

Review

Comprehensive Review of Hydrothermal Pretreatment Parameters Affecting Fermentation and Anaerobic Digestion of Municipal Sludge

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Abstract: Municipal solid waste treatment and disposal have become one of the major concerns in waste management due to the excessive production of waste and higher levels of pollution. To address these challenges and protect the environment in sustainable ways, the hydrothermal pretreatment (HTP) technique coupled with anaerobic digestion (AD) becomes a preferred alternative technology that can be used for municipal solid waste stabilization and the production of renewable energy. However, the impact of HTP parameters such as temperature, retention time, pH, and solid content on the fermentation of TWAS is yet to be well studied and analyzed. Hence this study was conducted to review the effect of hydrothermal pretreatment of thickened waste-activated sludge (TWAS) on fermentation and anaerobic digestion processes. Many studies reported that fermentation of TWAS at pretreatment temperature ranges from 160 °C to 180 °C resulted in a 50% increase in volatile fatty acid (VFA) yields compared to no pretreatment. However, for the AD process, HTP in the range of 175 °C to 200 °C with a 30–60 min retention time was considered the optimal condition for higher biogas production, with 30% increase in biodegradability and greater than 55% increase in biogas production. Even though there is a direct relationship between increased HTP temperature and the hydrolysis of TWAS, a pretreatment temperature range beyond 200 °C alters the biogas production. The solid content (SC) of sludge plays a crucial role in HTP, where in practice up to 16% SC has been utilized for HTP. Further, a combined alkaline-HTP enhances the process performance.

Keywords: hydrothermal pretreatment; thickened waste-activated sludge; fermentation; anaerobic digestion; volatile fatty acids; biogas



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1. Introduction

Population and economic growth coupled with climate change and food security have resulted in significantly increased usage of natural resources and energy consumption. The inevitable exploitation of natural resources has created increasing concerns worldwide. One of the major concerns is the excessive generation of waste [1], which becomes a basis for the current and future challenges of solid waste management [2]. These days, to address these challenges and protect the environment in sustainable ways, reduction, reuse, recycling, and recovery of natural resources have gained more attention [3]. Disposing of organic wastes as part of industrial or municipal wastes with improper treatment methods or no treatment at all results in detrimental effects on the environment. Landfills of organic wastes, as an example, exhibit emissions of greenhouse gases because of the anaerobic decomposition of the waste [4]. These conventional habits of putting organic wastes in landfills have created potential pollution of soil and groundwater resources resulting from the landfill leachate [1,5].

It was estimated that the volume of worldwide municipal wastewater produced in 2020 was 360–380 km³/year and it is predicted to increase by 24% by 2030 and by 51% by 2050 [6,7]. In 2017, the annual global municipal sewage sludge production rate was estimated to be 45 million tons as dry solid (DS) [8]. The USA and Canada produced 14 and 1.2 million tons of municipal sewage sludge, respectively [9,10]. According to Shanmugam et al. [11], global sewage sludge production is predicted to reach 127.5 million tons as DS by 2030. The most-used thickening processes for municipal sewage include gravity thickening, dissolved air flotation, rotary drum thickening, and centrifuge. The type of thickening selected is usually determined by the size of the WWTP, its physical constraints, and the planned operations further downstream. Stabilization is usually achieved using chemical, biological, and thermochemical treatments [12]. The typical form of chemical stabilization is alkaline stabilization by adding lime (or lime and waste solid materials) to the thickened liquid sludge to raise the pH to greater than 12 for several days [13]. Recently, ozonation and other advanced oxidation processes such as peroxone have been used for chemical stabilization prior to biological stabilization [14]. Biological stabilization can be either aerobic [15] or anaerobic [16]. According to the WEF Manual of Practice [17], AD is generally applied for WWTPs treating wastewater inbound flows greater than about twenty million liters per day, whereas AS is typically applied in smaller WWTPs. On the other hand, there are a range of thermal stabilization technologies such as drying, torrefaction, hydrothermal carbonization, hydrothermal liquefaction, pyrolysis, gasification, and incineration. Drying is an evaporation process achieved by boiling the sludge. Torrefaction is a thermochemical process performed at atmospheric pressure at 200–300 °C, for a relatively low residence time [18]. Hydrothermal carbonization is performed at 180–250 °C, and the residence time ranges from 0.25 to 2 h [19]. Hydrothermal treatment is performed at 300–360 °C under pressurized water, and the residence time ranges from 0.25 to 1 h [20]. Pyrolysis involves applying heat in a gaseous or liquid environment without oxygen [19]. Gasification is a process that converts carbonaceous organic or fossil-based materials at high temperatures (>700 °C) without combustion, while incineration must be performed above 850 °C [21].

Anaerobic digestion (AD) has been used worldwide, as it can be employed with various types of organic waste streams. In modern wastewater treatment plants, the anaerobic digestion process becomes a practical solution to sustainable waste management practices and is considered an environmentally friendly technology for municipal solid waste treatment and disposal [22–24]. According to Elbeshbishy et al. [24], applying the anaerobic digestion process to produce renewable energy or bioenergy has been recognized as an energy-efficient process with a smaller environmental imprint. Compared with other technologies like landfilling and incineration, the anaerobic digestion process has also significantly reduced the volume of sludge [23,25,26]. In addition, the stabilized sludge produced during the AD process can be used as organic fertilizer for agricultural purposes [23].

The anaerobic digestion process is an environmentally friendly method of bioenergy production, as it reduces numerous problems originating from inadequate disposal. Even though the AD process consists of different stages to achieve its goal, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis, hydrolysis is known to be the rate-limiting step [27,28]. Thus, suitable pretreatment is required to enhance digestibility by improving the hydrolysis stage [27–29].

Several pretreatment methods are used to increase the anaerobic digestibility of organic wastes for processing. These include chemical, biological, mechanical, and thermal pretreatments [29,30]. These pretreatment technologies change the complex organic structures by breaking chemical bonds and increasing the process of hydrolysis and biogas production [31]. Between the two, physical pretreatment methods are mainly used because of their low investment and operating suitability [30]. It also has a relatively greater advantage when it comes to environmental conditions. For example, chemical pretreatment yields secondary pollution [25], and biological pretreatment conditions have difficulty

controlling the process [30]. Combined treatment has the difficulties of both the chemical and biological treatments [25,30].

Thermal pretreatment is a type of pretreatment whereby organic waste is exposed to heating at different temperatures and pressures. The temperature could range between 50–295 °C [29,30] depending on the intended use. Thermal pretreatment can be hydrothermal, steam injection, or microwave heating, based on the method used [26,32].

Hydrothermal pretreatment (HTP) is considered one of the most effective and popular methods of thermal pretreatment of municipal solid wastes [31]. The application of HTP is well-documented for its improvement of dewaterability and enhancement of anaerobic digestion performance, as it alters the structure of the insoluble portion of organic matter into more biodegradable matter [26,31,33]. Hydrothermal pretreatment enhances the soluble chemical oxygen demand (SCOD) because of its degradation of macromolecular matter. HTP can significantly increase the hydrolysis of insoluble organic compounds in municipal solid wastes, resulting in a shorter hydraulic retention time for solubilization and a reduction in the total volume of the reactor [2].

Several studies have been conducted to evaluate the effect of hydrothermal pretreatment on municipal sludge [1–3,26,29,31–37]. Accordingly, most of the results confirmed a positive effect on the fermentation/acidification process and biogas production. These studies also reveal that different results were obtained based on the composition and characteristics of the substrates used for the hydrothermal pretreatment process. Although hydrothermal pretreatment is used to degrade municipal solid wastes, there is no defined agreement on the range of heating temperature and retention time for solubilization and biogas production. Currently, the most successfully operated industrial-scale plants, such as Cambi, have used an HTP temperature range of 160–180 °C [31]. Therefore, the objective of this study is updating the standards for the effect of hydrothermal pretreatment of thickened waste-activated sludge for fermentation and the anaerobic digestion process. In this review, new correlations between the different operating parameters and the performance of the hydrothermal pretreatment were generated.

2. Hydrothermal Pretreatment and Sludge Disintegration

The degree of solubilization, which is often considered a performance indicator of the pretreatment process, states the ratio of the SCOD produced through the process by the particle COD of the influent substrate [35]. Figure 1 indicates the main effect plots for COD solubilization vs. HTP parameters, incorporating data from the literature. The impact of temperature, retention time, and solid content are illustrated as the main variables.

As seen in the figure, temperature directly correlates with COD solubilization, while retention time and SC have an indirect relationship. As the temperature of the HTP process increases to 200 °C, the COD solubilization increases, stabilizing afterward. The stabilization and slight decline in sludge solubilization should be due to the formation of toxic compounds such as melanoidin [33]. Furthermore, reducing retention time from 180 min to 5 min causes a decrease in COD solubilization, although it should be noted that the temperature plays a crucial role in COD solubilization, and retention time is dependent on the temperature it is combined with. However, it has been proven that retaining the sludge for a longer time does not significantly enhance COD solubilization. Moreover, as with retention time, solid content proved to adversely impact the sludge disintegration rate.

As seen in Figure 1, the highest COD solubilization of 50% is observed at a temperature of 200 °C, a retention time of 8 min, and sludge SC of 3%. Although these data indicate the better performance of the HTP in lower RT, SC, and higher HTP, the actual operation of the process depends on the impact of COD solubilization on the target by-product (VFAs or methane) as well as the feasibility of the operation. For example, HTP plants currently operate with higher SC sludge (16%), as a higher sludge volume can be treated. Further details on the impact of COD solubilization and its impact on VFAs and methane production are discussed in the following sections.

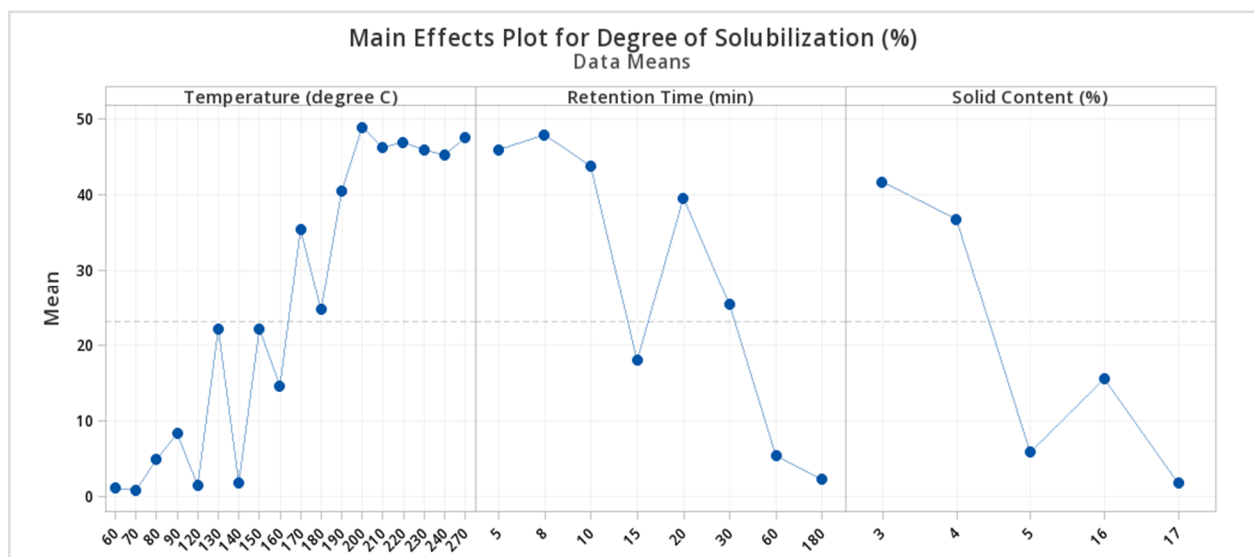


Figure 1. Main effect plot for the degree of solubilization after HTP vs. temperature, retention time, and solid content.

On the other hand, as shown in Table 1, there were some inconsistent and contradictory results for the degree of solubilization, and the variation is significant. For example, Xue et al. [38] reported a degree of solubilization of 85%, which is very high compared to most reports in the literature (20–50%), this was due to the high particulate SOD (pCOD) of about 158 g/L and the extended time for the pretreatment of 72 h, which are not common for HTP. Furthermore, Zang et al. [39] reported a low degree of solubilization of only 9.2%, which was due to the low temperature applied of 55 °C. Therefore, the contradictions in the results in the literature are mainly due to different in pretreatment conditions and/or the nature of the feedstock (source, solids content, pCOD content, sludge age, etc.).

Table 1. Studies on hydrothermal pretreatment of TWAS for VFAs recovery.

Substrate Characteristics (for the Raw Sample Only)						HTP Condition		System Configuration		Significant Results		Reference
Substrate	TCOD	TS	VSS	pH	Solid Content	Temperature	Retention Time	Reactor Mode	Temperature	Solubilization	VFAs Production	
	g/L	g/L	g/L	-	%	°C	min	B/S	M/T	%	g VFAs/L	
TWAS	49.6	34	22.7	6.3	3.4	150–240	5–30	Batch	Mesophilic	49.0	2.52	[29]
TWAS	62	44.19	33.38	ND	4.4193	150–270	ND	Batch	Mesophilic	46	3.31	[33]
TWAS (Lab scale)	108	99.8	75.7	ND	9.98	170	5–30	Batch	Mesophilic	48.1	0.52	[36]
TWAS (Pilot scale)	90.17	76.8	54		7.68	170	5–30	Batch	Mesophilic	ND	0.37	
TWAS	ND	40.59	31.86	6	4.05	120–200	60	Batch	Mesophilic	ND	2.94	[37]
WAS	166	167	ND	ND	16.7	60–180	15–180	Batch	Mesophilic	85	2.5	[38]
TWAS	68.68	60.15	45.26	6.41	15.67	35–55	30	Semi-continuous	Thermophilic	15.5	5.15	[39]
TWAS	88.8	ND	ND	7.6	ND	170–320	30	Batch	Mesophilic	ND	0.58	[40]
WAS	55.3	ND	ND	ND	ND	70–90	15–60	Batch	Mesophilic	17.8	2.74	[41]
Urban WAS	ND	12.91	8.58	7.15	1.29	60–120	ND	Batch	Mesophilic	43	ND	[42]
Industrial WAS	ND	13.44	7.92	8.07	1.34	60–120	ND	Batch	Mesophilic	67	ND	
WAS	134	ND	ND	6.4		130–180	ND	Semi-continuous	Mesophilic	22.3	4.54	[43]

ND: Not determined.

3. Hydrothermal Pretreatment and Fermentation

Various studies have been conducted to examine the effect of hydrothermal pretreatment on the fermentation of waste-activated sludge. Table 1 summarizes batch fermentation tests carried out to assess pretreated sludge potential for VFA recovery. All the studies reviewed were carried out at 35 °C in a thermostatic room, with anaerobic sludge from a

mesophilic anaerobic digester fed with raw secondary sewage sludge for the hydrolysis experiments. A wide range of pretreatment temperatures ranging from 60 to 270 °C, retention times from 30–180 min, and pressures within 5–8 bar were used for the fermentation processes under a mesophilic environment.

Most of the studies [33,36–40] reported a relatively increased VFA production under high temperature ranges from 160 °C to 180 °C. For the fermentation process to be efficient, other studies reported that an optimum temperature of 100 °C to 180 °C is required to disrupt the cell walls and make them readily available for biological disintegration [33,41]. A fermentation process operated below the standard temperature is likely to achieve low quantities of VFAs [39,41].

Most authors reported that 55–60% of volatile solids were destroyed, and sludge dewaterability was improved [37,40]. Furthermore, waste-activated sludge treated with the hydrothermal pretreatment technique resulted in a 35 to 50% increase in VFA yields compared with the raw sample, and a significant increase in SCOD has also been observed as compared to the raw samples [33,37,40,42].

Abe et al. [33] studied the effect of thermal pretreatment on thickened waste-activated sludge at different temperatures ranging from 120 °C to 200 °C and a 60-min retention time to reduce sewage sludge volume. This study revealed the highest gas production and VSS destruction efficiency of 77% at a VSS loading rate of 8 g/L/d. The digestion efficiency was about 30% higher than anaerobic digestion without sludge pretreatment. This study achieved the highest VFA production of 2.94 g/L at a pretreatment temperature of 200 °C.

Kim et al. [33] assessed the effect of hydrothermal pretreatment of waste-activated sludge to enhance biogas production by anaerobic digestion at a temperature range of 150 to 270 °C. According to this study, the solubilization of particles significantly increased from 3 to 31% after HTP. VFA production of 3.31 g/L was achieved, which is a five-times increase compared to the raw sample at a pretreatment temperature of 210 °C. Xue et al. [38] also studied the effect of thermal hydrolysis on organic matter solubilization and anaerobic digestion of high-solid sludge. The study also concluded that the best pretreatment temperature for VFAs and biomethane production from high-solid sludge is 160 °C.

Donoso-Bravo et al. [36] carried out laboratory and pilot-scale experiments to evaluate the influence of thermal pretreatment time on waste-activated sludge properties and anaerobic biodegradability. This study analyzed six experimental conditions from 0 to 30 min of hydrolysis time for a 170 °C pretreatment temperature. The degree of solubilization increased from 31% to 45% for laboratory-scale experiments and 47% to 70% for pilot-scale experiments. The highest VFA production of 0.52 g/L was achieved at a pretreatment temperature of 170 °C for a pilot-scale experiment. According to this study, HTP conditions had a positive effect on anaerobic biodegradability, and the maximum biogas production rate was more affected by pretreatment time than total biogas production.

Our previous study investigated hydrothermal pretreatment's impact on organic solubilization and anaerobic acidification of thickened waste-activated sludge [40]. For this study, 15 different hydrothermal pretreatment scenarios were developed, with pretreatment temperatures ranging from 150 to 240 °C, retention times 5 to 30 min, and pressures from 5 to 33.64 bar. Accordingly, the highest solubilization of 48% was achieved at the HTP condition of 200 °C. The highest VFA production yield of 5.38 g/L was obtained at the HTP condition of 190 °C.

On the other hand, Appels et al. [41] and Ennouri et al. [42] studied the effect of low-temperature thermal pretreatment on sludge solubilization. According to Appels et al. [41], the efficiency of the anaerobic digestion slightly decreased for sludge pretreated at 70 °C than 90 °C. At 90 °C pretreatment temperatures, VFA and biogas production slightly increased with the 60 min retention time. Ennouri et al. [42] also conducted research to address the effect of thermal pretreatment on the microbial populations' balance and biogas production during anaerobic digestion of WAS coming from urban sludge and industrial sludge. This study used a pretreatment temperature ranging from 60 to 120 °C. The highest

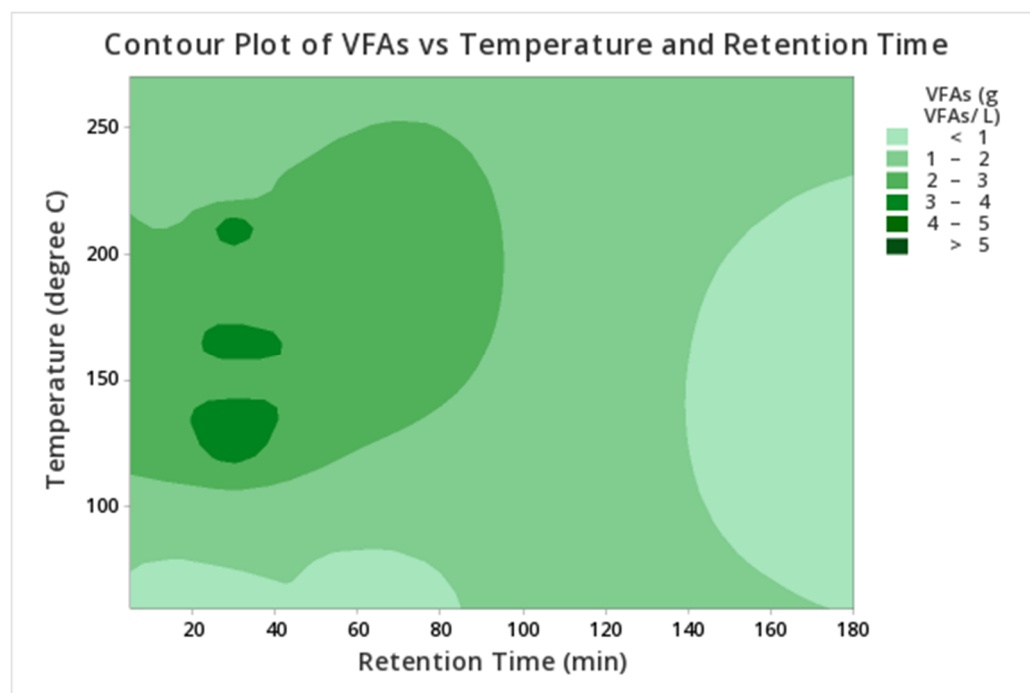
VFA yields of 0.23 g/L and 0.28 g/L were obtained with urban and industrial sludge, respectively, pretreated at 120 °C.

Table 1 also summarizes HTP operation in a semi-continuous configuration reactor. Though very few studies were carried out using this technology, Zhang et al. [42,43] conducted research on waste-activated sludge hydrolysis and short-chain fatty acid accumulation under mesophilic and thermophilic conditions.

According to Zhang et al. [42,44], the VFA yield increased from 0.07 gCOD/gVSS to 0.31 gCOD/gVSS under mesophilic conditions, indicating a 45% increase in VFA yield. Regarding the thermophilic condition, the highest VFA yield was 0.39 gCOD/gVSS, a 55% increase. These studies revealed slightly higher results when thermally pretreated samples were managed in a thermophilic environment than in a mesophilic condition, but most of the research reviewed was conducted in mesophilic conditions because the cost of heating is lower than thermophilic [44–46].

Morgan-Sagastume et al. [43] also conducted research using a semi-continuous reactor. This study focused on the production of volatile fatty acids by fermenting waste-activated sludge, pretreated in full-scale thermal hydrolysis ranging from 130 to 180 °C. Accordingly, a two- to five-times increase in VFA yield and a four- to six-times increase in VFA production rate was obtained compared to the fermentation of raw WAS.

Generally, HTP parameters impact VFA production differently, and Figure 2 explains these correlations. Figure 2a illustrates the relationship between COD solubilization and two main HTP factors, temperature and RT, while higher VFAs are produced as the temperature increases up to 200 °C and retention time goes below 60 min. Figure 2b shows the impact of COD solubilization on VFA production during anaerobic fermentation based on the data from the literature. As the sludge disintegration rate increases, the VFA-producing bacteria function better by converting the readily biodegradable compounds to VFAs. The high COD solubilization during HTP overcomes the hydrolysis challenge and impacts the fractionation of the VFAs. It has been reported that different HTP conditions are associated with an enhancement in the production of certain types of VFAs [44,45], while in general, acetic acid has been reported to be the most abundant VFA, followed by propionic acid.



(a)

Figure 2. Cont.

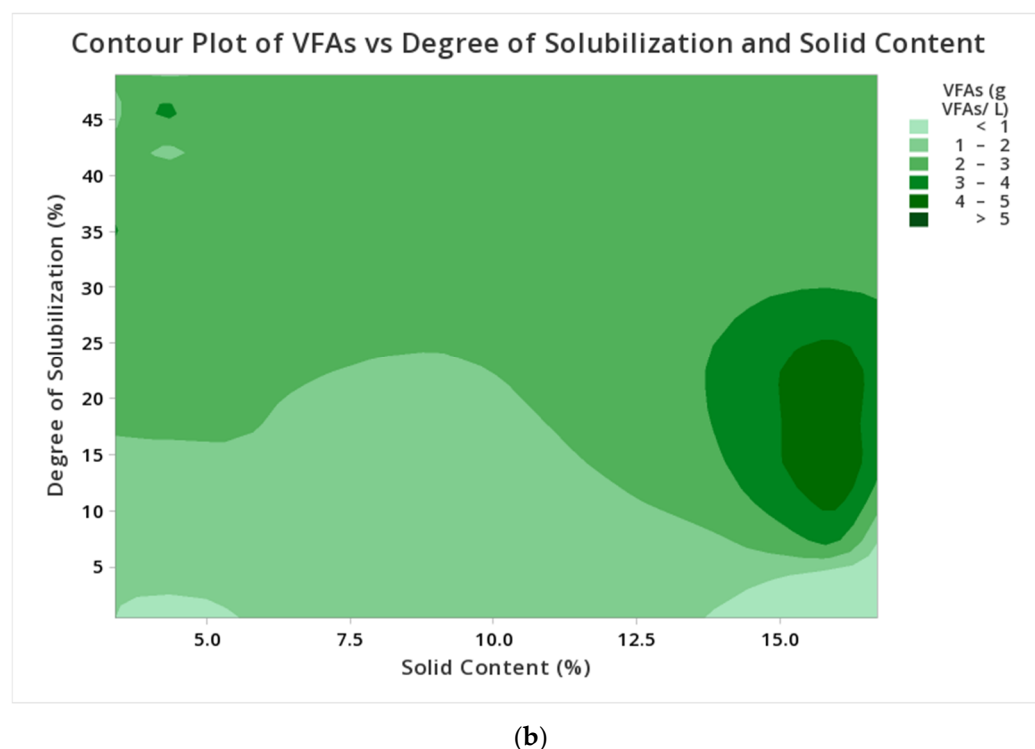


Figure 2. Contour plots for VFA production vs. solubilization and hydrothermal pretreatment parameters, (a) Contour plot of VFA vs. temperature and retention time, (b) Contour plot of VFA vs. COD solubilization due to HTP and solid content of sludge.

In conclusion, most of the reviewed studies on the fermentation of TWAS revealed that the HTP condition operated both in batch and in semi-continuous reactors increased dissolution of organic matter and suspended-solid removal efficiency. Moreover, higher VFA yield was observed at pretreatment temperature ranges from 160 °C to 180 °C, RT ranges between 8–30 min, and SC of 3–18%.

4. Hydrothermal Pretreatment and Anaerobic Digestion

Several studies have been conducted to assess the effect of HTP on the anaerobic digestion of thickened waste-activated sludge. These studies were conducted at pretreatment temperature conditions ranging from 70 °C to 275 °C, matching with different retention times of 30 to 180 min. According to the findings of these studies, a pretreatment temperature in the range of 175 °C to 200 °C with a 60 min retention time was the optimal condition for increased biogas production [1,5]. Even though higher pretreatment temperatures resulted in increased biogas production, the temperature range beyond 200 °C showed a significant reduction in biogas production. Reported temperature increases above 200 °C may result in the formation of melanoidins or the Maillard reaction [47], which results when sugars and amino acids combine at high temperatures. The Maillard reaction could significantly retard biomethane production during hydrothermal pretreatment.

Table 2 summarizes various studies conducted using the HTP technique in batch reactors. Most of the studies reviewed showed a direct linear relationship between temperature increase and biomethane production up to 200 °C. Generally, up to a 35% increase was observed in the biodegradability of waste-activated sludge, resulting in higher biogas production, although severe temperatures beyond 200 °C can negatively impact the AD process. Recent studies have shown that hydrothermal pretreatment of WAS subjected to a pretreatment temperature range of 100 °C to 300 °C resulted in improved SCOD concentration by around 35% compared to the raw sample [33,48–50]. The optimum thermal temperature was also reported to be between 180 °C and 210 °C for increased biogas production, which is 55% higher compared to untreated samples [33].

Table 2. Studies on hydrothermal pretreatment of TWAS for biomethane recovery.

Substrate	Substrate Characteristics (for the Raw Sample Only)					HTP Condition		System Configuration		Significant Results		Reference
	TCOD	TS	VS	pH	Solid Content	Temperature	Retention Time	Reactor Mode	Temp	Degree of Solubilization	Methane Production Yield	
	g/L	g/L	g/L	-	%	°C	min	B/S	°C	%	mL CH ₄ /g VS	
WAS	62	44.19	33.38	ND	4.4	150–270	30	Batch	Mesophilic	47.4	240	[33]
WAS				7.15	14.6	170	60	Batch	Mesophilic	ND	155.5	[34]
WAS	166	167	150.3	ND	16.7	60–180	15–180	Batch	Mesophilic	ND	1070	[38]
WAS	ND	12.91	8.58	7.15	1.3	60–120	30	Batch	Mesophilic	ND	420	[39]
	ND	13.44	7.92	8.07							370	
WAS	55.3	ND	ND	ND	ND	70–90	15–60	Batch	Mesophilic	17.8	378	[41]
WAS	52.4	39.1	28.5	7.76	3.9	40–80	60–300	ND	ND	20.3	ND	[48]
WAS	169	ND	ND	ND	14	75–200	15–90	Batch and continuous	Mesophilic	ND	230	[49]
WAS	169	ND	ND	ND	14	75–200	15–90	Batch and continuous	Mesophilic	ND	230	
TWAS	0.75	ND	ND	ND	ND	140–370	30–360	Batch	Mesophilic	ND	286	[50]
WAS1	17.4	17.2	12.1	ND	1.7	130–170	30	Semi-continuous	Mesophilic	ND	228	[51]
WAS2	17.7	16.9	12.5	ND	1.7	130–170	30	Semi-continuous	Mesophilic	ND	330	
TWAS	51.6	49.8	36.8		4.9	150–170	30–60	Batch	Mesophilic	15.7	28	[52]
WAS	27.7	38	26	6.7	3.8	121	30	Batch	Mesophilic	17.6	135	[53]
WAS	ND	157.4	108.2	ND	15.7	175	60	Batch	Mesophilic	0.5	200	[54]
TWAS	54.6	110	40	7.5	10–11	160–180	30–240	Batch and continuous	Mesophilic Thermophilic	41 37	250 200	[55]

ND: Not Determined.

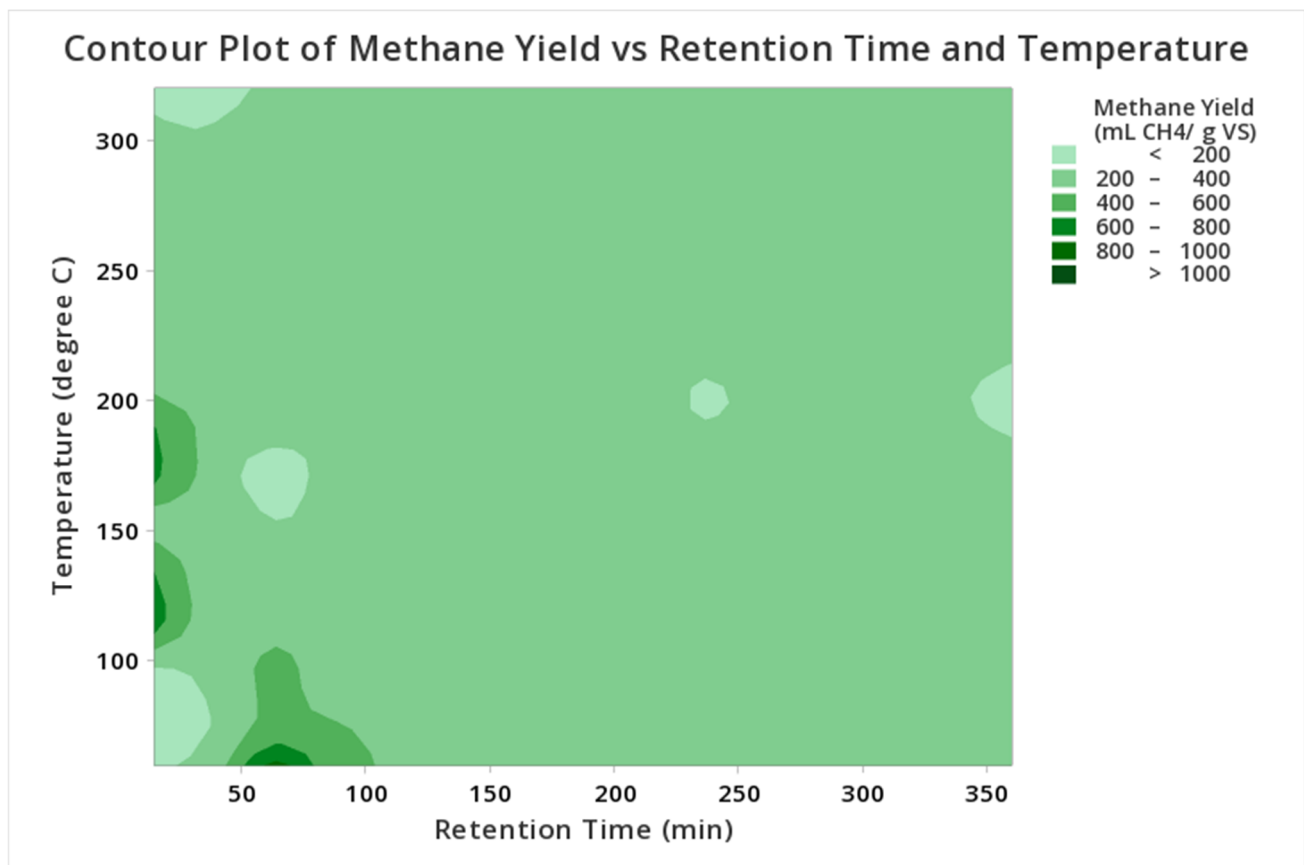
Temperature and retention time are considered the two most important parameters that affect the hydrothermal pretreatment of WAS. Almost all the reviewed articles have addressed the effect of pretreatment temperature on biogas production. Most of the studies reported that HTP increases the hydrolysis of WAS up to a specific temperature range. Some of the articles reported that temperatures higher than 180 °C result in a decrease in the biodegradability of sludge [33,34,51,52]. Others reported that pretreatment temperatures higher than 200 °C caused an adverse effect on the AD process [1,34]. Therefore, depending on the nature of the waste, the temperature point where inhibitory compounds are formed is different.

On the other hand, retention time significantly affects the solubilization and degradability of organic matter when the waste is processed at a low pretreatment temperature [39,41,48,53]. However, compared to temperature, retention time shows little effect on the hydrolysis of WAS when treated with a temperature greater than 100 °C [1]. These findings are proven by Figure 2a, illustrating different combinations of temperature and RT and their impact on methane production.

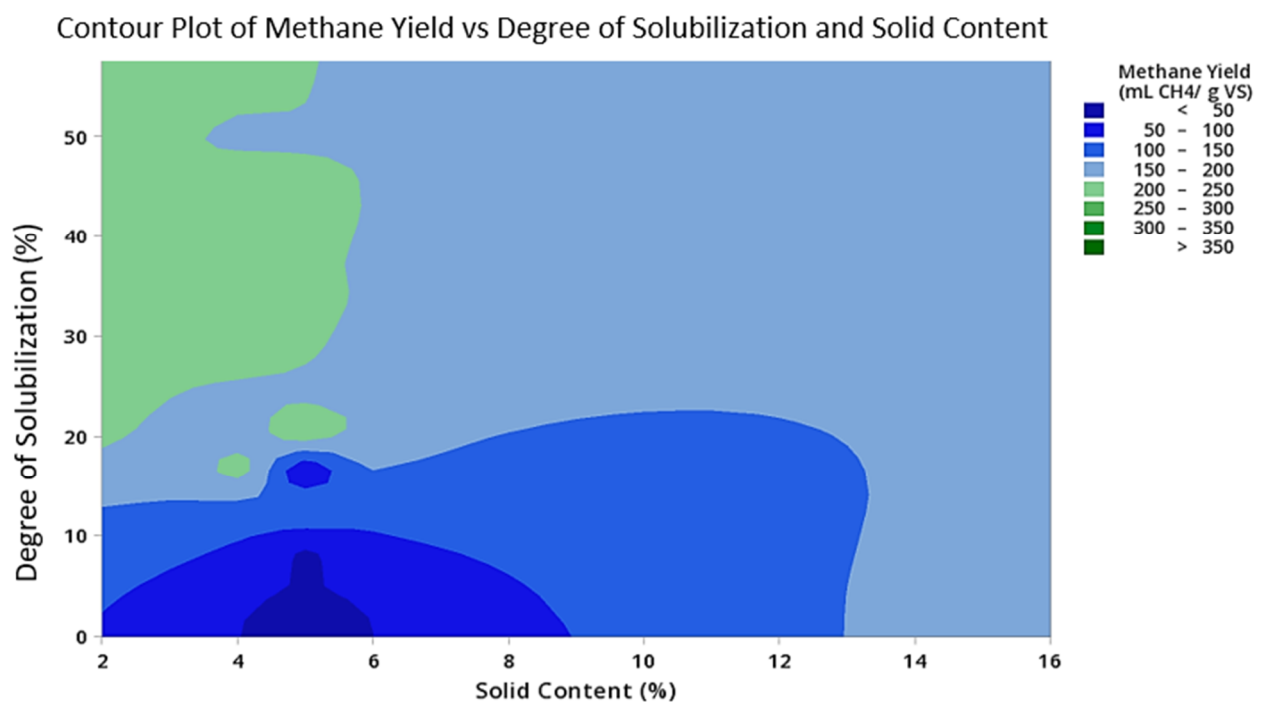
Further, the SC of the sludge significantly impacts methane production ($p < 0.005$). As the sludge SC increases to 12% there is higher methane production potential. Figure 3b shows the relationship between SC and methane production yield based on the literature findings studied in this article. As seen in the Figure 3, increasing the SC results in an increase in methane yield but the highest methane production was observed for the 3–6% SC, while keeping in mind that this was due to COD solubilization. As mentioned earlier, COD solubilization directly impacts methane production, and the higher the COD solubilization, the better the AD performance.

Ferrentino et al. [52] studied the effects of thermal hydrolysis (TH) pretreatment on anaerobic digestion (AD) under mesophilic conditions (35 °C). In this study, thickened sludge from a wastewater treatment plant (WWTP) was thermally treated under two different temperatures (150 °C and 170 °C) and reaction times (30 and 60 min). The study revealed a significant increase in soluble COD compared with the untreated or raw sludge when processed at a pretreatment temperature of 170 °C for 60 min. The thermal hydrolysis pretreatment of the sludge also accelerated the AD process and resulted in increased biogas yield ranging between 17 and 24%. On the other hand, Chen et al. [50] researched the hydrothermal conversion of sewage sludge, focusing on the characterization of liquid products and their methane yields under different temperatures (170–320 °C) and residence times (0.5–6.0 h) through AD. Results showed that the methane yield achieved 286 mL CH₄/g COD when the pretreatment temperature was 170 °C. In comparison, methane yield was decreased to 136 mL CH₄/g COD at 320 °C. The methane yield also decreased with the increase in residence time beyond 0.5 hrs.

Xue et al. [38] studied the effects of thermal hydrolysis on organic matter solubilization and anaerobic digestion of high-solid sludge under mesophilic conditions. This study showed that pretreatments at high temperatures (120–160 °C) accelerated the digestion rate and increased the biogas yield following biomethane production tests (BMP). Meanwhile, Liu et al. [54] investigated the effect of thermal pretreatment on municipal biomass wastes' physical and chemical properties. Their results showed a 34.8% methane yield increase and a doubled methane production rate after thermal pretreatment at 175 °C/60 min. Qiao et al. [34] also studied the evaluation of biogas production from different biomass wastes with or without hydrothermal pretreatment. After hydrothermal pretreatment at typical conditions (170 °C at 60 min), the biogas production of municipal sewage sludge increased 67.8% compared with the untreated sample. This high number might be due to the nature of the sludge source, as the sludge in this study was collected from a WWTP that uses a biological A/O process and membrane bioreactor, which results in different sludge than that collected from a typical activated-sludge process in terms of solid content and characteristics. Furthermore, the authors diluted the sludge by adding tap water before applying the thermal pretreatment.



(a)



(b)

Figure 3. Contour plots for methane production, (a) methane yield vs. temperature and retention time, (b) methane yield vs. degree of solubilization and solid content.

Nazari et al. [48] examined the relationship between the degree of solubilization and biodegradability of wastewater sludge in anaerobic digestion by low-temperature thermal pretreatment. According to this study, the optimum temperature, reaction time, and pH of the process were 80 °C, 5 h, and pH 10, respectively. This research showed that thermal pretreatments, carried out on seven different municipal wastewater sludges under the optimum operating conditions, produced an increased COD solubilization of 20.3% compared to the untreated sludge. The research also reported that the treatment did not significantly affect methane yields. Ennouri et al. [42] reported an increase in biogas production was obtained with urban (420 mL CH₄/g VS) and industrial sludge (370 mL CH₄/g VS) pretreated at 120 °C.

Appels et al. [41] also assessed the influence of low-temperature (70–90 °C) thermal pretreatment on sludge solubilization, heavy metal release, and anaerobic digestion. At a higher pretreatment temperature of 90 °C, the biogas production increased significantly, up to 378 mL CH₄/g VS for 60 min, whereas the anaerobic digestion efficiency slightly decreased for sludge pretreated at 70 °C.

Observation of HTP impact on AD in batch experiences was also validated through more reliable experiments in semi-continuous mode. Table 2 also reports the hydrothermal pretreatment of waste-activated sludge followed by semi-continuous BMP experiments. Results from semi-continuous experiments also confirmed the findings of the batch BMPs reporting the optimum pretreatment temperature of 170–190 °C with retention time ranging between 15–90 min.

Bougrier et al. [51] conducted research to investigate and compare the impact of thermal sludge pretreatments on the semi-continuous anaerobic digestion of two waste-activated sludge samples collected from different urban wastewater plants. The studies were conducted at thermal pretreatments of 130–170 °C and a pH of 10 for a 30 min retention time to enhance anaerobic digestion performance compared with untreated raw samples. This research revealed that an organic sludge processed at a pretreatment temperature of 170 °C resulted in a significant increase in anaerobic digestion performance, with an 80% improvement in biogas yield and removal of matter. Choi et al. [49] also assessed the enhancement of methane production in anaerobic digestion of sewage sludge by thermal hydrolysis pretreatment using a temperature range of 75–200 °C and 15–90 min retention time. This study found the optimal conditions at 180 °C of reaction temperature and 76 min of reaction time. On the other hand, Wei et al. [56] studied the effects of HTP on the performance of two-stage anaerobic digestion of food waste. They reported that the highest biomethane yield, 591 mL/g VS, was obtained at an HTP temperature of 140 °C, which was about 12% higher than that obtained from the untreated sample. In another study, the biomethane yield of 878 mL/g VS was achieved from pretreated food waste with an HTP at 220 °C, compared to 637 for the untreated sample [57].

Furthermore, aside from the main HTP parameters (temperature, RT and SC), combining the HTP with other pretreatment methods significantly influenced the sludge disintegration properties. Table 3 summarizes studies on HTP combined with either chemical, mechanical, or biological pretreatments. It was found that the combination of HTP with another pretreatment has a high potential of enhancing the COD solubilization by up to 50%. Among all the pretreatments, the HTP and alkaline combination is one of the most promising technologies utilized in the industry.

In conclusion, thermal hydrolysis pretreatment has a reasonably positive effect on the AD process [1–3,10,13,15,17]. For instance, pretreatment by thermal hydrolysis under high temperatures between 160–200 °C and retention time of 0–60 min has an important effect on process enhancement. This pretreatment temperature and retention time are considered optimum conditions for relatively higher VFA and biogas production. On the other hand, operating the thermal hydrolysis process below or above the standard condition might affect the desired output.

Table 3. Studies on Combined hydrothermal pretreatments prior to AD.

	Substrate	Pretreatment Condition	Process	Impact on Solubilization	Impact on BMP	Reference
1	WAS	Alkaline HTP—pH 12 using 10 M NaOH + 134 °C for 30 min	continuous, 15-day SRT	37% disintegration degree, 28% improvement in VS reduction	130% improvement in daily methane production	[54]
2	WAS	Alkaline HTP—0.2 mg NaOH/mg VS + 190 °C, 10 min	BMP	36% solubilization of VS	113% increase in methane production	[58]
3	pulp and papermill sludge	HTP and enzyme—150 °C for 10 min + Accelerate 1500, 0.07 g/g VS at 50 °C for 72 h	thermophilic BMP	COD solubilization increased by 9 times	methane yield increased by 19%	[59]
4	pulp and papermill sludge	ultrasonic and HTP—45 kHz, 30 min, 150 °C for 10 min	thermophilic BMP	COD solubilization increased by 9 times	methane yield increased by 31%	
5	pulp and papermill sludge	ultrasonic, HTP and enzyme—45 kHz, 30 min, 150 °C for 10 min, accelerate 1500, 0.07 g/g VS at 50 °C for 72 h	thermophilic BMP	COD solubilization increased by 10 times	methane yield increased by 21%	
6	sugarcane bagasse	HTP and alkaline, 180 °C for 20 min and 8.5% Ca (OH) ₂	BMP	83 and 46% degradation of hemicellulose and lignin	47% increase in methane production	[60]
7	algal bloom	HTP and acid, 2% H ₂ SO ₄ , 135 °C for 15 min	2 stage fermentation	Increased sugar yield by 94.5%	33% increase in methane production	[61]
8	WAS	FNA and heat—0.7 mgHNO ₂ -N/L, 55 °C, 24 h, pH 5.5	BMP	-	26% methane improvement compared to control and 16% improvement in FNA only	[62]
9	TWAS	FNA, acid and alkaline combined with HTP—170 °C, 30 min	BMP	COD solubilization increased by almost 50% with thermochemical pretreatment	45–55% improvement in methane production compared to the raw sample	[63]

5. Full-Scale Hydrothermal Pretreatment Technologies

Thermal hydrolysis becomes a vital part of the AD process to decompose and disintegrate substantial parts of the solid portions of the sludge into simpler and soluble molecules [23]. Different literature has reported that the anaerobic digestion process could achieve up to 60% reduction of solids after the thermal hydrolysis process [1,2,26,29,31,33,34]. Thermal hydrolysis also improves sludge dewaterability [26,31,33].

Table 4 summarizes some of the commercial methods that have been developed for the thermal hydrolysis of primary and secondary sludge, biosolids, and biomass before and after the AD process. The methods were developed based on the type and characteristics of the sludge being processed. Each technology defined its own specific thermal temperature condition and retention time for improved biogas production and solubilization of solids. Every year thousands of dry ton waste is treated using these large scale facilities (Figure 4).

Table 4. Comparison of commercially available full-scale hydrothermal pretreatment/post-treatment technologies.

Technology	Mechanisms				Reactor Mode	Waste	Heat Transfer	Sludge Flow	Number of Installations in WWTPs by 2021	Footprint
	Retention Time	HTP Conditions Temperature	Solid Content	Steam Injection						
Cambi	30 min	165 °C	12–15%	Yes	Series of batch tanks	Primary and secondary sludge	Intermittent Steam Injection Based on Timers and Number of Reactors	Pumps	41	No
Exelys	30 min	165 °C		No	Continuous plug flow reactor	Primary and secondary sludge	Continuous Steam Injection	Pumps	3	No
Haarslev	20 min	165 °C		Yes	Continuous plug flow reactor	Biosolids	Continuous steam injection	Pressurization	ND	Yes
Lystek		75 °C	13–16%	ND	Continuous plug flow reactor	Biosolids	Low pressure steam injection	Pumps	ND	No
Sustec	30 min	165 °C	10–12%	No	Continuous plug flow reactor	Biomass	Continuous steam injection	Pumps	1	No
Lysotherm	30 min	165 °C	3–5%	No	Continuous plug flow reactor	WAS	Continuous steam injection	Pumps	3	No

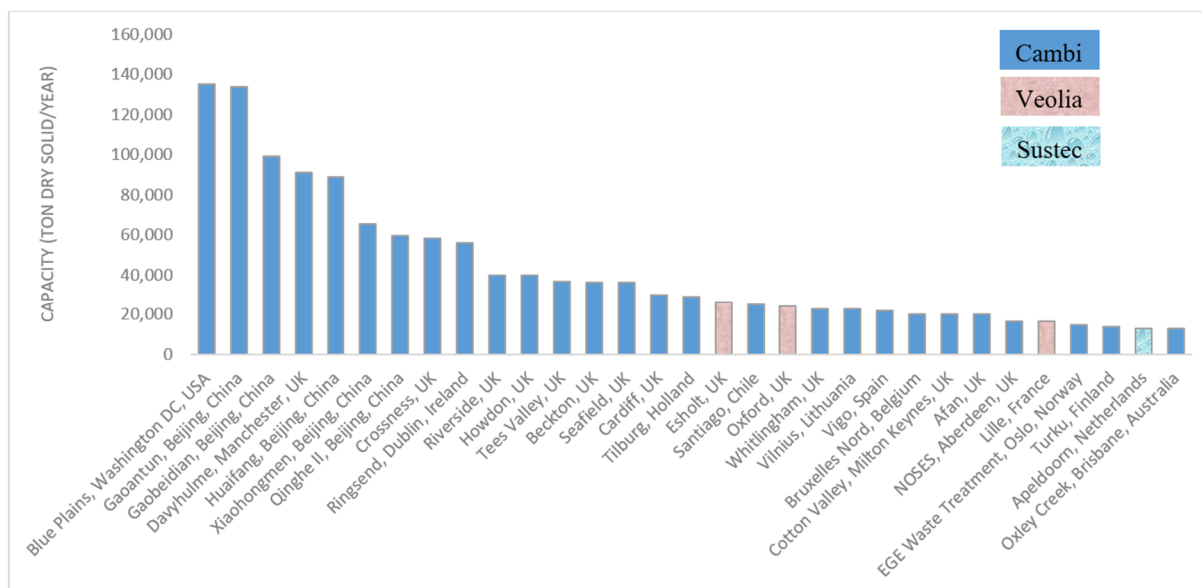


Figure 4. Largest full-scale thermal hydrolysis plants as of 2021 (Source: Adapted from companies' websites).

Cambi, Inc. (Asker, Norway) has developed a thermal hydrolysis process based on the type of sludge being processed. This company reported setting the HTP condition at 165 °C for a 30 min treatment depending on the characteristics of the processed sludge. A significant improvement in biogas production by about 150% is reported. The solubilization of solids is about 30%, as per the company's website. The patented thermal hydrolysis process (THP) is a pretreatment of sludge combined with anaerobic digestion. Here, THP works by dissolving and disintegrating sludge using pressure and temperature. To increase the efficiency of THP, the sludge needs to be dewatered at around 16% solid concentration before passing to the equalization tank. The equalization tank is responsible for accommodating large flow-rate variations, which is essential for thermal pretreatment to function at a constant flow rate. The pre-heated sludge is then introduced to the reactor and heated again, with the higher temperature reaching 165 °C and 8 to 9 bar pressure. After 30 min of retention time, the treated sludge is pumped into the flash tank with a solid concentration of approximately 12% to 15%.

Exelys, a subsidiary of Veolia group, has reported solubilization of solids by 30% at 165 °C for 30 min, increasing biogas production by 150%. When HTP is associated with conventional digestion, it also delivers around a 40% reduction of sludge, which could be readily available for disposal, and 30% more biogas production. The process works in batch mode, combining thermal hydrolysis and anaerobic digestion. The dehydrated sludge goes through a batch thermal hydrolysis phase during which steam is injected into reactors operating under specific pressure (9 bar) and temperature (165 °C) conditions for approximately 30 min. The process handles all kinds of organic, industrial, or municipal sludge and can also handle grease. The advantages of using such thermal hydrolysis pretreatment processes are reduced sludge volume, improved sludge quality, and increased biogas production.

6. Conclusions

The article review conducted by this research reviewed the parameters affecting the hydrothermal pretreatment prior to fermentation and AD. The impact of individual parameters such as temperature, RT, pH, SC, and combined HTP and other pretreatments were analysed. According to this study, HTP improves the solubilization and biodegradability of the TWAS and enhances VFA and biomethane production.

The following major conclusions are drawn:

- HTP condition operated both in batch and semi-continuous reactors increased dissolution of organic matter and suspended-solid removal efficiency.
- Most of the reviewed articles on fermentation of TWAS revealed that higher VFA yields were observed at pretreatment temperature ranges from 160 °C to 180 °C. Waste-activated sludge treated with the hydrothermal pretreatment technique resulted in a 35 to 50% increase in VFA yields compared with the raw sample.
- Temperature, retention time, and solid content are considered the most important parameters affecting the hydrothermal pretreatment of TWAS, while the temperature is the dominant factor.
- HTP in the range of 175 °C to 200 °C with a 60 min retention time was the optimal condition for increased biogas production. At the optimum condition, a 30% increase in biodegradability of waste-activated sludge was generally observed, which resulted in higher biogas production.
- Most of the studies reported that HTP increases the hydrolysis of WAS up to a specific temperature range. The temperature range beyond 200 °C showed a significant reduction in VFA and biogas production. In addition, a lower temperature cannot efficiently decompose the complex organics in the AD process unless combined with other pretreatment techniques.

To further understand the impact of thermal hydrolysis on fermentation and AD, further research is required to intensify these processes. There is a great potential for reducing the HRT of the AD with HTP integration, therefore studying HRTs from 8 to 20 days would be valuable. Another gap in the literature to be filled is the different configurations of the HTP, fermentation, and AD, varying the HTP parameters and HRT of the fermentation and AD.

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