CHAPTER 1
INTRODUCTION

1.1 Problem Statement

Thailand faces difficulties in managing waste sustainably and the continuous increase in municipal waste streams, from 10.80 million tons (1992) to 15.16 million tons (2010), has aggravated the problem (Pollution Control Department, 2011). Of the total waste generated, only 38% was properly managed through existing waste disposal systems: sanitary landfill, mixed system, and incineration. Thailand lags behind the waste separation. A consolidated unsorted waste into landfill is still the main disposal route in the current practices. There is a serious gap between the existing landfills system, 94 sanitary landfill sites are in operation throughout the country, and the waste quantities. While new landfill sites face difficulty in obtaining public acceptance for new landfill sites and waste generation keeps growing, utilization of waste as a source of alternative energy by biogas process is a promising solution. Thailand has renewable energy plans, with the Ministry of Energy's Renewable Energy Development Plan (REDP) aiming to increase the share of alternative energy mix to from 7% to 20% (approximately 5,600 MW) of energy demand by 2021. This goal includes the generation of 160 MW of energy from waste by 2022 (currently 13 MW). Anaerobic digestion (AD) of the sorted organic fraction of municipal solid wastes (OFMSW), like food waste and market waste, is one of the target renewable energy sources has been recommended for the maximizing the recycling and usage of the waste components.

Food waste, a methane (CH_4) rich biogas substrate (Banks *et al.*, 2011), is the single largest component of the waste stream in Thailand, representing 40% of municipal solid waste (MSW). Both food waste and market waste characterized by relatively high organic matter (85-95% of volatile solid, VS) and moisture content (75-85%), have been counted as a suitable feedstock for the anaerobic digestion process. But the heterogeneity of food and market waste, including the variability of their chemical compositions and a wide range of waste degradation rates, has a strong influence on the levels of waste bioconversion and biogas production under conventional single-phase condition. Elevated levels of volatile fatty acid (VFAs) from readily biodegradable fractions (e.g., carbohydrates) fermentation result in a drastic pH drop at an early stage. Low pH reduces the methanogenic bacteria activities causing an accumulation of VFAs, also known as a symptom of a 'sour or stuck' (biologically inactive) digester, which then slowdowns the VFAs production. Excessive intermediate VFAs are not only regarded as product inhibition of hydrolysis-acidogenesis, but also as a strong substrate inhibition of methanogenesis resulting in eventual process failure. A toxic effect on the bacterial growth by fermentation acids has been related to the molecular form of the acid: dissociated-undissociated, depending upon environmental pH and acid concentration. As its ability to freely move across the cell membrane following the pH difference (ΔpH) between the external medium and intracellular pH is higher than that of the ionized form, the undissociated acid is regarded as a much more potent cell growth inhibitor.

To overcome this problem, two practical methods were tested: (1) dilution of the digester content with water; and (2) adjustment of liquid phase pH. This work focused on improving the acidogenesis condition for treating food waste and market waste with parallel control of undissociated VFAs inhibition. These conditions were also tested on high solid content of food waste (15% TS).

1.2 Literature Review

1.2.1 Food Waste

Food waste (called garbage in American English) is one of the three greatest components MSW (food waste, paper products, and yard wastes) that are suitable for the bioconversion process (Worrell and Reinhart, 2002). The last two are also valuable in biochemical processing due to their high cellulose content.

Food waste is one type of biodegradable waste. There are several factors affecting the composition and quantity of food waste, such as the geographical location, season, dietary habits, standard of living, etc. Typically, food wastes in MSW include uneaten food and food preparation wastes from residences, commercial establishments (e.g. restaurants and markets), institutions (e.g. school and hospitals), and some industrial sources (e.g. factory cafeterias or lunchrooms).

In Bangkok Metropolitan, the solid waste generation rate increased from 3,260 tons per day by year 1985 to 9,400 tons per day by year 2003. On average, Bangkok waste has a bulk density in the range of 0.34-0.40 kg/l and quite high moisture content, around 46-56%. Total solid content is 44.44-53.54% (Department of Public Cleaning, Bangkok Metropolitan Administration). The organic fraction in MSW consists of food waste (44.34%), paper (11.89%), and yard waste (5.67%). In addition, the remaining inorganic fraction is composed of plastics (22.43%), glass/stone (3.51%), metals (1.71%), textile (5.52%), and rubber/leather (1.95%) (Asian Institute of Technology, 2004). Food waste is the main component of solid waste in Bangkok. When wood and leaves are added up to the food waste and categorized as organic waste, the amount can be as high as 53% (Table 1.1).

Table 1.1 Waste composition of Bangkok at transfer station in year 2009

Waste type	Percent
Food waste	44.34
Wood and leave waste	5.67
Textile	5.52
Recyclable plastic	3.25
Glass	2.70
Rubber	1.95
Metal	1.71
Bone and shell	1.54
Foam	1.44
Recyclable paper	1.19
Stone and ceramic	0.81
Non-recyclable paper	10.70
Non-recyclable plastic	19.18

(Source: Department of Environment, Bangkok Metropolitan Administration, 2009)

Table 1.2 Average composition of solid waste from several sources

Composition of waste	Source of waste (Percentage by weight)								
	Household	Apartment	Hotel	Shopping center	Restaurant	Market	Temple	Academic institute	Office building
Food waste	48.09	42.02	43.43	33.07	53.34	58.81	40.02	23.79	29.86
Paper	1.08	17.84	14.24	20.07	10.40	9.91	12.55	34.95	28.86
Plastic and foam	15.63	15.10	14.94	21.16	13.09	14.56	16.65	16.44	17.59
Tires	2.21	2.64	2.24	1.96	2.37	3.03	2.40	2.04	2.83
Leather	0.53	1.77	1.86	1.81	2.54	0.83	1.84	0.53	2.35
Textile	2.60	2.24	1.59	2.39	1.65	0.95	2.53	1.51	2.66
Wood	2.55	3.44	2.69	2.05	3.03	1.22	5.29	5.96	2.54
Glass	6.26	8.92	6.93	10.58	4.50	4.01	10.96	3.91	4.53
Metal	4.79	2.76	3.82	1.69	6.06	1.19	1.98	2.23	2.97
Stone	3.03	1.51	5.60	0.68	0.69	2.68	2.26	0.90	1.74
Hazardous waste	3.60	0.62	1.98	1.15	1.78	0.41	1.76	6.62	3.72
Others	0.62	1.15	0.67	2.77	0.54	2.39	1.76	1.1.1	0.80

(Source: Department of Public Cleaning, Bangkok Metropolitan Administration, 2001)

1.2.2 Market Waste

Wet markets, also called fresh or street markets, are open food markets selling meat, fish, fruits and vegetables, and sometimes live animals. Table 1.3 reports the average percentage spent in a typical month by type of retail outlet (wet market, supermarket/hypermarket and other) for five food categories (fruit and vegetable waste, fresh meat, fresh meat, packaged goods, and beverages).

In 2007, Thailand generated approximately 15 million metric tons of MSW, of which about 22% was generated in the Bangkok area. MSW include households, commercial and business establishments, fresh markets, institutional facilities, and construction and demolition wastes. MSW is generally collected and treated by local governments. The main component of MSW is food waste (approximately 49%), followed by plastic (18%) and paper (13%). There are no specific data on fresh market waste generation at the national level in Thailand. It was estimated that the composition of fresh market waste is similar to that of MSW. It was estimated that wet market waste represents about 9% of the total MSW generated in Thailand, i.e., approximately 1.35 million metric tons per year. In September 2009, there were 1,536 fresh markets registered, of which 145 were located in Bangkok, 75 in Chiang Mai, and 57 in Lampang (Figure 1.1).

Table 1.3 Average percentage spent by type of retail outlet for different food product categories

Area	Wet market	Supermarket	Other
Fresh fruit and vegetables (FFV)	55.5%	36.8%	7.6%
Fresh meat	53.4%	40.3%	6.1%
Fresh fish	62.4%	31.0%	7.1%
Package goods	30.1%	59.9%	10.0%
Beverages	17.9%	69.1%	13.0%

(Source: Gorton *et al.*, 2011)

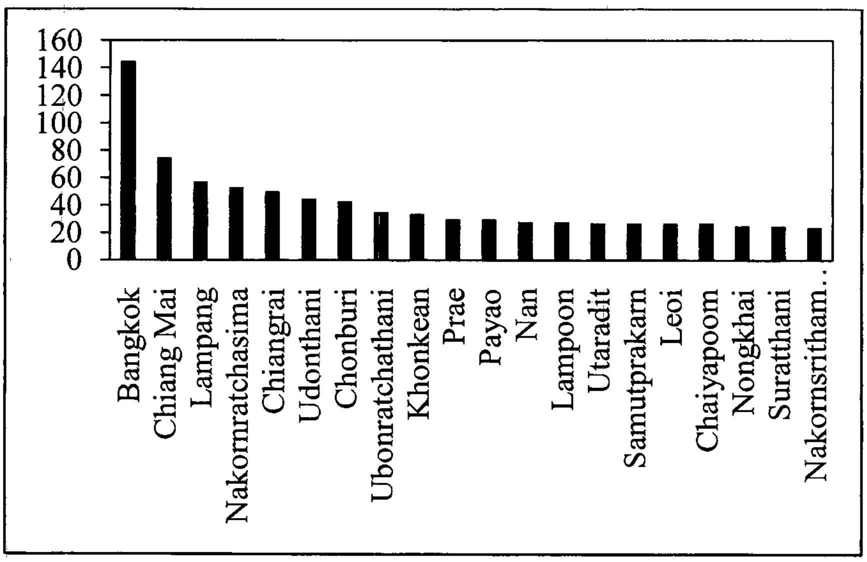

Figure 1.1 Top 20 provinces with the highest number of registered markets
(Source: Bureau of Food and Water Sanitation, 2009)

It was reported by the Food Marketing Institute that in fresh markets in Thailand wastage levels were highest for fruit and vegetables (10%), followed by seafood wastage (8-9%) and meat wastage (6%). In general, market waste and MSW are collected and treated at the same sites (open dumps or landfills). However, there are a few initiatives and pilot projects to treat market waste on-site through anaerobic digestion. In Bangkok, MSW are mainly disposed in landfills (81%), while in the rest of Thailand. MSW is mainly disposed of in open dumps (65%). In the absence of specific data, it was assumed that market waste disposal methods are similar to that of MSW.

Table 1.4 Ultimate methane yields of fruit and vegetable wastes and manures

Fruit and vegetable waste	Methane yield m^3 per kg VS (SD in parentheses)
Banana peel (Robusta variety)	0.277 (0.007)
Mango (Neelum variety)	0.373 (0.012)
Lemon pressings	0.473 (0.011)
Rotten tomato (mean of varieties)	0.298 (0.012)
Onion outer peel	0.400 (0.014)
Cauliflower leaves	0.190 (0.009)
Cauliflower stem	0.331 (0.013)
Potato peel	0.267 (0.017)
Turnip leaves	0.314 (0.010)
Radish shoots (pale pink variety)	0.304 (0.012)
Garden pea pods (seeds removed)	0.390 (0.013)
Carrot (leaves)	0.241 (0.008)
Carrot (petiole)	0.309 (0.010)
Garden beet (leaves)	0.231 (0.008)

(Source: adapted from Ward *et al.*, 2008)

1.2.2 Variables Affecting Anaerobic Digestion Processes

Various factors affecting the biodegradation of the waste in anaerobic digestion processes are described below.

1.2.2.1 Composition of the Waste

Nutrient composition and concentration of the raw waste are factors that influence the anaerobic digestion process. The more food wastes that are present, the more rapid is the gas production (Gunnerson and Stuckey, 1986). Paper is degraded at a slower rate even though it is also classified as organic or biodegradable waste, while other materials, such as plastics, and lignocellulosic materials, such as wood, resist anaerobic biodegradation. Generally, sources and compositions of food and market wastes are different. Major components of food waste are starch and fat and oil, while market waste comprises mostly cellulose and lignin (Towprayoon *et al.*, 2003). Fruit and vegetable wastes tend to have low TS and high VS, and are easily degraded in an anaerobic digester (Table 1.4). The rapid hydrolysis of these feedstocks may lead to acidification of a digester and the consequent inhibition of methanogenesis. It was found that many carbohydrate-rich feedstocks require either co-digestion with other feedstocks or the addition of alkaline buffers to ensure a stable performance (Knol *et al.*, 1978).

1.2.2.2 Moisture Content

Moisture content is one of the most important parameters in the anaerobic digestion process because the nutrients for the microorganisms must be dissolved in water before they can be assimilated. The moisture content may promote not only bacterial movement, but also affect to the mass transport limitation in high-solids organic wastes (Lay *et al.*, 1997). This factor also relates to the balance between the production of VFA by acidogenic bacteria and the conversion of acids to methane by methanogenic bacteria. Increasing the moisture content from 61% to 75% leads to a 10 to 20 fold increase in the rate of conversion over short periods of time (Buivid, 1981). Similar to the results obtained by Barlaz *et al.* (1990), higher moisture contents (55%) in shredded refuse led to more rapid acid accumulations. They also found that methane production was not always observed at low moisture content (35%).

Leachate recirculation is one of the options to maintain the moisture content in the digestion process since it can both increase the moisture content in a system and provide the various nutrients, bacterial seeds and enzymes for methanogens and solid/liquids. Reinhart and Al-Yousfi (1996) reported that the leachate recycling not only improves the leachate quality, but also shortens the time required for stabilization from several decades to 2-3 years.

However, since levels of recirculation volumes too high result in an imbalance between acidogenesis and methanogenesis because they inhibit the production of fermentation products (volatile organic acids and alcohols), the leachate recirculation should be properly adjusted. According to Borzacconi *et al.* (1997), the leachate recirculation can lead to the inhibition of methanogenesis because it may cause high concentrations of organic acids (low pH), which are toxic for the methanogens. A similar result was obtained by Sponza and Agdag (2004) in an experiment where anaerobic bioreactors were operated without leachate recirculation while the other two reactors were operated with a leachate recirculation rate of 9 l/day (13% of the reactor volume) and 21 l/day (30% of the reactor volume). After 220 days of an anaerobic process, they observed that the pH, chemical oxygen demand (COD), VFA concentrations, methane gas production, and methane percentages in the bioreactor that had a leachate recirculation rate of 9 l/day were better than in the other reactors.

1.2.2.3 Nutrient Requirements

One of the factors in the stability of the anaerobic digestion is the nutrient requirements of microorganisms. Nutrient deficiencies lead to digester failure. Nitrogen and phosphorus are the major nutrients (macronutrient) required for anaerobic digestion; in addition, some micronutrients (K, Mg, Ca, Fe, Mn, Mo) are necessary for bacterial growth (Adhikari, 2006). The relationship between the amount of carbon and nitrogen can be expressed in terms of the carbon to nitrogen ratio (C/N). A C:N ratio of 20-30 or 25-30 (Polprasert, 1996) is considered an optimum value for anaerobic digestion. High C/N ratio is an indication of rapid consumption of nitrogen by methanogens, which leads to lower gas production, whereas a low C/N ratio causes ammonia accumulation that leads to an increase in the pH value and the pH value exceeding 8.5 is toxic to methanogens. Therefore, nutrients should provide be provided in the optimal ratio of concentrations.

In general, many anaerobic organisms in digesters are also found in the wastes of animals and human beings. While these organisms will develop naturally in the digester, the degradation process can be initiated more rapidly by seeding the wastes with sewage sludge, which also serves as an additional source of moisture (Gunnerson and Stuckey, 1986).

1.2.2.4 Mixing

In a solid waste digestion, mixing increases the contact between the microorganisms and the food supply (solid waste). In practice, leachate recirculation helps to promote the mixing of seed and nutrients with MSW during the digestion process. Furthermore, mixing also minimizes the settling of grit and reduces the buildup of scum; other advantages of mixing are summarized in Table 1.5.

Table 1.5 Advantages of mixing digester content

Eliminating of reducing scum build up
Eliminating thermal stratification of localized pockets of depressed temperature
Maintaining digester sludge chemical and physical uniformity throughout the tank
Rapid dispersion of metabolic wastes (products) produced during substrate digestion
Rapid dispersion of any toxic materials entering the tank (minimizing toxicity)
Prevent deposition of grit

(Source: Gerardi, 2003)

Mixing does not need to be continuous to achieve an acceptable destruction of VS because it is costly. For example, three to six periods of routine mixing per day may be an efficient pattern. In addition, methane-forming bacteria are very sensitive to rapid mixing. Consequently, continuously washing out of methane-forming bacteria in the effluent may occur (Gerardi, 2003). Speed of mixing also affects to anaerobic digestion process; under low mixing (80 rpm) conditions, the system is able to absorb the disturbance of shock load (Gómez *et al.*, 2006).

1.2.2.5 Particle Size

The particle size of waste influences the biodegradation rate. A smaller particle size provides more surface area for the microorganisms to attack (Gunnerson and Stuckey, 1986). The result of Kayhanian and Hardy (2004) indicated that the rate of methane production was inversely proportional to the average feedstock particle size. However, a too small particle size might lead to the compaction of the waste and lower optimal moisture content (Hartmann and Ahring, 2006).

1.2.2.6 Temperature

Temperature is one of the most important factors affecting the microbial activity within an anaerobic digestion process. Depending on the typical temperature ranges for optimum activity bacteria can be classified as phychrophilic, mesophilic, and thermophilic, as shown in Table 1.6. The conventional anaerobic digesters can be operated either at mesophilic or thermophilic temperatures or at ambient temperature in the case of tropical countries, where the control of temperature is not a common practice (Sánchez *et al.*, 2001).

Table 1.6 Typical temperature ranges for various bacteria

Type	Temperature, °C	
	Range	Optimum
Psychrophilic[a]	-10 - 30	15
Mesophilic	20 - 50	35
Thermophilic	45 - 75	55

[a]also called cryophilic
(Source: Tchobanoglous *et al.*, 1993)

Generally, higher temperature results in higher metabolic activities. Thermophilic conditions allow more methane production than mesophilic conditions.

However, the study in a two-phase digester on highly biodegradable OFMSW by Pavan *el al.* (2000) showed a different result. They identified that an increase of temperature in the hydrolytic phase up to thermophilic levels does not improve either yield or kinetics.

In general, fluctuations in temperature influence both methane-forming bacteria and volatile acid-forming bacteria. A 10°C temperature increased can stop methane production or methane-forming bacterial activity within 12 hours, while volatile acid production increases. Changes in the activity of different groups of volatile acid-forming bacteria result in changes in the relative quantities of organic acids and alcohols produced during fermentation. Changes in the quantities of organic acids and alcohols that are used directly and indirectly as substrates by methane-forming bacteria affect the overall digester performance.

1.2.2.7 pH

The pH is known to influence enzymatic activity because each enzyme is active within only a narrow and specific pH range, and displays maximum activity at an optimum pH, generally from 6.7 to 7.5 (Adhikari, 2006). The optimal pH values for acidogenesis and methnogenesis are different. Acidogens can tolerate a pH as low as 5.5 but methanogens are inhibited at such low values. In general, mehanogenes are very sensitive to pH. Most methanogenic bacteria function is in a pH range between 6.7 and 7.4, and the rate of methanogensesis may decrease if the pH is lower than 6.3 or higher than 7.8 (Lay *et al.*, 1997). A acceptable ranges of pH values for a primary digester and secondary digester are 6.6 to 7.0 and 6.8 to 7.2, respectively (Gerardi, 2003).

The sharp drop in the rate of methanogenesis below pH 6.3 may be related to the fact that methane production proceeds at a slower rate than the production of organic acids; the sharp drop in the rate above pH 7.8 may be related to a shift in NH_4^+ to the toxic, unionized NH_3 form. A study conducted by Lay *et al.* (1997) showed that the rate of methane production in high-solids sludge digestion may fail if the pH is lower than 6.1 or higher than 8.3. Ammonia produced from degradation of protein provides the buffering to the system. Nevertheless, if the concentration of ammonia increased to a pH range of 6.8-7.3, the system becomes toxic. When the pH in an anaerobic reactor decreases, feeding should be stopped and the buffering capacity should be increased by adding calcium carbonate, sodium bicarbonate or sodium hydroxide (Adhikari, 2006).

1.2.2.8 Inhibitory and Toxic Substances

The toxic effect depends on the concentration of the toxic substrate in the system and the ability of the microorganisms to tolerate that effect. Volatile acids, such as acetate, butyrate, propionate, cause alkalinity (Alk) decrease and a drop in pH. According to Hanaki *et al.* (1994), propionaic acid is believed to be the most toxic VFA appearing in anaerobic digestion, and its oxidation to acetic acid is the slowest among all VFAs. This report also showed a reduction of the hydrolysis rate due to an accumulation of VFA.

Free ammonia (NH_3), also called unionized ammonia, is another toxic substance to anaerobic digestion process. Generally, ammonical nitrogen from degradation of organic nitrogen compounds (protein) exists in two forms: ammonium ion (NH_4^+) and free ammonia. Free ammonia is toxic to the anaerobic digester, whereas ammonium ions are nutrients for microorganisms. The existing free ammonia and ammonium relates to the pH value of the system. At high pH value (> 8), the main form of ammonical ammonia is free ammonia; this form is more inhibitory than the ionized ammonium. Free ammonia can affect the anaerobic digester by inhibiting the enzyme that synthesizes methane. In general, dissolved ammonia and ionized ammonia are measured together and this total amount is reported in terms of ammonia concentration, which can lead to the inhibition of anaerobic digestion (Mata-Alvarez *et al.*, 2000). Gerardi (2003) reported that ammonia concentrations greater than 1,500 mg/L at high pH may result in digester failure, while Kayhanian (1999) revealed that ammonia inhibition occurs at the concentration of 1,200 mg/L.

1.2.2.9 Substrate Loading Rate and Retention Time

Organic loading rate (OLR) is a measure of the biological conversion capacity of the anaerobic digestion system. Feeding the system above its sustainable OLR, overloading, results in low biogas yield due to an accumulation of inhibiting substances, i.e. fatty acids, in the digester slurry. Therefore, the feeding rate of the system must be set in the optimal range. OLR is a particularly important control parameter in continuous systems. In a one-stage system, acidogenic and methanogenic reactors are combined in one vessel. Increasing the feeding rate of the substrate promotes the acidogenic activity, and the formation of mainly acetate, carbon dioxide (CO_2) and hydrogen is increased, whereas the methanogenic population cannot increase its activity to the same extent causing an imbalance of acidogenic and methanogenic bacteria in the system. Many biogas plants have reported system failure due to overloading. The OLR is typically expressed as weight of organic matter (VS or COD) per bed volume of reactor in a certain period of time, i.e. kg COD or VS per cubic meter of reactor. It is also linked to the retention time for any particular feedstock and anaerobic reactor volume.

In 1984, wastes from the processing of many fruits and vegetables, such as apple press cake, extracted sugar beet pulp, pineapple pressings of asparagus waste, were utilized as feedstock for anaerobic digestion by Lane. The experiments were performed using wastes which were diluted with water to 10% TS; a gas yield and methane content of 0.429-0.568 L/g TS fed and 50-65%, respectively, were obtained. The results also concluded that the maximum accepted loading rate for fruit waste is 3.5 kg TS/m^3 d. Overloading of digesters, continuous stirred tank reactor (CSTR), with loading of fruit and vegetable wastes above 4 kg TVS/m^3.d was also reported by Lane (1979), the result being a fall in pH and gas yield, and an increase in the CO_2 content of gas produced.

Mata-Alvarez and Llabrés (1992) examined the performance of the mesophilic one-stage completely stirred reactor for the treating of the organic fraction of the waste coming from a large food market. The OLR of 6 kg TVS/m^3.d was found to be a limiting condition for similar waste digestion. High biodegradability, large and fast VFA production of this waste stressed the validity of this OLR limit.

Recirculation rate is a significant parameter in the operation of a two-phase system (Viturtia and Meta-Alvarez, 1989). High COD and total volatile fatty acid (TVA) were produced from the food waste in the acid formation step and caused nuisance to the fixed film reactor. Recirculation of leachate could reduce COD and increase OLR in the anaerobic methanogenesis reactor; however, low methane production was obtained. In the case of market waste, an acceptable methane production yield was obtained in higher OLR due to less acidity production. Therefore, it should be aware of the appropriate OLR for food waste and market waste because of its impacts on the performance of the reactor (Towprayoon *et al.*, 2003).

Another important parameter affecting the overall efficiency of the anaerobic digestion system is the presence of VS, because these present the organic matter in a feed waste. This parameter is measured as the solid content minus the ash content, as obtained by complete combustion of the feed wastes. Volatile solid comprises the biodegradable VS (BVS) fraction and the refractory VS (RVS). High VS content with low RVS is more suitable for anaerobic digestion (Monnet, 2003).

A semi-continuously mixed tubular mesophilic tubular anaerobic digester of fruit and vegetable waste into biogas was investigated by Bouallagui *et al.* (2003). Varying condition of TS (4%, 6%, 8%, and 10%) and HRT (10, 12, 15, and 20 days) were applied. The best results were obtained for the HRT of 20 days with an OLR of 2.8 kg TVS/m^3.d, while the highest biogas production yield (0.7 m^3/kg VS added) was found with a feed concentration of 6%.

1.2.3 Monitoring Parameters of Anaerobic Digestion

1.2.3.1 Specific Gas and Methane Yield

Specific gas production and methane yield are directly related to the extent and rate of feed conversion and the anaerobic process efficiency. However, a low gas production should not be used as an indicator to confirm system failure, as it just shows a low biodegradation of substrate. Both specific gas production and the ultimate methane yield are expressed as m^3 CH_4/kg VS added. The methane content of biogas is a good indicator of process stability (Adhikari, 2006). Methane content is a function of hydrogen to carbon ratio of the biodegradable fraction; generally, it has a normal range of 50-60% of MSW (Chynoweth *et al.*, 1994).

1.2.3.2 Volatile Solids Destruction

The net change or loss in volatile matter is also a measure of biodegradation of the feedstock in anaerobic digestion process. It is more appropriate to use VS loss rather than the TS loss since the destruction of the former is related to organic matter.

1.2.3.3 VFA, pH, and Alkalinity

All organic acid, pH and alkalinity can influence the anaerobic digestion performance. The alkalinity value can show both how able the reactor is to buffer acidic shock loads and how efficient the system is. The normal range of alkalinity is between 1,000 to 5,000 mg/L as $CaCO_3$. Acceptable alkalinity concentrations in a primary digester and secondary digester are normally 1000-2000 and mg/l 1500–3000 mg/l, respectively (Gerardi, 2003).

Under overloading rate and in the presence of inhibitors condition, the removal of hydrogen and organic acid is not as fast as they are produced. This condition results in an increase in VFA concentration and buffer depletion, which leads to a decreased pH. Since the accumulation of VFA will occur before the drop of pH can be observed, generally, VFA is an early warning indicator of system failure.

1.2.4 Type of Anaerobic Digester

Anaerobic digestion can be classified into different categories, such as those based on the operating temperature, stages of operation, feeding mode, etc.

1.2.4.1 Based on Bacterial Growth

In a suspended growth system, the bacteria are suspended in the reactor. Mixing promotes the bacteria or biomass to distribute through the digester. Suspended growth anaerobic digester is suitable for the treatment of particulate, colloidal and soluble wastes, whereas large digester volume is required to provide the necessary SRT, and the treatment efficiency may be reduced due to loss of bacteria in the digester effluent. One option to solve such problem is a fixed film anaerobic digestion.

The basic fixed film digester design consists of a tank filled with supportive media, i.e. gravel, plastic, and rock, on which a consortium of bacteria attaches and grows as a slime layer (biofilm). Wastewater flow can be in either the up flow or down flow mode. When the organic matter passes through the media-filled reactor, the attached and suspended anaerobic biomass converts both soluble and particulate organic matter in the waste to biogas. Soluble organic compounds will be absorbed (diffused into) by bacteria, whereas insoluble organic compounds are adsorbed or attached to the surface of the bacteria (Gerardi, 2003).

Immobilization of the bacteria as a biofilm prevents washout of slower growing cells and provides biomass retention time. Because the bacteria are not continuously washed out along with the effluent, there are more bacteria in the biofilm reactor than in the conventional suspended-growth designs. Furthermore, less time is needed to degrade in the fixed film system, allowing operation at short HRTs, i.e. in the range of 2 to 6 days. Reactors with a biofilm are widely used, such as in the alcohol, sugar, canning, starch and paper industries. Its high kinetic performances make it possible to treat even high strength wastewater.

1.2.4.2 Based on Phase of Operation

Anaerobic digestion process can be grouped into single-phase and multi-phase systems, mainly two-phase digesters. Two-phase systems consist of two separate tanks, whereas single stage digesters consist of only one tank or reactor. Single stage is more easily upset than two-stage digesters because the latter can provide the optimal condition for two bacterial groups, acidogen and methanogen. In fact, acid forming bacteria grow more quickly than methane forming bacteria and are also more tolerant of fluctuations in the operational conditions; therefore, an imbalance between acid production rate and methane production rate often occurs. This imbalance causes a decrease in alkalinity and pH that result in system failure.

Single- and two-phase anaerobic digestions of vegetable wastes under mesophilic and thermophilic temperatures were compared by Verrier *et al.* (1987). Significant higher methane production was obtained in the two-phase system under mesophilic conditions and a maximal overall methane production of 5 L CH_4/l d was obtained in this study. In general, there are advantages and disadvantages with both one- and two-phase separation, but this study showed that a two-phase system process is efficient when treating easily degradable solid wastes, while the single-phase system is more sensitive to overloading, especially when accumulating propionate. The authors also found that two-phase systems are highly stable and can proceed with high peak loading when using fixed film reactors for the methanogenic phase.

The two-phase anaerobic digestion of a mixture of fruit and vegetable wastes (FVW) has been studied in different works. The two-step technology applied by Rajeshwari *et al.* (2001) allowed the conversion of over 94% of vegetable market waste into biogas. Likewise, in the study performed by Ruynal *et al.* (1998), various kinds of FVW were fed to a two-phase anaerobic digestion in which the hydrolysis-acidification step occur in an anaerobic sequencing batch reactor (ASBR) and the methane fermentation in a fixed film reactor (up flow mode). A degradation above 87% and a biogas production yield of about 0.29 l per g of input total COD were obtained in this experiment.

The balance between the acidification and methanation in an anaerobic reactor can be adjusted by changing the pH, temperature and organic loading. Zoetmeyer *et al.* (1982) studied the influence of pH in the range from 4.5 to 7.9 on the acidogenesis of a simple substrate, and recommended the pH range of 5.7-6.0 for the acid formation reactor to provide a stable and most favorable substrate for the methane production.

1.2.5 Previous Study in Anaerobic Digestion of Food and Market Waste

The degradation of each component of the food waste is affected by the environmental conditions in the system. Carbohydrate, cellulose and protein have their own optimum retention time and pH for degradation. Therefore, the adequate adjustment of the environmental conditions for food waste degradation depends on the state of degradation. In the early stage, rapidly degradable matters (e.g. carbohydrate) cause a pH drop and product inhibition. High dilution rate (4.5 L/d) is maintained in the initial day to move produced VFA to the methane reactor quickly, and a lower dilution rate should be applied after 2 days for the enhanced degradation of slowly degradable matters such as cellulose and protein. It was reported that cellulose degradation increased at high retention time, whereas protein degradation increased at both high retention time and neutral pH (Han and Shin, 2004).

In 1992, Mata-Alvarez and Llabrés confirmed the high biodegradability of the organic fraction of food waste from a vegetable market. Four HRTs (8, 12, 14, and 20 days) were tested, the highly ultimate methane yield of 0.478 m^3 CH_4/ kg VS added was obtained from the experiment. In 1993, Mata-Alvarez *et al.* used the mixture of fruit and market waste, which was diluted to 4.51% as a feedstock in two-phase digesters. The digestion was operated under mesophilic temperature by using digested pig manure as inoculums. The overall methane composition computed over the total digestion period was 69.7%, while a specific biogas production of 0.742 m^3 biogas kg^{-1} VS was found.

Argelier *et al.* (1998) evaluated the influence of the initial substrate concentrations on VFA production. Food wastes (TS content of 43.8%) were digested at a mesophilic temperature (35°C) in completely mixed reactors. Three dilutions of substrate (1/25, 1/10, and 1/5) corresponding to 1.75%, 4.38%, and 8.76% of TS and five values of OLR: 2, 5, 10, 12.5, and 25 kg COD/m^3 d were studied. It was found that substrate 1/10 led to 14 g VFA/l at a loading rate of 12.5 kg COD/ m^3 d and a HRT of 3.7 d. The main VFA produced were especially acetate and butyrate. Substrate diluted 1/5 led to 26.1 g VFA/l at a loading of 5 kg COD/ m^3 d and a HRT of 15.1 d, but biomass production was not optimal.

The biogas and methane yields of the food waste collected from California were evaluated using a batch anaerobic digestion at 50°C. An analysis of the contents of food waste indicated that food waste contained balanced nutrients for anaerobic microorganisms. The results showed that the average methane yield was 348 and 435 mL/g VS, respectively, after 10 and 28 days of digestion, while the average methane content of biogas was 73%. The average VS destruction was 81% at the end of the 28-day digestion period. These indicated that the food waste is a highly desirable substrate for anaerobic digestion (Zhang *et al.*, 2007). Cho *et al.* (1995) determined the methane yields of different food waste at 37°C and 28 days of digestion time. Methane yields were 482, 294, 277, and 472 mL/g VS for cooked meat, boiled rice, fresh cabbage, and mixed food waste, respectively. Heo *et al.* (2004) reported a methane yield of 489 mL/g VS obtained from a traditional Korean food that consisted of boiled rice (10-15%), vegetables (65-70%), and meat and eggs (15-20%) after 40 days at 35°C.

In 2002, the use of rumen microorganisms to enhance cellulolytic activity in short generation times was investigated by Han and Shin (2002). The authors found that the acidogenic fermentation efficiencies of food waste were 71.2 and 59.8% at 3 d^{-1} for rumen microorganisms (from the stomach of a cow) and mesophilic acidogens (from an acidogenic reactor treating food waste), respectively. They also reported that rumen microorganisms had enhanced waste degrading capability, especially of cellulosic material (i.e. vegetables). In addition, these authors also studied the effects of adjusting the dilution (D) rate to improve acidogenic fermentation of food waste in a continuous flow reactor. The dilution rate of 1, 2, 3 and 4 d^{-1} was studied in the initial stage, and the dilution rate of 3 d^{-1} was shown to provide the most consistent fermentation efficiency. In the next step, the dilution rate was reduced from 3 d^{-1} to 3, 2, 1, and 0.5 d^{-1}. They found that the efficiency of the fermentation increased from 71.2 to 82.0% by reducing dilution rate from 3 to 1 d^{-1}.

Market waste is another interesting feedstock in anaerobic digestion system. Fruit and vegetable wastes, such as apples, asparagus, carrots, and green peas from canning factories, were digested at loading rates varying between 0.8 and 1.6 kg VS/m^3d and a retention time of 32 days under mesophilic temperature (Knol *et al.*, 1978). The results showed an average biogas yield varied from 0.3 to 0.58 m^3/kg VS. The authors concluded that an anaerobic digestion is a suitable process for the treatment of fruit and vegetable waste. Although the composition of the carbohydrate-rich substrates tends to produce a suboptimal digestion, this is may be resolved by the alkali addition, adjustment of the loading rate and the use of mixed substrates.

Ranade *et al.* (1987) presented the anaerobic digestion of vegetable market waste in a non-stirred floating dome type biogas plant. Different HRT of 5, 10, 20, and 30 days were studied with 5% TS. The results revealed that market waste is rich in easily degradable substrate, such as starch, fat, protein and soluble sugar while its cellulose, hemicellulose and lignin content is less. It was found that the VFA content at 5 and 10 days HRT was very high compared with that at 20 and 30 days HRT. In addition, this HRT was favorable for the conversion of propionate, butyrate and valerate to acetate, the substrate for methanogenic bacteria. It was thus concluded that an HRT of 20 to 30 days is suitable for the anaerobic digestion of market waste. Furthermore, the data collected over the period of 75 days showed that the maximum production of biogas, 35 L/kg MW d, was obtained at 20 days HRT.

The effects of feeding different fruit and vegetable wastes, such as mango, pineapple, tomato, jackfruit, banana and orange, were studied at different loading rates and at hydraulic retention times (HRT). The maximum biogas yield of 0.6 m^3/dg VS added was obtained at a 20 days HRT and 40 kg TS/m^3 d loading rate, while a methane content in the range of 51-53% was recorded (Viswanath *et al.*, 1992).

In 2001, Turajane investigated the solid waste degradation behavior and compared the methane production efficiency with and without leachate recycling. Three different leachate recirculation rates of 10, 25, and 50 percent (OLR around 782, 1,674, and 2,603 g COD/m^3 d^{-1}) were applied in the study. A total solid of 25-30%, the percentage of TS in vegetable and fruit wastes were collected, was used as raw material for the anaerobic digestion process. The result showed that the highest biogas production and methane content of 129.14 L and 52.45%, respectively, were found in the highest leachate recirculation rate of 50%.

1.3 Objectives

1.3.1 To improve the volatile fatty acid formation from food and market waste during the acidogenic anaerobic digestion process.

1.3.2 To study the performance of a two-phase fixed film anaerobic digestion system of food and market waste.

1.4 Scope of the Study

1.4.1 Mixed food waste in this study was collected from the cafeteria of King Mongkut's University of Technology Thonburi and made into a desired solid content with tap water.

1.4.2 Mixtures of fruit and vegetable waste from a fresh market, the Thungkru (Prachauthit 61) Market, in Bangkok, were used as representative market waste. Only decomposable fractions, such as vegetable and fruit waste, were used and prepared based on the data obtained from the market waste composition study, which comprised vegetable waste (80%) and seasonal fruits (20%).

1.4.3 The hydrolysis yield and acid yield reported here are shown as the apparent (not the actual) values, since the methanogenic phase was reached.

1.4.3 All experiments were carried out under designated laboratory conditions in a batch experiment mode.

1.4.4 The pH was adjusted to the desired value with sodium bicarbonate ($NaHCO_3$) and sulfuric acid (H_2SO_4).

1.4.5 Increasing the OLR was tested by pumping liquid from the acidogenic reactor into the methanogenic reactor with a discontinuous feeding regime by increasing the organic load (fed once a day) or shortening the retention time (fed more than once a day). The OLR tests in the stepwise approach were performed daily.

1.5 Output/Outcome

1.5.1 Understanding the production of total VFA and undissociated fraction, and their inhibition of the anaerobic digestion process, which often occurs for heterogeneous solid waste treatment.

1.5.2 Improving the VFA production condition can be used as baseline data for process operation and control for treating food and market waste in an anaerobic digestion system.

1.6 Conceptual Framework

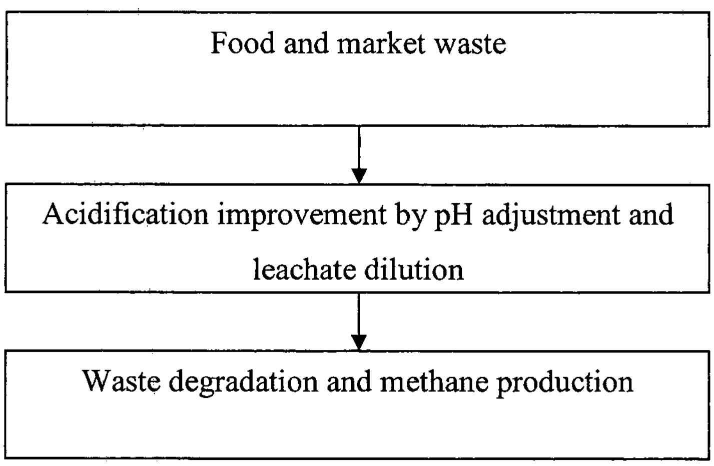

Figure 1.2 Conceptual framework