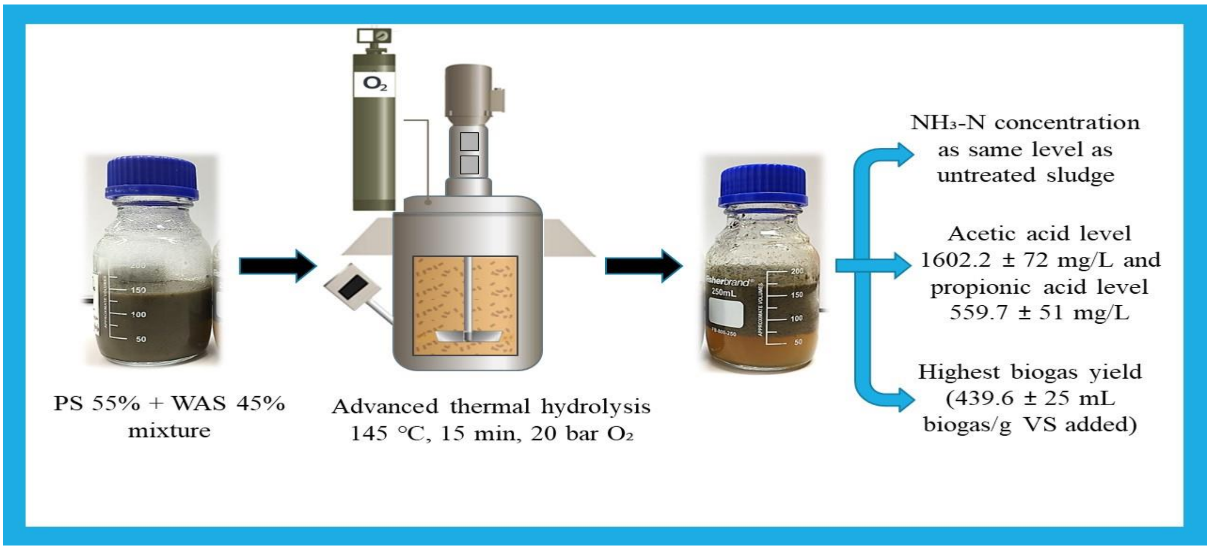
The sludge used in this study was a mixture of primary sludge (PS) (55 %) and waste-activated sludge (WAS) (45 %), which is already biodegradable because of the high percentage of primary sludge (80 % VS/TS). Therefore, this sludge required a lower pre-treatment temperature of THP compared to only WAS. Consequently, the most vital aspect that must be considered before choosing a THP condition is the kind of sludge used. This study showed that using a mixture of PS and WAS sludge will reduce the cost of separating the sludge and reduce the energy used by lowering the pre-treatment temperature from 160 ℃ to 145 ℃. Additionally, the most crucial advantage is the significant enhancement in the biogas production by 2.6 times compared to the untreated sludge and an additional 45% compared to the biogas production at 160 ℃, 30 min which is the current commercial condition from Cambi® THP.

Operating THP at a low temperature of 145 ℃ can minimise the release of NH_3-N, which can reduce the production of inhibitors for the methanogenesis process. Additionally, THP at 145 ℃ for 30 min, provided the highest amount of acetic acid and a low concentration of propionic acid, resulting in a more biodegradable condition for sewage sludge.

The next chapter investigates the effect of ATHP on enhancing biogas production and compares it with THP for the tested sludge.

Chapter 5

A novel strategy for integration of oxidation within advanced thermal hydrolysis of sludge



Chapters 3 and 4 delved into the impact of THP on the solubilisation of sewage sludge and the inhibitory compounds affecting methanogenic bacteria. The optimal conditions for THP were identified as 145 °C for 30 min. Within this chapter, an ATHP that combines THP with oxygen was explored to further enhance the effects of THP. A mixture of 55 % PS and 45 % WAS, derived from the same source as the sludge used in THP, underwent pre-treatment using ATHP at temperatures ranging from 100 °C to 145 °C. The processing time varied from 5 to 30 min, while the oxygen pressure ranged from 10 to 30 bar, all prior to AD. Notably, ATHP at 145 °C for 15 min under 20 bar O_2 pressure emerged as the condition yielding the highest biogas yield, reaching 439.6 mL biogas/g VS added. This marked a 13% increase compared to the biogas yield achieved by the optimal THP conditions.

The content of this chapter has been published, details in the footnote. The theme has been modified to improve the flow and readability of the thesis, details in the footnote.

Ngo, P. L., Young, B. R., & Baroutian, S. (2024). A novel strategy for integration of oxidation within advanced thermal hydrolysis of sludge. *Chemosphere*, *348*, 140676. https://doi.org/10.1016/j.chemosphere.2023.140676

5.1 Introduction

The thermal hydrolysis process has been implemented successfully as a pre-treatment step before anaerobic digestion of sewage sludge for more than 20 years [83]. The technology brings excellent potential for a circular economy approach where the biogas yield from anaerobic digesters will increase by up to 45 % to become an energetically self-sufficient process and produce more energy for operating the whole plant [10]. Also, by applying THP, digestate AD will become a pathogen-free biosolid (class A biosolid) which can be used directly for soil reclamation [18, 120].

By using high temperatures (up to 200 °C) and pressure (up to 25 bar) to disrupt particles and microbial compounds to release intracellular and extracellular material, THP not only helps to increase the biogas production but also shortens digestion time to minimise the volume of the anaerobic digester [43]. Conversely, the intense temperature required for operating THP was reported, which caused some challenges when the technology was adopted.

These challenges include high energy consumption and forming inhibitory compounds in the form of coloured refractory dissolved organic matter [83]. This dissolved organic matter, mainly melanoidins, is derived from browning reactions when the treatment temperature of THP is elevated above 150 ℃ [83]. Wang *et al.* [121] and Ahmed *et al.* [122] found the melanoidins from THP-treated sludge contain furan derivatives, i.e., 5-HydroxyMethyl Furfurals, which obstruct the microbial activities during methanogenesis. The inhibitory effect on the biodegradability of the sludge can result in a 10 to 35 % reduction in biogas production [122]. Additionally, the dark colour of melanoidins will invalidate downstream ultraviolet disinfection [16]. These refractory dissolved organic substances in the returned stream after dewatering also affect nitrogen removal in mainstream wastewater treatment, which can threaten the natural water bodies after the wastewater treatment plant effluent is discharged [123].

Table 5-1. Literature on the effect of temperature, operation time and presence of additional chemicals on biogas production after ATHP of sludge

Reference	**Sludge type**	**ATHP**			**Flash**	**Result**
		Temp. (°C)	**Time**	**Additional chemicals**		
Abelleira-Pereira *et al.* [9].	Secondary sewage sludge	115	5 min	0.2 oxygen supplied/ oxygen stoichiometric of H_2O_2	Yes	Equivalent methane production as THP at 170 °C, 30 min
Takashima and Tanaka [38]	Sewage sludge	170	1 h	0.01 g O_3/ g VS added	No	Biogas production increased by 60% when compared to untreated sludge
Takashima and Tanaka [38]	Sewage sludge	170	1 h	5 bar of O_2	No	Biogas yield was lower than that of sludge treated by THP with same temperature and time conditions
Cacho Rivero and Suidan [39]	Mixture of primary sludge and waste activated sludge (1:1)	90	18 h	0.10 g H_2O_2/g VSS influent	No	Provided the highest percentage of methane, 71.5% in the volume of biogas
Liu *et al.* [124]	Waste activated sludge	64.7	19 h	0.12 g CaO_2/ g VSS	No	Maximum short-chain fatty acids reached 336.5 mg COD/ g VSS, and the highest percentage of acetic acid (70.1%)
Valo *et al.* [125]	Waste activated sludge	90	1 h	150 mmol H_2O_2/L	No	No increase in the biodegradability of the sludge
Valo *et al.* [125]	Waste activated sludge	90	1 h	150 mmol H_2O_2/L + 5 mmol $FeSO_4$/L	No	Biogas production increased by 16 % when compared to no $FeSO_4$

VSS: Volatile suspended solids; VS: Volatile solids; COD: chemical oxygen demand

Therefore, the advanced thermal hydrolysis process has been investigated. This novel sludge pre-treatment method was developed based on the combination of Fenton's peroxidation and THP [83, 126]. By utilising Fenton's peroxidation, ATHP can be run at milder conditions, alleviating the energy consumption, colour of the sludge, and production of refractory dissolved organic substances. Abelleira-Pereira *et al.* [9] reported that with hydrogen peroxide (H_2O_2), ATHP was only required to operate at 115 °C for 5 min to achieve equivalent methane production compared to THP operated at 170°C for 30 min (Table 5-1).

There were some studies that analysed the synergistic effect of THP with H_2O_2 [9, 20, 39], with calcium peroxide (CaO_2) [124], and with ozone (O_3) [38]. These studies and their findings are summarised in Table 5-1.

While adding oxidation chemicals such as H_2O_2 or CaO_2 into sludge can minimise the processing temperature of ATHP, the chemical residues in the sludge after being treated should not be ignored. Although Abelleira-Pereira *et al.* [9] concluded that ATHP operated at 115 °C for 5 min yielded equivalent quantities of methane as THP at 170 °C for 30 min, the author also found that the addition of H_2O_2 can made the soluble organic content less biodegradable.

Xu and He [127] highlighted that the presence of H_2O_2 significantly lowered methane production because adding H_2O_2 promotes the direct formation of highly reactive oxidants, such as hydroxyl radicals. These hydroxyl radicals are much more harmful to methanogenesis than oxygen. Similarly, Climent *et al.* [50] reported that THP operated at 110 to 134 °C for 20 to 90 min exhibited no significant change in biogas yield. Cacho Rivero and Suidan [39] also experienced significant biogas yield drops at H_2O_2 dosage higher than 0.1 g H_2O_2/g VSS influent. Thus, there is a need for a new oxidant that can replace H_2O_2 to alleviate the reaction temperature without inhibiting biomethanation.

Ngo *et al.* [128] noticed hydrothermal deconstruction can occur during THP at 145 °C when there is the presence of oxygen. This finding shows the potential of oxygen to replace H_2O_2 in ATHP. With the same hypothesis, Takashima and Tanaka [38] tested the effect of O_2 on the enhancement of anaerobic biodegradability of biowastes. However, the authors operated ATHP at 170 °C and yielded a lower biogas production with O_2 at 1 bar and 5 bar compared to the control (THP).

In this study, ATHP was operated at lower temperatures ranging from 100 °C to 145 °C in 15 °C intervals and at different processing times and O_2 concentrations to evaluate the influence of these factors on the solubilisation of the sludge and biogas production. This chapter highlights conditions whereby O_2 starts to have an effect and biogas production is optimised. Given the absence of previous studies involving the addition of O_2 to THP under mild treatment conditions, the outcomes of this study could aid in the development of a potentially environmentally friendly sludge pre-treatment method. This may help address the current challenges associated with THP.

5.2 Materials and methods

5.2.1 Materials

The sewage sludge used in this study was a mixture of primary sludge (55 %) and waste-activated sludge (WAS) (45 %) obtained from the Mangere wastewater treatment plant in Auckland, New Zealand. After collection, the sludge was stored at -4 °C in a laboratory freezer. The sludge was thawed at 4 °C in the refrigerator 24 h prior to usage.

The main characteristics of the sludge were: total COD (tCOD) = 145.8 ± 3.1 g/L, soluble COD (sCOD) = 12.7 ± 0.3 g/L, total solids (TS) = 68.5 ± 0.2 g/L, volatile solids (VS) = 54 ± 0.2 g/L, total nitrogen (TN) = 2.8 ± 0.01 g/L, ammonia nitrogen (NH_3-N) = 0.295 ± 0.004 g/L, pH = 5.78 ± 0.01.

Nitrogen gas and oxygen gas were utilised for pressurising the reactor. These gases were acquired from BOC Ltd. (Auckland, New Zealand). The calibrating gases for gas chromatography (a mixture of carbon monoxide, carbon dioxide, oxygen, and nitrogen) were also purchased from BOC Ltd. (Auckland, New Zealand). The reference standards for VFAs calibration, including chromatographic grade acetic acid, propionic acid, butyric acid, and valeric acid, were acquired from Sigma-Aldrich (Auckland, New Zealand). The inoculum used for anaerobic digestion came from recycled digestate of biodigesters at the Mangere wastewater treatment plant in Auckland, New Zealand.

5.2.2 Advanced thermal hydrolysis

A 1 L autoclave reactor (Amar Equipment Ltd, India) equipped with a flash tank was used for advanced thermal hydrolysis reactions (Figure 3-1).

A volume of 300 mL of sewage sludge was loaded into the reactor for each run, and the reactor was pressurised with oxygen and nitrogen gases. Oxygen dosages were tested at three different partial pressures: 10, 20 and 30 bar. The quantities of oxygen were based on the optimum ratio between supplied and stoichiometric oxygen of 0.2 obtained from Abelleira-Pereira *et al.* [9] and Liu *et al.* [124]. For the experiments run at 10 and 20 bar of oxygen, nitrogen was used to pressurise the vessel to 30 bar to maintain the same pressure between all runs. The operating pressure ranged from 36.6 to 43.1 bar, depending on the reaction temperature.

Based on results from Ngo *et al.* [128], hydrothermal deconstruction can occur at the lowest tested temperature of 145 °C. This study conducted ATHP experiments at four reaction temperatures of 100 °C, 115 °C, 130 °C, and 145 °C for 5 min, 15 min, and 30 min reaction times. The reaction time starts when the designated temperature is reached inside the reactor. The heat up time required to achieve the desired internal temperatures was around 15 to 20 min. The mixing speed of the impeller was chosen at 300 rpm. After the processing time was completed, the sludge was flashed into the flash tank and removed for anaerobic digestion and analysis. All tested conditions were conducted in triplicates.

5.2.3 Anaerobic digestion

In this study, lab-scale anaerobic digestion was undertaken using the water displacement method in a batch process. Rasapoor et al. (2016) describe this method in further detail. The system encompassed three bottles, one 100 mL bottle for anaerobic digestion, one 1000 mL bottle containing water, and one 500 mL bottle for collecting water. Three bottles were connected using Tygon E-3603 flexible tubing. Rubber washers were applied to prevent gas leakages. The washers were positioned between the cap and gas outlet port of digestion bottles (100 mL bottles) and water displacement bottles (1000 mL bottles).

The digester bottles were filled with 80 mL of substrate and inoculum with a ratio of substrate to inoculum (S:I) of 1:2 (VS basis), which was reported as the optimal range by Haider *et al.* [109]. Once filled, digester bottles were flushed with nitrogen gas for 5 min to initiate the anaerobic conditions before fastening the caps [110]. All bottles were then placed in an incubator for 21 days. The temperature of the incubator was kept at 35 ± 1 °C to maintain mesophilic conditions [107]. The biogas generated from the 100 mL digester bottle engendered pressure to push water in the 1000 mL bottle containing water to the collection bottle.

Experiments were performed in triplicate. Also, three digesters were set up with only inoculum to analyse the biogas generated from the inoculum.

The weight of water collected daily in the 500 mL bottles was used to calculate the biogas yield produced from the substrate by using equation (1) retrieved from Rasapoor et al. (2016):

$$Y_{\mathrm{t}} = (V_{\mathrm{t}} - Y_{\mathrm{i,t}}.m_{\mathrm{i}})/m_{\mathrm{s}}\text{ , mL biogas/g VS added} \qquad (1)$$

In which, Y_t is the cumulative biogas (mL biogas/g VS added) produced by substrate at time t; V_t is the total volume (mL) of water measured at the time t; $Y_{i,t}$ is the cumulative biogas (mL biogas/g VS added) generated by the inoculum at the time t, m_i is the mass of VS of inoculum added (g), and m_s is the mass of added VS of substrate (g) to the digester.

5.2.4 Analyses

Total solids and volatile solids were analysed based on methods 2540D and 2540E from Standard Methods of The American Public Health Association [111]. tCOD and sCOD were evaluated using Hach high-range COD test kits (20 - 1500 mg/L) (method 8000). A high-range nitrogen ammonia reagent set was used to evaluate the concentration of nitrogen-ammonia (NH_3-N) based on the Salicylate method (method 10031). The Platinum-Cobalt method (method 8025) was applied to measure the colour of the sample.

Shimadzu QP2010 Plus gas chromatograph (GC-FID) (Kyoto, Japan) furnished with flame ionisation detection was utilised to assess the concentration of VFAs, including acetic acid, propionic acid, butyric acid, and valeric acid. A nitroterephthalic-acid-modified polyethylene glycol (PEG) column (DB-FFAP, 30.0 m × 0.53 mm × 0.5 µm, Agilent Technologies, US) was deployed in the GC. The selected carrier gas for the equipment was Helium. At the start, the sample was injected into the column. Thereafter, the temperature of the column was heated up to 40 °C and maintained for 2 min before elevating up to 180 °C at a rate of 10 °C/min. The temperature of the column was kept at 180 °C for 26 min.

The off-gas composition was assessed using an SRI GC (8610c) 2010 gas chromatograph (Torrance, California, USA), which was equipped with thermal conductivity detection (TCD) (for hydrogen and oxygen) and flame ionisation detection (FID) (for carbon monoxide and carbon dioxide). The gas samples were vented out of the reactor vessel (at the end of THP and before the sludge was flashed to the flash tank), then introduced into a Hayesep D Pre-column

(0.5 m in length) followed by the Hayesep D Column (2 m in length). Helium was employed as the carrier gas for the experiment. The Hayesep D Column was initially heated to 50°C and maintained at this temperature for 1 min. Subsequently, the column temperature was raised to 90 ℃ at a rate of 10 ℃/min and held at 90 ℃ for 3 min. Finally, the column temperature was ramped up to 270°C at a rate of 30°C/min. Identification of the carbon dioxide peak was accomplished by aligning reference standard gas retention times with those of the sample peaks. The sampling of off-gas led to a decrease in reactor pressure by 1 bar.

5.2.5 Solubilisation degree

To evaluate the influence of ATHP on the solubilisation of sewage sludge, solubilisation degree (SD%), the ratio between sCOD and tCOD, was employed. The relation between SD% and sCOD and tCOD is presented as Eq. (25) [22]:

$$\mathrm{SD\%} = \frac{\mathrm{sCOD}}{\mathrm{tCOD}} 100\% \tag{25}$$

5.2.6 Statistical analysis

The experimental data from different ATHP pre-treatment conditions were analysed using a two-factor ANOVA analysis. The *p*-value of each factor was applied to interpret the effect of temperature, time and O_2 pressure of ATHP conditions on enhancing the solubilisation degree of sludge and the biogas production. The effect was considered significant if $p \leq 0.05$.

5.3 Results and discussion

5.3.1 Solubilisation degree

As seen in Figure 5-1, ATHP remarkably impacts solubilising sludge at very mild temperatures and very short reaction times. With ATHP operated at 100 ℃, 5 min, and 10 bar of O_2, the sCOD of sludge increased by 1.1×10^3 mg/L from 11.4×10^3 mg/L to 12.5×10^3 mg/L (Figure 5-1b) and the solubilisation degree of the sludge increased by 1.7% (Figure 5-1a).

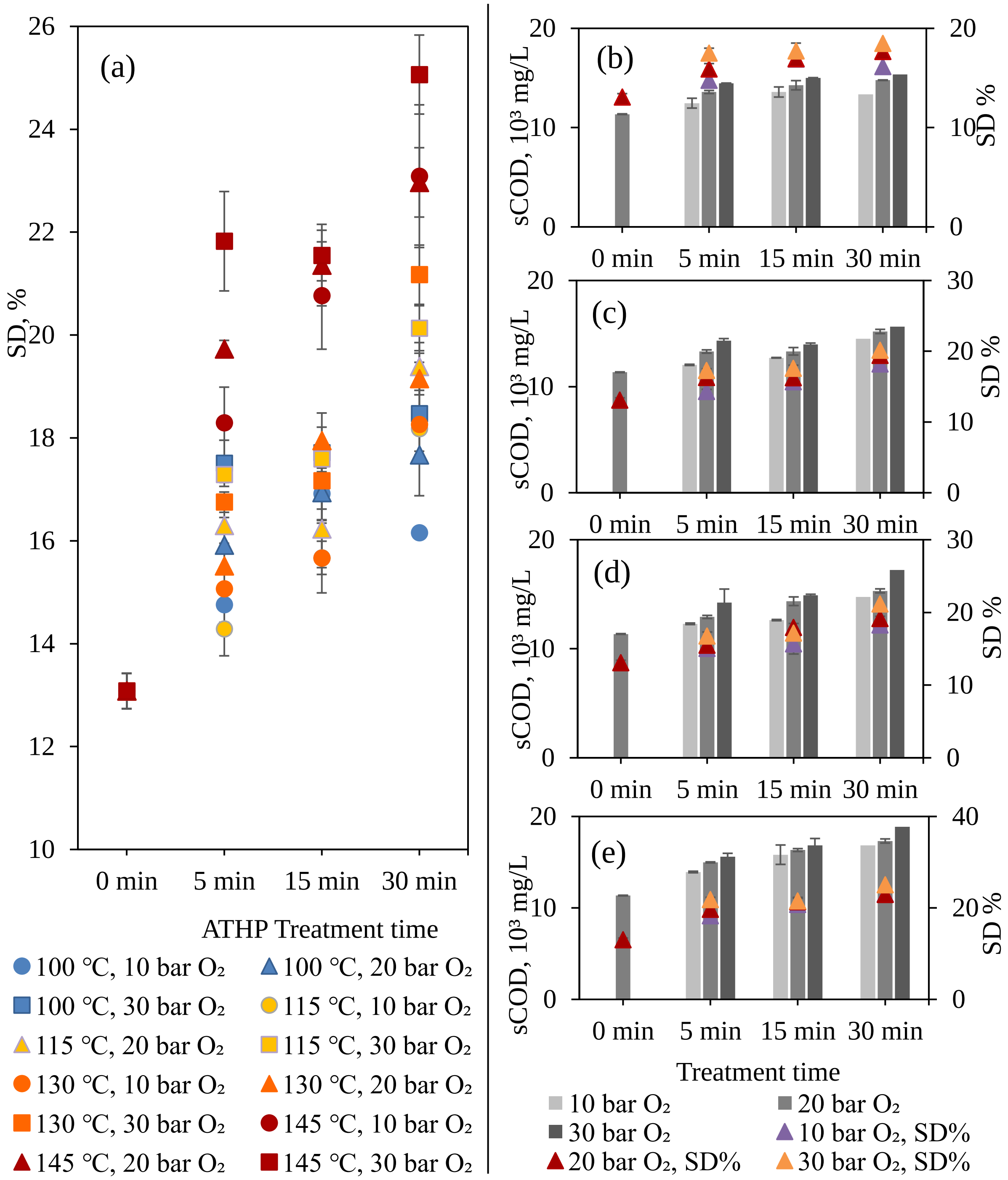


Figure 5-1. sCOD and SD% of sludge after being treated at different ATHP conditions; (a) SD%; (b) ATHP for 110 °C; (c) ATHP for 115 °C, (d) ATHP for 130 °C, (e) ATHP for 145 °C

The impact on the solubilisation degree of sludge was enhanced when the pressure of O_2 increased. When the pressure of O_2 was 30 bar, sCOD of treated sludge rose to 14.5 ×10^3 mg/L when operated at 100 °C for 5 min (Figure 5-1b). This increase is three times higher than at 10 bar of O_2. The influence of O_2 on solubilising the sludge showed an increase at every treatment condition time and temperature (Figure 5-1). The *p*-value from ANOVA analysis was less than 0.01 (Table 5-2). It is concluded that the impact of O_2 on sludge solubilisation was significant statistically.

Table 5-2. Two-way ANOVA of the effect of temperature and O_2 pressure on sCOD of treated sludge

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
Temperature	75.66	1.7E-21	2.06
O_2 pressure	124.99	6.3E-17	3.26
Interaction	1.34	0.21	1.85

The highest solubilisation of sludge (25%) was achieved at ATHP for 145 ℃, 30 min, 30 bar of O_2 (Figure 5-1a), whereas the SD% level of the same sludge treated by THP for 145 ℃, 30 min in Ngo *et al.* [128] was 22 %. This displays the considerable involvement of O_2 in solubilising sludge. However, Abelleira-Pereira *et al.* [9] saw eight times increase in sCOD when H_2O_2 presented at the concentration 0.2 oxygen supplied/ oxygen stoichiometric of H_2O_2 in ATHP for 115 ℃ and 5 min showing the more substantial impact of H_2O_2 in solubilising sludge comparing to O_2.

Similar to THP, the solubilisation degree of sludge after being treated by ATHP increased when the treatment temperature was elevated. It was discovered that the energy from applied heat significantly enhances the reactivity of water, aiding it in breaking down the chemical bonds within complex molecules to generate simpler compounds [83, 91]. As a result, temperature plays a crucial role in enhancing the solubilisation of COD within the sludge. The highest SD% of treated sludge at all processing times and O_2 pressure occurred at 145 ℃ (Figure 5-1a). However, at lower reaction temperatures, the influence of time and O_2 pressure can outweigh the effect of temperature on solubilising sludge. For example, sludge treated at 115 ℃, 30 min, and 30 bar O_2 had an SD% of around 20.1 %, which is higher than that of the sludge treated by ATHP for 130 ℃, 30 min, 10 bar O_2 (18.3 %) and by ATHP for 130 ℃, 30 min, 20 bar O_2 (19.2 %) (Figure 5-1a). These results illustrate the interaction effect of temperature and O_2 concentration. However, this was not confirmed statistically. A *p*-value to test the significant interaction between temperature and O_2 pressure from ANOVA analysis was 0.21 (Table 5-2) which is much higher than 0.01 to be considered the interaction was significant.

Table 5-3. Two-way ANOVA of the effect of time and O_2 pressure on sCOD of treated sludge at ATHP 115 °C

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
Time	240.47	1.54E-08	4.26
O_2 pressure	131.64	2.17E-07	4.26
Interaction	7.11	0.007	3.63

The interaction effect between time and O_2 pressure was confirmed statistically only at 115 °C with a *p*-value is 0.007 (<0.01) (Table 5-3). At other tested reaction temperatures, the interaction between time and O_2 pressure on increasing sludge solubilisation was not confirmed statistically because the *p*-values are higher than 0.01. However, the interaction between time and temperature on solubilising sludge occurred at all tested O_2 pressure and was confirmed by *p*-values less than 0.01 (Table 5-4). The interaction between time and temperature was also confirmed that it is significant during THP [128].

Table 5-4. Two-way ANOVA of the effect of time and temperature on sCOD of ATHP-treated sludge

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
Time	172.25	3.69E-19	3.26
Temperature	62.17	4.92E-20	2.07
Interaction	3.80	0.0002	1.85

Figure 5-1d shows the highest level of sCOD in sludge was 18.88 $\times 10^3$ mg/L and was achieved with sludge treated by ATHP at 145 °C, 30 min and 30 bar of O_2. The subsequent highest values were obtained from sludge treated by ATHP at 145 °C, 15 min and 30 bar of O_2, and ATHP at 130 °C, 30 min and 30 bar of O_2 (17. 32 $\times 10^3$ mg/L and 17.23 $\times 10^3$ mg/L, respectively). It would be expected that longer treatment time or more severe reaction temperature would result in higher sCOD as the solubilisation degree of the same sludge treated by THP for 190 °C and 10 min was 45 % with sCOD was up to 31.4 $\times 10^3$ mg/L [128].

However, solubilisation degree is not only one factor in order to enhance the methanogenesis. Although sCOD is a necessary indicator for the bioavailability level of sludge, a high sCOD level does not always lead to high biogas yield due to other influencing factors, such as the presence of inhibitory compounds [83].

5.3.2 NH_3-N level in treated sludge

NH_3-N plays an essential role in synthesising protein and neutralising the acidic conditions from acidifying bacteria activities during anaerobic digestion [106]. However, at a high concentration, NH_3-N can poison methanogenic bacteria, which will cause a reduction in biogas production [115]. Methanogenesis could be completely inhibited if the level of free ammonia reaches 620 mg/L [116]. The optimum range for NH_3-N concentration for methanogenic bacteria was found to be from 50 to 200 mg/L [106, 107].

The concentration of ammonia nitrogen (NH_3-N) in the sludge after ATHP at 100 °C (Figure 5-2a), 115 °C (Figure 5-2b), and 130 °C (Figure 5-2c) was lower than that in the untreated sludge. The lower concentration of NH_3-N in treated sludge at these conditions may be due to the evaporation during the flash phase [128].

When the reaction temperature is below 150 °C, the main solubilisation is for carbohydrates, not proteins [64]. In the sludge structure, carbohydrates are found mainly in the cell membrane, whereas proteins are primarily found inside cells [64]. Thus, with mild reaction temperatures like 100 °C, 115 °C, and 130 °C, ATHP only could affect the exopolymers, which help to increase the solubilisation of carbohydrates; however, the cells have not ruptured yet to release the protein from inside the cells. As ammonia is released from the degradation of the protein in the sludge, with no extra protein from the cell lysis, the concentration of NH_3-N in the treated sludge at these reaction conditions did not increase.

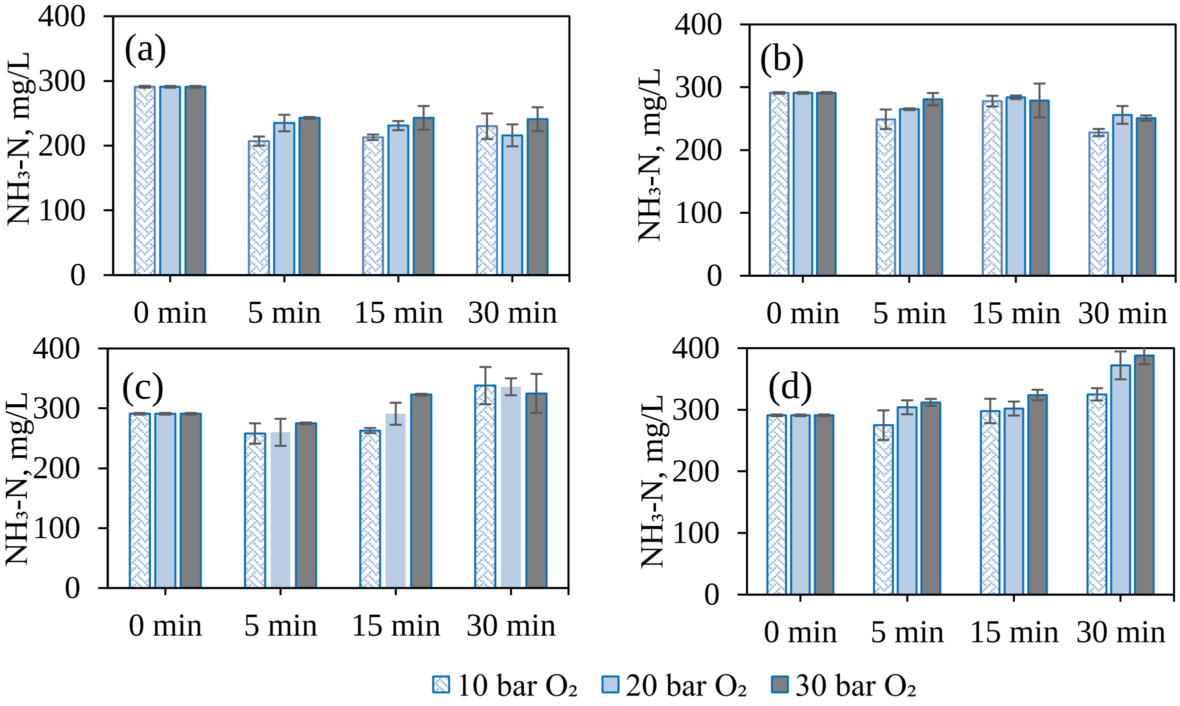


Figure 5-2. NH_3-N concentration in sludge after being treated at different ATHP conditions: (a) 100 °C; (b) 115 °C; (c) 130 °C; (d) 145 °C

With ATHP conditions at 145 °C for 5 min and 15 min, NH_3-N in treated sludge was as same level as in raw sludge (Figure 5-2d). Only with ATHP 145 °C, 30 min, 20 bar O_2, and ATHP 145 °C, 30 min, 30 bar O_2 the treated sludge has higher concentrations of NH_3-N, 372 mg/L and 388 mg/L, respectively compared to raw sludge (291 mg/L) (Figure 5-2d). These rises in NH_3-N concentrations indicates cell walls lysis has occurred during ATHP at 145 °C for 30 min, with 20 bar O_2 and 30 bar O_2. Bougrier *et al.* [64] found that the protein inside the microbial cells of the sludge flocs will only be released when the treatment temperature is higher than 150 °C. The rise in NH_3-N concentration in the sludge treated by ATHP 145 °C, 30 min with 20 bar O_2 and 30 bar O_2 shows the significant impact of O_2 on enhancing the hydrolysis process.

5.3.3 VFAs concentration in the sludge after advanced thermal hydrolysis

Figure 5-3 shows the highest amount of VFAs (around 3000 mg/L) in the sludge achieved after being treated at 100 °C. At this treatment temperature, the concentration of acetic acid and propionic acid in the treated sludge was also at its peak. The highest concentration of acetic acid reached 1954.5 mg/L when the sludge was treated for 30 minutes at 100 °C and 30 bar O_2 (Figure 5-3a). Similarly, the highest concentration of propionic acid, 1314 mg/L, was achieved when the sludge was treated at 100 °C for 5 minutes with 10 bar O_2 (Figure 5-3a). The propionic acid level in all the sludge treated at 100 °C was from 762.4 mg/L to 1314 mg/L (Figure 5-3a).

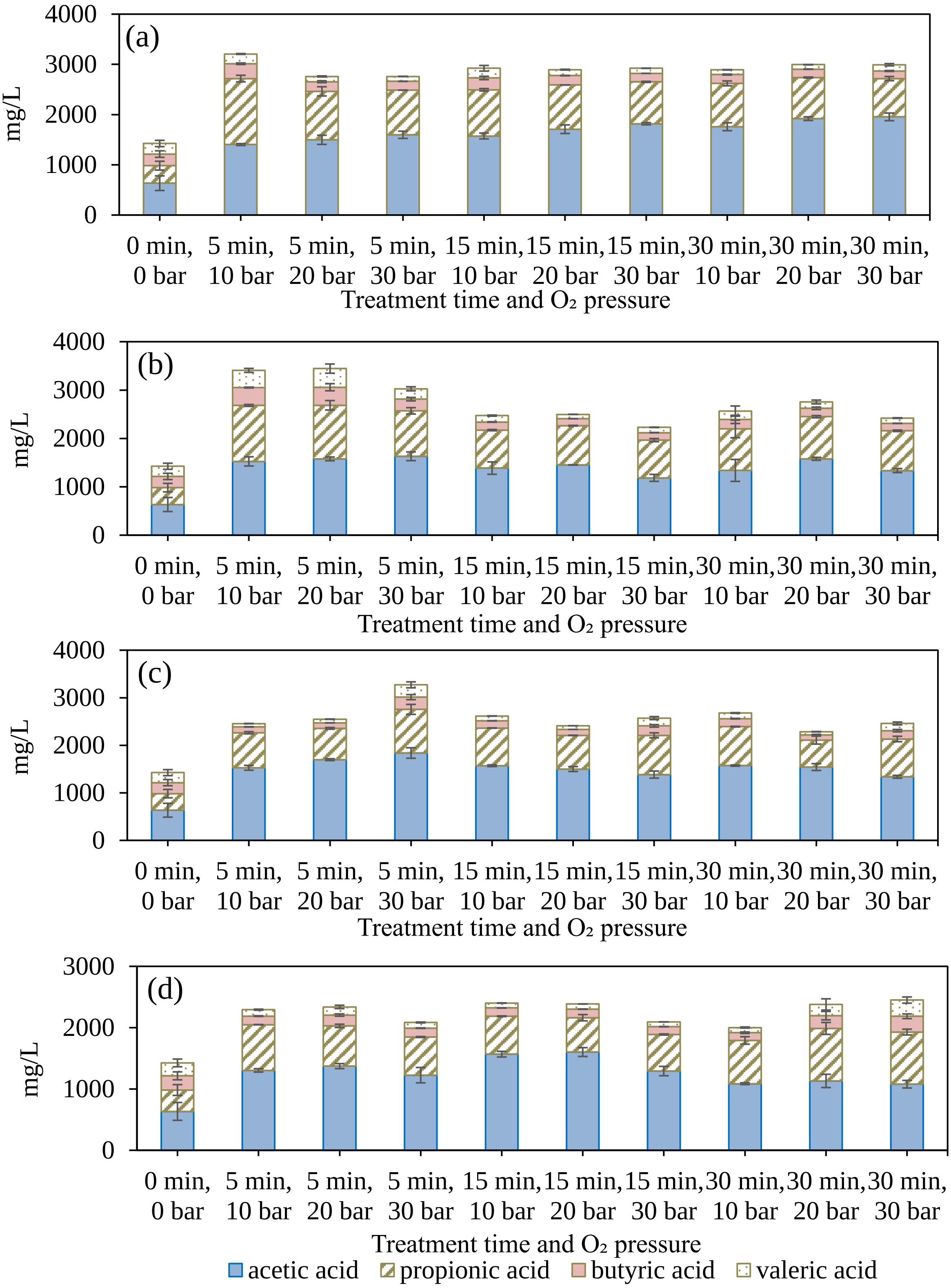


Figure 5-3. VFAs concentration in the treated sludge after ATHP (a) 100 °C; (b) 115 °C; (c) 130 °C; (d) 145 °C

Volatile fatty acids, with acetic acid in particular, serve as the primary substrates for methanogenesis in the anaerobic digestion process, ultimately converting into methane. However, detrimental effects occur when VFAs, particularly butyric and propionic acid, are present in high concentrations [117]. A butyric acid concentration of 8000 mg/L, for instance, can inhibit methanogenic archaea [118]. Similarly, propionic acid can impede methanogenesis at a concentration of 950 mg/L, leading to process failure [119]. To prevent adverse impacts on methanogenesis, the concentration of propionic acid should ideally remain below 500 mg/L [118]. As a result, conducting ATHP at 100 °C may not be suitable for pre-treated sludge aimed at enhancing biogas production, primarily due to the elevated concentration of propionic acid (> 700 mg/L) (Figure 5-3a). This is despite the fact that the treated sludge exhibited the highest concentration of acetic acid under these conditions.

The quantity of acetic acid in the treated sludge at 115 °C and 130 °C decreased in comparison to that in the treated sludge at 100 °C (Figure 5-3b, Figure 5-3c). The highest concentration of acetic acid observed in the treated sludge at these ATHP treatment temperatures was 1837.5 mg/L at 130 °C, 5 minutes, and 30 bar O_2 (Figure 5-3c). In contrast, ATHP at 145 °C yielded a higher amount of acetic acid in the sludge. The peak concentration of acetic acid, around 1602.2 mg/L, was achieved when the sludge was subjected to ATHP at 145 °C for 15 minutes with 20 bar O_2 (Figure 5-3d). Additionally, the level of propionic acid in the treated sludge at this treatment condition remained low (approximately 559.7 mg/L) in comparison to the sludge treated under other tested conditions. With a high concentration of acetic acid and a low level of propionic acid, ATHP at 145 °C for 15 minutes with 20 bar O_2 stands out as the optimal treatment condition for the tested sludge to maximise biogas yield.

5.3.4 Oxidative hydrothermal deconstruction

The production of CO_2 detected in the off-gas during ATHP (Figure 5-4) indicated hydrothermal deconstruction has occurred. Hydrothermal deconstruction (wet oxidation) can occur at temperatures of 150 °C and pressure of 20 bar, as noted in previous studies [42, 97-99]. When oxygen is present at elevated temperatures, it leads to the formation of free radicals like hydroxyl ($HO^{\cdot}$) and hydroperoxyl ($HOO^{\cdot}$). These free radicals have the capability to dissolve insoluble organic compounds, transform hydrolysis byproducts into simpler substances like organic acids and alcohols, or completely oxidise short-chain organics into CO_2, N_2, water, and residual ash [100].

The concentration of CO_2 measured from the off-gas of the reactor after ATHP started to be detected from reaction temperatures of 115 °C or greater (Figure 5-4). In ATHP operating at 115 °C and 130 °C, CO_2 was measured in the off-gas after 15 min reaction time. At 145 °C, CO_2 was recorded in the off-gas after 5 min of reaction time (Figure 5-4). This shows the significant impact of temperature on enabling hydrothermal deconstruction. Also, the amount of CO_2 analysed after ATHP at 130 °C, 15 min, 10 bar O_2 (81.8 mg/L) was almost double that of ATHP for 115 °C, 15 min, and 10 bar O_2 (46.6 mg/L) (Figure 5-4).

While it has been observed that hydrothermal deconstruction can occur from 150 °C [99], the presence of CO_2 in the off-gas from treated sludge at ATHP temperatures below 145 °C highlights the influence of O_2 on enhancing the hydrolysis process at moderate temperatures. The generation of CO_2 in the off-gas under these conditions indicates that complete deconstruction has taken place, converting organic compounds into CO_2. This can elucidate the reduction in VFAs in the treated sludge at ATHP treatment temperatures higher than 100 °C discussed earlier in section 3.3.

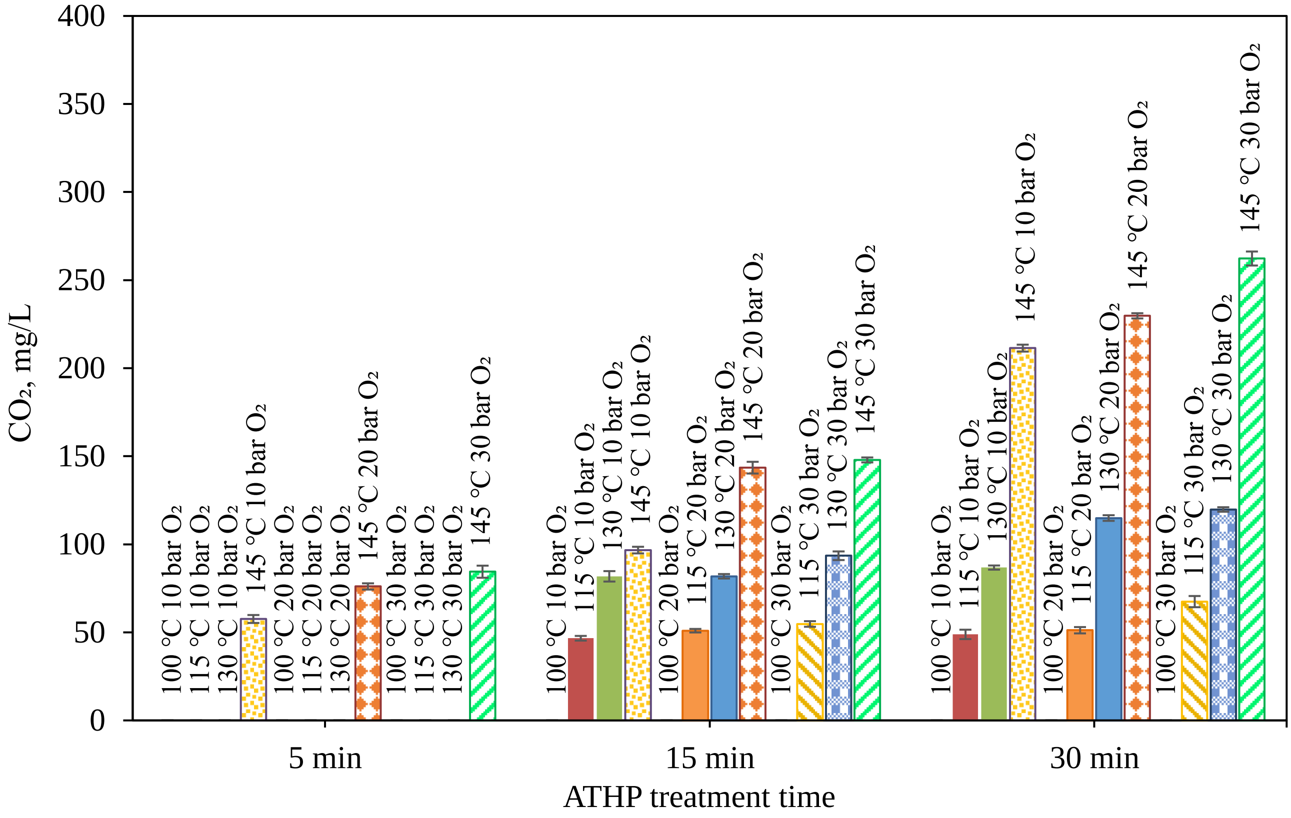


Figure 5-4. CO_2 content in the off-gas after ATHP

5.3.5 Biogas production

There was an interaction between reaction time, temperature, and the pressure of O_2 in influencing the biogas production shown in Figure 5-5. This is illustrated through the greater yield of biogas from sludge treated for 15 min at 130 °C and 30 bar O_2 when compared to 145 °C, and 10 bar O_2. The yields are 398 mL biogas/g VS added, and 390 mL biogas/g VS added, respectively. This interaction is confirmed statistically by ANOVA analysis of the interactions between reaction time and temperature (Table 5-5), temperature and the pressure of O_2 (Table 5-6), and between time and the pressure of O_2 (Table 5-7). All *p*-values are less than 0.01.

Table 5-5. Two-way ANOVA on the effect of time and temperature on biogas yield from ATHP-treated sludge

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
time	46.32	6.74E-18	2.07
temperature	62.80	1.83E-12	3.26
Interaction	5.25	6.08E-06	1.85

Table 5-6. Two-way ANOVA on the effect of temperature and O_2 pressure on biogas yield from ATHP-treated sludge

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
temperature	52.51	8.38E-19	2.07
O_2 pressure	46.29	1.12E-10	3.26
Interaction	3.65	0.0003	1.85

Table 5-7. Two-way ANOVA on the effect of time and O_2 pressure on biogas yield from ATHP-treated sludge

ANOVA

Source of Variation	*F*	*P-value*	*F crit*
time	52.51	8.38E-19	2.07
O_2 pressure	46.29	1.12E-10	3.26
Interaction	3.65	0.0003	1.85

The highest biogas yield (439.6 mL biogas/g VS added) was given by the sludge treated at 145 °C, 15 min, and 20 bar of O_2 condition, followed by sludge treated at 145 °C, 5 min, and 20 bar of O_2 condition (420 mL biogas/g VS added) (Figure 5-5). The biogas production enhancement from ATHP was around three times from 147 mL biogas/g VS added to 439.6 mL biogas/g VS added. This result proves that ATHP with O_2 enhances biogas production significantly.

Interestingly, the treatment condition that provided the highest amount of biogas yield was not the condition that brought sludge to the highest level of solubilisation. The solubilisation degree of treated sludge by ATHP 145 °C, 30 min, and 30 bar of O_2 was the highest (25 %) (section 3.1); however, lower biogas production (353.9 mL biogas/g VS added) was generated. This is lower when compared to the treatment condition at the same temperature but with lower O_2 pressure (20 bar) and shorter processing times of 5 min or 15 min (Figure 5-5).

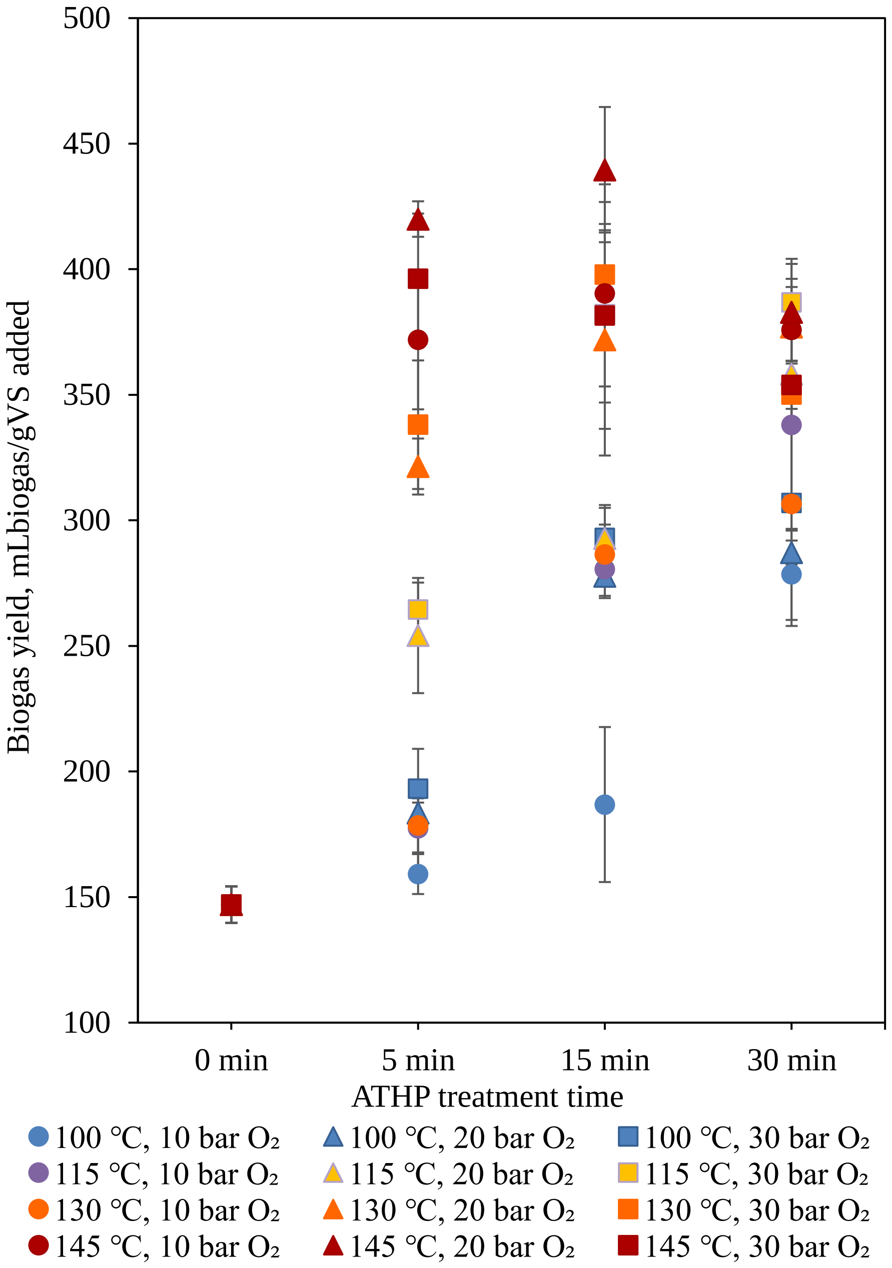


Figure 5-5. The biogas yield of sludge after being treated at different ATHP conditions

The lower biogas production from treated sludge by ATHP at 145°C for 30 min at 30 bar O_2, which has the highest SD%, indicates the presence of inhibitory factors. In Figure 5-2d, there is a considerable increase in NH_3-N concentration in the treated sludge at ATHP 145°C for 30 min at 20 bar O_2 and 145°C for 30 min at 30 bar O_2, with an increase of more than 81 mg/L. The NH_3-N levels in treated sludge at 145°C for 30 min at 20 bar O_2 and 145°C for 30 min at 30 bar O_2 were 372 mg/L and 388 mg/L, respectively. Given that a high concentration of NH_3-N can be detrimental to methanogenic bacteria [115], the elevated NH_3-N concentration in the sludge under these treatment conditions can account for the reduced biogas production despite the higher solubilisation degrees observed in these sludge samples.

Moreover, the presence of a high concentration of propionic acid in treated sludge under these conditions is also a contributing factor to the low biogas yield. The propionic acid level in the treated sludge at ATHP 145°C for 30 minutes at 30 bar O_2 was approximately 850.5 mg/L. Derimelk and Yenigun [119] determined that methanogenesis can be inhibited by propionic acid concentrations as low as 950 mg/L.

In contrast, when subjected to ATHP at 145 °C for 15 min and 20 bar O_2, the treated sludge exhibited a high concentration of acetic acid (1602.2 mg/L) and a lesser amount of propionic acid (559.7 mg/L) compared to the sludge treated under other tested conditions (Figure 5-3d). Additionally, the level of NH_3-N in the treated sludge at this treatment condition showed no difference when compared to that in the untreated sludge (Figure 5-2d). The low levels of propionic acid and NH_3-N, coupled with a reasonably high concentration of acetic acid and SD% in the treated sludge under ATHP at 145 °C for 15 min and 20 bar O_2, help explain why this condition yields the highest biogas production among those tested.

In comparison to the maximum biogas yield (389 mL biogas/g VS added) obtained from the tested THP discussed in Chapter 4, ATHP at 145 °C for 15 minutes and 20 bars of O_2 pressure increased biogas production from the treated sludge by 13%, raising it from 389 mL biogas/g VS added to 439.6 mL biogas/g VS added. This result highlights the positive impact of oxygen in enhancing the THP process. The presence of oxygen at 20 bar not only reduced the reaction time from 30 min to 15 min but also led to a 13 % greater volume of biogas generated.

5.4 Summary of chapter and conclusions

Advanced thermal hydrolysis with O_2 efficiently solubilises sludge and enhances biogas production. The highest biogas yield was 439.6 mL biogas/g VS added, three times higher than the control. This yield was achieved by ATHP treatment of sludge at 145 °C, 15 min, and 20 bar of O_2.

The treatment condition of ATHP, which results in the highest solubilisation degree of sludge (25%), was achieved by treatment at 145 °C, 30 min, and 30 bar of O_2. The solubilisation of the sludge would be expected to increase more with higher reaction temperature and longer processing time. Although ATHP for 145 °C, 30 min, and 30 bar of O_2 was the best condition to solubilise the sludge among the tested conditions, sludge treated by ATHP for 145 °C, 30 min, and 30 bar of O_2 generated less biogas than the those treated by ATHP with lower O_2 pressure and shorter time. This result can be explained by the high concentration of NH_3-N and propionic acid in the sludge treated by ATHP for 145 °C, 30 min, and 30 bar compared to other treatment conditions, which can negatively influence methanogenesis.

Compared to commercial THP operating around 160 °C, 30 min, using ATHP for 145 °C, 15 min can reduce the energy cost significantly and eliminate the effect of the dark colour of sludge.

The limiting factor in this study is the sludge used. As it was a mixture of primary sludge (55 %) and waste-activated sludge (45 %), it already achieved high biodegradability (VS/TS % was 80 %). This is the result of the high percentage of primary sludge. This sludge used could lead to less severe treatment conditions required. Therefore, further studies regarding ATHP and the synergistic effect of O_2 should be conducted to test the impact on WAS only.

While the comparison between THP and ATHP in this study demonstrates that the addition of 20 bars of O_2 pressure increased biogas production from the treated sludge by 13% and required a shorter reaction time, a future technical and economic analysis should be conducted to determine whether introducing oxygen to THP is a practical approach.

Chapter 6

Concluding remarks

6.1 Conclusions

The thermal hydrolysis process stands as an effective and dependable technology for the pre-treatment of sewage sludge in anaerobic digestion, with a successful industrial track record spanning over two decades. Numerous benefits of this technology have been documented, including improved dewatering, facilitation of higher loading rates, and enhancement of both biogas quality and quantity. Nonetheless, there remains room for substantial improvement if the formation of free radicals can be augmented at lower temperatures, thereby reducing the production of inhibitors like melanoidins and ammonia nitrogen.

The substantial variations in reported biogas production outcomes across different studies underscore the critical necessity for a comprehensive exploration of the mechanisms and influential factors related to thermal hydrolysis in the context of pre-treating wastewater treatment plant sludge. Moreover, advanced thermal hydrolysis presents a promising alternative technology that could potentially surmount the existing challenges of conventional THP. However, this technology requires further investigation, particularly concerning the optimal dosage of oxidation.

The primary purpose of this research project was to develop a comprehensive understanding of the main mechanisms involved in THP, with a specific focus on sludge solubilisation, the generation of inhibitory compounds for methanogenesis, and the enhancement of biogas production. Additionally, the project aimed to assess the impact of ATHP and its potential to address the limitations of THP. Specific tasks were devised to test these hypotheses. The following section provides a summary of the conclusions drawn from each task:

- First, noteworthy observations were made during the literature review encompassing both THP and ATHP. For THP, the increase in biogas production for AD varied widely, ranging from a significant 75 % enhancement in comparison to untreated sludge, to as low as 30%, contingent on the sludge characteristics. It was also observed that THP substantially intensified the browning of sludge. With an escalation in THP temperature from 140 °C to 165 °C, the sludge colour underwent a remarkable surge from 3837 PtCo/L to 12677 PtCo/L. This phenomenon introduces a drawback for UV disinfection when post-dewatering wastewater from digestate is reintroduced into the mainstream wastewater treatment process. Regarding ATHP, it was found that the technology could amplify the effects of THP, leading to a requirement for less severe reaction conditions. Nevertheless, the impact of ATHP with H_2O_2 proved to be unstable due to the adverse influence of residual H_2O_2 in the treated sludge on methanogenic bacteria.

- ❖ The experimental results found that there are two main solubilisation processes when THP is followed by flash depressurisation. Hydrolysis is the primary solubilisation mechanism which contributes to approximately 76 to 87 % of the increase in SD% of the sludge. However, flash depressurisation contributes considerably, from 13 % up to 24 % of the rise in SD%. Also, with flash depressurisation, THP can achieve the required solubilisation level in a shorter reaction time, within 10 min, which in turn can help reduce the dark colour of the sludge and the formation of inhibitory compounds for anaerobic digestion afterwards. At 190 °C with 10 min and 20 min reaction times with flash depressurisation, THP provided the highest SD% of the sludge (45 %). Additionally, a degradation/deconstruction reaction by the occurrence of wet oxidation happened when air or oxygen is available in the THP reactor headspace. In this study, hydrothermal deconstruction was responsible for 7 % of the tCOD loss.

- ❖ The results from this study revealed that employing a combination of PS and WAS sludge offers the potential to cut down on the expenses associated with sludge separation and decrease energy consumption through a reduction in pre-treatment temperature from 160 °C to 145 °C. Notably, the paramount benefit lies in the substantial increase in biogas production at THP 145 °C 30 min to 389 ml biogas/g VS added, reaching 2.6 times that of untreated sludge. Furthermore, an additional 45 % rise was observed at this treatment condition in comparison to biogas production from treated sludge at 160 °C for 30 minutes, which is the current commercial conditions of Cambi® THP. Additionally, by operating THP at a low temperature of 145 °C, the production of inhibitors for the methanogenesis such as NH_3-N, melanoidins and propionic acid can be minimised.

- Advanced thermal hydrolysis with O_2 efficiently solubilises sludge and enhances biogas production. The highest biogas yield observed was 439.6 mL biogas/g VS added, which is three times higher than the control and 13% higher than the maximum biogas production observed from the tested THP. This impressive yield was achieved through ATHP treatment of the sludge at 145 °C, 15 min, and 20 bars of O_2 pressure. In comparison to commercial THP processes that operate at around 160 °C for 30 min, utilising ATHP at 145 °C for 15 minutes could lead to significant reduction in energy costs and eliminate the issues associated with the dark coloration of the sludge.

Overall, the findings of this study suggest that the optimum condition for THP which can be applied to a mixed sludge consisting of primary sludge and waste activated sludge, is at 145 °C for 30 min. By using this condition, the costs associated with sludge separation and the energy requirements for THP are reduced. Importantly, the colour of the sludge treated under this mild condition will not pose problems for UV disinfection. Furthermore, the conclusions drawn from this thesis have confirmed the hypothesis that ATHP has the potential to replace THP. With the incorporation of oxygen, the maximum biogas yield increased by 13% compared to the yield obtained from THP pre-treatment. Moreover, the reaction time only needs 15 min at 145 °C.

6.2 Recommendations for future work

This novel study on THP and ATHP presents new opportunities for circular economy approach to sludge management. Nevertheless, due to the limited scope of the research, only a mixture of 55 % PS and 45 % WAS was tested. Recommendations for future work include the following:

- Different ratios of primary sludge and waste activated sludge within a sludge mixture should be tested to obtain a comprehensive understanding of the optimal conditions for the thermal hydrolysis process concerning various sludge types.
- The sludge mixture used in this study demonstrated high biodegradability, with a volatile solids to total solids ratio of 80 %, primarily due to the substantial proportion of primary sludge. This sludge could lead to less severe treatment conditions required. Therefore, further investigations concerning the advanced thermal hydrolysis process and the potential synergistic effects of O_2 should focus on assessing the impact when applied solely to waste activated sludge.

- For a complete assessment, a future technical and economic analysis should be conducted. This evaluation would determine whether the incorporation of oxygen into THP is a viable approach. It will be essential to weigh the benefits of higher biogas yield, shortened reaction time, and reduced reaction temperature against the costs associated with oxygen addition.
- To prepare for the scalability of the technology, piloting an ATHP model is recommended.

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