공학석사학위논문

Comparison Between Mesophilic and Thermophilic Anaerobic Digestions of Thermal Hydrolysis Pretreated Organic Wastes

열가수분해 전처리 유기성 폐기물의 중온 및 고온 혐기성 소화 비교 연구

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이 논문을 공학석사 학위논문으로 제출함

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LIU XIAOHUI의 공학석사 학위논문을 인준함

2018년 8월

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Abstract

Comparison Between Mesophilic and Thermophilic Anaerobic Digestions of Thermal Hydrolysis Pretreated Organic Wastes

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With the rapid growth of urban population and expansion of industries, the excessive production of organic wastes (e.g., food waste, swine manure, and waste activated sludge, etc.) has become a major environmental issue since last few decades. Anaerobic digestion (AD), by which microorganisms decompose organic compounds and convert them into renewable energy – methane, is widely accepted as a low-cost and sustainable alternative for organic wastes management.

The conventional AD is not profitable due to the low biodegradability of raw feedstocks. The rigid lignocellulosic biopolymers in swine manure, and to some extent, in food waste, the large fraction of cell wall/membrane and flocs found in waste activated sludge, encapsulate biodegradable organics and resist to be degraded by enzymes as well as microorganisms. Those natural characteristics greatly hinder the hydrolysis step in AD and limit biogas generation potential of aforementioned organic wastes.

In order to solve this problem, various physico-chemical methods prior to anaerobic digestion have been proposed for generating easily-degradable products, such as mechanical grinding, ultrasonic disintegration, chemical methods, thermal pretreatment, enzymatic and microbial application, etc. Among them, thermal hydrolysis pretreatment (THP), which utilizes high temperature and pressure to rupture rigid structures as well as disintegrate flocs, has been widely applied to sludge stabilization. However, the effects of THP on organic wastes are closely related to their intrinsic variabilities (e.g., nature, composition, and structure, etc.). The detailed comparison of THP's impacts on the biodegradability characteristics of food waste, swine manure, and waste activated sludge has not been revealed yet.

Generally, the AD of organic wastes is performed in a wide range of experimental conditions, from batch to continuous mode, and from mesophilic (30–45°C) to thermophilic (45–60°C) temperature regimes. In early researches, the influences of THP on anaerobic biodegradability of organic wastes are mostly evaluated at mesophilic temperature in lab-scale batch tests. The optimal temperature during subsequent AD after THP process is still unknown.

Therefore, the main objective of this study is to compare the impacts of THP and temperature (i.e., mesophilic and thermophilic) on various types of organic wastes (i.e., food waste, swine manure, and waste activated sludge). The biodegradability properties and overall mass balance of the three organic wastes with/without THP implement were investigated in BMP test. The AD feasibility and performance of raw/pretreated swine manure under both mesophilic and thermophilic temperatures were evaluated over a relatively long-term continuous stirred-tank reactors (CSTRs) operation.

The characterization results statistically revealed that THP enhanced volatile suspended solid (VSS) hydrolysis degree and solubilization of chemical oxygen demand (COD) for food waste, swine manure, and waste

activated sludge. THP led to a maximum 145.0 and 118.2% methane yield increase of swine manure and waste activated sludge, respectively except for that of food waste. Compared with mesophilic condition, thermophilic temperature did not show distinctive advantages as for enhancing methane generation potential of the three organic wastes in BMP test ($p > 0.05$). The mass balance analysis showed that the differences in overall methane production between raw and pretreated swine manure under the two temperature settings were not significant ($p > 0.05$) due to the loss of organic matters during pretreatment process.

The results of CSTRs operation demonstrated that the AD of pretreated swine manure obtained higher specific methane yield, greater organic solids reduction efficiency and higher COD solubilization level than that of raw substrates. Thermophilic temperature did not improve methane production of THP-treated swine manure, while leading to a lower methane generation from raw substrate due to a short-term free ammonia inhibition. The concentration of acetic acid exceeded the inhibiting threshold in thermophilic reactors, and the accumulation of propionic acid caused disturbance in the higher temperature situation.

In conclusion, THP was effective to improve the anaerobic biodegradability of swine manure and waste activated sludge. The methane reduction caused by organic substances loss should be taken into account. Thermophilic temperature did not significantly increase the methane production, and suffered higher risks of process unbalance and instability than that of mesophilic digestion.

Keywords: Anaerobic digestion; Thermal hydrolysis pretreatment; Mesophilic; Thermophilic; Organic wastes

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1. Introduction

1.1 Background

The production of organic wastes such as food waste, swine manure, and waste activated sludge, has increased at staggering rate in the last several decades. The main causes include rapid growth of urban populations, transition of living style, and dramatic industrialization, etc. Accumulation of those organic wastes as well as inefficient disposals result in numerous adverse impacts on environment and public health. At the same time, the availability of fossil fuels is decreasing, which forcing the worldwide demand for renewable and clean energy. Moreover, the increase of greenhouse gases in the atmosphere, which is caused by the consumption of fossil fuels as well as emissions from animal manure, leads to global climate change. Therefore, the development of sustainable and cost-effective technologies for organic wastes treatment, nutrients recycle, renewable energy production, and carbon footprint reduction, is an urgent and long-term issue faced by all of humanity.

Compared with various waste management methods (e.g., landfilling, composting, incineration, etc.), anaerobic digestion (AD) offers some advantages. During AD process, microbial consortia break down the organic matters and generate biogas in the form of methane and carbon dioxide. Through this biological process, the mass of wastes is reduced, nutrients and resources are recovered, and renewable energy is produced. Based on the above-mentioned facts, AD has been suggested as one of the most potential and sustainable strategies for organic wastes management, and attracted more and more attention from researchers and decision makers.

Although AD is favorable for degradation of organic wastes and biogas production, the first stage – hydrolysis, is commonly considered as a rate-limited step due to the existence of hare-biodegradable substances and rigid structures in solid organic wastes. Consequently, pretreatment methods prior to AD are proposed to improve hydrolysis and stabilization of organic wastes. Various pretreatment technologies, e.g., mechanical grinding, ultrasonic disintegration, chemical methods, thermal pretreatment, enzymatic and microbial pretreatments, have been investigated to improve the characteristics of organic wastes. Among the various alternatives, thermal hydrolysis pretreatment (THP) has been proven to be one of the most effective methods for sludge disintegration. During THP process, the flocs and cell structures are ruptured, the encapsulated organic matters are released into the digesters. Much more easily-biodegradable components are accessible to the microorganisms for subsequent degradation. However, the studies about the effects of THP on food waste and swine manure are relatively recent and limited.

There are many factors affecting the subsequent AD performance. In addition to substrate characteristics, temperature is one of the most influential factors (Labatut et al., 2014). Mesophilic (30–45°C) and thermophilic (45–60°C) temperatures are commonly suggested for AD process. Thermophilic condition is characterized with faster degradation rate, more pathogen reduction, and higher biogas production (Johansen et al., 2013) However, mesophilic AD is superior in terms of lower energy requirement, better stability and less inhibition risks (Labatut et al., 2014). Thus, mesophilic condition is mostly applied in AD plant in practice.

The lab-scale batch reactors are commonly utilized to predict the anaerobic biodegradability of specific organic wastes. The commercial-size, continuous-flow digesters are widely operated for biogas generation in most AD plant. There are many differences between batch reactors and

continuous-flow digesters. Except for the size and mode of operation, the thermodynamic conditions in continuous-flow digesters are constantly altered due to the periodic substrate feeding and accumulation of intermediate products (Labatut et al., 2011). However, in previous studies most evaluation of AD performance treating THP-treated organic wastes are performed in batch biochemical methane potential (BMP) test at mesophilic condition (Bonmati et al., 2001; Li et al., 2015; Xue et al., 2015; Zhou et al., 2013). The information from BMP assay is neither credible nor sufficient to predict the daily methane yields, process balance or stability in continuous-flow anaerobic digesters over a long-term operation.

Therefore, it is necessary to investigate the anaerobic biodegradability of food waste, swine manure and waste activated sludge before and after THP, and assess the overall mass balance with/without pretreatment. The optimal temperature for treating those organic wastes should be advocated as well. Furthermore, the applicability and feasibility of anaerobic digestion of raw and THP-treated swine manure in CSTRs over a relatively long-term operation should be presented and discussed for optimizing swine manure treatment.

1.2 Objectives

The main objective of this study is to reveal the effects of THP and temperature on the anaerobic digestion of food waste, swine manure, and waste activated sludge. The specific objectives are listed as follows:

(1) To investigate the effects of thermal hydrolysis pretreatment (THP) and temperature on biodegradability characteristics of food waste, swine manure and waste activated sludge

(2) To evaluate anaerobic digestion performance of raw/THP-treated swine manure in CSTRs under mesophilic and thermophilic conditions

(3) To assess the feasibility and process stability of raw/THP-treated swine manure under the two temperature regimes in CSTRs

1.3 Scope of study

The characteristics of organic wastes were analyzed to assess the influences of THP and temperature on the subsequent AD process. Both lab-scale BMP test and CSTRs were operated under mesophilic and thermophilic conditions. The physical-chemical parameters were monitored during operating period. The specific scope of this study is:

(1) Lab-scale anaerobic digestion

Lab-scale BMP assay and CSTRs were processed to evaluate the anaerobic biodegradability of organic wastes under mesophilic and thermophilic conditions. The optimal AD temperature for treating raw/THP-treated organic wastes was proposed.

(2) Determination of THP applicability

The methane generation potential and overall mass balance were considered for each type of organic wastes. The applicability and feasibility of THP for anaerobic digestion of organic wastes were evaluated.

(3) Assessment and monitoring of digestion process

The process stability and inhibitory factors were monitored continuously during digestion period. The relative phenomena and analysis will possibly be useful for optimization of THP as well as subsequent AD process.

2. Literature Review

2.1 Anaerobic digestion (AD)

Anaerobic digestion (AD) is a biological process and involves in various mechanisms. During AD process, microorganisms degrade organic matters in the absence of oxygen under suitable temperature regimes. Many kinds of bacteria break down complex organics into simple molecules, e.g., methane, ammonia, carbon dioxide, water, etc. AD is favorable for organic wastes management due to its advantages such as reduction of waste mass, elimination of unpleasant odor, reuse and recycle of nutrients, etc. The produced renewable energy – methane gas, can be used for heat, electrical energy, etc. AD has drawn much public attention and been widely applied for the treatment of municipal, industrial, and agricultural wastes for a long period.

Although some chemical reactions in AD are still not be recognized fully, the conventional anaerobic digestion process is commonly be divided to four major steps, i.e., hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The detailed biological process is shown in Fig 2.1.

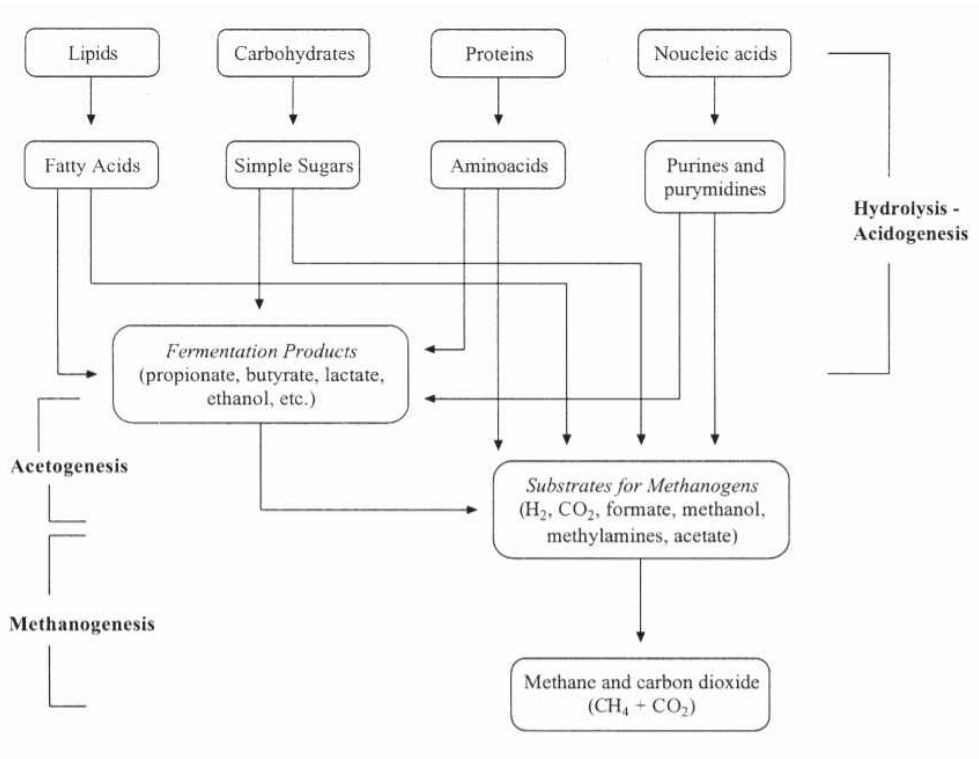


Fig 2.1 Bioconversion process during AD (Gavala et al., 2003)

2.1.1 Hydrolysis

Hydrolysis of organic substances is the first step in AD process. Under the effect of extracellular enzymes, hydrolytic or fermentative bacteria degrade complex macromolecules (e.g. carbohydrates, proteins, fibers, and fats, etc.) into soluble monomers or oligomers with the products of amino acids, sugars, and fatty acids (Surendra et al., 2014). For high solids organic wastes, hydrolysis is widely been treated as the rate-limiting step.

2.1.2 Acidogenesis

The second step – acidogenesis, includes fermentation and anaerobic oxidation (β-oxidation), which is carried out by fermentative acidogenic and acetogenic bacteria, respectively. During this process, the substances produced in hydrolysis stage (e.g., sugars, amino acids, and organic acids) are being fermented further by acidogenic bacteria into volatile fatty acids (VFAs), CO_2, H_2S, alcohol, and other by-products.

2.1.3 Acetogenesis

In the third step – acetogenesis, acetogenic bacteria converts VFAs and alcohols into CO_2, acetate, H_2. Acetate can also be formed from H_2 and CO_2 by acetogenic bacteria (Khanal et al., 2011). Acetate is known as methane precursors for methanogens.

2.1.4 Methanogenesis

In the final stage, acetate, H_2, and CO_2 are transformed into a mixture of CH_4 and CO_2 by acetotrophic and hydrogenotrophic methanogens. Decarboxylation of acetate contributes about 70% produced CH_4 gas. The left small fraction of CH_4 originates from formic, propionic and butyric acids, and other organic matters (Surendra et al., 2014).

2.2 Organic wastes

2.2.1 Food waste

The food waste management has become a main environmental issue at both national and global scale. It has been reported that as high as 30–50% food has been wasted in food supply chains in North America and Europe. The amount of discarded food waste accounts for 1.3 billion tons annually (Gustavsson et al. 2011). The excessive food waste has caused many environmental problems, such as odor, leachate in collection and transportation, etc. In order to solve this issue, many technologies such as anaerobic digestion, composting, combustion, gasification, and landfilling, have been proposed and applied in practice. However, disposal of food waste by landfilling has been prohibited due to its low efficiency, emission of greenhouse gases, and groundwater pollution by leaching problems (USEPA, 2000). High moisture content in food waste also limits the utilization of thermo-chemical conversion methods, such as combustion and gasification (Zhang et al., 2007). Besides, composting encounters some resistance due to the requirement of relatively large places, and high standard of ambient temperature. Among the various alternatives, AD is the potential solution for food waste management. Food waste has high level of organic matters such as carbohydrates, fats, and proteins. Those components are relatively easier to be degraded in AD process (Pham et al., 2015). The characteristic of food waste has made it become a good candidate for AD with high methane production potential as well as nutrients recovery value. Nevertheless, the AD process is easily be affected by accumulation of volatile fatty acids and inhibition of ammonia (Veeken et al., 2000; Braum et al., 2003). The improvement of food waste properties by promoting

solubilization, biodegradability, accelerating rate-limiting step may optimize the AD of food waste.

2.2.2 Swine manure

The thriving livestock breeding has caused excessive production of animal wastes such as cattle, chicken, and swine manure, etc. It has been reported that over a billion tons of livestock manure is produced annually in the United States (Kellogg et al., 2000). Livestock manure management has become an important issue since it leads to excess nutrients in water bodies, mosquito breeding, and greenhouse gas emissions.

Among the vast livestock wastes, the swine manure accounts for large proportion. Swine manure is characterized by rich nitrogen content, high buffer capability and large fraction of lignocellulosic materials. AD is suitable for treating swine manure due to the following advantages. The AD process occurs naturally in the combination of microorganisms already existing in manure and that in inocula (Jurado et al., 2013). The greenhouse gas emission is reduced by anaerobic digestion of animal manure.

The hydrolysis step is considered as rate-limiting procedure for AD of animal manure because of high fraction of hard-biodegradable polymers (e.g., cellulose, hemicellulose, lignin, etc.) as well as their solid matrix structures (González-Fernández et al., 2008). Cellulose consists part of crystalline and amorphous structure. These cellulose fibrils are mostly independent and weakly bound through hydrogen bonding (Laureano-Perez et al., 2005). Lignin is non-water soluble and optically inactive, contributing to the resistance of microbial/enzymes decomposition (Fengel and Wegener, 1983). Besides, the degree of polymerization, moisture content, available surface area also limit the hydrolysis of animal manure (Bonmati et al., 2001). Consequently, the biodegradability of swine manure is low, which hinders its

pervasive application in biogas plant. The pretreatments aiming at rupturing fiber structures, releasing inner nutrients to digesters, and enhancing solubilization of organic particulates may be favorable for the improvement of AD efficiency.

2.2.3 Waste activated sludge

Annually, there are about 30,000 tons of dry sludge mass being generated from wastewater treatment plants (WWPTs) in European Union (Jiang et al., 2014). During the sewage and industrial wastewater treatment, the coagulant chemicals are added into wastewater for the primary settling operation. Then, the supernatant of primary clarifier undergoes aeration with microorganisms, which are mainly composed of bacteria and protozoa. The bacteria and protozoa degrade the supernatant in organic matters in primary settling procedure, resulting in rich biomass sludge, which is known as waste activated sludge (WAS) (Gebreeyessus et al., 2016).

WAS contains high moisture content, which is unsuitable for landfilling or incineration. AD is generally utilized for WAS treatment because of its advantages such as volume reduction, stabilization, and biogas production. However, hydrolysis is considered as the rate-limiting step during AD process. The flocs, cell wall and cell membrane are relatively restricted to be decomposed by anaerobic bacteria. Besides, the AD process of WAS takes relatively long time, and requires big size of digesters. Consequently, WAS management has accounted for up to 50% of the operating expenses of in a WWTP, which represents a major issue and demands a suitable solution urgently (Appels et al., 2008).

2.3 Thermal hydrolysis pretreatment (THP)

In order to increase the hydrolysis degree of organic matters, many physico-chemical pretreatment methods prior to AD have been studied a lot in previous researches. The thermal hydrolysis pretreatment (THP) has been proven to be one of the most effective alternatives. During THP process, the substrates are heated with steam from boiler at high temperature and pressure. After the setting period, the substrates undergo sudden decompression, resulting in hydrolyzed products. The hard-biodegradable materials and their rigid structures are ruptured, and the inner readily biodegradable organic materials are released. Consequently, Much more easily-degraded components are available for microorganisms, and the biogas production is improved greatly.

The effects of THP are largely dependent on pretreatment conditions, substrate characteristics, and subsequent AD operation (Carrere et al., 2016). Early studies investigated a wide range of optimal temperature and reaction time for THP process. 160–190℃ is favorable for waste activated sludge treatment (Bougrier et al., 2007) although 170℃ and 30 min retention time is optimal condition (Yoneyama et al., 2006). Lower temperature (< 100℃) and higher temperature (> 100℃) in THP treatment of animal manure were studied (Bonmati et al., 2001; Mladenovska et al., 2006; Yoneyama et al., 2006; Ferreira et al., 2014). These treatments showed enhanced methane production of animal manure at batch mesophilic reactors. Higher THP temperature (> 175℃) led to a decrease of methane yield of food waste at mesophilic AD temperature (Ariunbaatar et al., 2014). Since hydrolysis is not necessarily considered as the rate-limiting step for food waste treatment, the improvement of hydrolysis of food waste may contributed to methanogens inhibition.

2.4 Influences in AD

In AD process, many factors affect the AD performance, stability, and applicability. In order to ensure a favorable and optimal digesting condition, the key parameters should be considered and monitored, and the inhibiting factors are needed to be repressed frequently.

2.4.1 Feedstock characteristics

The AD performance is highly related to the physical properties and chemical compositions of the feedstock. Input feedstock provides necessary nutrient source for anaerobic microbes. Carbon and nitrogen sources are essential for the growth and metabolism of microorganism in anaerobic digesters (Kougias et al., 2013). Carbohydrate is the main carbon source, and protein offers the main nitrogen source for microbial communities. Proteins are converted into ammonium, which may lead to inhibition of AD process when it is in high concentration. The different carbohydrate, lipid, protein and fiber contents in feedstock result in various anaerobic biodegradability of organic wastes (Khalid et al., 2011). Besides, physical properties such as moisture content, particle size, surface area, structure, etc. strongly affect the design and operation of anaerobic digesters (Haweks, et al., 1980), which also has an obvious impact on biogas production and digestion efficiency.

2.4.2 Temperature

Temperature has a direct impact on the microorganisms in terms of composition, growth rate and metabolism reactions. In addition, temperature also affects the physico-chemical properties of digesters with regard to the

components, process kinetics, and stability (Riau et al., 2010). AD generally takes place at mesophilic (30–45°C) or thermophilic (45–60°C) temperature conditions, although mesophilic temperature is the most application in practice.

The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the reaction rate. The rate constant is then given by

$$k = A \times e^{-\frac{E_A}{R \times T}} \qquad \text{(Eq. 1)}$$

where: k = rate constant of a chemical reaction,

A = pre-exponential factor,

E_A = activation energy,

R = gas constant, and

T = absolute temperature (in kelvins).

Compared with mesophilic condition, thermophilic temperature improves the solubility of organic compounds, accelerates degradation rate of organic wastes (Khalid et al., 2002), improves the destruction of pathogens, and enhances the grow rate of methanogenic archaea, resulting in higher biogas production (Ahring et al., 2002; Appels et al., 2008). However, the biogas production under thermophilic condition may be lower than mesophilic situation due to the generation of volatile gases such as ammonia, leading to the inhibition of methanogenic activities (Fezzani et al., 2010).

Mesophilic temperature behaves better than thermophilic condition in some respects. Mesophilic AD requires lower energy demand than thermophilic reactors. In addition, mesophilic digestion is more stable and less sensitive to environmental conditions. The risk of ammonia inhibition is lower in mesophilic digesters than that in thermophilic ones, which is especially

favorable to deal with substances with high concentration of ammonia (Chen et al., 2008).

2.4.3 pH

A wide range of suitable pH for anaerobic digestion has been reported by many previous researchers. The optimal pH for anaerobic digestion has been found to be in the range of 6.5–7.5 (Liu et al., 2008). Similarly, Ward et al. (2008) reported that the favorable pH range for AD was 6.5–8.2, while the suitable pH range for hydrolysis and acidogenesis was 5.5–6.5 (Kim et al., 2003).

pH value in anaerobic digester can be affected by temperature and influent substrates. pH determines microbial community, biochemical reactions, and thermodynamic equilibrium in AD process (Labatut et al., 2014). The accumulation of VFA results in pH decrease, which consequently inhibits methanogenic activities and reduces methane production. However, the higher pH also has negative impact on biogas generation and contributes to buildup high concentration of free ammonia.

2.4.4 Volatile fatty acids (VFAs)

VFAs are the intermediate products in the first two AD steps – hydrolysis and acidification. VFAs supply the essential carbon source for microorganisms. However, high VFAs concentration may causes suppression of methanogenic activity, decrease of pH value, and consequently results in failure of digestion. VFAs concentration has been treated as a reliable indicator for anaerobic digestion process (Murto et al., 2004). In previous findings, it has been reported that when the concentration of acetic acid and butyric acid concentrations less than 2400 and 1800 mg/L, respectively, no

obvious inhibition of the activity of methanogens occurred; when the concentration of propionic acid exceeds 900 mg/L, the methanogenesis was seriously inhibited (Wang et al., 2009). However, there is no widely-accepted VFAs inhibiting concentration, due to the fact that various digesters have different capability of VFAs consumption. Some digesters can operate stable and effective at certain VFAs concentration, while others face serious process failure and inhibition in that VFAs level.

2.4.5 Alkalinity

Although anaerobic digestion has been widely studied for a long period, short-term process failure occurs oftentimes. When VFAs are accumulated due to some factors (e.g., overloading, temperature change, etc.), an overflow of protons happens, which decomposes the bicarbonates in the aqueous solution and produces CO_2, and consequently decreases the pH value in reactors (Palacios-Ruiz et al., 2008). Thus, effective indicators are required to monitor the process, relieve the risks of digestion inhibition. Alkalinity represents the capability of a digester to resist change in pH, reflects the buffer capability in the case of OLR, pH, nutrients change. Alkalinity and VFA concentration have become the important monitoring parameters since they provide an indication of imbalance, instability, and even process failure (Sun et al., 2016). Since alkalinity is closed related to VFAs concentration, it is always combined with VFAs concentration to exhibit the digestion status.

2.4.6 Ammonia

Ammonia is the product of degradation of nitrogenous compounds such as protein and urea (Kayhanian, 1999). In anaerobic digesters, the main

inorganic ammonia nitrogen exists in the form of ammonium ion (NH_4^+) and free ammonia (NH_3) (Sprott et al., 1986) Ammonia is an essential source for microorganisms to synthesize cell membrane and maintain stable pH range in anaerobic digesters. However, excessive ammonia always results in inhibition of methanogenesis. The threshold of ammonia inhibition is different in various anaerobic digestion conditions due to the various substrate characteristics, temperature, pH, etc. Many researchers have found a wide range of inhibiting ammonia concentration in anaerobic digesters, changed from 1.7 to 14 g/L (Chen et al., 2008).

Free ammonia has been considered as the major inhibiting factor in AD process and is much more toxic than ammonium ion. The reason is that free ammonia has the ability to permeate membrane freely (De Baere et al., 1984), which may cause imbalance of pH, and/or potassium deficiency (Sprott and Patel, 1986; Gallert et al., 1998). Early studies reported that when the concentration of free ammonia less than 200 mg/L, the anaerobic digestion process maintains steady (Liu et al., 2002).

3. Materials and Methods

3.1 Substrates and inocula

3.1.1 Substrates

The raw food waste (RFW), swine manure (RSM) and waste activated sludge (RWAS) were collected from waste treatment plant. The three kinds of organic wastes were processed thermal hydrolysis pretreatment in Halla Energy & Environment Co., Ltd (Fig 3.1). The raw substrates was first mixed with water to ensure the 80% water content. The pretreatment capacity was 40 kg each time. Before THP process, the reactor A was pre-heated to 170℃. The substrates were fed into the reactor A and heated with the steam from boiler (190.7℃, 12 bar). The THP took 30 minutes for each treatment. After the setting time, the substrates processed by sudden depression in reactor B, and then released into the atmospheric flash tank. The THP-treated food waste (TFW), swine manure (TSM), and waste activated sludge (TWAS) were obtained. The raw and pretreated substrates (Fig 3.2) were stored in a –20℃ refrigerator to prevent the volatilization of organic compounds and deterioration.

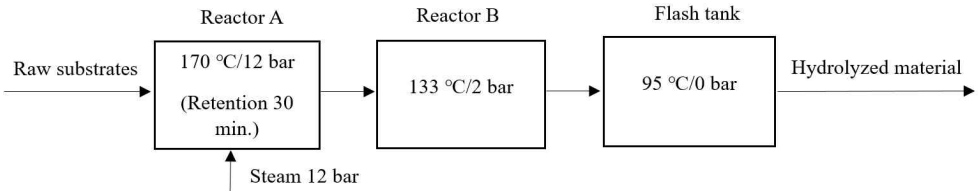


Fig 3.1 Simplified scheme of THP process

(a)

(b)

(c)

Fig 3.2 Raw and pretreated organic wastes: (a) food waste, (b) swine manure, and (c) waste activated sludge

3.1.2 Inocula

Sewage sludge was collected from one anaerobic digestion plant, which runs at steady state feeding with animal manure at mesophilic temperature. The inocula was passed through 500μm sieve to remove large particles. The inocula was acclimated at mesophilic (37±1℃) and thermophilic (50±1℃) conditions to eliminate endogenous biogas production.

3.2 Methods

3.2.1 Biochemical methane potential (BMP) test

3.2.1.1 BMP test design

Biochemical methane potential (BMP) assay was performed to evaluate methane generation potential of the specific substrates. The BMP operation was according to the design described by previous researchers as shown in Fig 3.3 (Angelidaki et al., 2009; Hansen et al., 2004; Müller et al., 2004). The total volume of serum bottle was 250 mL. The working volume was 100 mL, and the left fraction was used for headspace. The addition of substrates and inocula was based on a substrate-inoculum ratio of 1:2 (on VS base). After adding substrate, inocula and medium, the serum bottles were purged with N_2 for around three minutes. Then the serum bottles were tightly closed using rubber stoppers and aluminium crimps. The serum bottles were placed in two incubators, with the temperature of 35±1 and 50±1℃, for mesophilic and thermophilic conditions, separately (Fig 3.4). The agitation rate was 150 rpm for both incubators. In each incubator, three serum bottles without substrates addition were set for background (i.e., endogenous) methane production. The net methane production was calculated by subtracting methane production contributed from inoculum. The BMP test was carried out in triplicates. When there was no obvious biogas was generated in each assay vessel, the BMP test stopped.

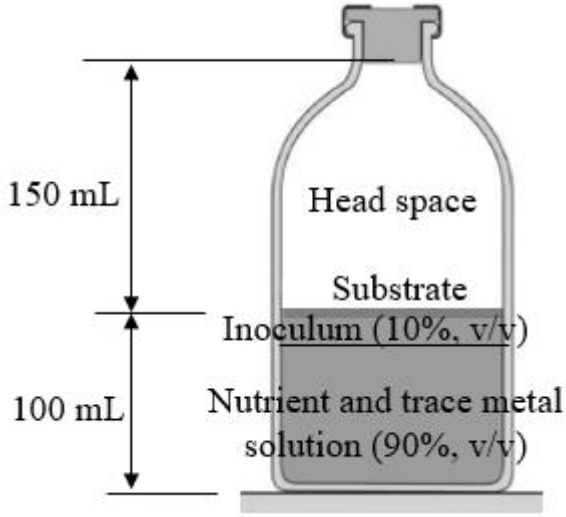


Fig 3.3 BMP assay vessel for anaerobic biodegradability test

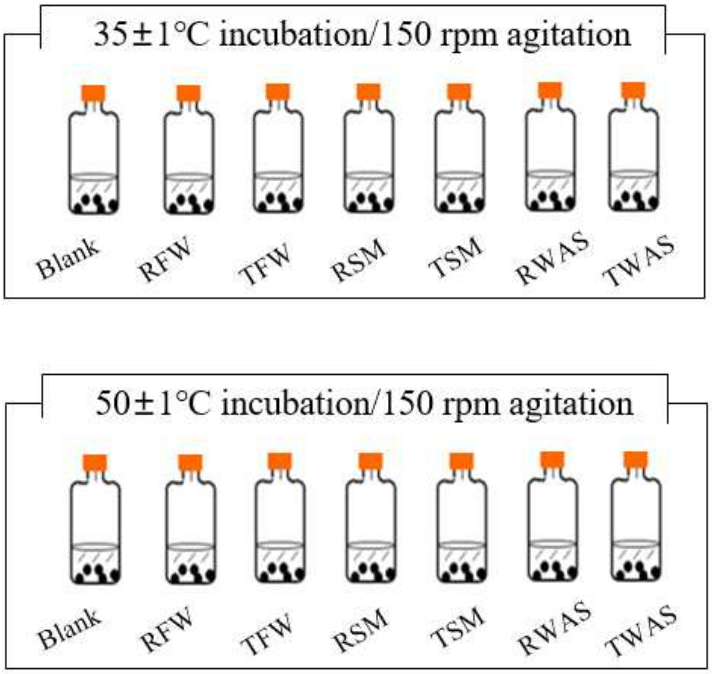


Fig 3.4 BMP assay setup

3.2.1.2 Kinetic study

The modified Gompertz model was utilized for kinetic studies.

$$M = P \times \exp[-\exp\frac{R_{max}e}{P}(\lambda - t) + 1] \quad \text{(Eq. 2)}$$

where: M = cumulative methane production (mL-CH_4/g-VS),

P = methane production potential (mL-CH_4/g-VS),

R_{max} = maximal methane production rate (mL-CH_4/g-VS·d^{-1}),

λ = lag phase time (day), and

t = time over the period (day).

The theoretical biochemical methane potential was based on the atomic composition of the waste material:

$$C_nH_aO_bN_c + (n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4})H_2O \rightarrow$$
$$(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8})CH_4 + (\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8})CO_2 + cNH_4$$

$$Theoretical\ methane\ yield = \frac{22.4 \times (\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8})}{12n + a + 16b + 14c} \quad \text{(Eq. 3)}$$

Methane-based degradability:

$$Biodegradability\ (\%) = \frac{Methane\ yield\ of\ BMP\ test}{Theoretical\ methane\ yield} \times 100 \quad \text{(Eq. 4)}$$

3.2.2 Continuous stirred-tank reactor (CSTR) operation

3.2.2.1 CSTR experimental setup

Two mesophilic and thermophilic continuous stirred-tank reactors (CSTRs) were operated in this study (Fig 3.5). The detailed design information was illustrated in Fig 3.6. The total volume was 10 L, and the working volume was 8 L for each CSTR. Before sealing, the CSTRs were purged with N_2 for more than 20 minutes to remove oxygen. The four CSTRs were placed in constant temperature room (37±1℃). Thermophilic CSTRs were equipped with water jacket and water tank. Water was heated to 50±1℃ in water tank, and then continuously moved through inlet to outlet of thermophilic reactors during experimental period. Tedlar bags were attached to the valves for biogas collection. The substrates feeding and effluent withdraw were performed everyday.

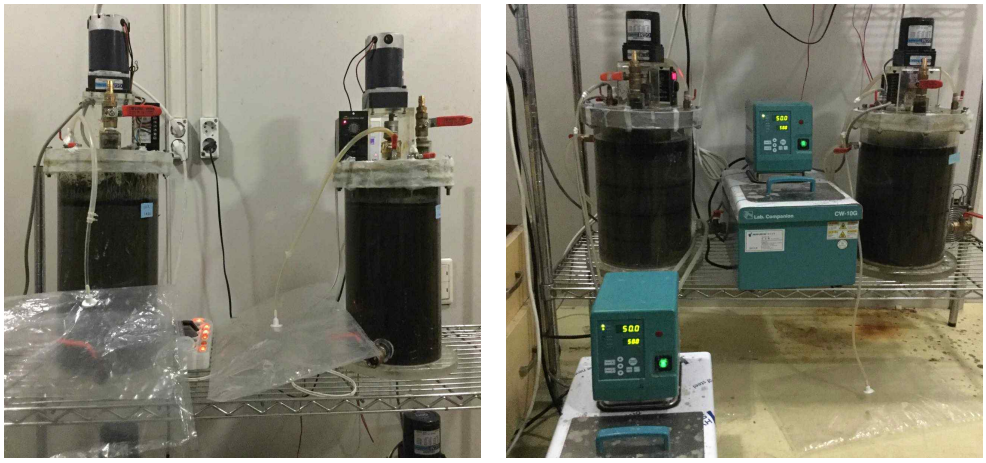


Fig 3.5 Pictures of mesophilic and thermophilic CSTRs

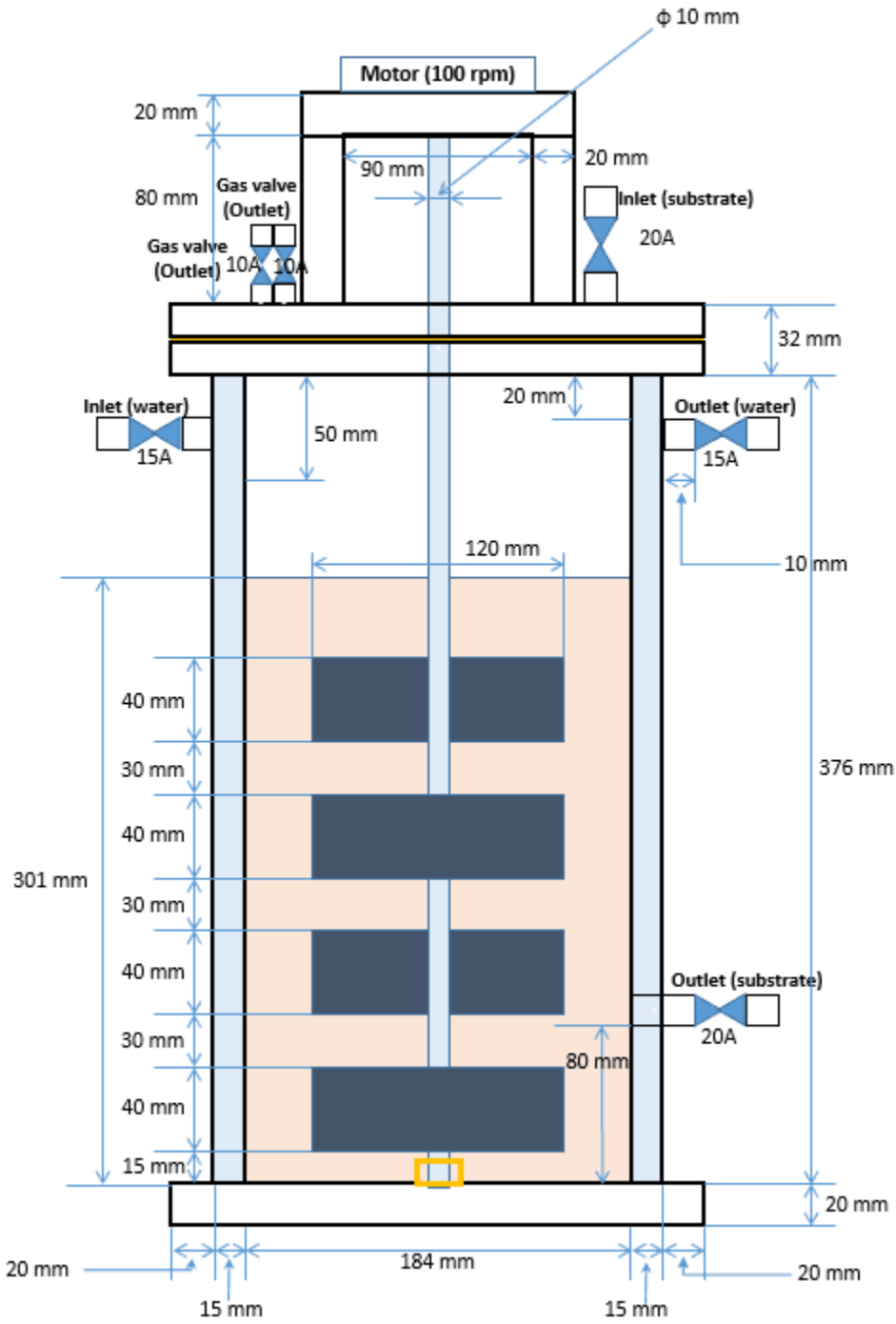


Fig 3.6 Schematic design of CSTR

3.2.2.2 CSTR operation design

The OLR of four CSTRs are 2.5 g-VS/L/d, and HRT are 18 days. The OLR stared from 0.5 g-VS/L/d for each CSTRs. The OLR was increased when the methane production tended to get stable in each reactor. The detailed operation schedule was listed in Table 3.1.

Table 3.1 CSTRs operation design

	Substrates	Temp. (℃)	OLR (g-VS/L/d)	HRT (day)
CSTR 1	Raw swine manure	37±1℃	2.5	18
CSTR 2	THP-treated swine manure	37±1℃	2.5	18
CSTR 3	Raw swine manure	50±1℃	2.5	18
CSTR 4	THP-treated swine manure	50±1℃	2.5	18

3.2.3 Analytical methods

3.2.3.1 Substrates and inocula characterization

Proximate analysis was performed according to the Korean standard test methods. The proximate analysis includes total solids (TS), volatile solids (VS), volatile suspended solids (VSS). TS was measured by weighting the residues after over-night drying (105℃). The VS was calculated by weighting the mass after igniting the dry samples in 550℃ for 2 hours. When testing the VSS fraction, the samples were filtered through weighted 0.45 μm glass-fiber filter. The residues in the filter were first dried over night at 105℃, and then ignited at 550℃ for 30 minutes. The VSS was calculated as the mass loss after ignition.

The components analysis was performed in Feed Research Institute (Korea Feed Association). The contents of moisture, crude fat, crude protein, ash, acid detergent fiber (ADF), and neutral detergent fiber (NDF) were measured using Korea standard analysis method. The hemicellulose contents were calculated as NDF-ADF. The carbohydrate content was determined by calculation, the contents of celloluse and lignin were tested by weighting method.

3.2.3.2 Biogas measurement

The biogas (i.e., methane and carbon dioxide) and nitrogen volumes in CSTRs were measured using a wet gas meter. The biogas composition was measured using gas chromatography (GC). In BMP test, the biogas composition measurement was carried out every two days in the first 20 days, and twice a week in the consecutive days. During CSTR operation, the biogas composition was measured everyday.

Table 3.2 GC setting condition for biogas composition measurement

Item	Conditions
GC	ACME 6100 (Younglin, South Korea)
Detector type	Thermal conductivity detector (TCD)
Column	80/100 Porapak N (Agilent Technologies, USA) 10 ft × 1/8 in × 2.1 mm SS
Oven temp.	Initial: 80℃, final: 120℃
Detector temp.	150℃
Injector temp.	150℃
Carrier gas	Helium (He)

3.2.3.3 VFA analysis

The measured VFAs in this study include acetic, propionic, butyric, isobutyric, isovaleric, and valeric acid. The VFAs were determined by high performance liquid chromatography (HPLC) systems. A 0.02 N H_2SO_4 were utilized as the flow rate of 0.6 $mL \cdot min^{-1}$ and the detection wavelength was 210nm.

Table 3.3 HPLC setting condition for VFAs measurement

Item	Conditions
HPLC	YL9100 (Younglin, South Korea)
Detector	UV/Vis 210nm
Column	C18 (4.6*250mm, 5μm)
Oven temp	30℃
Flow rate	0.6 mL/min
Injection volume	20μL
Mobile phase	0.02 N H_2SO_4

3.2.3.4 Alkalinity and FOS/TAC

The abbreviation TAC stands for total alkalinity, expressed in mg/L of calcium carbonate ($CaCO_3$). TAC was determined by titration, according to the method proposed by Nordmann (Nordmann, 1977). The sample of substrate was first filtrated through 0.45 μm filter, then the filtrate was titrated by 0.1 N of sulfuric acid solution (H_2SO_4) to an endpoint of pH 5.0. The calculation of TAC was according to the following equation:

$$Alkalinity, mg\ CaCO_3/L = \frac{A \times N \times 50{,}000}{mL\ sample} \qquad \text{(Eq. 5)}$$

where: A = volume of titrant at pH 5.0 (mL),

N = normality of standard acid.

The FOS value stands for the volatile fatty acids content and expressed in mg/L of acetic acid (CH_3COOH). The FOS/TAC value was present in German technical literature, and widely being used as an indicator of fermentation status. In practise, the FOS/TAC in the range of 0.3 to 0.4 stands for a well-digested process. The value exceeds 0.5 is a caution for indigestion and less biomass addition, and less than 0.2 always reflects a 'hungry' digester and requires rapid increase of biomass input. The FOS is measured based on Nordmann's method. The sample of substrate was continuously titrated from pH 5.0 to a second titration endpoint 4.4. The calculation of FOS was based on the following equation:

$$FOS = ((\frac{20}{A} \times B \times 1.66) - 0.15) \times 500 \qquad \text{(Eq. 6)}$$

where: A = volume of titrant at pH 5.0 (mL),

B = volume of titrant at pH 4.4 - volume of titrant at pH 5.0 (mL).

3.2.3.5 Water quality analysis

Water qualities of the substrates and effluents from CSTRs were measured using water quality analyzing kit products (Water Test Kit, Humas, South Korea). The measurements included concentration of total and free ammonia, total and soluble chemical oxygen demands (tCOD & sCOD). The samples were filtered through 0.45 μm filter before testing total ammonia and soluble COD concentration.

The concentration of free ammonia was related to pH, temperature, and total ammonia concentration. The free ammonia concentration was determined according to the following equation (Bonmati et al., 2001):

$$\frac{[NH_3]}{[TNH_3]} = \left(1 + \frac{10^{-pH}}{10^{-\left(0.09018 + \frac{2729.92}{T(K)}\right)}}\right)^{-1} \qquad \text{(Eq. 7)}$$

where: $[NH_3]$ = concentration of free ammonia,

$[TNH_3]$ = concentrition of total ammonia, and

$T(K)$ = temperature (Kelvin).

4. Results and Discussion

4.1 Effects of THP and temperature

4.1.1 Characteristics of organic wastes

4.1.1.1 Mass variation

Raw food waste, swine manure and waste activated sludge were performed by THP process in a pilot plant separately. The accurate information about input and output of food waste and waste activated sludge was not acquired. Only detailed mass variation of swine manure was shown in Table 4.1. The total mass weight changed due to the addition of water, evaporation of volatile matters, adherence of residues to the pipelines and reactor, and continuous steam supplement during thermal hydrolysis process.

Table 4.1 Mass weight of swine manure before and after THP process

			Unit	RSM			TSM[b]		
				T1[a]	T2[a]	T3[a]	T1	T2	T3
Input	mass	kg	(by wet wt.)	21	21	21		−	
Output	mass	kg	(by wet wt.)		−		30	43.5	53.3

[a] T1, T2, and T3 stands for three independent THP process

[b] The TSM from three treatments was homogenized and used as the substrate

4.1.1.2 Solids contents

The solids contents of raw and THP-treated food waste, swine manure and waste activated sludge were shown in Table 4.2. The TS contents in the three THP-treated wastes were decreased after THP process. This fact can be explained by escape of volatile matters in reactors, and the samples loss in the THP unit.

The VS contents after thermal pretreatment for three substrates were decreased, which can be explained by some dissolved macromolecular organic compounds hydrolyzed into small volatile molecules (e.g., VFA, CO_2, NH_3, etc.) under high temperature and high pressure condition.

The VSS/VS ratio represents the hydrolysis degree of organic particulates. The VSS/VS ratio decreased after THP process, from 66.3, 77.9, and 87.5% to 45.1, 55.6, and 79.5% for food waste, swine manure, and waste activated sludge, respectively. This result indicated that THP improved the solubilization of organic particulates in the three organic wastes.

Table 4.2 Solids content of raw and THP-treated substrates

Items	Unit	Raw substrates			THP-treated substrates		
		FW	SM	WAS	FW	SM	WAS
TS	(%, by wet wt.)	16.8±0.7	39.6±1.0	15.8±0.2	9.9±1.6	10.9±0.1	7.2±0.1
VS	(%, by wet wt.)	16.1±0.5	24.5±1.1	10.5±0.2	9.2±1.7	7.0±0.1	4.5±0.1
VSS	(%, by wet wt.)	10.6±0.7	19.9±0.4	9.2±0.6	3.9±0.3	2.0±0.1	3.6±0.1
VSS/VS	%	66.3	77.9	87.5	45.1	55.6	79.5

4.1.1.3 Components analysis

As shown in Table 4.3, raw food waste had relatively higher crude fat content (around 38%) than swine manure and waste activated sludge. This was because traditional Korea food products contained large fraction of meat, oil, etc. The carbohydrate and protein content of waste activated sludge were high due to the large fraction of microorganisms, which accounted for around half mass weight of waste activated sludge. The lignocellulosic biomass content (i.e., cellulose, hemicellulose, and lignin) reached up to 37.8% dry matter in raw swine manure. The amount of cellulose and lignin fluctuated in small range, while that of hemicellulose decreased after THP from 11.6 to 3.3%. The similar phenomenon was also observed in previous research (Beltrame et al., 1992; Horn et al., 2010; Estevez et al., 2012), which can be explained by the removal of hemicellulose sugars and loss of volatile compounds in the outlet of steam (Horn et al., 2011). The reduction of hemicellulose increased the mean pore size and available surface area of lignocellulosic material, which increased the likelihood of hydrolysis of cellulose (Grethlein, 1985).

Table 4.5 Components of organic wastes before and after THP

Components	Unit	Raw organic wastes			THP-treated organic wastes		
		FW	SM	WAS	FW	SM	WAS
Moisture	%, by dry wt.	4.5	2.05	3.5	5.2	3.6	2.2
Carbohydrate		37.6	43.8	31.7	32.6	38.9	28.6
Crude protein		19.2	13.8	28.0	21.0	27.2	25.9
Crude fat		32.5	1.6	0.1	32.3	2.7	1.1
Ash		6.2	38.5	36.7	8.8	27.6	42.2
Acid detergent fiber (ADF)		19.9	16.1	5.46	16.8	14.9	11.7
Neutral detergent fiber (NDF)		28.2	27.8	8.27	22.7	18.2	24.6
Cellulose		16.8	15.3	1.6	15.3	19.1	8.1
Hemicellulose		8.3	11.6	2.8	5.9	3.3	12.9
Lignin		8.7	10.9	3.8	9.1	6.1	10.1

4.1.1.4 Water quality

The sCOD/tCOD ratio of food waste, swine manure and waste activated sludge was increased after THP, indicating that THP improved solubilization of the organic compounds for the three substrates. The percentages of NH_3-N and PO_4-P were increased in the three organic wastes after THP. Ammonia nitrogen was treated as an evaluation of protein decomposition degree (Wang et al., 2014). Proteins were degraded to amino acids, which then converted into ammonia, carbon dioxide, etc. The increased ammonia nitrogen demonstrated that THP promoted the decomposition of proteins in food waste, swine manure, and waste activated sludge.

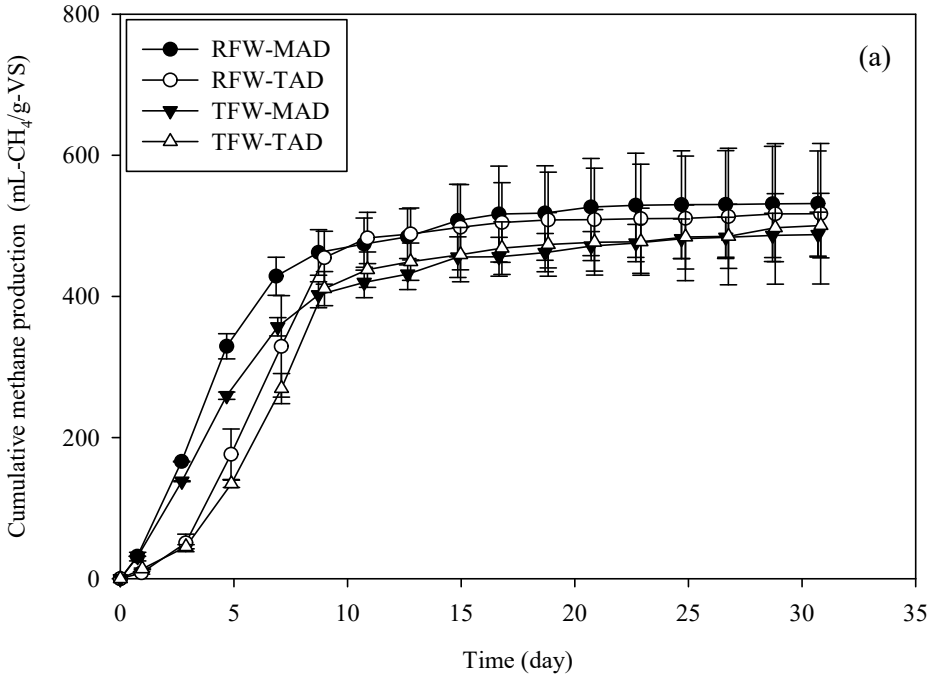
Table 4.4 Water quality analysis of raw and THP-treated substrates

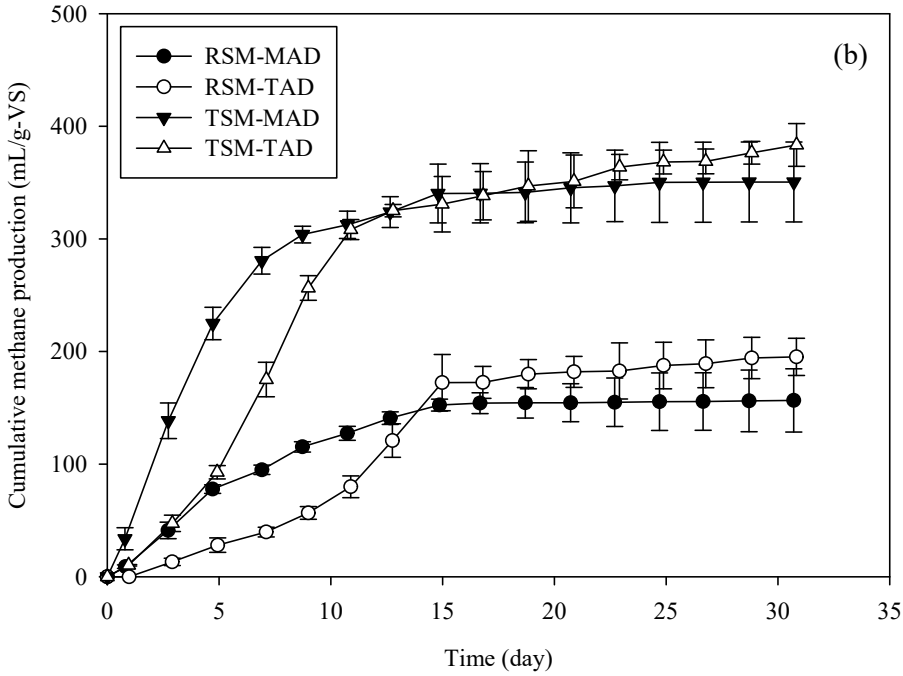
Parameter	Unit	Raw organic wastes			THP-treated organic wastes		
		FW	SM	WAS	FW	SM	WAS
tCOD	g/L	140.1±8.1	179.8±18.1	32.5±6.1	118.7±25.3	49.5±0.6	45.2±0.4
sCOD	g/L	45.5±0.6	11.5±1.0	5.7±1.1	42.0±0.8	29.1±1.6	21.6±0.8
sCOD/tCOD	%	32.5	6.4	17.5	35.4	58.8	47.8
NH_3-N	%, on TS	0.4±0.0	0.4±0.0	0.1±0.0	1.2±0.1	2.7±0.1	1.0±0.0
PO_4-P	%, on TS	0.2±0.0	0.07±0.0	0.0±0.0	0.3±0.0	0.8±0.1	0.001±0.0

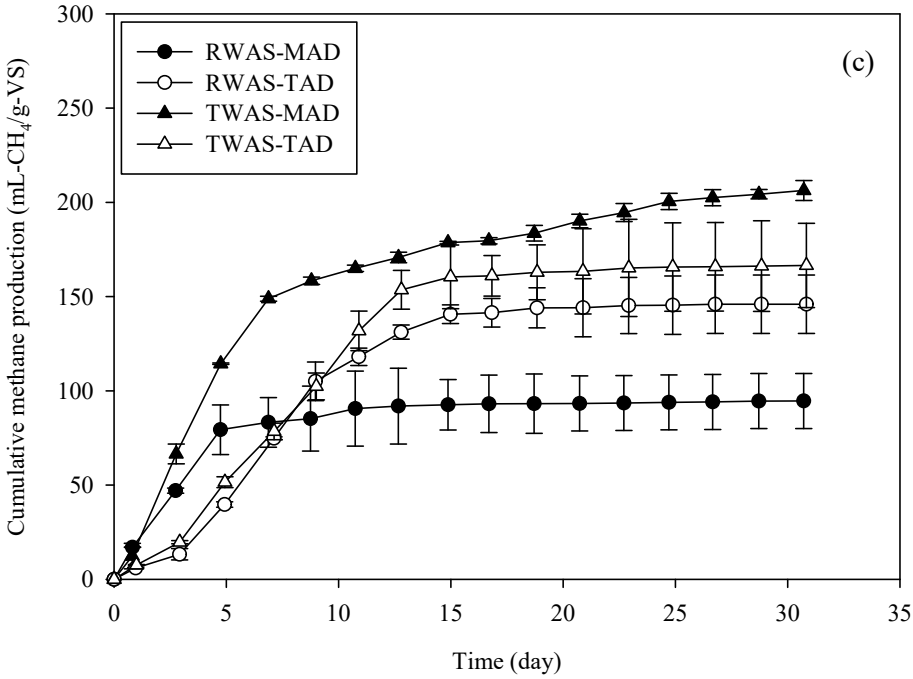
4.1.2 Anaerobic biodegradability in BMP test

4.1.2.1 Cumulative methane production

The methane generation potentials of food waste, swine manure and waste activated sludge under mesophilic and thermophilic conditions were assessed in BMP batch tests. As shown in Fig 4.1 (a), there were no significant differences in cumulative methane productions between RFW and TFW under MAD and TAD conditions ($p > 0.05$). The can be explained by food waste is mainly composed of carbohydrates, proteins, fats, which can be easily degraded in anaerobic digestion process. Thus, THP had limited influence on improvement of methane generation potential of food waste. Fig 4.1 (b) showed that THP increased cumulative methane production of swine manure, which reached up to 383.4 and 350.6 mL-CH_4/g-VS in TSM-TAD and TSM-MAD patterns, respectively. A steep increase of cumulative methane production was observed in TSM-MAD/TAD patterns, indicating the existence of easily-degradable matters. However, the cumulative methane production of raw swine manure was relatively low, 156.5 and 195.2 mL-CH_4/g-VS under RSM-MAD and RSM-TAD conditions were obtained. Higher temperature (i.e., thermophilic condition) did not show distinctive improvement of cumulative methane production for swine manure ($p > 0.05$). Fig 4.1 (c) showed that, for pretreated WAS, TWAS-MAD obtained the highest cumulative methane production (206.3 mL-CH_4/g-VS), followed by TWAS-TAD condition (166.5 mL-CH_4/g-VS). However, This result from raw WAS paradoxically exhibited opposite effects of temperature, where RWAS-TAD obtained higher cumulative methane production (145.9 mL-CH_4/g-VS) than RWAS-MAD (94.6 mL-CH_4/g-VS) ($p < 0.05$). Impurities in WAS samples, denaturation of proteins in WAS under high temperature may contributed to this phenomenon.


RFW-MAD
RFW-TAD
TFW-MAD
TFW-TAD
(a)
Cumulative methane production (mL-CH4/g-VS)
Time (day)
0
200
400
600
800
0
5
10
15
20
25
30
35


RSM-MAD
RSM-TAD
TSM-MAD
TSM-TAD
(b)
Cumulative methane production (mL/g-VS)
Time (day)
0
100
200
300
400
500
0
5
10
15
20
25
30
35

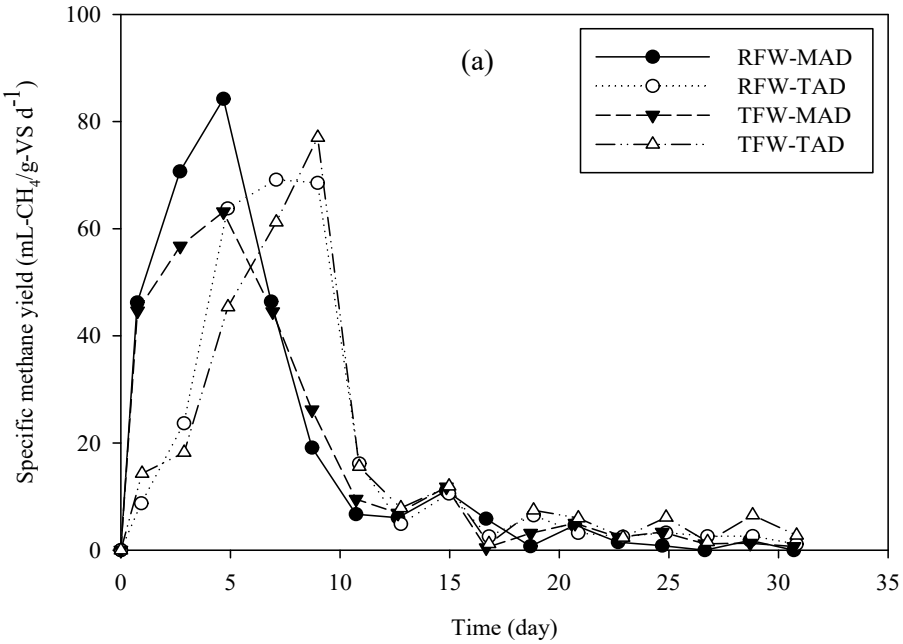


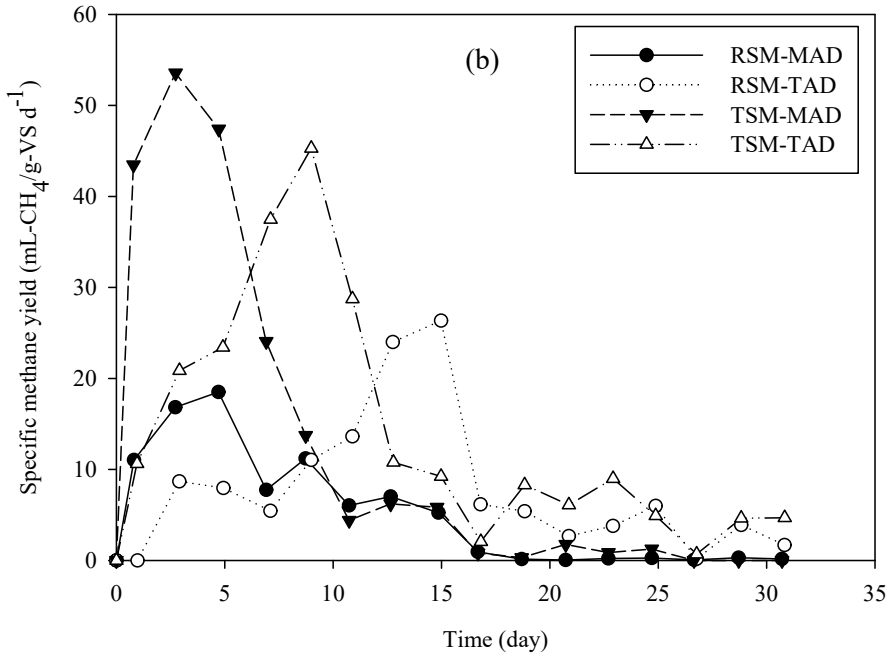
* MAD: mesophilic anaerobic digestion, TAD: thermophilic anaerobic digestion.

Fig 4.1 Cumulative methane production of (a) food waste, (b) swine manure, and (c) waste activated sludge

4.1.2.2 Specific methane yield

Fig 4.2 depicted the specific methane yield of food waste, swine manure, and waste activated sludge in BMP test. The specific methane yield reflects the biodegradability and degradable fractions of substrates. As shown in Fig 4.2, the main peak occurred relatively earlier, and its value was more pronounced than other peaks. After the decline of main peak, several smaller peaks followed until no obvious peaks can be observed. In the case of food waste, no obvious lag phase was found in four digestion conditions (i.e., RFW-MAD, RFW-TAD, TFW-MAD, and TFW-TAD). This probably due to the existence of large fraction of easily biodegradable components in food waste. The differences in the first peak value in the four conditions were not significant, indicating that THP and higher temperature (i.e., thermophilic) had no great improvement effect on methane generation potential of food waste. As for swine manure, an obvious prolonged lag phase was observed in RSM-MAD condition, which was probably caused by the inefficient decomposition of lignocellulosic materials under mesophilic temperatures. The values of specific methane yields of raw swine manure under mesophilic and thermophilic conditions were low, 18.5 and 26.3 mL-CH_4/g-VS • d^{-1} in RSM-MAD and RSM-TAD conditions, respectively. The rapid methane yields were observed in THP-treated swine manure, with the value of 53.5 and 45.3 mL-CH_4/g-VS • d^{-1} in TSM-MAD and TSM-TAD conditions, respectively. In the case of waste activated sludge, the maximum specific methane yield reached up to 27.8 mL-CH_4/g-VS • d^{-1} in TWAS-MAD condition, increased by 33.2, 51.1, and 64.0% than that in RWAS-MAD, RWAS-TAD, and TWAS-TAD conditions.


(a)
RFW-MAD
RFW-TAD
TFW-MAD
TFW-TAD
Specific methane yield (mL-CH4/g-VS d-1)
Time (day)
0
20
40
60
80
100
0
5
10
15
20
25
30
35


(b)
RSM-MAD
RSM-TAD
TSM-MAD
TSM-TAD
Specific methane yield (mL-CH4/g-VS d-1)
Time (day)
0
10
20
30
40
50
60
0
5
10
15
20
25
30
35

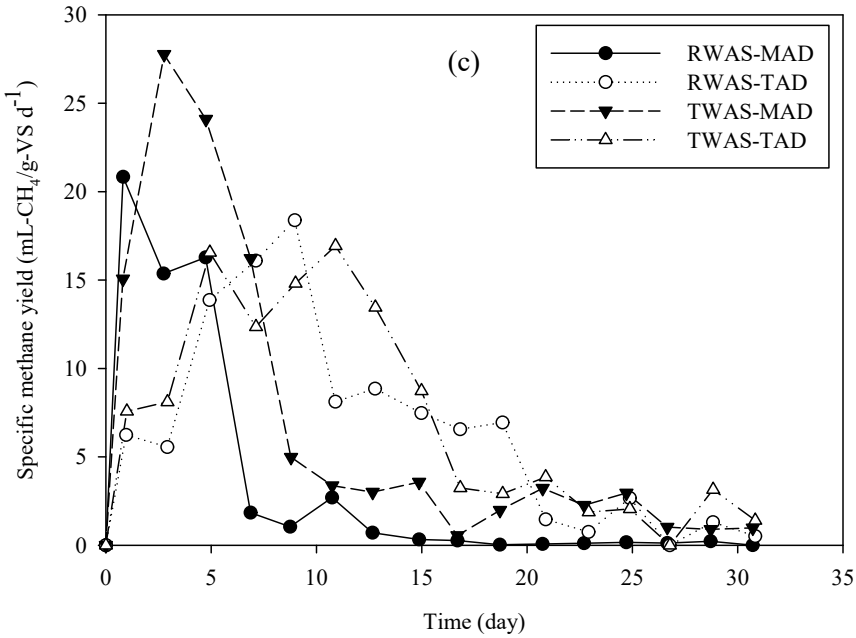


Fig 4.2 Specific methane yield of (a) food waste, (b) swine manure, and (c) waste activated sludge

4.1.2.3 Overall mass balance

Although the methane potentials of food waste, swine manure, and waste activated sludge were improved by THP, the loss of organic matters during THP process can not be ignored. The overall mass balance was considered on VS basis. Due to there was no accurate input and output data for food waste and waste activated sludge, only swine manure was analyzed for mass balance. After THP process, the mass recovery was low, only 57.8% was achieved. The comparison of cumulative methane production of 63 kg RSM and 126.8 kg TSM (i.e., the THP products from 63 kg RSM) under two temperatures was illustrated in Fig. 4.3. The results showed that there was no significant increase of cumulative methane production from TSM compared with that in RSM in both mesophilc and thermophilic conditions ($p > 0.05$).

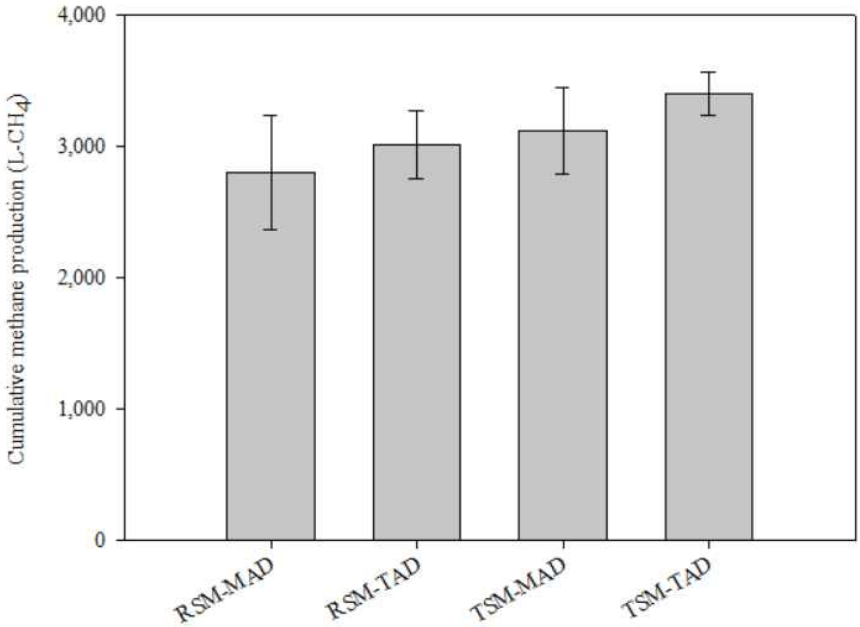


Fig 4.3 Cumulative methane production of total biomass

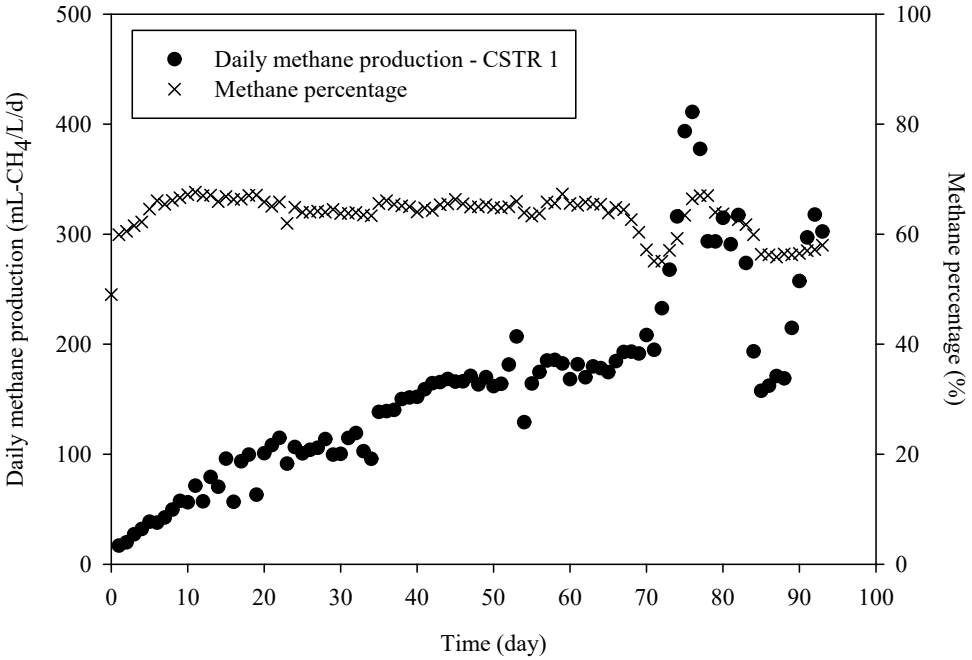
4.2 Anaerobic digestion performance in CSTRs

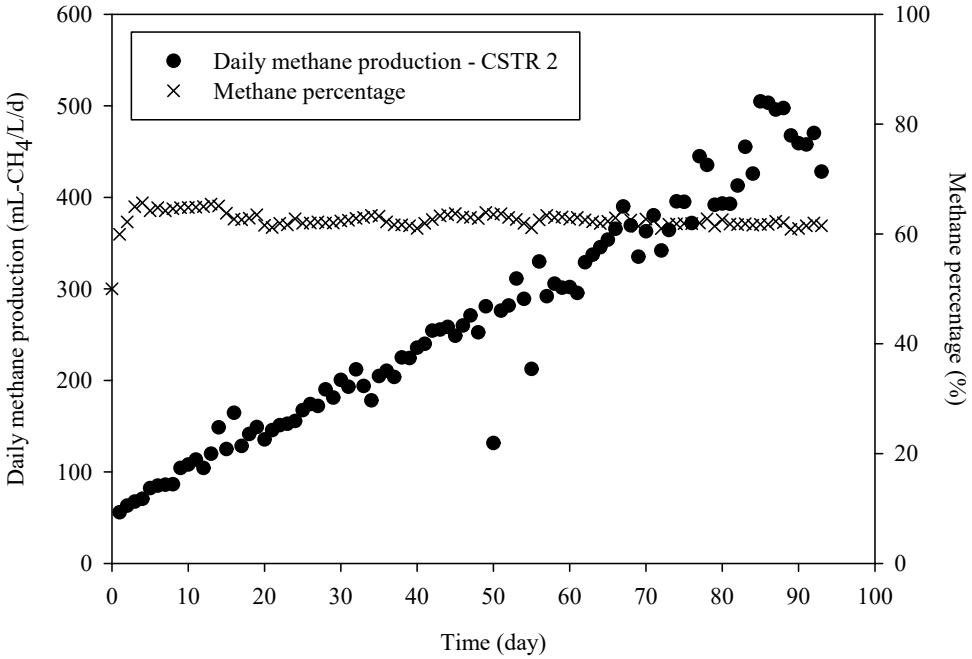
4.2.1 Methane production

4.2.1.1 Daily methane production and percentage

Two mesophilic CSTRs (37±1℃) and thermophilic CSTRs (50±1℃) CSTRs were operated in this study. As shown in Fig 4.4, the daily methane production in CSTR 2 (THP-MAD) & 4 (THP-TAD) were relatively higher than that in CSTR 1 (Raw-MAD) & 3 (Raw-TAD). This indicated that THP was effective to increase the methane production of swine manure. Compared with digesters feeding with raw substrate (CSTR 1 & 3), the increase of daily methane production was more stable in the reactors treating THP-treated swine manure (CSTR 2 & 4). And oo shock increase or decrease of daily methane was observed. Besides, thermophilic temperature did not show significant improvement of daily methane production compared with mesophilic condition (CSTR 2 vs. 4; CSTR 1 vs. 3).

The methane percentage of CSTR 1 & 2 were maintained around 56-67%, and that in CSTR 3 & 4 was low, 13 and 14% at the beginning stage, respectively. The methane percentage gradually increased and maintained in the range of 62-68%. The thermophilic reactors (CSTR 3 & 4) took longer time for acclimation than mesophilic ones (CSTR 1 & 2), which probably because the inocula was collected from mesophilic AD plant. The microorganisms thriving in mesophilic condition required longer time to adapt the thermophilic temperature.


Daily methane production - CSTR 1
Methane percentage
Daily methane production (mL-CH4/L/d)
Methane percentage (%)
Time (day)
0
100
200
300
400
500
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
90
100


Daily methane production - CSTR 2
Methane percentage
Daily methane production (mL-CH4/L/d)
Methane percentage (%)
Time (day)
0
100
200
300
400
500
600
0
20
40
60
80
100
0
10
20
30
40
50
60
70
80
90
100

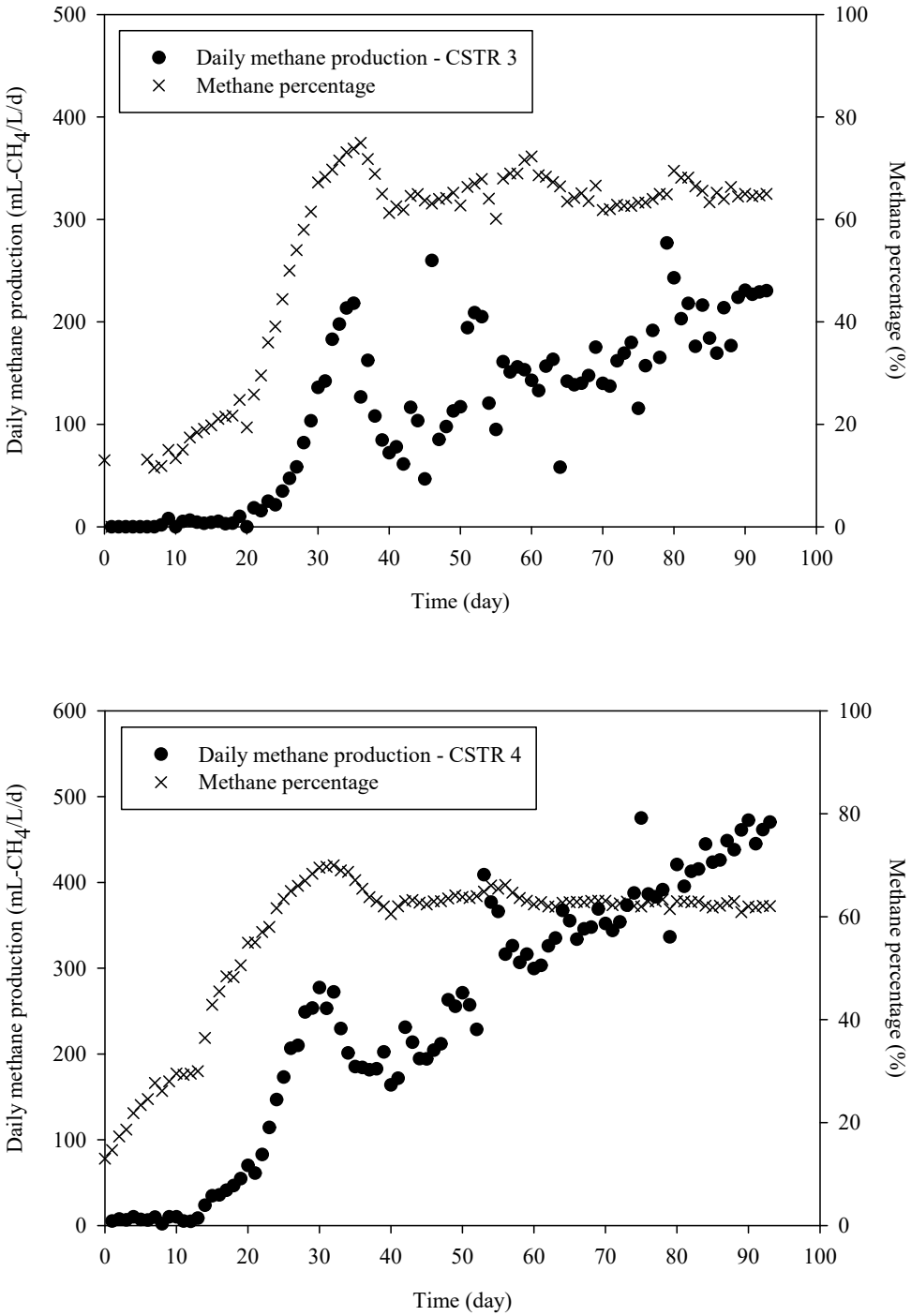
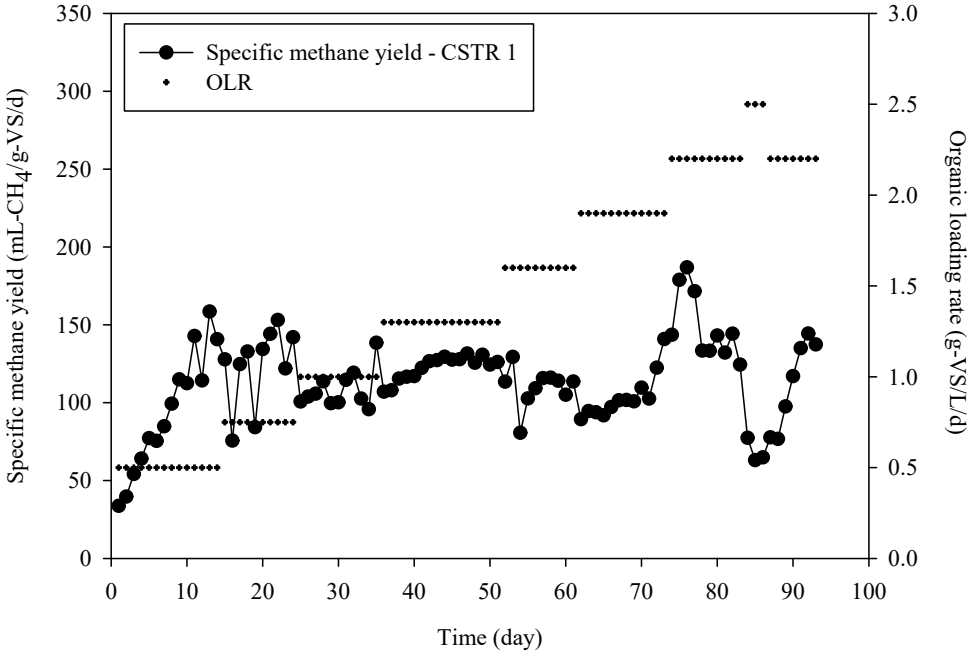
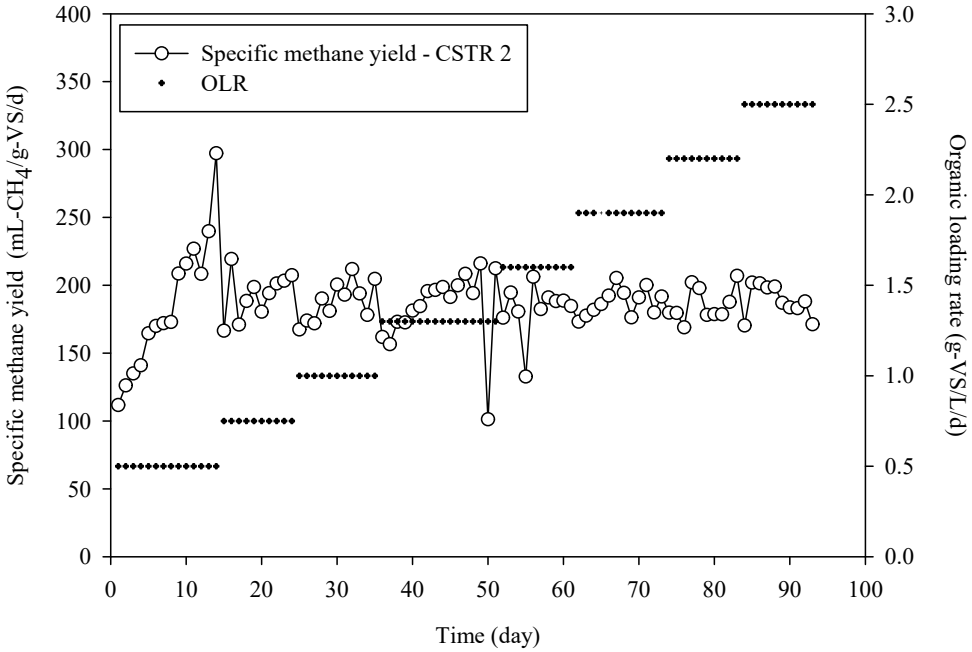


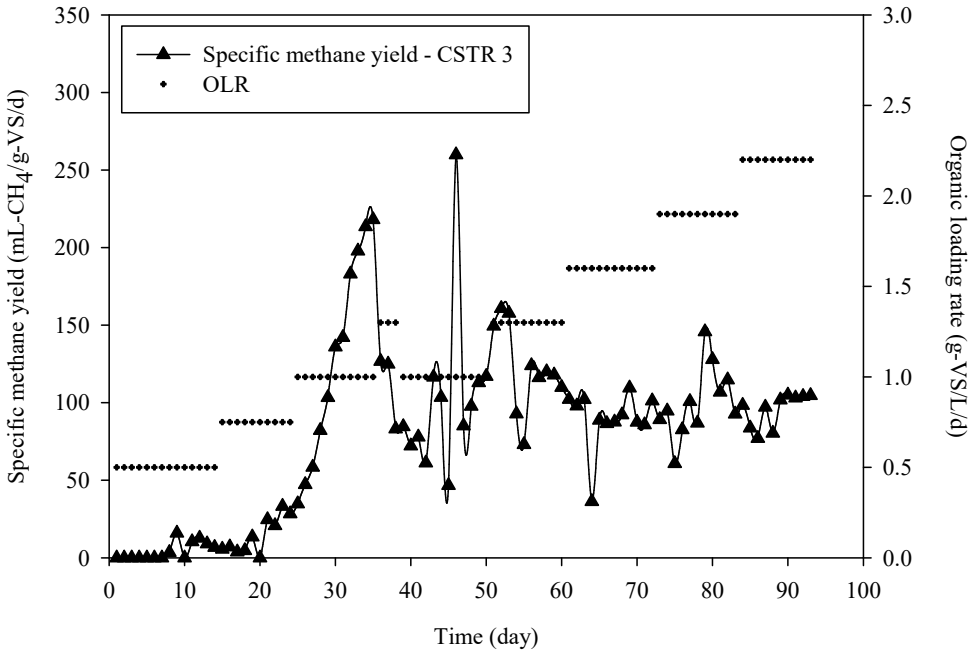
Fig 4.4 Daily methane production and percentage

4.2.1.2 Specific methane yield

The effects of THP and temperature (i.e., mesophilic and thermophilic) on the specific methane yield of swine manure were illustrated in Fig 4.5. The specific methane yield demonstrates the biodegradability of substrates, and organic loading rate (OLR) reflects the input amount of organic matters, which is expressed as gram of VS per unit area per unit time. With the increase of OLR, the specific methane yield of reactors fed with pretreated swine manure (CSTR 2 & 4) tended to be stable after day 35. In contrast, the specific methane yield of reactor treating raw swine manure (CSTR 1 & 3) was fluctuated wildly. The higher specific methane yields were obtained by pretreated swine manure, which in the most cases stayed within the range of 176.3-206.6 and 171.5-196.5 mL-CH_4/g-VS/d in CSTR 2 and 4, respectively. The specific methane yields in CSTR 1 & 3 were relatively low, which were less than 150 mL-CH_4/g-VS/d in most situations. No significant differences in specific methane yield were found in CSTR 2 and 4, showing that thermophilic temperature had few advantages to increase methane production of pretreated swine manure compared with mesophilic condition during stabilizing stage. However, the specific methane yield in CSTR 1 was higher than that in CSTR 3, mesophilic temperature behaved better than thermophilic condition when digesting raw swine manure.


Specific methane yield - CSTR 1
OLR
Specific methane yield (mL-CH4/g-VS/d)
Organic loading rate (g-VS/L/d)
Time (day)
0
50
100
150
200
250
300
350
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
10
20
30
40
50
60
70
80
90
100


Specific methane yield - CSTR 2
OLR
Specific methane yield (mL-CH4/g-VS/d)
Organic loading rate (g-VS/L/d)
Time (day)
0
50
100
150
200
250
300
350
400
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
10
20
30
40
50
60
70
80
90
100



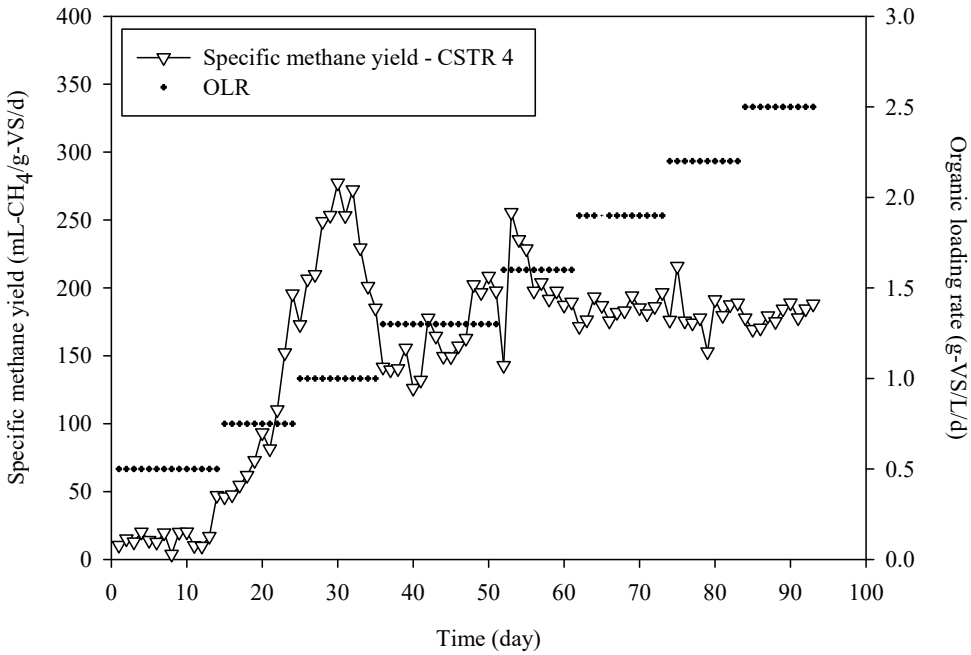


Fig 4.5 Specific methane yield of swine manure

4.2.2 Effluent quality

4.2.2.1 Solids reduction

The variations of TS and VS in effluents were shown in Fig 4.6. TS is one of the water quality measurement, which includes the amount of total dissolved solids and total suspended solids in water samples. The VS content represents the availability of organic matters that can be degraded into biogas. As shown in Fig 4.6, the total TS and VS contents increased gradually with the rising OLR. The TS contents in reactors fed with THP-treated swine manure (CSTR 2 & 4) were relatively lower than that in reactors fed with raw substrate (CSTR 1 & 3). And the similar trend was also observed for VS in effluents from four CSTRs. Besides, the highest VS content in most periods was found in CSTR 3 (Raw-TAD), the lowest one was obtained in CSTR 2 (THP-MAD). This tendency was consistent with that of methane production, demonstrating that the more VS reduction, the more biogas generation. Combined the higher biogas yield in CSTR 2 & 4 as shown in Fig 4.4, this result demonstrated that THP improved the solids reduction efficiency of swine manure.

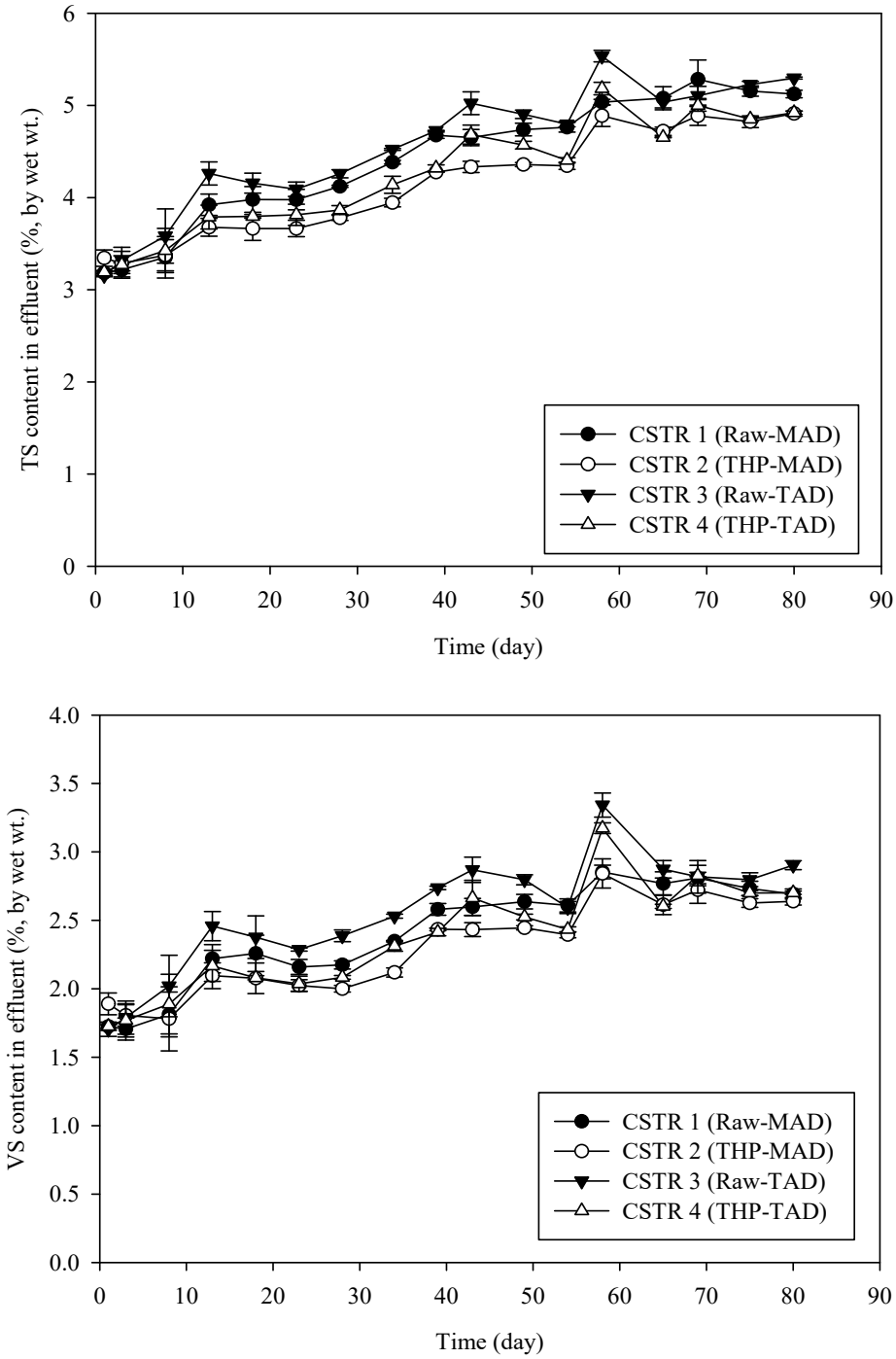
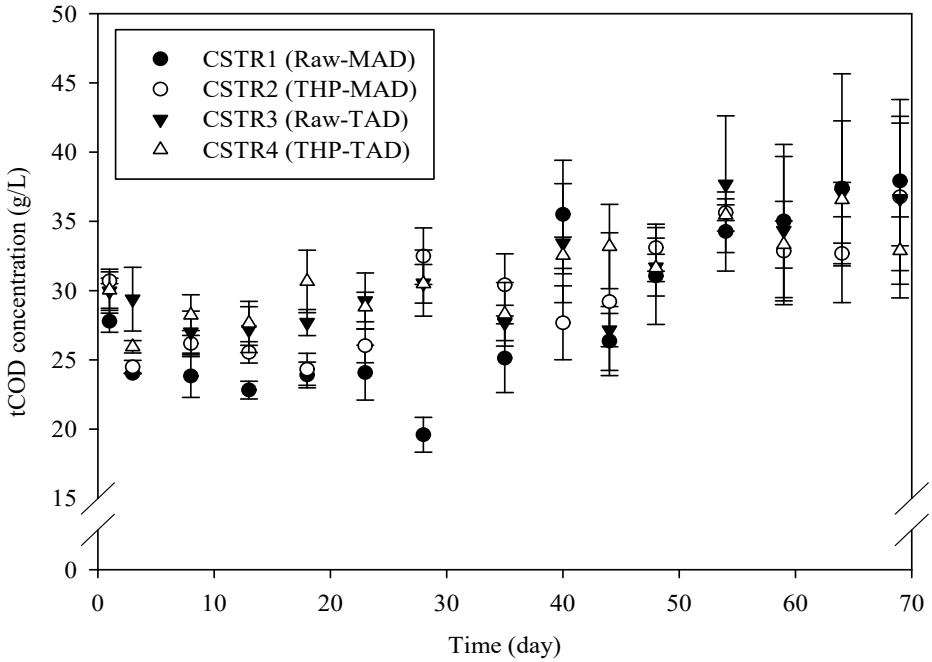


Fig 4.6 TS and VS contents in effluents

4.2.2.2 COD concentration

COD is normally used to quantify the amount of organic matters in waster samples. Total COD and soluble COD represent the particulate and soluble organic fractions, respectively. The tCOD concentrations in the effluents from four CSTRs were increased due to the rising OLR. The tCOD concentrations in the four reactor were more than 20 g/L, and no obvious differences in tCOD concentrations among the four CSTRs were observed.

The sCOD concentrations in reactors fed with THP-treated swine manure were higher than that treating raw substrate at the same temperature (CSTR 2 vs. 1; CSTR 4 vs. 3), showing that THP was effective to improve the solubilization of organic particulates of swine manure. The thermophilic reactors (CSTR 3 & 4) reached higher sCOD concentration than mesophilic ones (CSTR 1 & 2) in most cases. This result can be explained by higher temperature (i.e., thermophilic) improved the destruction efficiency of organic solids (Buhr et al., 1977). The OLR in CSTR 3 was lower than other three reactors after day 37, resulting a lower sCOD concentration than that in CSTR 2.



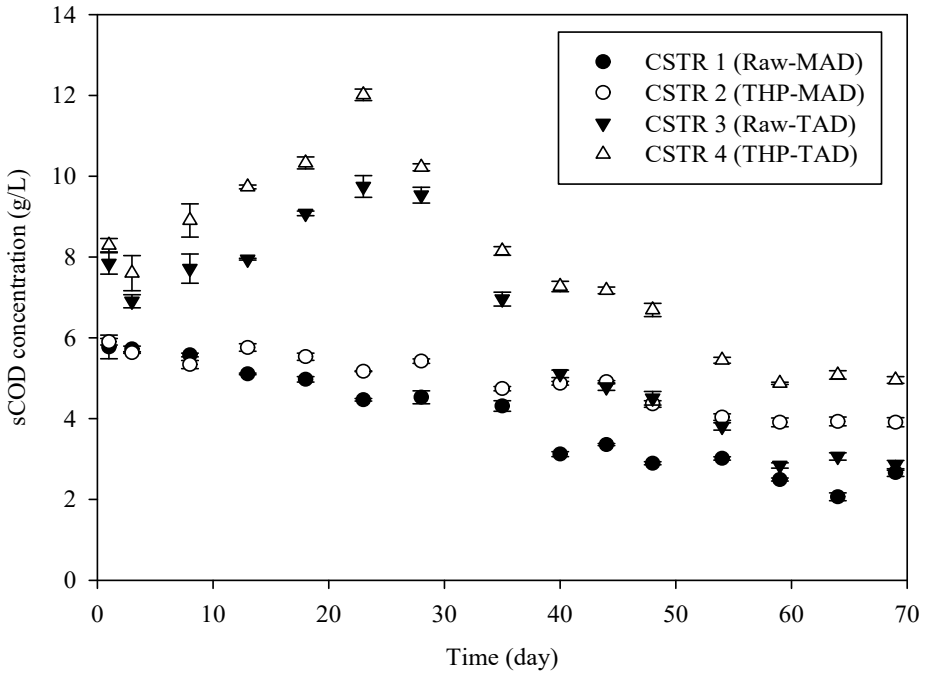


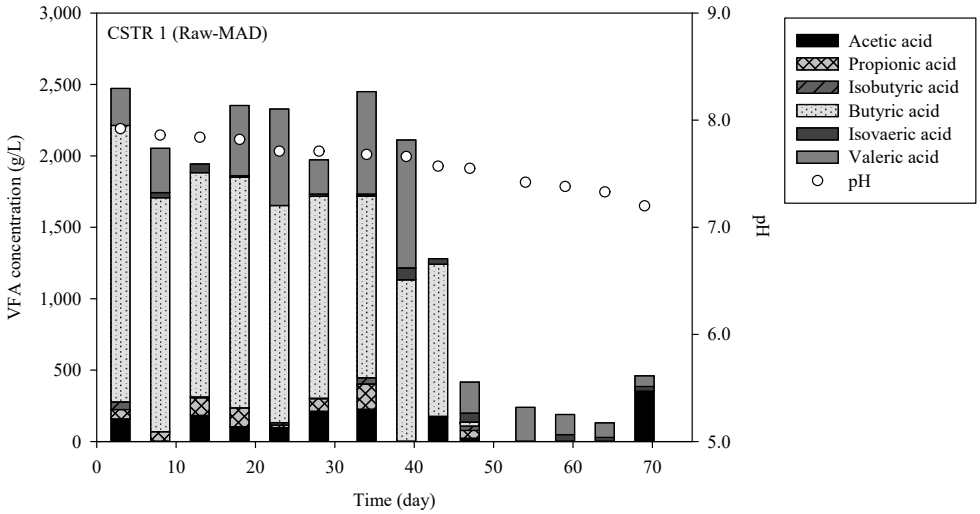
Fig 4.7 tCOD and sCOD concentration in effluents

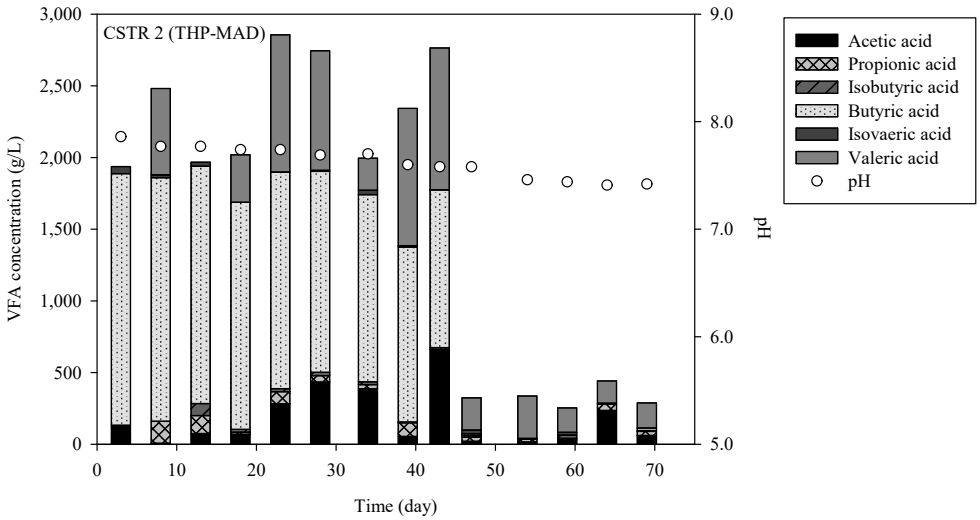
4.3 Process feasibility and stability

4.3.1 VFAs

The VFAs concentration and composition are suitable indicators for process instability (Ahring, 1995). Butyric acid was the dominant VFA at mesophilic condition (CSTR 1 & 2). Acetic acid, propionic acid, and butyric acid were prevalent at thermophilic condition (CSTR 3 & 4). Several factors such as pH, temperature, and organic loading, etc affected the composition of generated VFAs. The total VFAs concentration at thermophilic temperature (CSTR 3 & 4) was higher than that in mesophilic condition (CSTR 1 & 2). Acetic was one of the less toxic VFAs and the immediate precursor of methane and carbon dioxide. The acetic acid concentration was 3789.5 and 3645.9 mg/L at day 23 and 28 in CSTR 3, 3522.8 mg/L at day 23 in CSTR 4, exceeding the threshold of methanogenic toxicity caused by acetic acid accumulation, which was reported around 3,000 mg/L (Ahring et al., 1995). The propionic acid in CSTR 4 reached as high as 1024.9 and 1031.5 mg/L at day 44 and 49, higher than the inhibiting limitation - 900 mg/L (Wang et al., 2014), resulting in disturbance and unstable methane production. The accumulation of organic acids in CSTR 3 & 4 was a warning of instability warming, which leading to suppression of methanogenic activity, but not causing process failure. The total VFAs concentration declined after day 50, probably due to the well adaption of microorganisms.

The pH values in thermophilic reactors were higher than that in mesophilic ones. pH affected VFAs composition, especially acetic, propionic, and butyric acid (Bengtsson et al., 2008). The pH changes were small due to the highly buffer capability in the systems. The pH value fluctuated slightly during digestion process due to the accumulation of VFAs.


CSTR 1 (Raw-MAD)
VFA concentration (g/L)
pH
Time (day)
Acetic acid
Propionic acid
Isobutyric acid
Butyric acid
Isovaeric acid
Valeric acid
pH


CSTR 2 (THP-MAD)
VFA concentration (g/L)
pH
Time (day)
Acetic acid
Propionic acid
Isobutyric acid
Butyric acid
Isovaeric acid
Valeric acid
pH

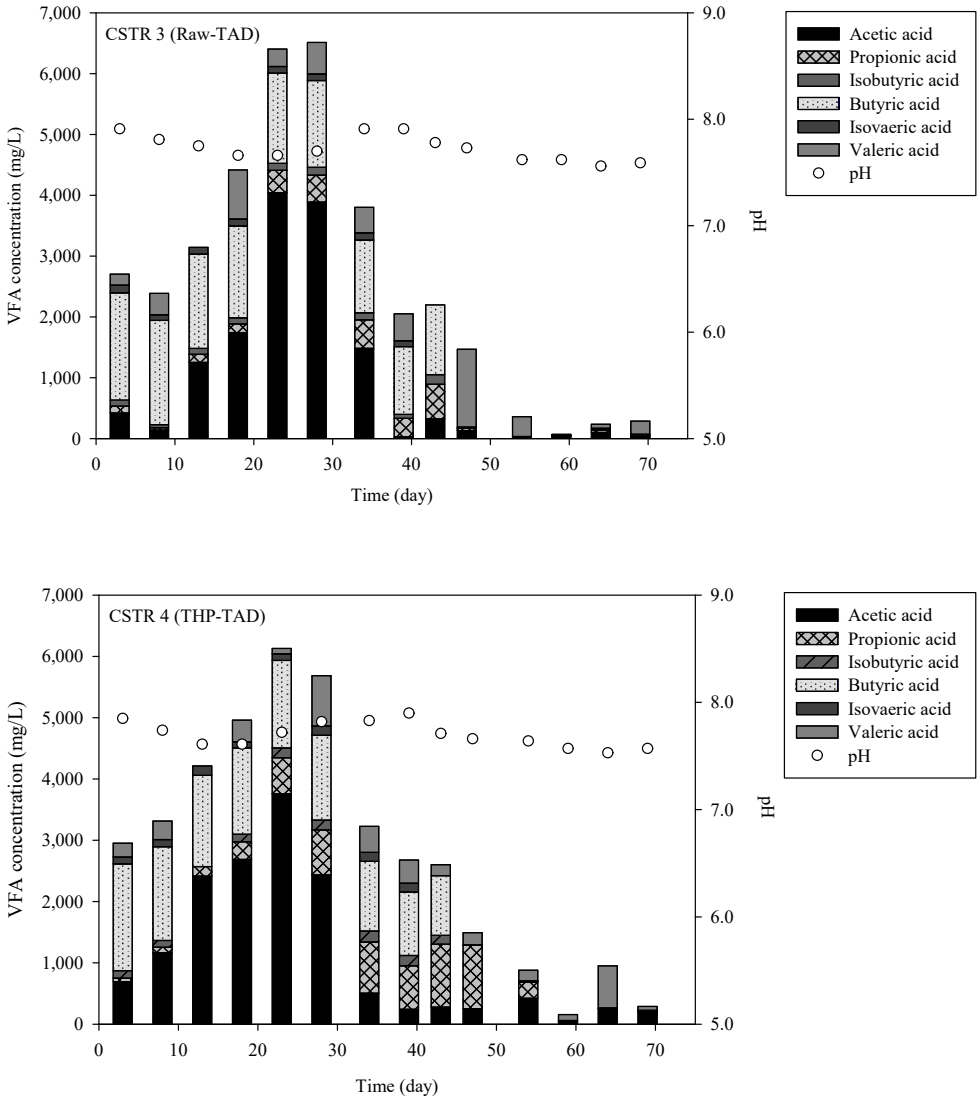
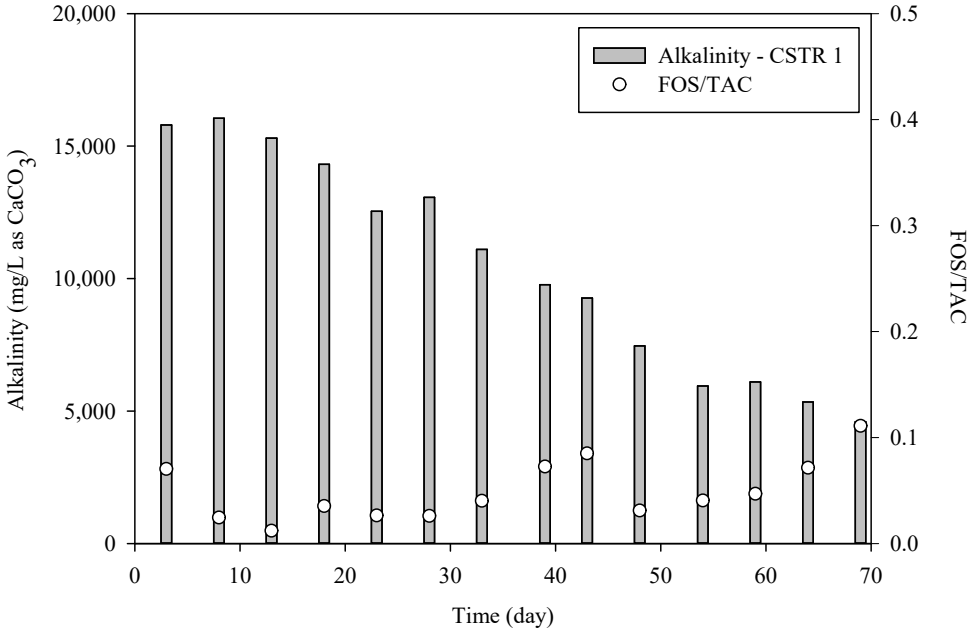


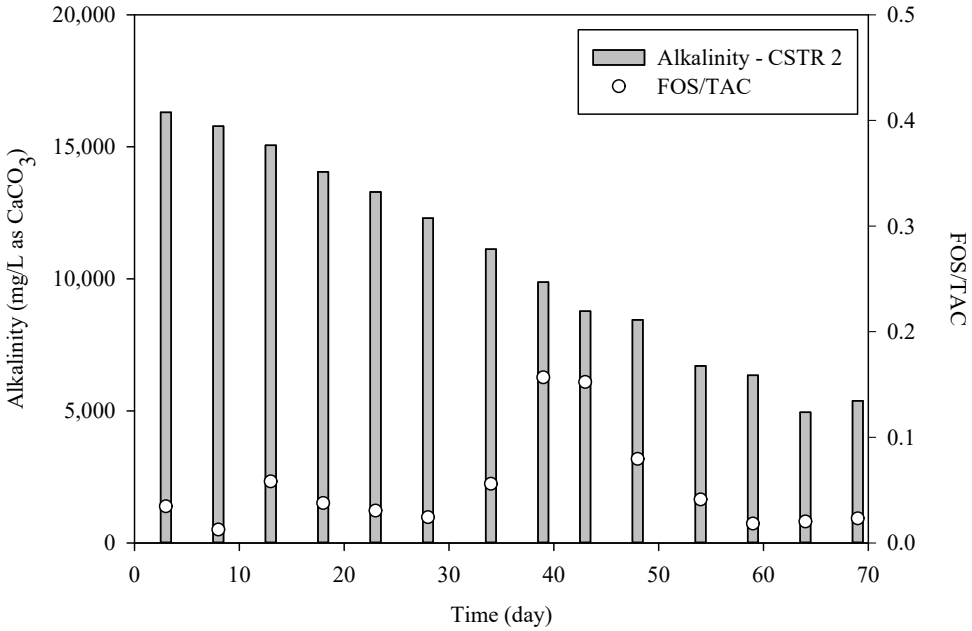
Fig 4.8 VFAs concentration under four digestion conditions

4.3.2 Alkalinity and FOS/TAC

As depicted in Fig 4.10, the alkalinity decreased gradually in the four reactors due to the VFAs accumulation during digestion process. The alkalinity was more than 5,000 mg $CaCO_3$/L at day 70 in each CSTRs, greater than the total VFAs concentration (expressed similarly). This indicated a favorable condition for stable process and methane generation (Pohland et al., 1963).

The FOS/TAC ratios in CSTR 1 & 2 were less than 0.1, showing a 'hungry' status in the two digesters during acclimation period. The FOS/TAC ratios in CSTR 3 & 4 were relatively higher than that in the two mesophilic reactors, and sometimes closed to 0.5 - threshold of an unstable and risky digestion process. However, the FOS/TAC had some limitations. From the day 35 to 50, the FOS/TAC ratio was closed to 0.2 in CSTR 3, representing a 'hungry' digester and requiring more feedstock imput. Nevertheless, the specific methane production in CSTR 3 was absolutely unstable due to over-loading, resulting the decrease of OLR to avoid undigestion in the following days (Fig 4.5). Some reasons may be able to explain this phenomenon. The given FOS was measured 'as acetic acid equivalent'. However, butyric acid and propionic acid took half amount of total VFAs at that period, which may led to inaccurate assessment. Besides, in the anaerobic digesters, the alkalinity is not only contributed by carbonates and biocarbonates sources. A high ammonia concentration could increase the alkalinity value, which consequently, decreased the FOS/TAC ratio and showed a misleading result of a 'hungry' digester. The FOS/TAC ratio may not be an accurate indicator for assessing the fermentation process of swine manure.


Alkalinity - CSTR 1
FOS/TAC
Alkalinity (mg/L as CaCO3)
FOS/TAC
Time (day)
20,000
15,000
10,000
5,000
0
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
30
40
50
60
70


Alkalinity - CSTR 2
FOS/TAC
Alkalinity (mg/L as CaCO3)
FOS/TAC
Time (day)
20,000
15,000
10,000
5,000
0
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
30
40
50
60
70

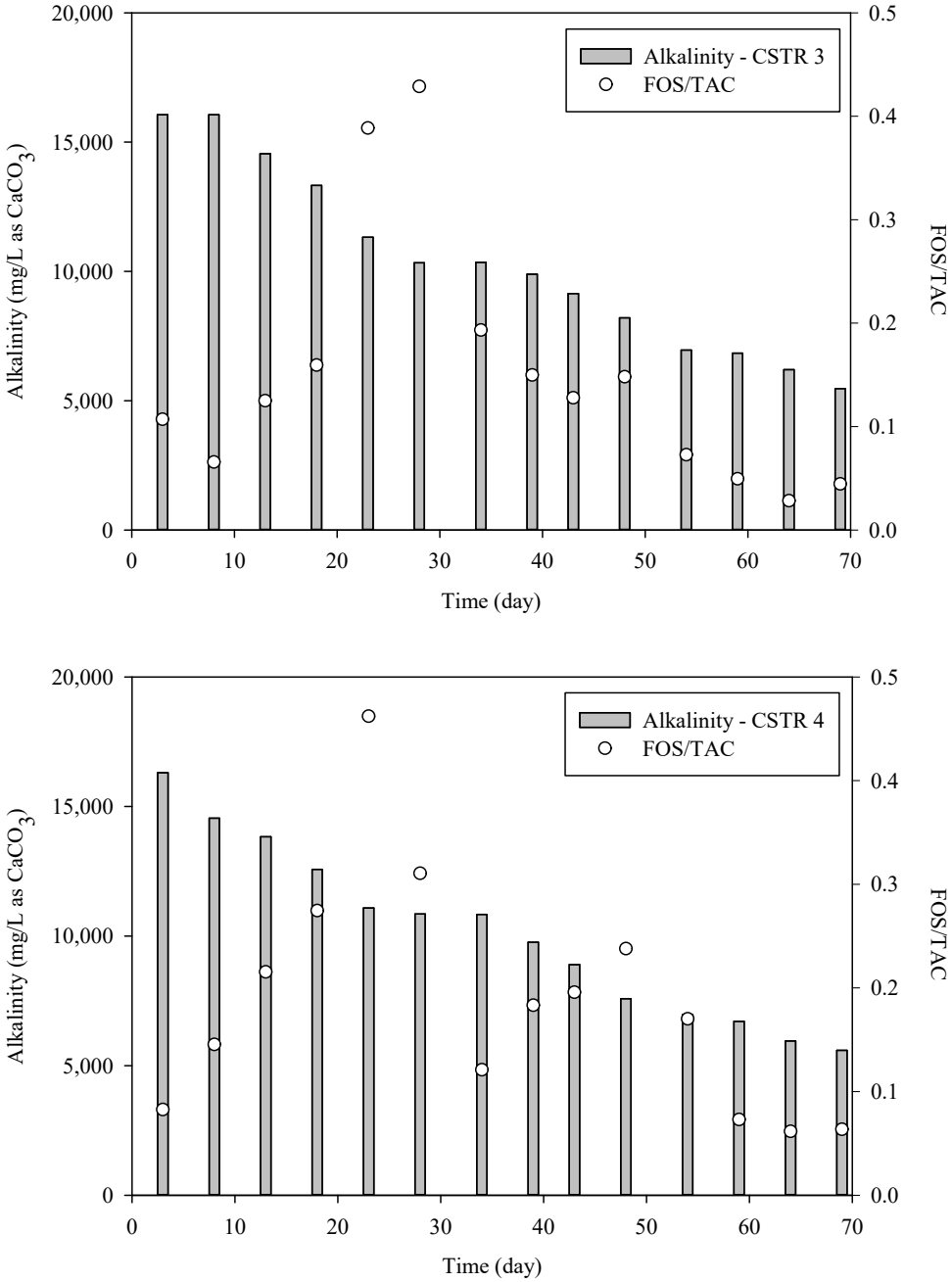


Fig 4.9 Alkalinity and FOS/TAC ratio in four digesters

4.3.3 Ammonia

The total ammonia concentrations in the four patterns were illustrated in Fig 4.11. No obvious differences in total ammonia concentration were found in CSTR 1, 2, 3, and 4. The concentration of ammonia maintained around 3,000 - 4,000 mg/L at early 30 days, and increased as high as 6,000 mg/L at day 38 and 43 due to the increasing organic loading in the four CSTRs. Then the ammonia concentration declined below 2,000 mg/L from day 70. The range of total ammonia concentration causing inhibition was wide, from 1.7 to 14 g/L, and its toxicity in digesters depends on feedstock, inocula, operating factors (e.g., temperature, pH), and acclimation periods (Chen et al., 2008).

The free ammonia is more toxic to methanogenic microorganisms than ionized nitrogen form (NH_4^+). The free ammonia concentration was closely related to pH, temperature, and total ammonia concentration. The concentrations of free ammonia were higher in thermophilic reactors (CSTR 3 & 4) than mesophilic ones (CSTR 1 & 2), which was caused by higher temperature and pH. The maximum free ammonia concentration reached up to 982.0 at day 39 in CSTR 3, which exceeded the reported limitation – 700 mg NH_3-N/L (Angelidaki and Ahring, 1994). Consequently, the daily methane production showed a sharp decline (Fig 4.4). This result proved that thermophilic digesters were more easily inhibited by free ammonia than mesophilic conditions (Angelidaki and Ahring, 1994; Braun et al., 1981). After day 45, the free ammonia concentration declined gradually as the OLR increased in the four CSTRs. This probably due to the well adaption of microorganisms to digester conditions, which consequently, improved the degradation efficiency of organic components.

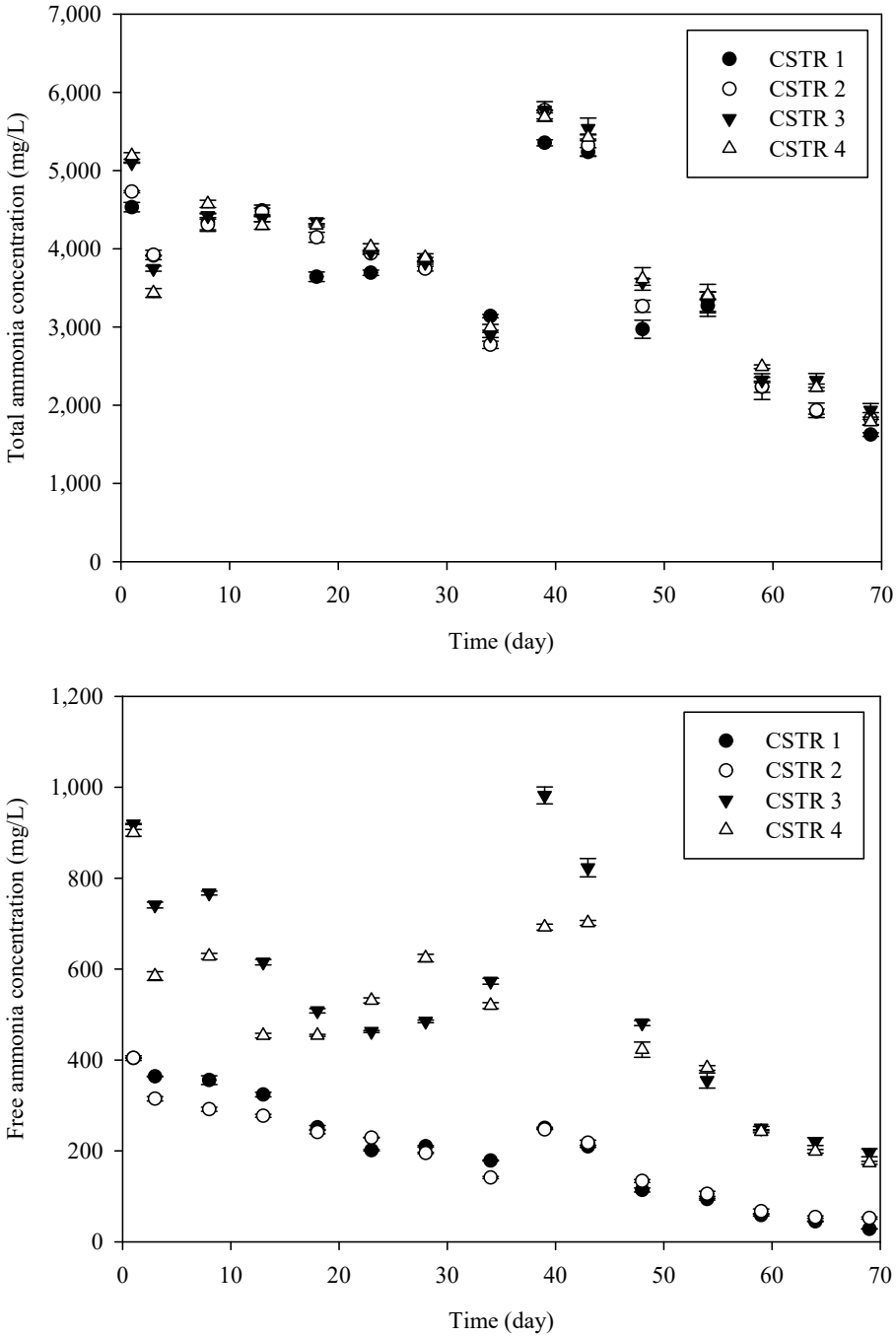


Fig 4.10 Total ammonia and free ammonia concentration

5. Conclusion

This study investigated the effects of thermal hydrolysis pretreatment (THP) and temperature (i.e., mesophilic and thermophilic) on the anaerobic digestion of food waste, swine manure, and waste activated sludge in lab-scale reactors. Biochemical methane potential (BMP) test was conducted for approximately 35 days to predict the methane generation potential of the raw and pretreated organic wastes at mesophilic and thermophilic conditions. Continuous stirred-tank reactors (CSTRs) were operated for more than 90 days to evaluate the anaerobic digestion performance as well as feasibility of raw and pretreated swine manure under the two temperature regimes.

(1) THP process improved solubilization of organic particulates in food waste, swine manure and waste activated sludge. THP resulted in higher biomethane potential of swine manure and waste activated sludge except for that of food waste. Thermophilic temperature showed no significant enhancement on the methane yield of food waste, swine manure, and waste activated sludge compared with mesophilic condition in BMP test. The loss of organic matters during pretreatment process limited the application of THP on organic wastes.

(2) THP was favorable to promote the anaerobic digestion of swine manure, by which increasing methane production, decreasing solids content in the effluent, and obtaining more stable process. Thermophilic temperature led to lower effluent quality in terms of higher sCOD and ammonia nitrogen concentration. Besides, the higher temperature did not induce significant improvement of the specific methane yield of pretreated swine manure.

(3) THP improved the feasibility and applicability of anaerobic digestion of swine manure in thermophilic condition. Thermophilic temperature was not recommended for the anaerobic digestion of raw swine manure due to short-term free ammonia inhibition. Besides, thermophilic digestion deserved more periodical monitoring compared with mesophilic condition due to the higher risks of process disturbances or instability caused by VFAs accumulation.

6. Further Studies

(1) One of the objective in this study was to compare the effect of temperature on the anaerobic digestion of food waste, swine manure, and waste activated sludge. The relative comparison of food waste and waste activated sludge was only conducted in BMP test. Due to the elimination of inhibiting factors in BMP test, it is unfaithful to apply the BMP results to CSTRs directly. Further studies are required to investigate more about the anaerobic digestion performance of pretreated food waste and waste activated sludge in continuously-flow reactors under the two temperatures.

(2) The range of 'mesophilic' and 'thermophilic' temperature are different according to various definition. In this study, the 37 and 50℃ were selected as the mesophilic and thermophilic condition settings. However, the two temperatures may be not that great to distinguish the microbial community, thermodynamic equilibrium, etc. in the anaerobic digesters. The higher temperature, e.g., 55℃ or higher, may required to strengthen the conclusions.

(3) In this study, only physico-chemical parameters (e.g., FOS/TAC, alkalinity, VFA, and ammonia concentration) were utilized as indicators to monitor the digestion status of organic wastes. However, anaerobic digestion is a multistep microbial process, which is influenced greatly by microbial interactions. The combination of both physico-chemical as well as microbiological criteria may assist to optimizing the digestion process as well as timely relieving inhibitory or toxic elements.

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초록

열 가수분해 전처리 유기성 폐기물의 중온 및 고온 혐기성 소화 비교 연구

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지난 수십 년 동안 도시 인구의 급속한 증가와 산업의 발전으로 인하여 유기성 폐기물 (음식물쓰레기, 돈분, 폐슬러지 등) 의 발생이 과도하게 증가하였고, 이들의 처리는 주요한 환경 문제로 대두되어 왔다. 혐기성 소화는 이러한 유기물을 분해하여 신재생 에너지로 활용될 수 있는 메탄가스를 발생시킬 수 있으며, 저비용 및 지속 가능한 폐기물 관리방안으로 받아들여지고 있다.

기존의 유기성 폐기물의 혐기성 소화는 원재료의 생분해도가 낮아 수익성이 부족하다. 돈분과 음식물쓰레기의 목질계 섬유 고분자와 폐슬러지 속 세포벽/막 및 플록은 생분해성 유기물이 압축됨에 따라 미생물과 효소에 의한 분해에 저항성을 갖는다. 이러한 특성은 혐기소화 과정 중 가수 분해 단계를 크게 저해하기 때문에 유기성 폐기물의 바이오 가스 발생량을 낮출 수 있다.

따라서 유기성 폐기물의 혐기성 분해가 잘 일어나도록 물리적 파쇄, 초음파 분해, 화학적 처리, 열처리, 효소 또는 미생물을 이용한 전처리 등 다양한 물리 화학적 전처리 방법이 제안되었다. 그 중에서 열 가수분해 전처리는 고온 고압을 이용하여 유기물 속 단단한 구조를 파쇄하고 플록을

분해는 방법으로 폐슬러지 처리에 광범위하게 적용되어왔다. 열 가수분해 전처리의 효과는 유기성 폐기물의 고유한 성상 (예: 특질, 조성 및 구조 등) 과 밀접하게 관련되어 있다. 그러나 열 가수분해 전처리가 음식물쓰레기, 돈분 및 폐슬러지의 생분해도에 미치는 영향에 대한 자세한 비교가 수행된 바는 없다.

본 연구에서는 회분식 및 연속식 반응조와 중온(30-45˚C) 및 고온(45-60˚C) 조건으로 유기성 폐기물의 혐기성 소화에 대한 실험을 수행하였다. 선행연구에서는 열 가수분해 전처리가 유기성 폐기물의 혐기성 생분해에 대해 미치는 영향은 대부분 실험실 규모의 중온 회분식 반응조로부터 평가되었다. 그러나 열 가수분해 이후 혐기성 소화 시 최적 온도에 대해 밝혀진 바가 없다.

따라서, 본 연구의 주요 목적은 열 가수분해와 온도가 여러 유기성 폐기물(음식물쓰레기, 돈분, 폐슬러지)의 혐기성 소화에 미치는 영향을 비교하는 것이다. 본 연구에서는 BMP (Biochemical Methane Potential) 실험을 통하여 음식물쓰레기, 돈분, 폐슬러지의 원 시료 및 열 가수분해 처리 시료의 물질 수지와 더불어 생분해도 양상에 대하여 분석하였다. 또한, 장기간 연속식 교반형 반응조 운전으로부터 유기성 폐기물의 원 시료 및 열 가수분해 처리 시료의 중온 및 고온 혐기성 소화 시 타당성 및 안정성을 평가하였다.

성상 분석 결과로부터 음식물쓰레기, 돈분, 폐슬러지의 열 가수분해 처리가 가연성 부유 고형물의 가수분해도와 화학적 산소 요구량의 용해도를 증가시키는 것을 통계적으로 확인하였다. 열 가수분해는 돈분 및 폐슬러지의 최대메탄발생량을 각각 145.0, 118.2%로 증가시켰으며 음식물쓰레기의 최대메탄발생량에는 변화가 없었다. 고온 혐기성 소화는 음식물쓰레기, 돈분, 폐슬러지의 잠재 메탄 발생량을 중온 조건보다 유의미한 수준으로 증가시키지는 않았다 ($p > 0.05$). 물질 수지 분석 결과에 따르면 돈분의 경우 전처리에 의한 유기물 손실이 커서 실질적인 메탄 발생량은 감소하였다.

연속식 교반형 반응조를 운전한 결과, 돈분의 열 가수분해 처리는 비메탄 발생량과 유기성 고형물 제거율, 화학적 산소 요구량의 용해 수준을 증

가시키는 것을 확인하였다. 고온 반응조에서는 아세트산 농도가 저해 기준을 초과하였으며 프로피온산의 축적으로 반응조의 불안정성이 증가하였다. 전처리하지 않은 시료의 중온 혐기성 소화조에서 일시적으로 자유 암모니아 (Free ammonia) 농도가 증가하였다.

결론적으로, 열 가수분해는 돈분과 폐슬러지의 혐기성 생분해도를 효과적으로 증가시켰다. 그러나 열 가수분해에 따른 유기물 감소가 전체적으로 메탄 발생량을 감소시키는 것을 고려할 필요가 있다. 고온 조건은 중온 조건보다 메탄 발생량을 유의미한 수준으로 증가시키지 않았으며, 소화 공정의 불균형 및 불안정성을 높이는 것으로 나타났다.

주요어: 혐기성 소화; 열가수분해 전처리; 중온 조건; 고온 조건; 유기성 폐기물

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Appendix

1. Elemental analysis of raw and pretreated substrates

Element	Unit	Raw organic wastes			THP pretreated organic wastes		
		FW	SM	WAS	FW	SM	WAS
C	%, dry basis	55.2±0.1	32.5±0.1	28.3±0.1	44.5±0.1	38.6±0.4	30.5±0.1
H		8.3±0.0	4.6±0.1	4.8±0.0	6.5±0.1	4.8±0.1	4.3±0.0
O		31.1±0.1	30.5±0.1	29.4±0.2	35.9±0.1	27.6±0.1	24.7±0.1
N		3.2±0.1	2.4±0.0	4.8±0.0	5.1±0.1	4.4±0.01	4.8±0.0
S		0.3±0.0	0.6±0.0	1.5±0.0	0.3±0.0	0.8±0.0	1.7±0.1
C/N	–	16.8±0.3	13.2±0.2	5.8±0.1	8.8±0.1	8.7±0.1	6.3±0.1

2. Kinetic parameters estimated by Modified Gompertz model

Substrates	AD conditions	P (mL/g-VS)	R_{max} (mL/g-VS d^{-1})	λ (day)	R^2
Food waste	Raw-MAD	519.9	79.6	0.6	0.994
	Raw-TAD	511.9	83.1	2.7	0.998
	THP-MAD	472.5	59.8	0.4	0.994
	THP-TAD	483.5	70.8	2.9	0.995
Swine manure	Raw-MAD	156.3	15.6	0.3	0.994
	Raw-TAD	196.3	17.0	5.1	0.985
	THP-MAD	343.2	50.0	0.2	0.993
	THP-TAD	367.3	38.6	2.2	0.994
Waste activated sludge	Raw-MAD	92.7	19.0	0.2	0.991
	Raw-TAD	146.1	16.9	2.5	0.999
	THP-MAD	192.4	23.0	0.1	0.978
	THP-TAD	167.9	16.8	2.1	0.996

3. Experimental and theoretical methane production

Substrate	AD conditions	Experimental CH_4 production(mL/g-VS)	Theoretical CH_4 production (mL/g-VS)	Methane-based degradability (%)
FW	MAD	531.6±74.4	663.7	80.1
	TAD	517.2±99.5	663.7	77.9
	THP+MAD	487.6±31.8	521.5	93.5
	THP+TAD	500.3±45.7	521.5	95.9
SM	MAD	156.5±28.0	640.8	24.4
	TAD	195.1±16.4	640.8	30.4
	THP+MAD	350.5±35.5	655.9	53.4
	THP+TAD	383.4±18.9	655.9	58.4
WAS	MAD	94.5±14.5	596.1	15.8
	TAD	145.9±15.5	596.1	24.4
	THP+MAD	206.2±5.2	738.2	29.9
	THP+TAD	166.5±22.3	738.2	22.5