

CHAPTER 4

ANAEROBIC MARKET WASTE DIGESTION

4.1 Introduction

The aim of this study was to improve the anaerobic digestion of market waste. Fruits and vegetables residues from a local wet market in Bangkok were used as representative of the market waste feedstock. Rapidly digestible wastes like fruit and vegetable wastes are difficult substrates due to the high acid release in the start up. Improving the first step of the AD process was the main purpose in the initial experiment with respect to the generation of the maximum possible of hydrolyzed-acidified products. The behaviors of a conventional one phase and a two-phase system were determined both in terms of waste degradation efficiency and methane yield. Aiming to acquire more data on the anaerobic digestion of a fruit and vegetable market for practical application, the study worked with raw market waste in solid form without water addition, in the range of 8-10%TS, depending on the variation of market waste composition in each sampling. Like food waste, three consecutive batch experiments were designed. These were 1) the effects of pH variation on hydrolysis-acidogenesis 2) the influences of pH control and leachate dilution on hydrolysis, VFA production and inhibitory undissociated VFA profile in acidogenic reactor, and 3) the comparative performance study of one and two-phase anaerobic digestion of market waste.

4.2 Methodology

4.2.1 Market Waste and Seed Sludge Preparation

Market wastes were collected (before the waste collection service started) from the Tungkru market of Bangkok. Approximately 60 kg of samples on a wet weight basis were brought to the laboratory and sorted manually to remove any non-fruit and vegetable waste. A quartering technique was adopted in order to eliminate the effect of waste composition variation, which depends on the season. Sorting studies were carried out 3 times covering weekdays and weekend to characterize the distribution of market waste composition.

- 1) mix waste together with spade,
- 2) divide waste into 4 quarters and separate these waste from each other,
- 3) remove two opposite quarter,

- 4) mix the two retaining quarters together again, and
- 5) repeat this process until achieve the amount of waste required.

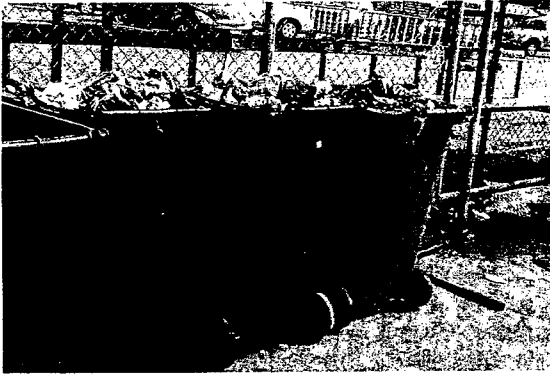
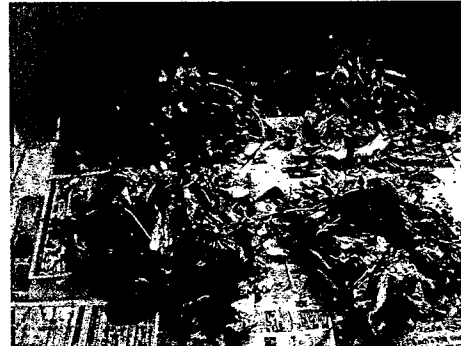


Figure 4.1 Source sorted market waste at Thungkru market



(a) Mixed waste



(b) Separate waste to 4 groups



(c) Select 2 groups from 4 groups



(d) Market waste sample

Figure 4.2 Quartering sampling method

It was found that market waste from Thungkru included cabbage (30%), Chinese kale and Chinese white cabbage (20%), other vegetables (30%), and seasonal fruit (20%) on wet weight basis. To control the substrate characteristics and variation, a simulated market waste (based on waste type sorting study results) was used for all experiments.

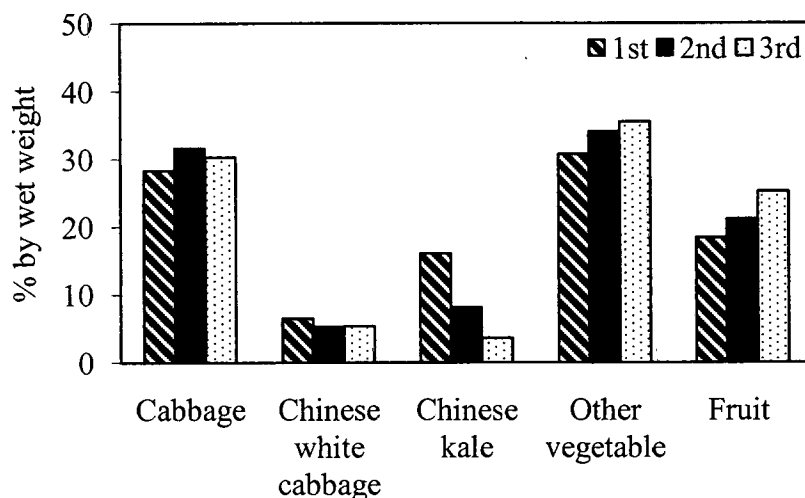


Figure 4.3 Market waste composition of Thungkru market

Table 4.1 Feeding market waste component used in all experiment

Waste type	Wet weight (%)
Cabbage	30
Chinese kale	10
Chinese white cabbage	10
Other vegetables	30
Seasonal fruit	20

The anaerobic sludge was taken from the Up flow Anaerobic Sludge Blanket (UASB) reactors of pig farm wastewater treatment plant in Ratchaburi, Thailand. The concentrations of TS and VS in the seed sludge of the pH experiment were 32.5 g/l and 22.8 g/l, respectively, with a pH of 7.0. In the acidogenesis improvement study, pH was 7.18 with TS and VS of 39.5 and 26.2 g/l, respectively. Mixture of fruit and vegetable waste was shredded down to a small particle size by manual to providing larger surface area. Market waste (no water addition) and seed sludge in the ratio of 70/30, v/v, were added to acidogenic reactor. After 1-2 day of the operation, the leachate pH monitoring and leachate recirculation were started.

4.2.2 Experimental Set-up and Operation

The laboratory set-up was divided into three parts. The two first experiments - 1) the effect of pH (5, 6, and 7) on acidogenesis and 2) the effect of pH adjustment and dilution on VFA production- were set-up and operated with the procedures previously described for the anaerobic food waste digestion (see detail described in Section 3.2.2.1 and 3.2.2.2). Four sets of experiments, M1 with a leachate dilution, M2 with a neutral pH, M3 with a neutral pH followed by dilution, M4 with a stepwise pH adjustment, and MC without pH adjustment as the control reactor, were conducted at room temperature for 119 days. The performance of M1, M2, and M3 was compared with MC, where no leachate recirculation, pH adjustment or leachate dilution was carried out. Mixing in all the experimental reactors (except for MC) was performed via leachate recirculation from the bottom through the upper part of the reactor in the upward direction once a day using a peristaltic pump (Masterflex model 7520-47) at a flow rate of 12 l/d. To extract the organic content generated from the market waste feedstock, leachate collection and recirculation was initiated the day after the start-up. Approximately only 10 ml of leachate was sampled for the daily analyses to prevent disturbing the naturally leaching leachate volume in the digester.

Table 4.2 Operational process of anaerobic market waste study

Operation phase	Dilution 'M1'	Neutral pH 'M2'	Neutral pH along with dilution 'M3'	Control 'MC'
Period I		-Add buffer (d10-d41)	-Add buffer (d10-d41)	-Without leachate recirculation and pH adjustment
Period II	-Leachate dilution : 6 times (d24, d35, d50, d70, d83, d97)		-Leachate dilution :3 times (d53, d70, d83)	
Regular leachate recirculation				

In the final experimental part, two sets of experiments were designed. These were: 1) one-phase batch system with stepwise pH, and 2) two-phase digestion system. Two acidogenic reactors were operated separately (M4 and M5). Each acid digester was packed with the mixture of 70% by volume fruit and vegetable waste and 30% by volume

anaerobic seed without the addition of any water. The leachate recirculation and pH adjustment were made on the next day after the start-up due to a low solid waste leachate leaching on the start-up. One reactor served as stepwise pH control starting from pH 4.5 to 6.5 by using solid sodium bicarbonate (NaHCO_3) as a buffering agent, while the other one (M5) was later coupled with the up-flow methanogenic fixed film reactor. Before the acid digester was coupled to the methanogenic fixed film reactor in a two-phase system, small amounts (10.5 g) of NaHCO_3 were added into M5 during the initial operation period (day 1 and day 2) to support the acid formation.

The packing material was initially inoculated with seed sludge from a pig farm wastewater treatment plant and then acclimated for 3 months using fruit and vegetable residues; cucumber, watermelon and tomato, as the substrates (this step was done in 15-l separated tank). Prior to combination (with an acidogenic reactor), on day 5 and day 7, the methanogenic fixed film reactor was fed with fruit and vegetable juice as substrate to facilitate the biofilm formation on the supporting medium. An acidogenic reactor coupled to a up flow fixed-film reactor was started on day 12 after the F5 had stopped producing gas (after the end of feeding, gas production stopped on day 11).

The combination of acidogenic reactor 'M5' and methanogenic reactor 'FF' was operated in discontinuous batch mode at the HRT of 24 hours. The methanogenic effluent was circulated back to M5 through the port installed at upper part of the reactor sidewall. Acidogenic leachate from the bottom of the M5 was fed to the fixed film reactor at different OLR, ranging from 1.0 to 3.8 g COD/l d (Table 4.3). The organic load was increased in a stepwise fashion in order to accelerate the biogas production. The combination of M5 with methane reactor was ended when the concentration of UA of M5 reached the threshold level for methanogenesis (30-60 mg/l). After day 74 (since the end of the combination), F5 was operated using the leachate self-recirculation mode until the end of the experiment. Biogas was separately collected from each reactor (M4, M5, and FF) by the water displacement method via an outlet installed on the top of the reactor. At the end of batch run, the remaining amount of volatile organic solid was analyzed both in terms of VS reduction and mass carbon balance in both acidogenic reactors (M4 and M5). The properties of the market waste feedstock and effluent were analyzed according to standard methods (APHA, 2005)

Table 4.3 One phase and two-phase operational process of market waste

Operational phase	Two phase		Single phase acid reactor 'M4'
	acid reactor 'M5'	fixed film reactor 'FF'	
Phase I	-Frequency of leachate recirculation, 4 times/day, everyday		
	-Add buffer (d1-d2)	-Acclimated anaerobic seed with vegetable and fruit juices: 2 times (d5 and d7)	-Increase pH in stepwise manner (add buffer; d1-d29) d1-d2: pH 4.5
Phase II	-Coupled with fixed film reactor (d12-d24)		d3-d12: pH 5.5
	-Load with fixed film effluent with the same volume as acidogenic leachate load to fixed film	-Load with acidogenic leachate d12-d14: OLR 1.2-3.8 g COD/l d d20-d24: OLR 1.0-2.2 g COD/l d	d13-d24: pH 6 d25-d29: pH 6.5
Phase III	-Decoupling (d25)		
	-Self recirculation (d25-d37)	- Monitoring the production of biogas	

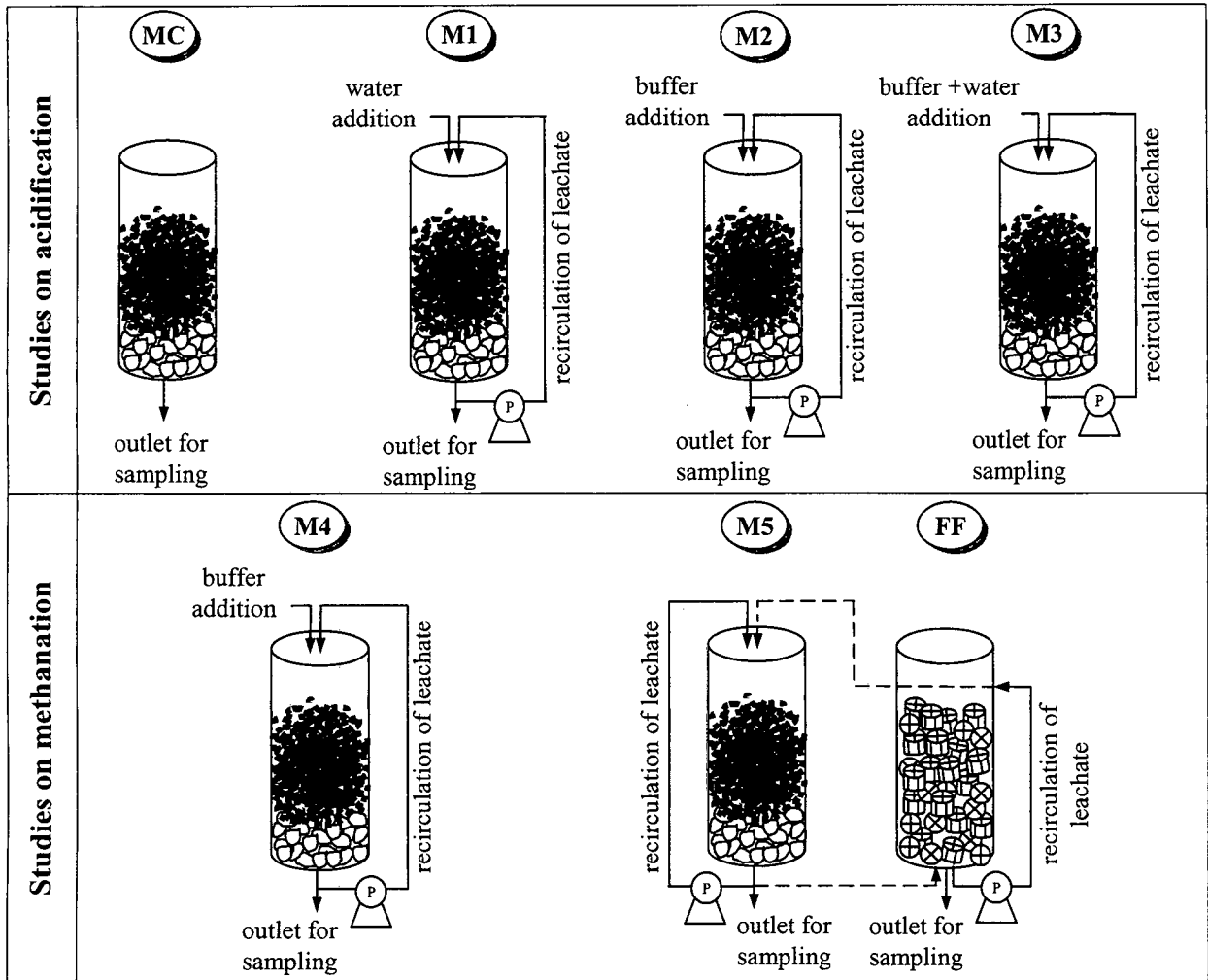


Figure 4.4 Schematic diagram of the reactor set-up

4.3 Results and Discussion

4.3.1 Market Waste Characteristics

The compositional quartering technique showed that the feedstock market waste (from Thungkru market) consisted of the following components: 30% cabbage, 20% Chinese kale and Chinese white cabbage, 30% other vegetables, and 20% seasonal fruit (Table 4.4). This composition represented the actual composition of the largest fruit and vegetable market, Seimummuang, in Thailand, which including cabbage, Chinese white cabbage, other vegetables, and fruit of 40, 20, 20, and 20%, respectively (Tubtong, 2007). The major types of market waste found during the initial sampling were putrescible fruit and vegetable residues like tomato and orange. In the late collection, a seller chose to introduce cheap for low fruit quality instead of discharge, so small amounts of fruit sent to waste container. The chemical characteristics of market waste feedstock are presented in

Table 4.5. Fresh market waste contains high amounts of organic matter, which indicates a high VS content, specifically $88\pm 1\%$ on a dry weight basis (data taken from an average of 3 samples). The moisture content of market waste is high ($90\pm 1\%$), which facilitates anaerobic digestion, bacterial movement, mass transport, and nutrient assimilation by microorganisms. The total carbon content approached 50%. The C/N ratio was approximately 100:4.4-6.3, which is similar to the result of 100:5.4 obtained by Tubtong (2010). This value was in the optimum C/N ratio for the bioconversion of vegetable biomass to methane, which was 100-128:4 (Kivaisi and Mtila, 1998). A basic analysis showed that carbohydrates (17.4-32.4%) and proteins (13.9-19.7%) were the main components, while lipids (2.8-3.9%) were a minor component of the market waste. Carbohydrate content may affect digester function. Knol *et al.* (1978) stated that much easily digestible carbohydrate in substrate, as in fruit and vegetable waste, caused rapid acid formation, suboptimum pH, and then disturbed methane production and even complete digester failure.

Table 4.4 Market waste compositions of Thungkru market and Seimummuang market

Waste component	Thungkru market			Seimummuang ^a market
	1 st	2 nd	3 rd	
Vegetable (%WW)	81.6	78.9	64.8	-
Cabbage	28.3	31.6	30.3	40
Chinese white cabbage	6.5	5.2	5.4	20
Chinese kale	16.1	8.1	3.6	-
Other vegetables	30.7	34	35.5	20
Fruit (%WW)	18.4	21.1	25.2	20
Density (kg/l)	0.217	0.227	0.315	-

^a Tubtong (2007)

Table 4.5 Market waste characteristics

Parameters	Thungkru (Present work)	Thungkru (Kayee, 2003)	Seimummuang (Tubtong, 2007)
pH	4.83±0.46	-	5.0
Moisture content (%WW)	90.46±1.34	90.23	90.2
Total solid (%WW)	9.55±1.34	9.76	9.8
Volatile solid (%DW)	88.38±1.36	86.54	86.5
Ash (%DW)	11.63±1.35	12.46	13.5
Carbon content (%DW)	49.10±0.75	48.07	48.1
Hydrogen content (%DW)	5.26±1.37	-	-
Carbohydrate (%DW)	23.93±7.69	-	-
Total protein (%DW)	17.65±3.29	-	-
Total lipid (%DW)	3.25±0.57	-	-
Total nitrogen (%DW)	2.76±0.51	2.63	2.6
COD (g/kg DM)	1031.7±6.1	-	-
Cellulose (%DW of carbon)	-	-	49.1
Hemicellulose (%DW of carbon)	-	-	37.4
C/N	100:5.6 (or 18.2)	18.3	100:5.4

Note: DW = Dry weight, WW = Wet weight

4.3.2 Effect of pH on Acidogenic Phase of Market Waste AD

4.3.2.1 Leachate pH and Alkalinity

Figure 4.5 presents the changes in the pH, alkalinity and TVA/Alk ratio of three different pH tests. The rather low pH, ranging from 4.38-5.29, of fruit and vegetable substrates is a concern under conditions of low buffering capacity and rapid acid built-up of the readily degradable fraction, which could inhibit further hydrolysis-acidification. These characteristics caused the fluctuation of pH, particularly during the initial digestion, and resulted in a poor performance or failure of the digester. Large amounts of buffer were supplied to adjust the pH to desired value of 6 and 7 (0.17 and 0.31 g NaHCO₃/kg DM). But controlling pH 6 and 7 were unable to handle the system during the first 24 days of the operation, thereby the concentrations of leachate SCOD and VFA reported here were possibly underestimated. The pH decreased rapidly in all flasks, especially at pH 6 and 7, indicating an accumulation of VFA and insufficient buffer capacity to prevent pH change.

This agrees with Marouani *et al.* (2002) who showed that the anaerobic treatment of fruit and vegetable wastes at 8% TS in a batch digester was inhibited by the VFA accumulation and irreversible decreasing pH problems.

One of the criteria for judging digester stability is the TVA/Alk ratio. The alkalinity and TVA/Alk ratio of pH 5, 6 and 7 in this study was 0.84-1.74, 2.47-3.93, and 2.54-6.83 g CaCO₃/l, and 4.8-8.0, 2.5-5.0, and 2.4-4.1, respectively. A high TVA/Alk ratio, above 0.8, in all reactors indicated their processes instability (Khanal, 2008). Reduction in the alkalinity level during day 16-21 of pH 6 and 7 indicated an insufficient buffer capacity to maintain pH and buffer the VFA produced in these digesters. The mixture of vegetable wastes was quickly digestible (Converti *et al.*, 1999). The high amounts of biodegradable matter of vegetable waste meant a larger and faster VFA production (Mata-Alvarez *et al.*, 1992), thereby it is essential to ensure an adequate alkalinity. For a stable digestion, alkalinity should be in the range of 2,000-4,000 mg CaCO₃/l (Sharma, 1999). Lane (1984) suggested that for the balanced digestion of fruit and vegetable waste, the alkalinity should not be less than 1,500 mg/l, which means that the TVA/Alk ratio should not exceed 0.7. The study by Bouallagui *et al.* (2009) also revealed the anaerobic digestion limitations from a rapid acidification, decreasing the pH and stressing the methanogenic bacteria activity, showing that these effects could be prevented by addition of co-substrates with high nitrogen content like abattoir wastewater, and waste activated sludge on the fruit and vegetable waste digestion. Additional waste showed that a highly buffered system such as the high nitrogen content co-substrate contributed to a high amount of ammonia, and permitted anaerobic digestion of fruit and vegetable waste in terms of methane production and the organic matter bio-degradation enhancement, as well as the process stability. A decrease in the proportion of TVA/Alk of pH 7 on day 40-55 may be related to the TVA conversions to the gaseous phase, implying a marked decline in TVA concentration together with a noticeable increment in methane content, climbing from 3.0% (day 45) to 33.7% (day 55) (see Table B.3).

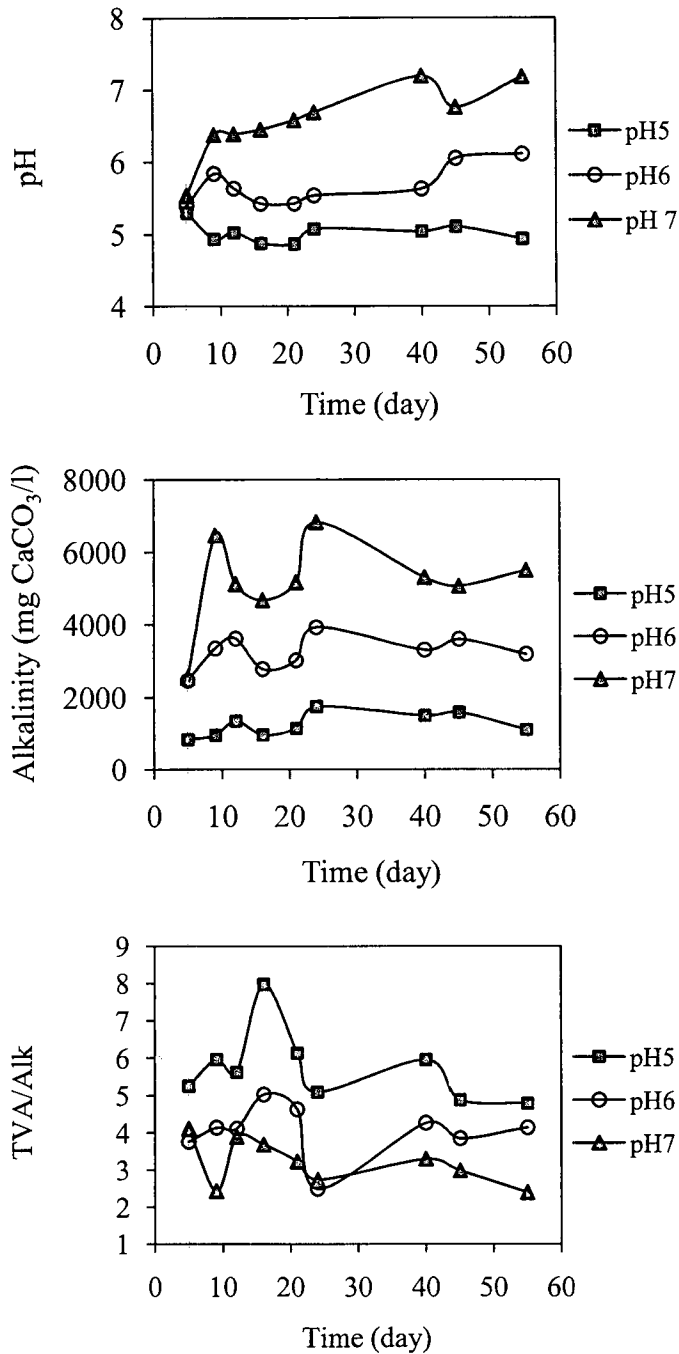


Figure 4.5 Changes in the pH, alkalinity and TVA/Alk at operating pH 5, 6, and 7

Remark : Incomplete pH adjustment of pH 6 and 7 for a 24-day operation period

4.3.2.2 Soluble COD and TVA

As seen in Figure 4.6, more hydrolysis products were detected in the first 16 days of the operation when compared to the following days. In all pH tested, SCOD started immediately from an initial values of 5.5, 9.5, and 13 g SCOD/l to reach the maximum values of 10.1, 20.5, and 21 g SCOD/l at pH 5, 6, and 7, respectively, on day 16, (Table B.1 to Table B.3), and then stabilized thereafter. The highest hydrolysis yield was noticed at pH 7 (144.3 g HAc/kg DM), followed by pH 6 (122.5 g HAc/kg DM) and pH 5 (88.7 g HAc/kg DM). The pH values for the hydrolysis reported here were relatively higher than those reported as optimal in the literature. The lowest optimum pH value for hydrolytic step reported by Witty and Märk (1983) is 4.2 to 4.6, while most of the authors recommended a pH comprised between 5 and 6. However, some authors reported higher pH values for hydrolysis; 6.5 or from 6 to 7. Verrier *et al.* (1987) concluded that anaerobic liquefaction of vegetable wastes is not satisfactory unless the control pH is above 6.5.

The VFA concentration at pH 5, 6, and 7 ranged from 4.38 to 8.90, 9.29 to 14.88, and 10.43 to 19.91 g HAc/l, respectively. The variation of TVA concentrations at pH 6 and 7 behaved in a similar way. Their concentrations reached the peak values of 14.9 g HAc/l (pH 6) and 19.9 g HAc/l (pH 7) on days 12 and declined thereafter. The drop in TVA concentration at pH 7 during days 45-55 coincided with the sharp increase in methane concentration from 3.0% (day 40) to 33.7% (day 55). There was a slight increase in TVA concentration at pH 5 with the maximum rate of 0.45 g HAc/l d, from 4.38 (initial day) to 8.90 g HAc/l (day 40). A higher acid production rate was obtained at pH close to neutral, 0.82 (pH 6) and 1.35 g HAc/l d (pH 7). The maximum acid yield of 117.2 g HAc/kg DM was obtained at pH 7, followed by 90.1 g HAc/kg DM 6 (pH) and 76.5 g HAc/kg DM (pH 5). As can be seen from Figure 4.6, the concentration of undissociated acid responsible for acid production inhibition at pH 7 was lower than that of lower pHs (pH 5 and 6). Since operating pH 7 showed the highest yields for hydrolysis and acidification, it was selected as the optimum pH for acidogenic phase. This finding was in line with the result reported by Verrier *et al.* (1987) using vegetable waste in the batch experiment. They found that both the liquefaction and acidogenesis peaked when maintaining the pH around 6.5.

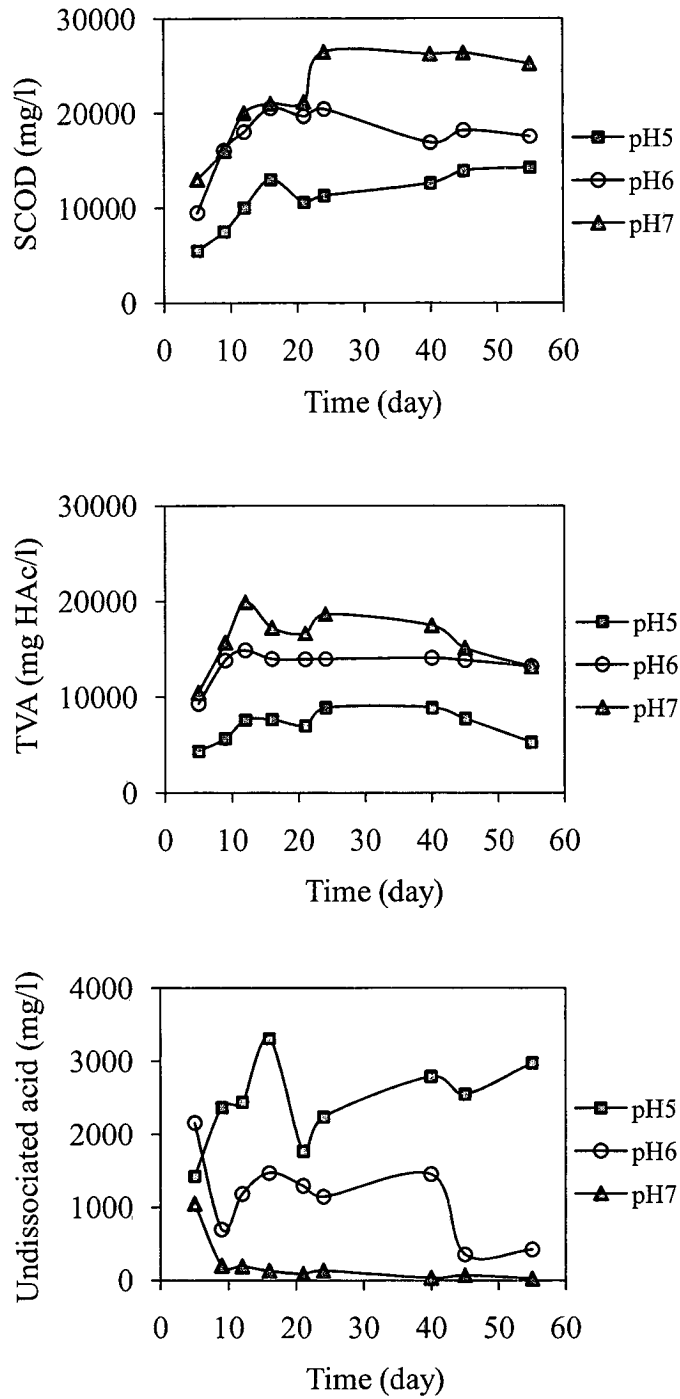


Figure 4.6 Variation of the SCOD, TVA, and undissociated VFAs with different pHs

Remark : Incomplete pH adjustment for pH 6 and 7 in the first 24 days of operations

4.3.2.3 Inhibitory Undissociated VFA Level for Acidogenesis of Market

Waste

From the highest TVA concentration of pH 5, 6, and 7 (8.9, 14.9, and 19.9 g HAc/l), it can be interred that their corresponding undissociated VFAs of 2787, 1184, and 195 mg/l were responsible for the inhibition level of acidogenesis. Babel *et al.* (2004) showed a similar plot from a digester experiment with pineapple (Figure 4.7). They reported that the inhibitory levels of undissociated acids for acidogenesis of pineapple peel were 2300, 650, and 120 mg/l at pH 5, 6, and 7, respectively. The undissociated weak acid forms can move freely across the microbial cell membrane and lower the intracellular pH, which explains their toxicity. The minimum inhibitory concentration of the undissociated acid that prevents growth reflects the resistance of microorganisms: the higher is the value, the higher is the resistance. Although there is the similar plot between the market waste and pineapple peel, mixed different feedstocks (like market waste) may be more resistant to undissociated acid than single waste (pineapple). There are examples of single waste rich in toxic constituents such as limonin in citrus wastes and most of them are deficient in nitrogen (such as mango and pineapple processing wastes) (Viswanath *et al.*, 1992). It has been found that if some of these wastes were used individually as feedstock for biogas production, there was souring of the digesters leading to digestion failure (DNES report cited by Viswanath *et al.*, 1992). Similar effects are described by Murto *et al.* (2004), mixing of difference wastes could offer in better digestion performance by reduce the negative effects of toxic compounds on degradation process. The concentration of undissociated acid showed a trended increase as pH decreased. The determinations of the threshold acid concentrations and the relationships indicated above can be used to estimate the allowable organic load or TVA level for the operation of a full-scale anaerobic market waste treatment.

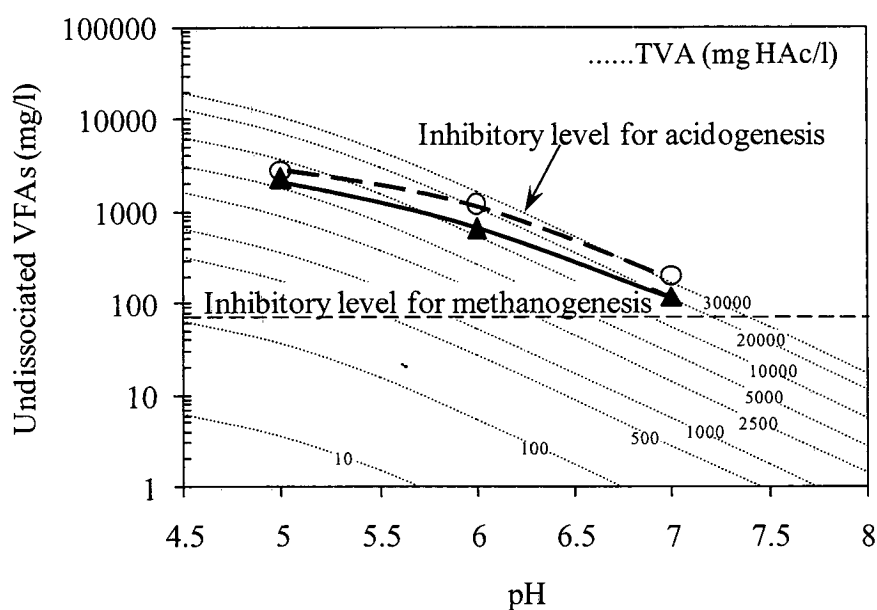


Figure 4.7 Inhibitory level for acidogenesis of market waste (○) and pineapple peel (▲)

Figure 4.8 presents the distribution of individual VFAs (iVFA) at pH 5, 6, and 7. As can be seen, their distributions were quite similar in all pH tested; in decreasing order of concentration the iVFA found were: butyric, acetic, propionic, valeric, and iso-butyric. The butyric and acetic acids were the two most prevalent VFAs, and the sum of them accounted for nearly 60% of the total. Propionic ranked the third in all cases, and the rarest VFA measured was iso-butyric acid. The individual VFA can serve as an efficient indication of process imbalances. In literature, some authors (Suwannakham and Yang, 2005; Horiuchi *et al.*, 2002) found that propionic acid is the main product during glucose acidification at pH 6 to 8, while acetic acid is the top iVFA in protein fermentation. Weiland (2010) proposed that the propionate/acetic acid ratio more than 1 as an indicator for digester failure, if the propionic concentration is higher than 1000 mg/l. Ahring *et al.* (1995) suggested that the concentration of both butyrate and iso-butyrate could be used as a reliable indication of process failure. The relatively high concentrations of butyric and valeric acids were an indication of low acetogenic activity. Likewise, the high acetic acid concentration compared with that of the propionic acid, was indicative of low methanogenic activity.

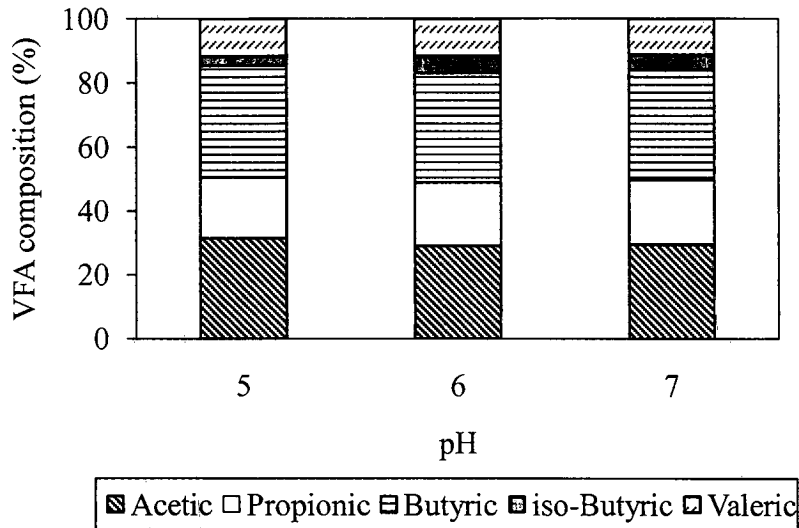


Figure 4.8 The iVFA distribution at different pH conditions

Remark : Incomplete pH adjustment for pH 6 and 7 during day 0-24

4.3.3 Acid-Phase Improvement by pH Adjustment and Leachate Dilution

4.3.3.1 COD Solubilization and VFA Production

To enhance the hydrolysis-acidification and consequently improve the methane production, four acid reactors were operated, with and without pH control in batch run for 119 days. The results for the uncontrolled pH digester were used as the baseline data for comparison with the results from both the controlled pH and the diluted leachate conditions. This study determined the effects of pH adjustment and leachate dilution on the anaerobic digestion of market waste in a single-phase reactor, focusing on the hydrolysis-acidogenesis stage, where undissociated acids are produced.

1) Effect of pH Adjustment

From the previous study, it was clearly found that controlling the pH 7 showed the best performance in term of hydrolysis and acid yields by reducing the concentration of inhibitory (undissociated) organic acid at low pH. Influence of neutral pH control on hydrolysis-acidification was further verified in the scaling-up reactor to find out the way to avoid an acid stress, which could further improve the production of soluble COD and VFA for biogas production. Process performance of M2 is presented in Figure 4.9. SCOD and VFA continually increased from 24.7 to 26.9 g/l and 11.4 to 15.6 g HAc/l, respectively, during the first 5 days (the TVA/SCOD rose from 0.46 to 0.58). After day 5,

the concentrations of SCOD and TVA were relatively stable, on average, 27.2 g/l and 16.1 g HAc/l, respectively (Table B.7) indicating the inhibition of hydrolysis-acidogenesis. The build-up of VFA led to the depletion of buffer capacity (from 1.12 to 0.58 g CaCO₃/l), directly affecting the pH. The initial pH of 5.06 of fruit and vegetable residues mixed with seed sludge decreased and was as low as 4.27 (day 5), but then, through the indigenous buffer capacity of market waste and seed sludge mixtures, reached 5.16 (day 7). A sudden increase in TVA content, especially on day 5, consumed the digester alkalinity, leading the pH to drop below 5 and the TVA/Alk to be up to 26.7. Under such low pH, organic acid was expected to be undissociated and they pass freely through cell membrane of microbes, thus inhibiting their growth and ultimately affecting the process of conversion rate in the hydrolysis/acidogenesis reactor (Warnecke and Gill, 2005; Vavilin *et al.*, 2001). Reporting on the hydrolysis/acidogenesis of food waste using leach bed reactor (LBR), Xu *et al.* (2011) showed that the LBR for treating food waste should be artificially buffered for the higher conversion rate and better processing performance.

The hydrolysis inhibition, indicated by the stable concentration of SCOD and TVA after 5 days, may be linked to the high inhibitory undissociated fraction, ranging between 1,119 and 2,081 mg/l. These results revealed that low pH and accumulation of VFA during the initial stage of market waste treatment subsequently affected the hydrolytic-acidogenic stage in single stage reactor. Because of the rapid acid release during the initial operation, which subsequently results in decreased pH, impeding the acidogen and methanogen activities, poor treatment performance was obtained.

The external buffer (NaHCO₃) addition was started after 9 day of operation to counter the declining alkalinity. Neutral pH showed an improvement of the COD and VFA production. The TVA/Alk ratio sharply decreased from, on average, 12.7 (before buffer) to 1.3 (after buffer). The SCOD concentration substantially increased from 27.6 (day 9) to 46.7 g/l (day 77). TVA followed the same trend as SCOD, as it rose from 15.8 g HAc/l on day 9 to 40.7 g HAc/l on day 39 and reached a peak value of 42.7 g HAc/l on day 77. These results indicated the extended acidification at the neutral pH condition in spite of its acid generation rate (0.92 g HAc/l d), which is nevertheless comparatively lower than in the uncontrolled pH (1.23 g HAc/l d). The buffer supplementation was stopped on day 41. No positive observation on acid production was found after the end of external alkalinity addition, based on the VFA generation rate. One may assume that the chemical alkali addition can sustain a steady production of high levels of TVA with pH-

balanced environment, thus solving inhibition of acidogenesis. But a substantial buffering in an acid digester treating large amounts of readily available content in market waste could be a problem due to the cumulative VFA produced. McCarty (1964) and Grady and Lim (1980) reported that controlling the pH by sodium bicarbonate may results in toxic effects that will inhibit the microorganisms if the level is above 8000 ppm of sodium. Volatile acids represent a critical control parameter of anaerobic digestion (Fernández *et al.*, 2008). High concentrations of hydrolysis/acidogenesis products i.e. SCOD and VFA in the leachate, can cause process inhibition in a one-stage system (Bhattacharya *et al.*, 2008). According to ten Brummeler *et al.* (1991), hydrolysis of biowaste was severely inhibited under VFA concentrations up to 33 g/l. Chemical supplementation by adding sodium bicarbonate to maintain alkalinity showed no sustainable beneficial effect on methanogenesis, with a very poor methane content and relatively stable in VFA level (36 g HAc/l, on average). Similarly, Veeken and Hamelers (2000) also found that a complete inhibition of anaerobic hydrolysis of biowaste was met at VFA levels of 40-50 g VFA-COD/l. Generally, under the optimal condition, the digester pH increases due to the process stability and the optimal methanogen ability. Then VFA is converted to methane and carbon dioxide. The relatively stable concentrations of SCOD and TVA, on average, 43.6 g/l and 39.1 g HAc/l, respectively, accompanied by low methane content (max. 9.1%) indicated process instability, despite the fact that a relatively low undissociated VFA (9.1 to 98.5 mg/l) was obtained early upon the initial buffer addition.

Anaerobic market waste treatment process encountered some difficulties in the startup phase due to large quantities of readily degradable matter and solid form. The current study suggested that digestion of fruit and vegetable wastes without the control of VFA (large amount of buffer) concentration is likely to result in poor digester performance or failure of the digester. It clearly showed that the methanogenesis onset for easily digestible substrates like fruit and vegetable wastes is associated with other resistance factors beyond the level of undissociated VFA. Grady and Lim (1980) stated that little acid inhibition will occur in anaerobic digester even at neutral pH condition since the undissociated acid is a function of both total VFA and pH. This result therefore indicated that the presence of a high concentration of VFA strongly influences the acidogenesis performance as well as the undissociated VFA.

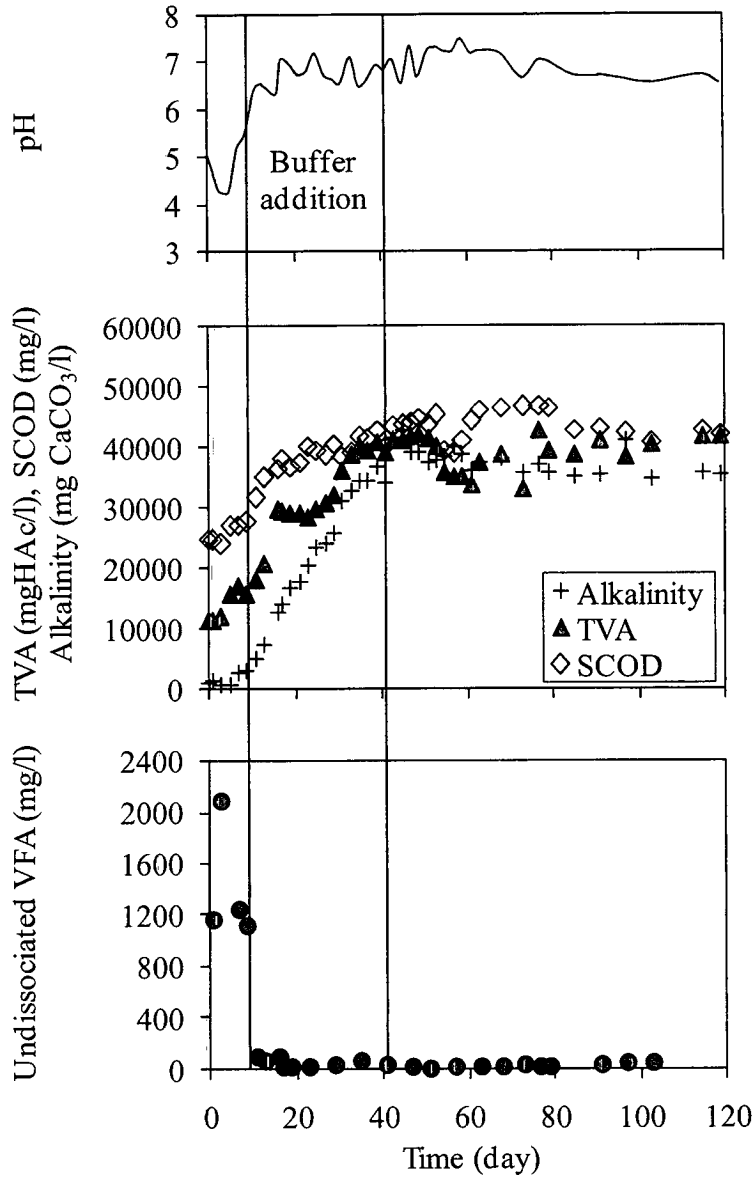


Figure 4.9 Process performance of neutral pH control reactor

As seen in Figure 4.10, the fermentation TVA product was almost similar to the SCOD leached out, TVA/SCOD approached 0.9 on day 31 and it remained in high range of 0.7 to 1 throughout the run. This means that no accumulated monometric product occurred or, it can be indicated that fermentation of monomers proceeds faster and the hydrolysis of particulate polymers seem to be the rate-limiting step for solid digester like market waste (Veeken and Hamelers, 2000).

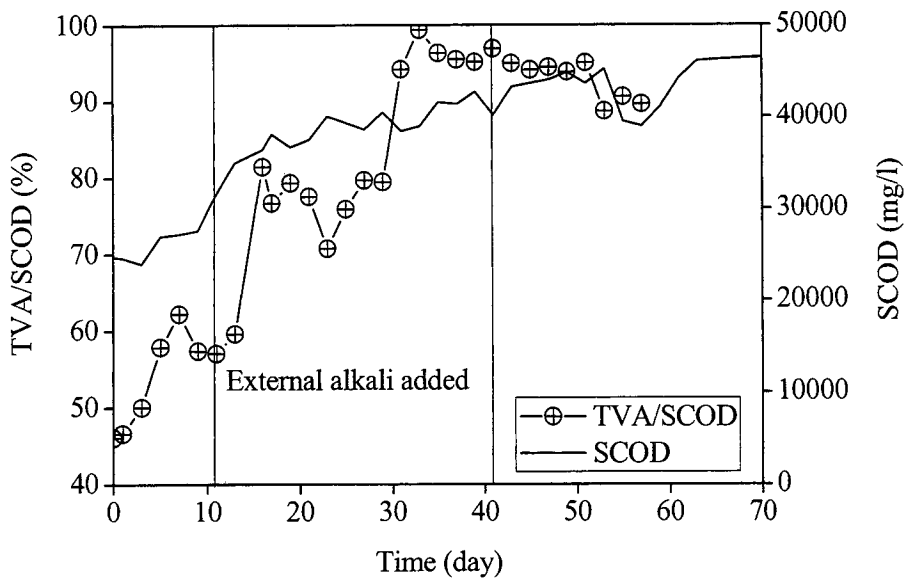


Figure 4.10 Changes in the SCOD and SCOD/TVA of neutral pH reactor

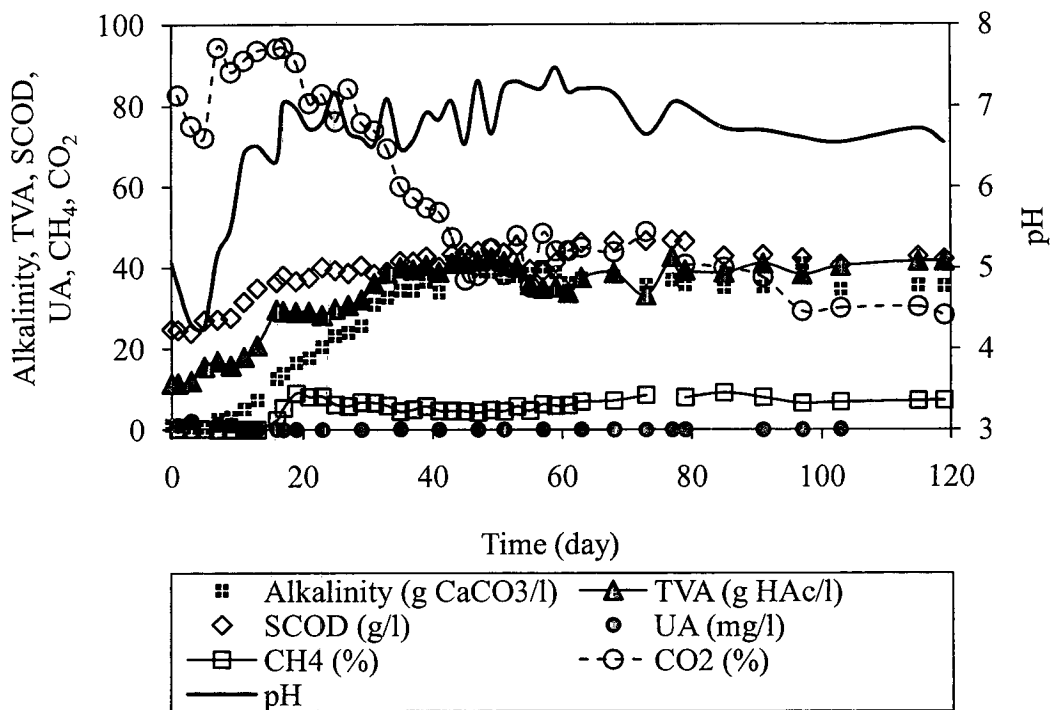


Figure 4.11 Overall performance of neutral pH reactor of market waste

2) Effect of Dilution

In this work, an attempt was then made to investigate the effect of the dilution to extract the organic content generated from the market waste feedstock. As acid accumulation causes the inhibition of hydrolysis-acidogenesis, it was assumed that the lower the VFA concentration is, the higher is the amount of acid produced. To prevent disturbance of the naturally leaching leachate volume in the digester, a withdrawal of only 150-250 ml of acidogenic liquid was fixed, which was then replaced with an equal amount of fresh water. As the dilution application related to the leachate strength changes, their concentrations could be misleading for the interpretation of the dilution technique efficiency, and thus the term of the VFA generation rate was followed instead. The degree of dilution in this study could not represent the true value since the effluent leachate after dilution was analyzed with a delay. In the first 23 days before the application of the dilution, the pH dropped from the initial value of 4.74 to 4.40 after 3 days of operation, and then increased to above 5 on day 13. The rather stable pH in this period was expected to be related to the protein content of market waste. The study of Jash and Ghosh (1996) using organic residues (rice straw, cow dung, and jute stick) as substrate observed that the pH of the digesting mass of batch digestion decreased initially because of the VFA accumulation, dropping to a minimum in 4-7 days and gradually increased to about 7 thereafter. Total alkalinity of the fermented product showed a rise from the initial 402 to 3,323 mg CaCO₃/l without external buffer addition.

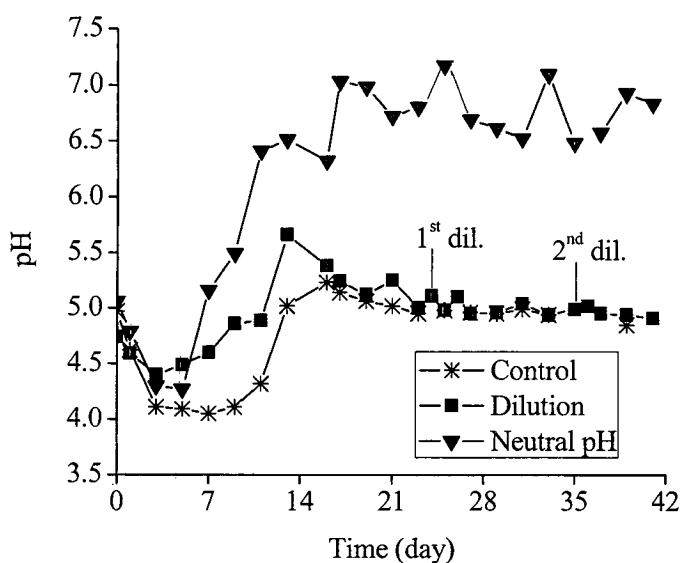


Figure 4.12 Leachate pH profiles of buffered and unbuffered reactors

A high SCOD extraction of 24.1-28.7 g/l was noticed in the leachate on the second week, and remained thereafter above 25 g/l. The maximum concentrations of SCOD (29.6 g/l) and TVA (19.6 g HAc/l) were attained after two weeks of operation with the rate of TVA generated of 1.76 g HAc/l d. Jash and Ghosh (1996) stated that the pH is the most important single factor affecting the solubilization rate. An imbalance between the acidogenesis and methanogenesis led to the accumulation of VFA. Lowering pH by addition of acid induced a decrease in the rate of solubilization. The anaerobic digestion process was severely impeded when the pH dropped below 5. Achieving the maximum VFA formation rate within the first 5 days of the digestion period revealed the rapidly biodegradable nature of the market waste. The VFA in the undissociated form, increasing from 1,242 mg/l (start-up) to 5,350 mg/l (day 23), was suspected to be one cause of hydrolytic-acidogenic inhibition.

The dilution technique applied first on day 24 by the 150-ml acidogenic leachate was replaced with an equivalent amount of fresh water, resulting in leachate strength reduction from 28.8 g COD/l (24.3 g HAc/l) to 25.2 g COD/l (19.3 g HAc/l) on the subsequent day, or accounting for 13% dilution degree (based on SCOD value). The rate of VFA production of 1.19 g HAc/l d was obtained by the first dilution practice. The undissociated VFA sudden decreased from 5350 to 529 mg/l before it shifted to 1869 mg/l, which corresponds to a reduction above 65%. The following dilutions were introduced on day 35 (2nd), day 50 (3rd), day 70 (4th), day 83 (5th), and day 97 (6th). The acid production in all dilution tests, ranging from 0.21 to 1.01 g HAc/l d, was decreased compared to the value before the dilution was applied. This finding contradicted the data available in the literature. In the anaerobic digestion of single feedstock (pineapple), Babel *et al.* (2004) found that at lower VFA concentration, the digester had a tendency to produce more acids than at high concentration, from 0.205 g/l d to 0.411 (2nd), 0.397 (3rd), and 0.44 g/l d (4th) under the 42 to 62% dilution applied (based on VFA concentration change). A similar result in one-stage batch packed with 145 g of glass-silage and 750 ml of distilled water suggested that COD solubilization and VFA production can be improved through leachate replacement with/without pH adjustment performed (Jagadabhi *et al.*, 2010). Rajeshwari *et al.* (2001) found the strength of the leachate increased within 4 hours of water addition; fresh water was recirculated in place of concentrated leachate, indicating the possibility of further extraction of the organic material from solid wastes. Low value of

waste to liquid ratio resulted in reduced strength of leachate but early extraction of higher fatty acids in the leachate.

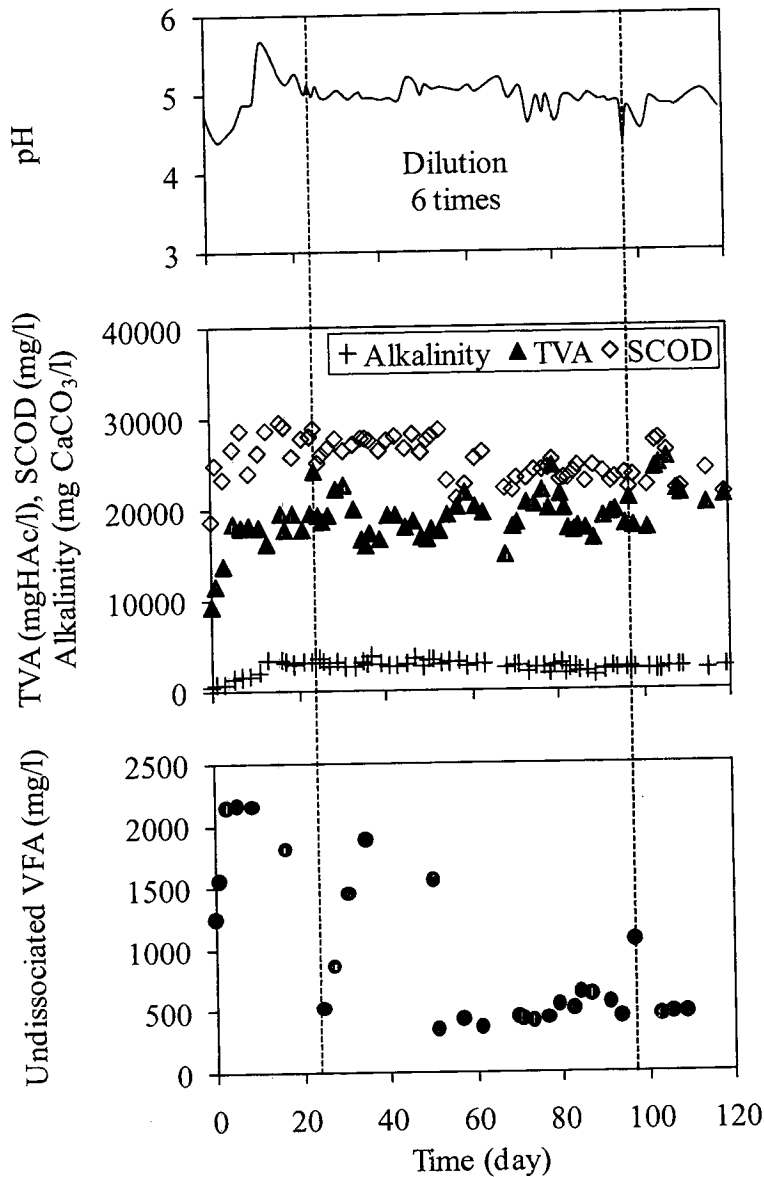


Figure 4.13 Liquid phase characteristics of dilution application

Dilution of leachate did not show evidence of VFA production improvement, implying a declining rate of VFA production. This result is probably related to the greater heterogeneity of the market waste, which introduces excessive resistances to mass transfer that become rate-limit, together with the rather low percentage of dilution using in our study, estimated to be no more than 20%. However, this study was planned

with the aim to get realistic data that could be used to scale up the technology for treating market waste. For this reason, introducing excessive dilution to facilitate the process may give misleading results for the goal of the present work. Therefore, based on the scope of experiment design, the hypothesis of acid enhancement by leachate dilution did not seem to be valid for the present market waste tests.

Table 4.6 Change in TVA and undissociated VFAs by dilution

No	Day	TVA concentration (mg HAc/l)		Undissociated VFAs (mg/l)		Rate of TVA generation (g HAc/l d)
		Before dilution	After ^a dilution	Before dilution	After ^b dilution	
1	24	24,339.5 ^c	22,700.3 (d31)	5,350.5	528.5	1.19
2	35	16,659.0	19,444.2 (d41)	1,869.4	2,701.2	0.63
3	50	16,710.4	21,757.3 (d59)	1,543.6	343.4	0.67
4	70	17,967.8	24,609.4 (d79)	435.6	425.3	0.68
5	83	17,733.2	19,894.7 (d94)	500.4	637.6	0.21
6	97	21,188.7 ^c	25,641.9 (d106)	1062.6	456.3	1.01

^a the maximum value

^b early detected value after dilution application

^c seed washed out

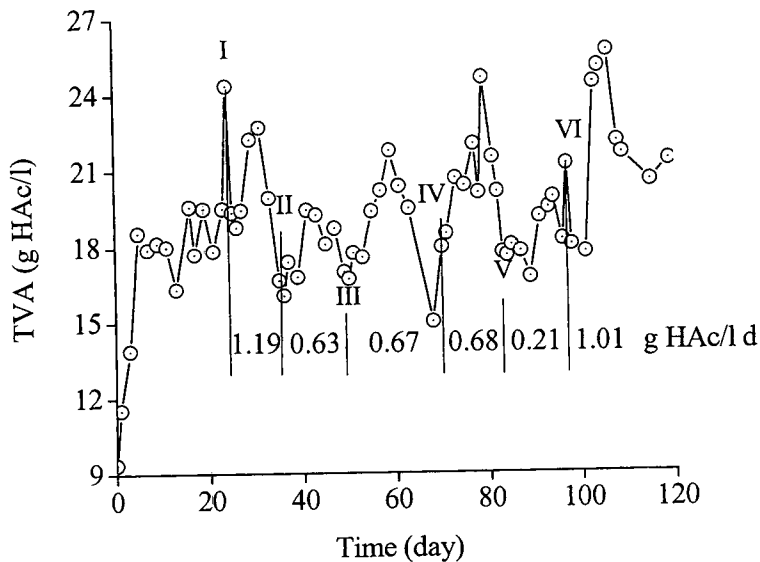


Figure 4.14 The VFA generation rate of applying dilution

As aforementioned, the TVA extraction profile of market waste reflected the addition of external buffer for improving alkalinity capacity. Figure 4.15 showed the overall performance of anaerobic market waste degradation without any regulation (no buffer, no agitation), or control reactor 'MC'. The rapid VFA production and fluctuating pH values noticed during the initial 11 days of the operation denoted the acidifying nature of the market waste feedstock and/or the indigenous buffer capacity of the system. Guerrero *et al.* (1999) reported that pH during acidogenesis may vary as the system tends to buffer itself. In the control condition, the market waste can be fermented naturally. The pH was always in the pH range of 4.05 to 5.23 with alkalinity level ranging from 0.08 to 3.4 g CaCO₃/l. Weiland (2010) stated that the accumulation of VFA will not always lead to a pH drop, due to the buffer capacity of the substrates.

The stability of the pH (4.8 ± 0.4) and the gradual increase of alkalinity were achieved without any necessity of chemicals addition, though a buffer capacity fluctuation could be seen during the first 11 days of the operation by its fermentation nature with a TVA generation rate of 0.63 g HAc/l d. One interesting point about the acidification process is that the great variation in pH and alkalinity was registered only in the control digester, in which the highest pH value observed was 5.23, whereas a quite consistent increasing trend of these parameters was shown in another uncontrolled pH digester with leachate recirculation (dilution reactor). Hydrolysis-acidogenesis of MC was rapid a few days after the start-up period and seemed stable thereafter as the easily digestible fractions declined. The SCOD and TVA increased from 25.7 to 35.2 g/l and 10.7 to 28.6 g HAc/l by digestion time of 119 days with yields of 0.48 g COD/g VS and 0.38 g HAc/g VS, respectively. Introducing liquid recirculation in dilution reactor accelerated the hydrolysis of particulate matter; increasing moisture content, promoting mass transfer and redistributing the enzymes and microbes (Lü, *et al.*, 2008).

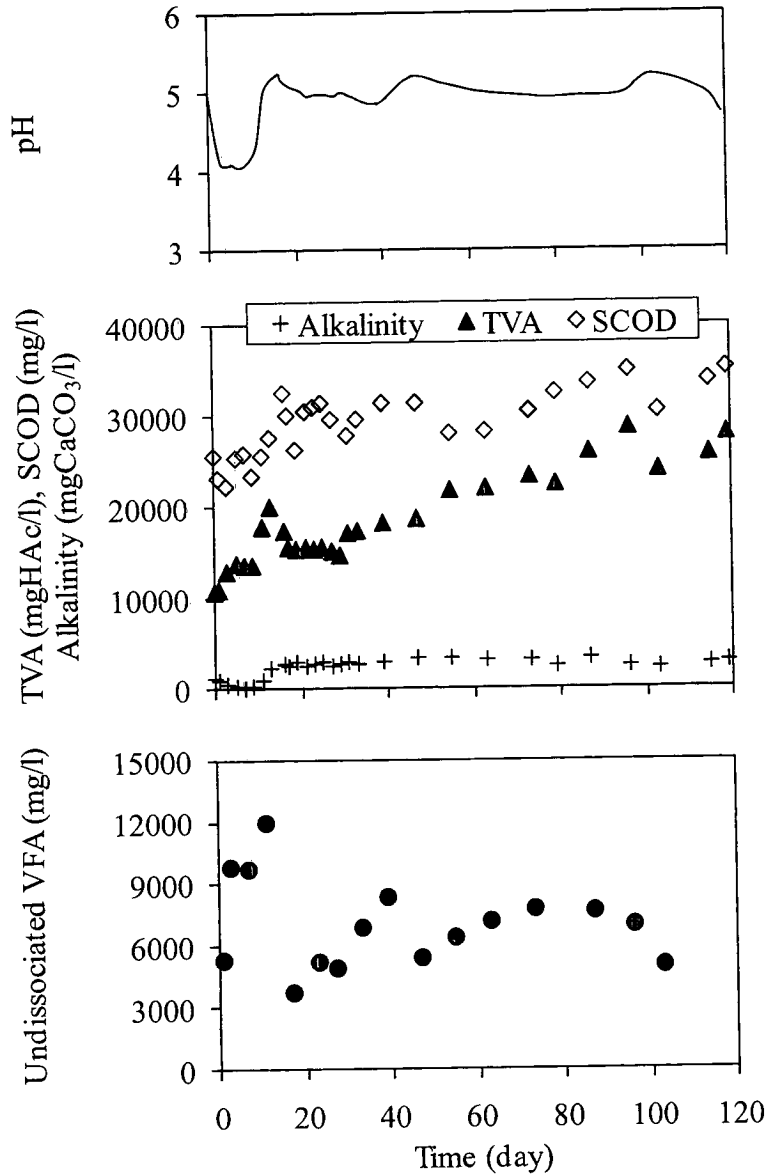


Figure 4.15 Liquid phase profile of control reactor

Concerning the TVA/SCOD, the ratio of dilution increased over 0.9 by the third dilution application (Figure 4.16). A high VFA/SCOD ratio represents the amount of solubilized matter converting to VFA and this value also expresses the degree of success of acidification (Maharaj and Elefsiniotis, 2001). The dilution of leachate could improve acidification. Nevertheless, in the reactor MC (without any regulation), the ratio of TVA-SCOD near 0.8 was also high, implying that the formation of non-VFA soluble organic remained low and indicating that acidogenesis was not a critical step of anaerobic market waste digestion. The high VFA/SCOD experienced in both reactors hinted that

hydrolysis was the rate-limiting step for treating market waste, a lignocellulose-containing material.

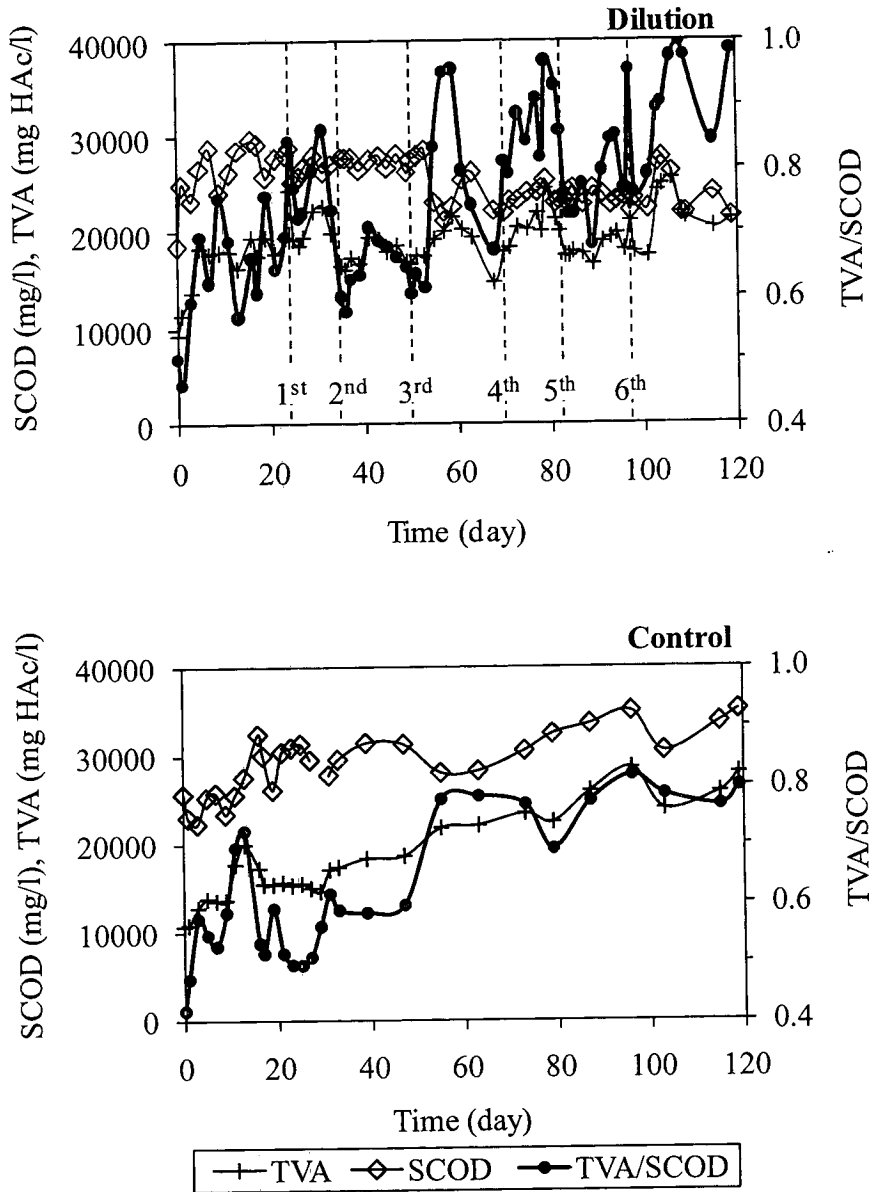


Figure 4.16 Changes in SCOD and TVA of dilution and control reactors

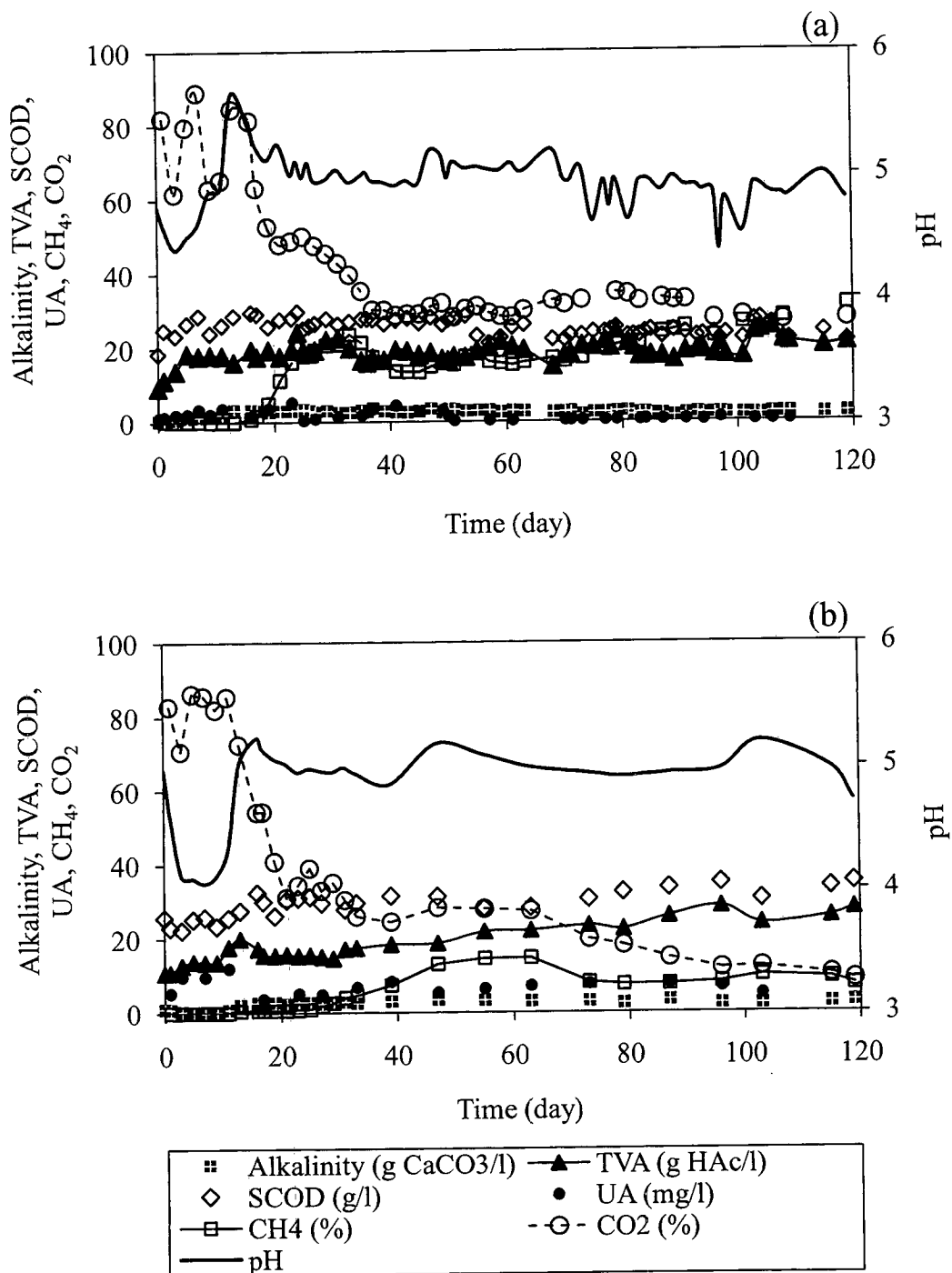


Figure 4.17 Overall performance of dilution reactor (a) and control reactor (b)

3) Effect of Dilution after Neutral-pH Adjustment

Integration of a pH control-dilution method setup was built for examining its impact on the hydrolysis and acidogenesis of solid market waste. The acidogenesis performance using the dilution technique was studied and compared, with and without neutral pH control. Results showed that during the 31 days of pH adjustment period, consistent increases were seen in both the SCOD and TVA concentrations. The concentrations of SCOD and TVA peaked on day 47 and 43 with a value of 45.7 g/l and 44.3 g HAc/l, respectively, and the TVA/SCOD ratio was almost 1. The hydrolysis and acid yields were 0.64 g COD/g VS and 0.54 g HAc/g VS, respectively. TVA concentration increased up to 71% when pH increased from 4.9 ± 0.2 (dilution reactor) to 6.7 ± 0.3 . The results mentioned above showed the positive effect of the pH adjustment on VFA production.

The dilution technique was introduced after the neutral pH operation showed the steady-state performance. It started on day 53 by a 150-ml withdrawal of liquid digester was substituted by same amount of distilled water. It was found that the acid generation rate increased from 0.82 g HAc/l (neutral pH control) to 1.12 g HAc/l, followed by a declining rate of 0.80 and 0.54 g HAc/l d on the second (day 70) and the third dilution (day 83), respectively (Table 4.7). The TVA/SCOD ratio remained high, 0.86 on average (Figure 4.18). Additional tests run with leachate dilution after applying pH adjustment led to the same conclusion: COD solubilization and VFA formation were enhanced but the methanogenic performances were limited. Delivery of dilution water through the acidogenic reactor with an attempt to reduce the concentration of inhibitory materials accumulated in the first AD process for further acid production could not provide the expected result. High TVA concentration by neutral pH control seems to be the cause of the methanogenic phase hindrance under single-phase reactor. It is also noteworthy that in reactor M1, in which leachate was diluted, the methane content surpassed that of other digesters, suggesting that the TVA concentration plays a critical role in the treatment of readily biodegradable market waste. However, it should be noted that the dilution degree applied in the present work was considerably lower than that of most of other reports.

Table 4.7 Effects of introducing leachate dilution

Performances	Dilution without pH control		Dilution with pH control	
	Before dilution (day 0-13)	Dilution ^a	Neutral pH (day 0-41)	Dilution ^b
Mass SCOD (g)	86		120	
Mass total VFA (g HAc)	75		103	
Acid production rate (g HAc/l d)	1.76	1.19 (1 st) 0.63 (2 nd) 0.67 (3 th) 0.68 (4 th) 0.21 (5 th) 1.01 (6 th)	0.82	1.12 (1 st) 0.80 (2 nd) 0.54 (3 th)
Undissociated VFA (mg/l)	1242-5350	343-4378	9-158	12-54

^a the 1st, 2nd, 3rd, 4th, 5th, and 6th dilution were operated on day 24, 35, 50, 70, 83, and 97, respectively

^b the 1st, 2nd, and 3rd dilution were operated on day 53, 70, and 83, respectively

In any case, dilution techniques either with or without pH adjustment seemed to be less advantageous on the hydrolysis-acidogenesis, while the pH adjustment played a strong role on the improvement of hydrolysis-acidogenesis. However, it must be stressed that, contrary to the literature, in our case a dilution with tap water was carried out at low dilution degree (5.3 ml/g VS_{added}). In the buffer supplied reactors (M2 and M3), the TVA concentrations were relatively high. This finding supports the importance of maintaining the system pH near neutral and indicated that both TVA and undissociated acid affected the reactor performance of market waste digestion. COD solubilization and VFA production could be improved through pH adjustment with or without leachate replacement.

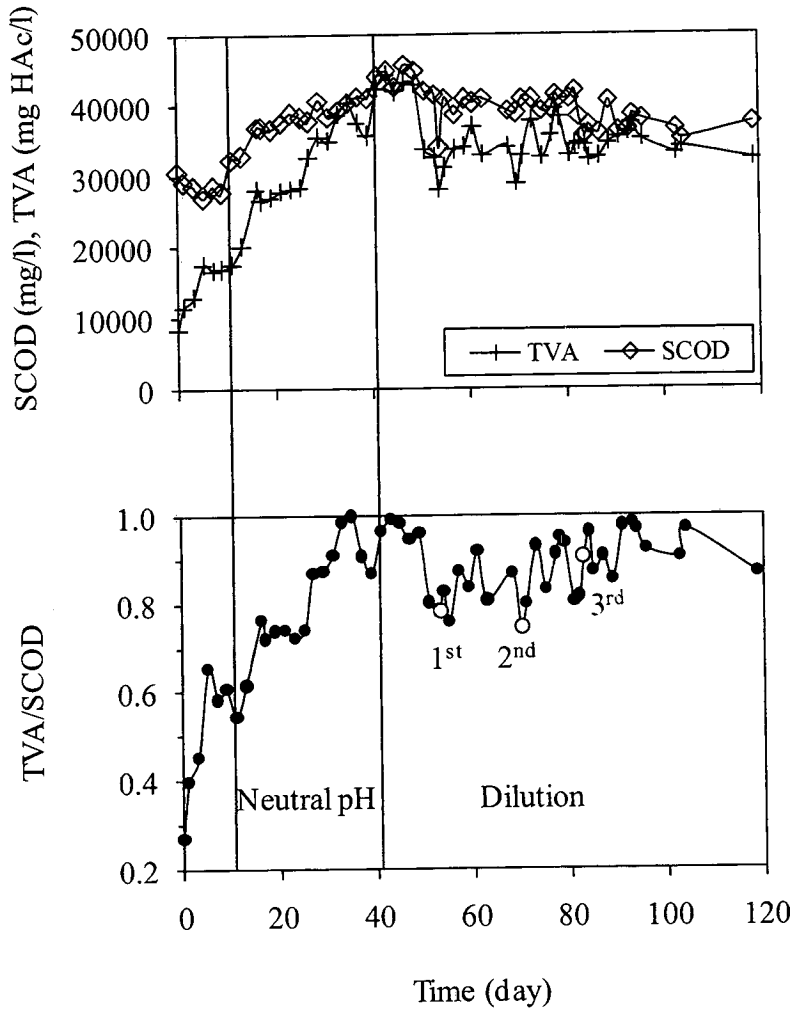


Figure 4.18 Variations of TVA and SCOD in the leachate of reactor M3

4.3.3.2 Inhibition by Undissociated Acid

Neutral pH conditions showed the lowest undissociated acid concentration, ranging from 9 to 158 mg/l. This level of undissociated VFAs was closer to 195 mg/l, which was the inhibitory level for acidogenesis obtained from our previous study (see Figure 4.7). Results showed that operation at neutral pH minimized undissociated VFA inhibitor and enhanced VFA production. The production of VFA was rapid, indicative of the status of activation of acidogenic bacteria in the initial period but the decline of VFA formation appeared later may be related to the inhibitory effect from high undissociated fraction. The high VFA production noticed in all buffered reactors indicated an imbalance between the VFA production and consumption, and such high VFA concentration inhibits the hydrolysis-acidification even though the undissociated fraction did not exceed the

inhibition levels for methanogenesis. The failure encountered with the neutral pH control could be linked to the disruption of the high-accumulated TVA level. The inhibitory effects of the unbuffered batch reactor (MC) with low acid production rate of 0.63 g HAc/l d seemed to be related to the low pH, high TVA and high undissociated acid levels.

Table 4.8 Performance under pH adjustment and dilution application

Parameter	No adjust pH (control)	pH adjustment ^a (neutral pH)	Dilution	
			Without pH adjustment ^b	With pH adjustment ^c
pH	4.05-5.23	6.32-7.47	4.39-5.20	6.34-7.32
TVA (g HAc/l)	10.7-28.6	18.0-42.7	15.0-25.6	17.5-44.3
Undissociated VFAs (mg/l)	3,748-11,968	9-98	343-4,378	9-158 (neutral pH) 12-54 (dilution)
Max. CH ₄ content (%)	14.7	9.1	31.8	15.3 (neutral pH) 5.8 (dilution)
VS reduction (%)	48.8	79.5	51.9	81.4

Note: Results were obtained from ^a day 11-119, ^b day 24-119, and ^c day 53-119

4.3.3.3 Biogas Composition

Due to a deficiency in the gas collecting apparatus, gas production results could not be shown, so the gas composition (CO₂ and CH₄) was used instead as an indicator of process performance. Figure 4.19 shows the evolution of biogas composition. Carbon dioxide was the major biogas constituent, which was always higher 60% during the first 10-days period. The methane contents of gas produced for the first 9-days in the buffered reactors (M2 and M3) were negligible ($\leq 1.26\%$), and then increased to 9 and 15% by day 17 and 16, respectively. Later, they declined with time reaching 4.2 and 5.5% after day 46 (M2) and day 52 (M3) from the start-up. Applying dilution after neutral pH (CH₄ 5.8%) was not efficient to promote methanogenesis. High TVA concentration accompanied by the low methane content (max. 15.3%CH₄) from both supplied buffer reactors (M2 and M3) indicated an AD process limitation despite the fact that most of their undissociated forms (9-98 mg/l) reached the methanogenesis threshold level (30-60 mg/l). The methane

content of M1 was very low at the start-up (3%CH₄, on average), and then gradually increased to reach 20% by the 4th dilution and 30% by the 6th dilution. Methane production was found to be very low at all the pH tests, meaning that methanogenesis was adversely affected from the condition employed.

The results showed that the methane production in the one phase system treating market waste suffered from the large VFA produced. A rapid acidification decreasing system pH and hindering the activity of methanogens is a major limitation of anaerobic digestion of fruit and vegetable waste (Misi and Forster, 2001; Bouallagui *et al.*, 2005). The maximum methane concentration (31.8%) was observed in M1 without buffer addition, while methane content was negligible at other conditions tested. Methanogens are far more sensitive to the accumulation of VFAs than the acidogen. Low VFA concentration by leachate dilution reduced inhibitory products (VFA and UA) and the pH adjustment led to the high accumulated VFA level impeding the methane production under one phase system.

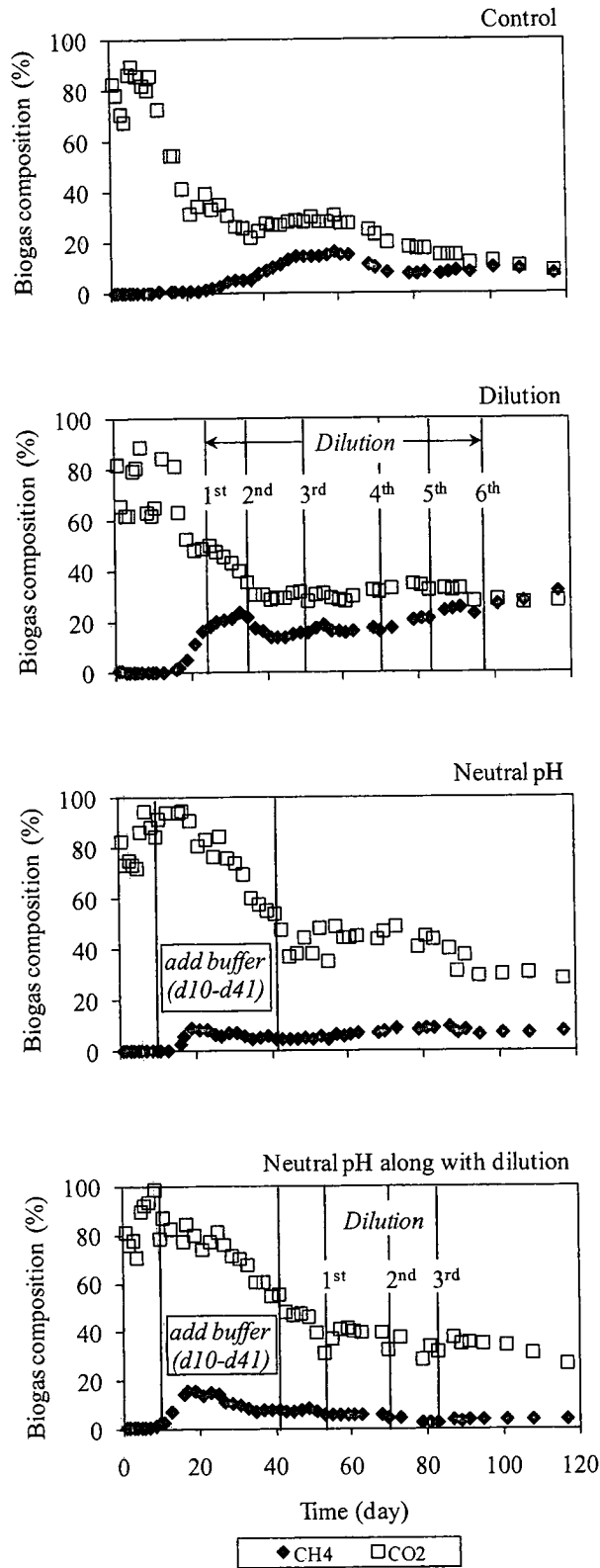


Figure 4.19 Gas content in acid-phase market waste digestion

Among the four reactors, the highest VS reduction was noticed in supplied buffer reactors either with or without dilution (79.5% in M2 and 81.4% in M3). These results clarified that the pH adjustment improved the rate and extent of hydrolysis/acidogenesis of particulate substrate like market waste with an efficient control of undissociated VFA. But it was speculated whether or not its benefits on acidogenesis are needed for such high readily degradable substrate like market waste. As aforementioned, acidogenesis seemed not to be the limiting factor for anaerobic market waste digestion. In general, hydrolysis is the rate limiting step if the substrate is in particulate form (Veeken and Hamelers, 1999) and the anaerobic degradation of cellulose-poor wastes like fruit and vegetable wastes is limited by methanogenesis rather than by the hydrolysis. The TVA/SCOD of both unbuffered reactors (MC and M1) showed the high value, above 0.8, without external alkali served, indicating the high acidification degree. By contrast, the excess intermediate VFA forming by neutral pH adjustment put up extremely resistant methanogens, leading to an imbalance between VFA production and consumption in one phase reactor, as evidenced by the accumulated TVA in the buffered reactors. The requirement for neutral pH of methanogens has long been known. Despite this, however, extreme acidification was induced in both M2 and M3, which suffered from intensive VFA raise and poor biogas composition.

The methane production was found to be always very low at all conditions tested, meaning that methanogens were adversely affected by the conditions employed. It should be noted that the goal of this experiment was to find a feasible way to improve the hydrolysis-acidogenesis by eliminating inhibitory products for further coupled with methanogenic digester in two phase system, not to create, at least in this work, a two-phase system together with pH adjustment. In the subsequent investigations dealing with this theme, however, proper VFA and undissociated VFA productions were much more crucial. A final experiment was then made articulating two separate concepts; one phase based accelerating VFA production was prohibited and a two phase system with natural fermentation in acid digester. Two sets of experimental reactors were designed, namely: 1) one-phase batch system with stepwise pH 'M4' and 2) two-phase system by periodic combination of the acid digester 'M5' and a methanogenic reactor 'FF'.

4.3.4 Batch One Phase and Two-Phase Treating Market Waste

4.3.4.1 Single-Phase Anaerobic Reactor with Stepwise pH Gradient 4.5 to 6.5

In the previous study, a large buffer amount was supplied to buffer the high amount of VFA produced. However, extreme buffer addition can cause disadvantageous circumstances for methanogenic bacteria. The possibility of one phase treating fruit and vegetable market waste, easily digestible and carbohydrate rich-substrates (Tenca *et al.*, 2011), was carried out with external buffer addition in stepwise increasing pH to prevent the occurrence of rapid acid formation. Total VFA and undissociated fraction as the critical control parameters were closely observed in our study.

1) SCOD and VFA Degradation Evolution

Due to the rather low pH (4.83) of market waste, a buffer was introduced at the start-up with aim of maintaining leachate pH not less than 4.5. However, a drop in pH from 4.58 to 4.49 on the next day could be attributed to the increase of the SCOD and TVA levels from 20.3 to 23.7 g/l and 7.69 to 8.46 g HAc/l, respectively, suggesting the need for buffer supplementation. On day 2, addition of sodium bicarbonate to adjust the pH resulted in a drastic increase in pH from 5.6 on day 3 to 7.18 on day 4 followed by a gradual decrease, and reached pH 5.41 by day 11. The daily pH oscillation occurring in this course indicated the consumption of easily digestible substrate. Subsequently, the runs started at pH 5.77 and stabilized at 6. The TVA generation rate of 0.45 g HAc/l d was quite lower than that obtained by pH 5.5. In this respect, further build up of SCOD and VFA extraction was done on day 21 by letting the pH climb up to 6.5, but the reactor M4 kept showing a constant TVA generation rate of 0.47 g HAc/l d. Buffer addition was continued until day 29 at a pH closed the neutral range, with the total amount of buffer 0.3 g NaHCO₃/g VS_{added} (~10 times lesser M2).

The hydrolysis and acidification products of the experimentally stepwise pH gradient 4.5-6.5 are showed in Figure 4.20. The profile of the SCOD showed an initial, increase until the methanogenesis started and later, the solubilization decreased until the end of the biodegradation process was reached. The high initial leachate SCOD value and rapid SCOD extraction noticed during the initial 5 days of operation were attributed to the simple wash-out of the soluble organics of the feedstock nature. The concentrations of SCOD during the second week, at a pH around 5.6, were relatively stable, around 26.8±1.6 g/l. The maximum SCOD concentration of 32.5 g/l was recorded

on day 16 and remained nearly constant thereafter. The stable COD may be due to product inhibition. Xu *et al.* (2013) reported that a slowdown of acid production might be related to the depletion of easily digestible substrates, and the hydrolysis of cellulose and hemicelluloses became the rate-limiting step. Cysneiros *et al.* (2012) found approximately 45% and 65% of solids were hydrolysed within the first 7 and 14 days, respectively, indicating that the rate of hydrolysis slowed down with time. Jagadabhi *et al.* (2010) reported the onset of inhibition of hydrolysis occurred when reaching VFA level 9 g/l (pH 5.6) while Siegert and Banks (2005) reported similar inhibition of cellulolytic activity at TVA concentrations of 2 g/l.

As indicated in Figure 4.20, TVA contents increased as a function of external buffer addition. For 29-days with addition of an exogenous buffering agent, the reactor M4 showed a remarkable increase of TVA concentration, reaching the peak of 22.4 g HAc/l. The TVA concentration behaved in a similar way as SCOD. The TVA generation rate sharply increased and reached the maximum rate of 1.38 g HAc/l d within 8 days of operation period. This study revealed that introducing external buffer to the acid reactor has a strong effect on the acidification process. Bioconversion of fruit and vegetable organic matter into VFA (SCOD→VFA) was calculated as the ratio between effluent VFAs and SCOD; $VFA_{out}/SCOD_{out}$, which defines the fraction of the effluent COD due to VFAs. A slight inhibition of acidogenesis occurred in the day 2 as indicated by the low representation of VFAs in the SCOD (37%). The production of VFA did not account for all the SCOD in the reactors, suggesting that other soluble compounds were present in the leachate.

The COD and TVA values of leachate from reactor M4 were compared with the results of the previous investigation in which the reactors were started with a neutral pH value (M2 and M3). The initial neutral pH control and the stepwise increasing pH produced a similar result in which there was no remarkable increment of the cumulative COD and TVA leached out from them after the buffer addition ended. The cumulative VFA production in M2 and M3 (0.5-0.6 g VFA/g VS_{added}) was higher than that of M4 (~0.1 g VFA/g VS_{added}), which could be attributed mainly to the buffering effect. Under the drastic drop in buffer usage of M4 (~10 time lesser M2), the present study has shown a lower VS reduction efficiency of 61%, which is 23% lower than in the neutral pH control (80%). Therefore, controlling the system pH effectively enhanced the hydrolyzed and acidified products as confirmed from these results. Similarly, in the treatment of

MSW, a ligno-cellulosic material, with various alkalis, hydrolysis was enhanced (Bhattacharya *et al.*, 2008). The author found the addition of strong bases such as NaOH or $\text{Ca}(\text{OH})_2$ can increase the solubilization of organic matter through depolymerization reactions of lignin-cellulose complex.

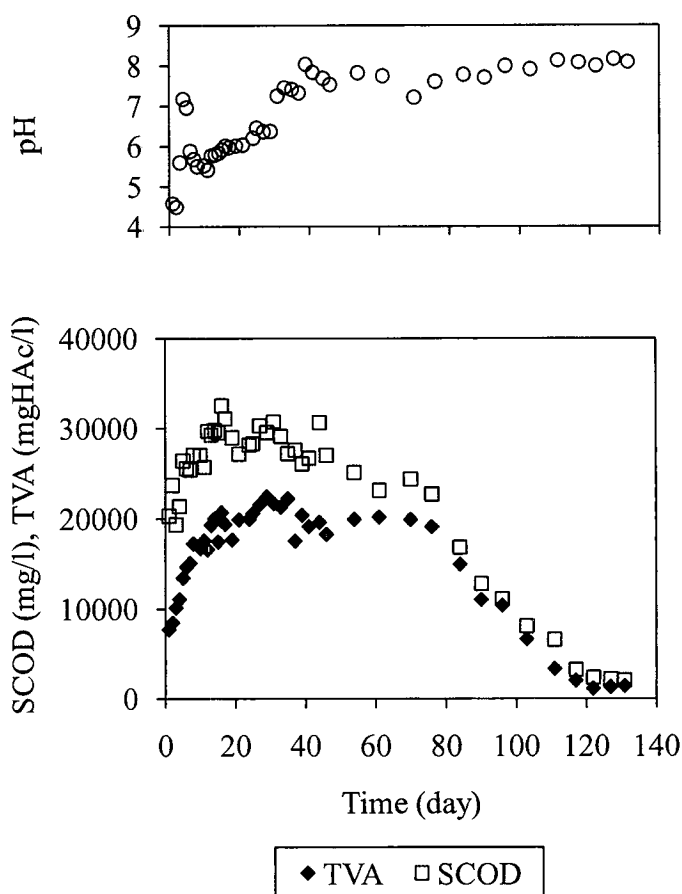


Figure 4.20 Variation of pH, SCOD and TVA by stepwise increasing pH 4.5-6.5

2) Biogas and Methane Production

Figure 4.21 shows the methane and gas production by the stepwise pH adjustment (M4). The distributions of methane content in biogas samples were between 3.8% and 24.8%, as carbon dioxide accounted for $56 \pm 5\%$ of the biogas, indicating acidogenesis as the dominating process during the initial operation period. Negligible biogas volume was detected during the early stages of digestion. There was a rather long lag time before the biogas production noticeably measured on day 44 with a slight increase in methane concentration from 4.6% (start-up) to 24.8% (day 29), and then reaching 56% by day 39. This suggested that methanogens were not active or that their concentrations

were insufficient during the start-up. Day 70 after reactor start up, a remarkable increase in biogas production was measured, reaching 60% CH₄, indicating the onset of methanogenic phase, with a gradual decrease in the concentration of undissociated acid. This indicates that the acid reactor became progressively more methanogenic and SCOD and VFA were converted to biogas inside the one phase reactor. The rate of biogas production stabilized at only about 0.36 l/d, some 5.7 times lower than in the two-phase system (section 4.3.4.2). The biogas production for 108-days operation was 21.6 l of which 69% was methane. This corresponded to 0.2 l CH₄/g VS_{added}. In this respect, the successful employment of pH control for biogas production in single-phase system had been already achieved by raising the pH in a stepwise manner.

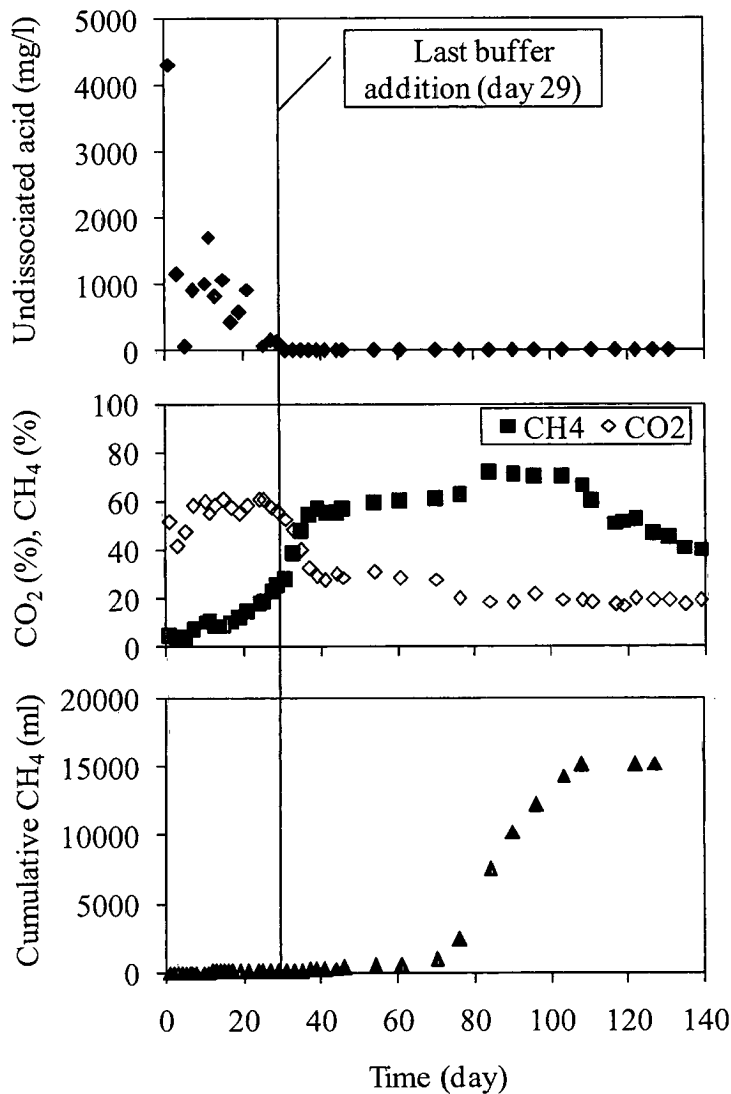


Figure 4.21 Gas production and undissociated VFA by stepwise pH adjustment

The variations of undissociated acid shown in Table 4.9 indicate a strong undissociated VFA control by pH adjustment. Undissociated fraction gradually decreased from 4323 mg/l (start-up) to 10 mg/l, by 31-days of the stepwise increasing pH process. The undissociated VFA concentrations of 9.1 to 98.5 mg/l were in good agreement with the recommended inhibitory undissociated acid level for methanogenesis. When the undissociated fraction was in the recommended threshold level for methanogenesis, the methane production kept increasing continuously.

Table 4.9 Undissociated acid concentrations with pH gradient 4.5 to 6.5

Operation time	pH	Undissociated acid (mg/l)	
		Before buffer addition	After buffer addition
Day 1th	4.5	4,323.0	1,151.4
Day 3rd	5.5	1,151.4	57.2 ^a
Day 12nd	6.0	1,718.1	833.5
Day 25th	6.5	932.7	80.5
Day 29th	>7.0	128.2	9.5

^a temporary drop

As aforementioned, methanogenesis failed to develop at the high TVA concentration. Methane could not be formed in the single-phase reactor, which operated at the relatively high TVA concentration of 10.7 g HAc/l and a concentration of undissociated acid above 3.7 g/l, respectively. These results were clearly observed in the previous batch runs under extreme buffer addition ~ 3 g NaHCO₃/g VS_{added} (M2), where methane release was always low. The presence of methane was never higher than 16% in all the neutral pH control reactors (M2 and M3). Failure encountered with the control reactor (MC) may be linked to TVA accumulation and formation of large amounts of undissociated VFAs. The undissociated acid concentrations of 4-12 g/l of uncontrolling pH were far above the inhibitory limits for methanogenesis reported in literature.

In this study, we introduced the stepwise increased pH procedure into the market waste treating process in order to resolve the difficulties noted above. Keeping the pH with proper dosage of NaHCO₃ prevented pH from dropping too low during the initial period and led to further enhancement of the VFA released. A sufficiently low TVA was essential for the development of a stable anaerobic digestion process. Interestingly, biogas was enriched in CH₄, when there was ~ 2000 fold difference between TVA and UA

concentrations, whereas CH₄ concomitantly increased from 47 to 71% of the total biogas. Therefore, it suggested that a well-adjusted proportion of TVA and UA could avoid the stressing problem in a single-phase system.

The possible inhibitory effects of high buffer additives and the adverse effects of undissociated form to the degradation process have been abated by the stepwise pH method. Nevertheless, the stepwise pH increase for anaerobically treated market waste may have an adverse effect on a lag phase in methane formation and low methane yield (Figure 4.21). In our case, there was no measured biogas for over 40 days, which in practice is associated with the larger size of tank requirement. Reduced buffer turned into lower accumulations of VFA and, consequently, lower SCOD and VFA yield resulted in lower VS reduction efficiency. In the previous study (as defined in M2 and M3) which initially controlled pH set point at 7, an 80% of VS reduction was achieved after introducing 3.13 g of NaHCO₃/g VS_{added}. Under the drastic drop in buffer usage of 0.3 g NaHCO₃/g VS_{added} (~10 time lesser M2), the present study has shown a lower VS reduction (efficiency of 61%), 23% lower than that observed under neutral pH control. In conclusion, the pH control at neutral value was the best performing reactor on a hydrolysis-acidification as it showed the highest yields, which in practice is associated with the separated phase. A continuous supply of buffer in the early acid phase of the reactor overcame the acid stress problem, thus enabling further methanogenesis in one stage system. In addition, it is therefore clear that the pH control regime created either by the initially controlling pH set point of 7.0 (M2 and M3) or stepwise increased pH (M4) was an effective amendment for inhibiting the production and accumulation of undissociated acid. Both pH control modes produced a similar evolution of the undissociated acid but the stepwise increasing pH delayed initiation of methanogenesis.

4.3.4.2 Two-Phase System

1) COD and VFA Production in the Acid Reactor

1.1) Before Coupled with Methanogenic Reactor

The final part of this study was carried out to determine the market waste degradation efficiency under the separated phase condition; therefore, a low amount of buffer was supplied into the system. Performance of the two stage systems was monitored in terms of VFA production, methane production and VS removal. The characteristics of the effluent leachate of M4 and M5 were similar by the first 10 days from

the start-up because the reactors were operated in a similar manner (Figure 4.22). Prior to combination, digester M5 was given sodium bicarbonate (10.5 g) on day 1 and day 2 aiming to support the TVA formation as well as suppress the undissociated VFA concentration. A gradual rise in pH was found from 4.64 (day 1) to 6.30 (day 4) before drop to 5.47 (day 11). Leachate SCOD and TVA reached the peak values of 27.5 g/l and 16.3 g HAc/l, respectively, within the first 10 days of the operation. The SCOD concentration of reactor M5 increased ~20% from the initial SCOD which was lower than the ~60% increase in SCOD found in reactor M4. It could be clearly seen that the undissociated acid concentration was strongly affected by pH control. There was a temporary drop in undissociated acid concentration during the alkali addition from 3126 mg/l (start-up) to 563 mg/l (day 5) and increased thereafter to 1621 mg/l (day 11), surpassing the critical level for methanogenesis as reported elsewhere. Carbon dioxide was the main gas generated while the few methane concentrations were measured, indicating that acidogenesis was the main reaction in this stage as well as seen in M4.

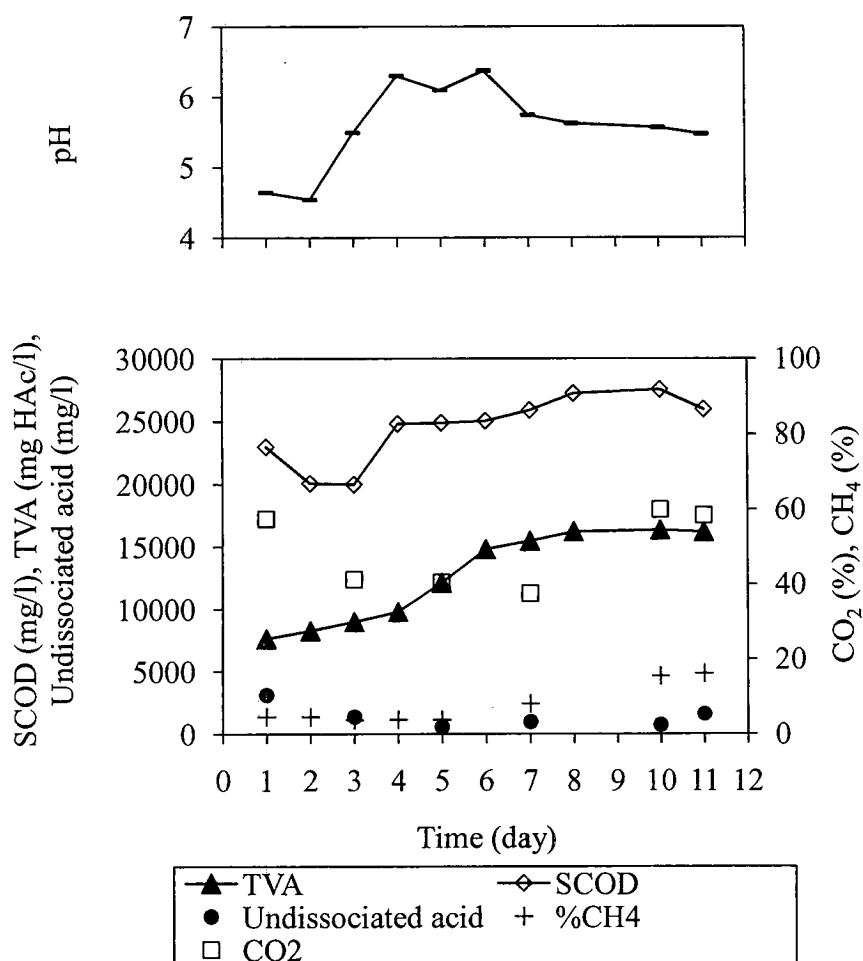


Figure 4.22 Leachate characteristics and biogas production of M5 before combination with FF

1.2) M5 Coupled with Methanogenic Reactor

When M5 became stable, the methanogenic fixed film reactor was coupled with F5 on day 12. Acidogenic leachate from M5 was fed into the methanogenic reactor in up flow mode before the methanogenic effluent from FF recirculated to F5 with the same volume. Fixed film reactor was initially fed with acidogenic leachate at OLR of 0.6 g COD/l d before the methanogenic effluent with high pH (7.92) and low strength leachate (SCOD 1,575 mg/l and TVA 681.9 mg HAc/l) was circulated back to M5. A slight increase in pH was noticed, from 5.56 to 5.67, by the first combination, and the corresponding undissociated acid concentration slightly decreased from 1,375 to 1,043 mg/l on following day.

To accelerate the biogas production, increasing OLR to 1.3 g COD/l d was employed in the second combination (day 14). The OLR was increased in steps of 0.6, 1.3, 1.8 up to 3.8 g COD/l d. A rapid fall in the leachate TVA and SCOD concentrations caused a strict OLR adaptation. Accelerating OLR to 3.8 g COD/l d was made on the fourth combination (day 16) at which point M5 had low strength leachate; therefore, resuming OLR at a reduced loading of 0.4 g COD/l d was done on the fifth combination (day 19). Effluent SCOD ranged between 220 mg/l and 3477 mg/l with a COD removal efficiency varying between 86% and 99%, indicating the conversion of intermediate VFA by the methanogen activity in fixed film reactor, thus resulting in the generation of biogas. The notably high SCOD and TVA in the outlet found on day 14 and 15 could be due to the washout of biomass from the methanogenic reactor. The pH of the methanogenic effluent always remained over 7.65 throughout the run. Alkalinity was sufficiently high with a TVA/Alk ratio consistently below 0.3, indicating a stable methanogenesis performance. A COD reduction of 98% was achieved at the maximum OLR of 3.8 g COD/l d. The concentration of the methanogenic effluent COD fell as the experiment continued, however, it stabilized at >85%COD removal irrespective of the OLR. Coupling the acid reactor with the fixed film reactor was terminated on day 24 under a strict acid leachate fed.

With 12 days of coupling period (or 9 times of combinations), gradually declining concentrations of TVA and undissociated acid of M5 appeared. The results of anaerobic digestion of market waste in coupled acid and anaerobic methanogenic reactors as depicted in Figure 4.23 showed that the undissociated acid content in M5 (34.5 mg/l) reached the threshold level for methanogenesis on the sixth combination.

Interestingly, the reactor 'M5' has shown continuous increments in methane with the sharp increase in TVA/UA. This can be attributed both to a drastic drop in TVA/undissociated acid (TVA/UA), shifting from around 13 to almost 2000, and to the neural pH reached.

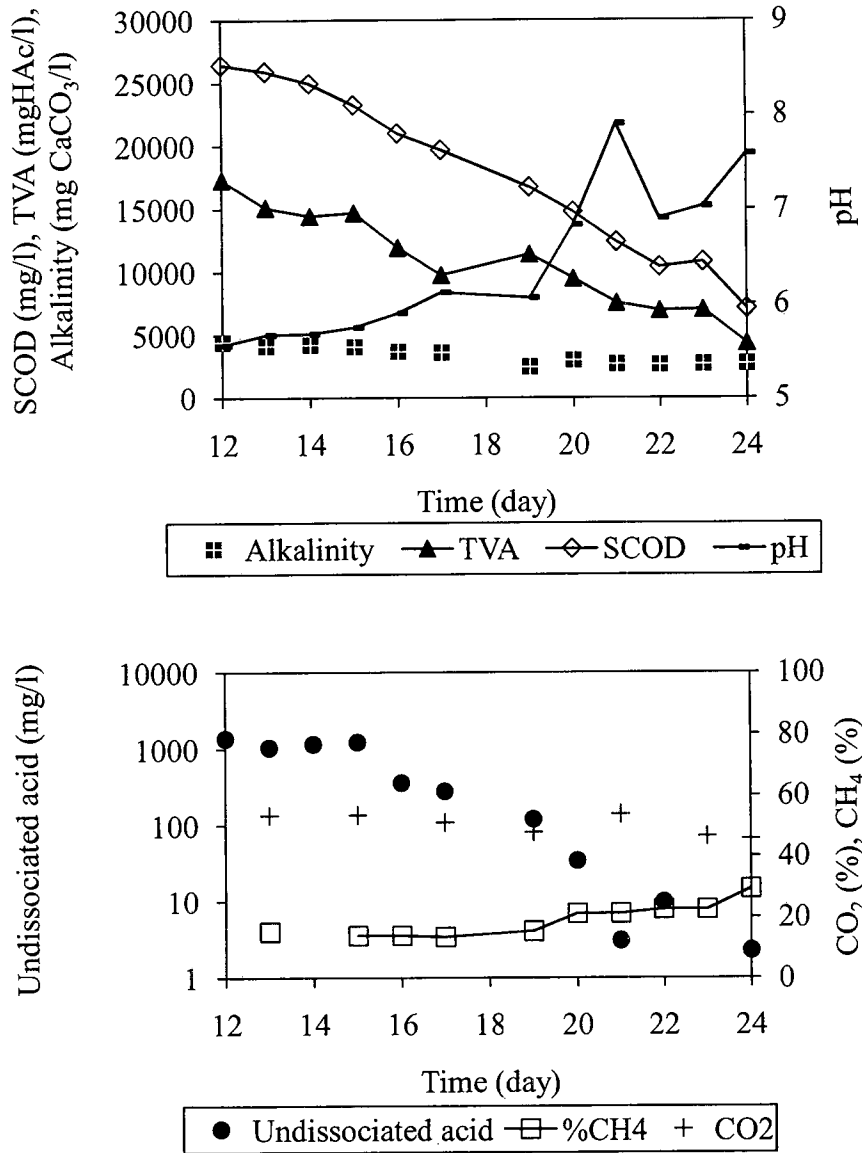


Figure 4.23 Leachate characteristics and biogas production of M5 coupled with FF

2) Relation between OLR and Biogas Production

The performances of the methanogenic reactor versus organic loading were determined with regard to COD removal and biogas production (Figure 4.24). The OLR was started at 0.6 g COD/l d at the beginning of the operation and switched to 1.3 g COD/l d, and a remarkable effluent fluctuation from SCOD 0.32 to 3.48 g/l was also found. This variation was likely the result of a partial washout of biomass from the methanogenic reactor. During the coupling period of stepwise increase in the loading rate there was, however, a negligible variation in the pH of fixed film reactor, 7.89 ± 0.2 . The concentration of alkalinity detected in the effluent averaged 2.52 g CaCO_3/l , corresponding to a TVA/Alk ratio of 0.31. This remained below the threshold of 0.4 for optimum performance (Rincón *et al.*, 2009), indicating stable methanogenic conditions.

Low concentrations of TVA (less than 0.7 g/l) were kept during all the OLRs studied, which showed that the high concentrations of acids from the hydrolytic-acidogenic stage and fed into the methanogenic reactor were easily removed for OLRs of 0.6 to 3.8 g COD/l d and a HRT of 24 h. Apart from the observed high TVA level on day 15, the more than 85% COD removal with increasing loading rate showed a stable performance of the methanogenic fixed film reactor. The amount of volatile material expressed as VFA that was passed from the acidogenic reactor M5 to the fixed film reactor was insufficient to account for the maximum OLR for the methanogenic fixed film reactor. Consequently, a rapid increase in OLR at 3.8 g COD/l d loading rate was applied. The maximum OLR obtained at this stage was 3.8 g COD/l d with a 95% COD removal, on average. The COD removal efficiency hinted that within the coupling period, the OLR could have increased more aggressively without any compromises in the performance of the methanogenic reactor. The increase in OLR did not affect the COD reduction for the entire period of operation, as the COD reduction always remained in the range of 93 to 99%, while the effluent pH was >7.6 under the conditions used. The biogas production rate, the methane yield ($0.3 \text{ l CH}_4/\text{g VS}_{\text{added}}$) and the methane content (60-74 v/v% CH_4) of the biogas were satisfactorily high. In other words, the result suggested the possibility of minimizing the start up time required to treat market waste.

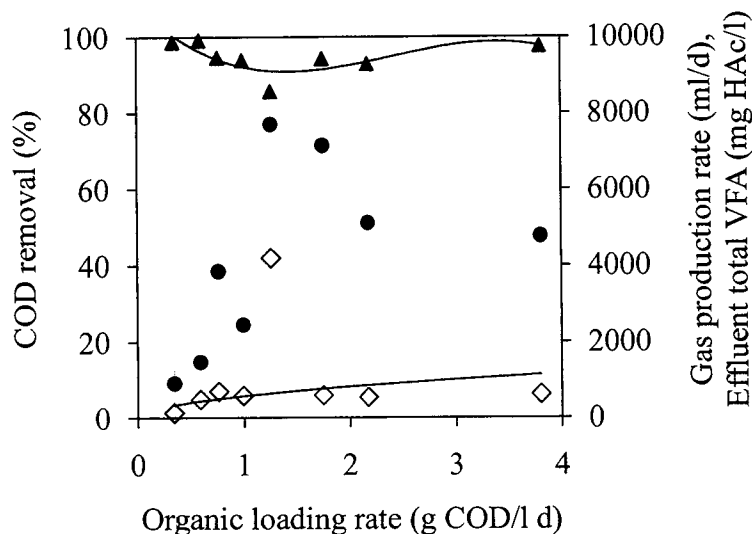


Figure 4.24 Effect of different OLRs on the volumetric gas production rate (●), COD removal (▲) and effluent VFA (◇)

Table 4.10 Degradation of VFA composition in fixed film reactor during coupling period

OLR (g COD/l d)	AA (g/l)		PA (g/l)		BA (g/l)		iBA (g/l)		VA (g/l)	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
0.6	3.08	0.59	1.66	0.30	3.61	0.47	0.11	0.028	0.67	0.17
1.3	3.53	0.62	1.68	0.32	3.76	0.53	0.12	0.033	0.73	0.18
1.8	4.26	0.74	2.05	0.38	4.71	0.59	0.15	0.031	0.91	0.18
2.2	1.32	0.55	0.66	0.30	1.30	0.41	0.049	0.026	0.34	0.16
3.8	1.75	0.61	0.90	0.33	1.75	0.50	0.070	0.030	0.38	0.17

The leachate SCOD of reactor M4 ($0.3 \text{ g NaHCO}_3/\text{g VS}_{\text{added}}$) was ~60% increased from the start, which was comparatively a 3 times higher increase than in the M5 ($0.1 \text{ g NaHCO}_3/\text{g VS}_{\text{added}}$). The observation agrees with the higher acid yield and SCOD/TCOD ratios observed for the buffered reactors (M2 and M3) compared to the unbuffered reactor (MC and M1) as discussed early. This was the beneficial effect of external buffer addition on enhancing hydrolysis-acidification, which led to the 1.3 times extra SCOD released. However, when considering the reactor performance in terms of VS reduction and the methane production, the performance of reactor M5 was better than that M4 even though the SCOD extraction of the former was lower than that of the latter. The

VS reduction of reactors M4 and M5 were found to be 61% and 73%, respectively. This indicated that methane is being formed from non-VFA components or that further acidification and conversion of soluble polymers is taking place within the methanogenic reactor. In any case, this finding is in agreement with the report of Wang *et al.* (2005); the recycling of buffered leachate in the acidogenic reactor for hydrolysis was beneficial in leaching more VFA and COD. As the waste degradation degree and methane production of the two-phase system were higher than those of the one phase system (see section 4.3.4.3), the pH control may not be a strong factor affecting the AD performance of market waste treatment under the two phase system. Thus, the way to reduce the amount of external buffer using the methanogenic effluent as water dilution instead was verified in the next study.

Figure 4.25 shows the evolution of methane content in the headspace of reactor M5. The methane percentage reached 60% on day 33, or by 9 days after the end of decoupling. By this time, the measurement of the volumetric methane production had commenced in both reactors (M5 and FF). The biogas production of M5 was 5.67 l, of which 2.96 l was methane, whereas the methanogenic fixed film reactor produced 38.2 l of biogas, of which 23.9 l (66%) was methane. Thus, the total methane yield was 0.3 l CH₄/g VS_{added}, of which 87% was obtained in the methanogenic reactor. It was higher than the yield of 0.15 l CH₄/g VS_{added} generated by the single-phase system 'M4' (210-day operation period). Hence, with phase separation and methanogenic effluent as the dilution water, better performances were achieved in a shorter time. The process was completed and a high level of cumulative methane production was achieved in less than 37 days. The methane yield in this study was consistent with a previous study by Rajeshwari, *et al.* (2001) on the processing of solid vegetable market in a two-stage digester, which had a methane yield of about 0.2 l CH₄/g VS added. Babae and Shayegan (2011) utilized fruit and vegetable waste for the production of biogas. They tested different OLRs (1.4, 2, and 2.75 kg VS/m³ d) at a fixed HRT of 25 days at mesophilic temperature. The authors obtained a yield of 0.12-0.4 m³ biogas/kg VS with a methane concentration of 49.7-64%, and reported that the methane composition decreased at higher OLRs.

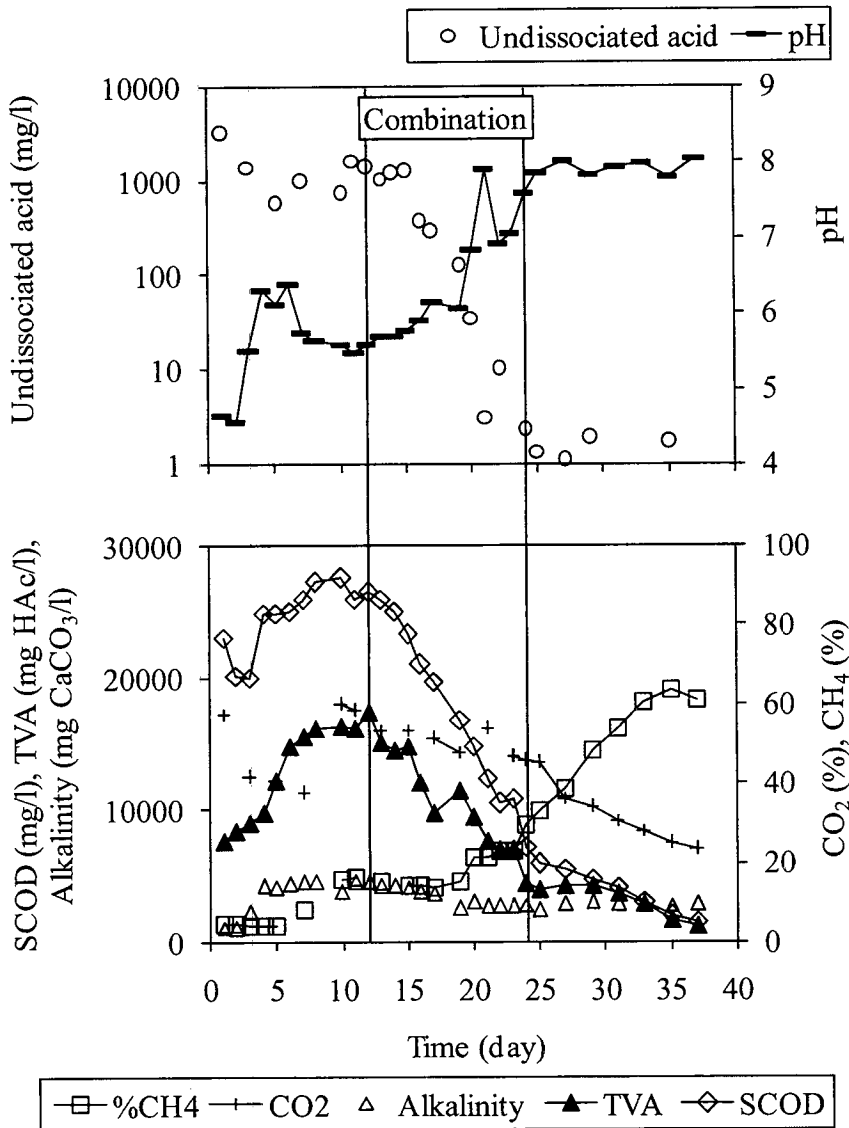


Figure 4.25 Leachate characteristics and biogas production of two-phase system

4.3.4.3 Phase Comparison and Mass Balance Analysis of Anaerobic Digestion of Market Waste

1) iVFA Profile of Single and Two-Phase System

The analysis performed by gas chromatography showed that the predominant volatile fatty acids were acetic and butyric acids, with concentrations higher than other acids (propionic acid, iso-butyric acid, and valeric acid) at both the reactor M4 and M5 (Figure 4.26). The concentration of some of the iVFAs of batch reactor M4 during the initial 10 days of operation exceeded the threshold levels reported to cause process inhibition. For instance, acetic acid levels were 2.0-4.2 g/l and exceeded the threshold

level of 0.8 g/l reported to cause process inhibition (Hill and Holmberg, 1988). The concentrations of iso-butyric (0.05 and 0.1 g/l) and valeric acids (0.35 and 0.81 g/l) also exceeded the levels of 0.005 and 0.015 g/l, respectively, reported to cause inhibition (Wu *et al.*, 1995). As fruit and vegetable market wastes are carbohydrate rich-material, the rapid accumulation of acetate during present study indicated that carbohydrates were more readily degraded than nitrogenous materials and lipids (Jagadabhi *et al.*, 2010). An accumulation in acetic acid observed in reactor M4 may have inhibited the hydrolysis of carbohydrate (Lü *et al.*, 2008), because high concentration of acetate influences intracellular pH, ATPase, and the fatty acids composition of the cell membrane, thus affecting the biodegradation of the organic matter, VS reduction 61% (single phase system) versus 73% (two phase system).

Similarly, the concentrations of acetic acid of M5 before coupled with FF ranged between 1.6 and 4.5 g/l, while the butyric acid concentrations varied between 0.3 and 5.8 g/l. This concentration was higher than the inhibitory acetic acid concentrations reported in the literature, where it was shown that concentrations higher than 788 mg/l caused failure in the process and low stability (Hill *et al.*, 1987). Iso-butyric was also produced but its concentration was <0.75 g/l from day 16 onwards. A small build-up of longer chain VFA such as iso-butyric, n-butyric and valeric acids compared with acetic acid in the present study indicated that the former VFAs were easily biodegraded to form acetic acid (Jagadabhi *et al.*, 2010). As compared to M4, which operated a one stage, M5 approached methenogenesis much faster than under single phasing condition because iVFAs of reactor M5 were kept low by coupling with methanogenic reactor. This observation implied greater benefit of the two-stage anaerobic market waste treatment over the single stage system.

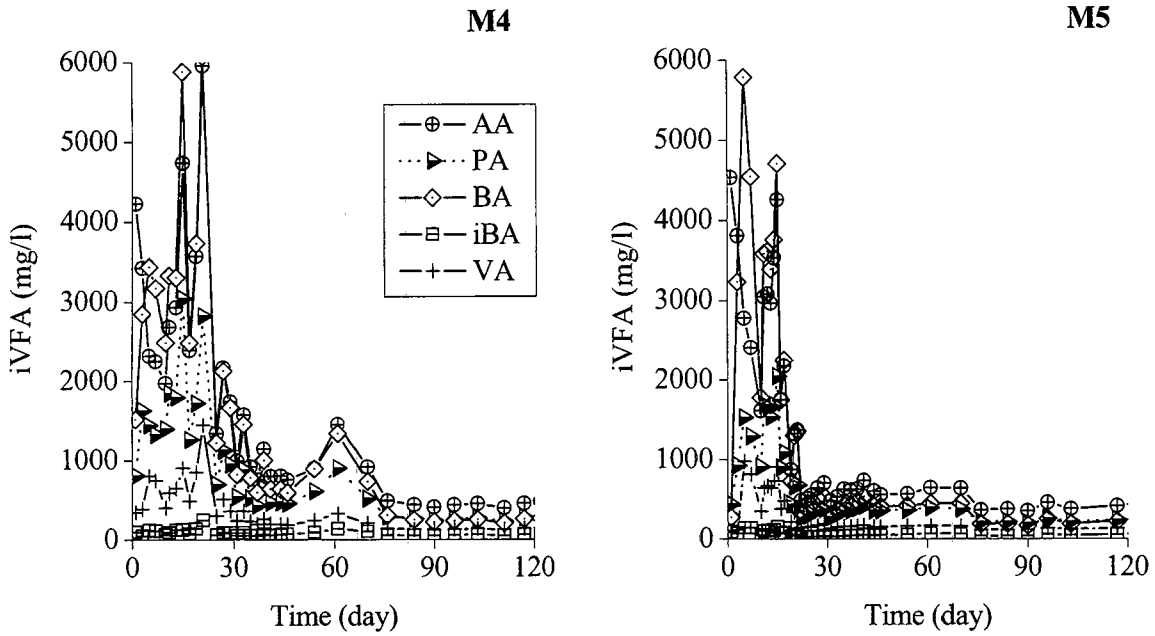


Figure 4.26 iVFA profiles of acidogenic reactor M4 (single-phase) and M5 (two-phase)

Regarding the iVFA concentration at the effluents of the methanogenic reactor, the most prominent ones, acetic and butyric acids, were noted. The variation of the different volatile fatty acid concentrations with the OLR in the methanogenic reactor is shown in Figure 4.27. The acetic acid concentration was 551 ± 88 mg/l for all the OLRs tested, and it only increased to 740 mg/l for the last OLR studied (3.8 g COD/l d). A high number of VFAs, including valeric acid, was no greater than 13% that of the overall VFA production. Demirel and Yenigun (2002) found that propionic inhibits methanogen growth when its level is above 951 mg/l. In the present methanogenic reactor a maximum concentration of propionic acid, the major inhibitory VFA type for methane formation (Wijekoon *et al.*, 2011), of 376 mg/l was achieved at the highest OLR studied, and this concentration was always below the failure limit value mentioned in the literature. This was accompanied by high methane composition, between 60% and 74%.

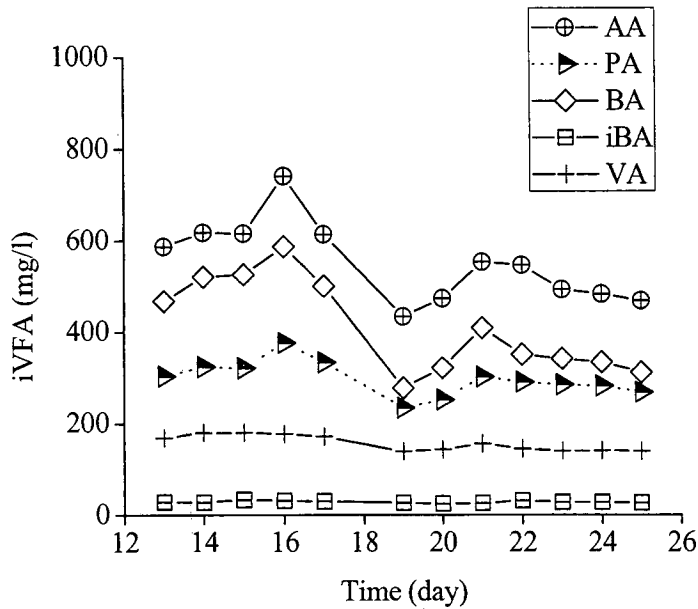


Figure 4.27 iVFA profiles of methanogenic fixed film reactor

2) Biogas and Methane Production

The maximum methane production rate ($2 \text{ l CH}_4/\text{d}$) of anaerobic digestion of market waste under the two-stage system was 5.7 times greater than that of one stage process ($0.4 \text{ l CH}_4/\text{d}$). The methane yield was 2 times higher than that obtained in the single phasing condition ($0.15 \text{ l CH}_4/\text{g VS}_{\text{added}}$). In addition, the level of undissociated acid reached 1 mg/l , a much lower value than that necessary to achieve the methanogenesis.

Rapid flush out of inhibitory products, TVA and undissociated VFA, in the two phase operation led to a fast entrance into the methanogenesis phase in M5 ($60\% \text{CH}_4$ reached on day 33) with a 29-fold higher production of volumetric methane than that of M4 for the same time point, whereas a prolonged runtime, including a lengthy lag phase, totalizing around 61 days was required for methanogenesis initiation under the single phase reactor. The methanogenic reactor promoted the hydrolysis-acidification by stabilizing the pH in the first stage reactor and flush out inhibitory product (VFA and undissociated acid). The recycled effluent could retain alkalinity and microorganisms in the system, and in this case water addition is reduced as well because the methanogenic effluent functions as dilution water. As can be seen in the previous study, circulating leachate between a landfill and a methanogenic reactor offers the advantages of a high

alkalinity effluent in the methanogenic reactor to buffer the pH and the presence of adapted microorganism to inoculate the landfill reactor, which improved the performance of landfill system (Chynoweth, *et al.*, 1992). Lü *et al.* (2008) indicated that the recirculation of methanogenic effluent introduced alkalinity into hydrolysis reactor, avoided the pH descending during the initial acidogenesis. Methanogenic effluent could dilute the inhibitory effects of organic acids, alleviating accumulation of fermentative products in the acidogenesis environment, promoting the development of methanogenic bacteria activity. The authors also found that the increased OLR, diluted the inhibitory products in the acidogenic pocket. O' Dwyer *et al* (2001) stated that hydrolysis was a surface-depended reaction. Liquid flow enhanced the mass transfer around the substrate surface, so as to reduce the inhibitors (TVA and undissociated acid) accumulation in heterogeneous zones, improve the mobility of enzymes and increased the probability of enzymatic accessibility to substrate surface. The author indicated that the methanogenic effluent played a role of pH buffer. Similar result reported by Vavilin *et al.* (2003), the recirculation of methanogenic effluent into first stage reactor could introduce alkalinity, buffer the pH fluctuation, dilute the inhibitors, and increase the total enzyme activities in hydrolysis environment (Zhang *et al.*, 2007). Therefore, partial recirculation of methanogenic effluent was required to promote hydrolysis. However, the ratio of TVA/UA should be controlled at a reasonable value, i.e. TVA/UA 2000:1. A high ratio of TVA/UA means that the level of undissociated acid in the leachate is acceptable. Cysneiros *et al.* (2008) suggested that recirculation of leachate from the methanogenic reactor is important in maintaining conditions suitable for hydrolysis of municipal solid waste in a leach-bed reactor (first phase acidogenic reactor). This was considered to be due to the washing out of VFAs from the first reactor, which consequently prevented the inhibition of hydrolytic microorganisms.

The leachate strength reduction in the acidogenic digester after coupling with the methanogenic reactor in the two-phase system also provided benefits for biogas production in the acidogenic digester, as indicated by the boost in methane generation in M5. The VS removal increased from 61% (one-phase) to 73% (two-phase), with a corresponding increase in CH₄ production. The use of the leachate dilution with the methanogenic effluent recirculation through the acid reactor allowed the digester M5 to achieve methanogenesis in just 37 days, while M4 showed a late onset of methanogenesis.

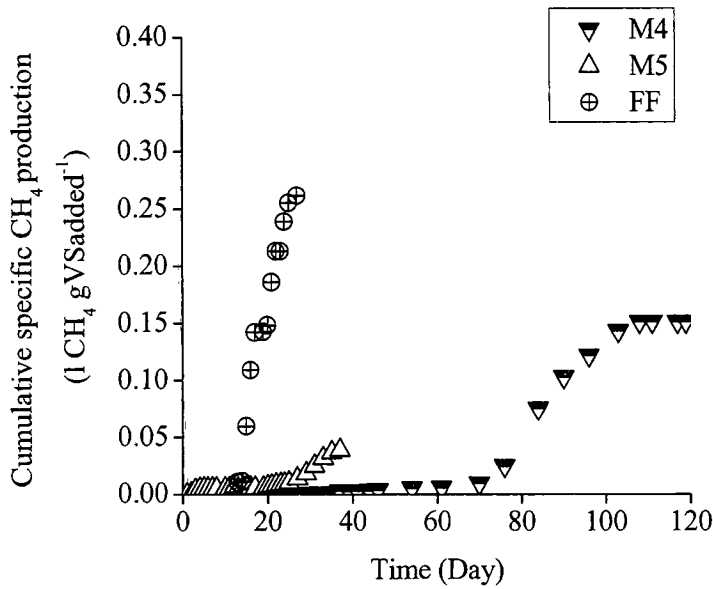


Figure 4.28 Cumulative specific CH₄ production of one and two-phase based on VS added

3) Carbon Mass Analysis

Carbon mass balance analyses of the one-and two-phase system treating market waste were conducted and the results are shown in Figure 4.29. It can be seen that the market waste under a two phase process was mainly transformed into gaseous products, which accounted for 40% (26%CH₄ + 15%CO₂) of the total carbon in the substrate, and a liquid phase COD 21%, while organic carbon in solid form was only around 7%. Also as shown in Figure 4.29, when market waste was treated by the single phase reactor the amount of carbon of gas phase and liquid phase was only 18% (13%CH₄ + 5%CO₂) and 5%, respectively, which was lower than that generated by the phase separation condition previously mentioned. Most carbon (23%) remained in the organic solid form.

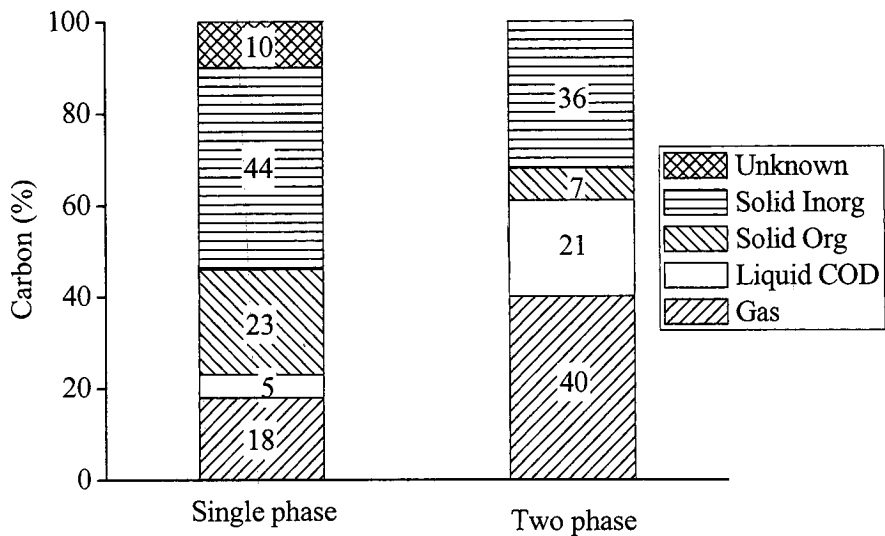


Figure 4.29 Carbon balance analysis of anaerobic market waste treatment

Two major factors are involved in the problem of readily degradable fruit and vegetable wastes. One is the fast degradation of organic composition of the market waste. The main component is carbohydrate, which is rapidly degraded in the anaerobic fermenter during the acidogenesis, stressing additional biodegradation of slowly degradable fraction; such as hemicelluloses and lignin, resulting in a poor overall process performance. The second factor stems from the first. As the products of acidogenic phase are organic acids, the pH in the digester decreases, leading to improper methane production by the methanogenic microorganisms. The process most widely used to avoid the effects of organic acid accumulation is the control of the pH. Aiming at resolving the rapid VFA build-up encountered at the start-up phase using the stepwise increasing pH method had shown that the intermediate VFAs were not converted to biogas immediately because of differences in the rates of acidogenesis and methanogenesis under the single phasing condition. In the operation of a single-stage system, careful attention has to be paid to the balance of pH, TVA, and undissociated acid levels. In our study, the two-phase system, as means of avoiding an external buffer source, the leachate dilution used low strength methanogenic effluent instead of fresh water in the first stage reactor. Recirculation of the methanogenic effluent alleviated the accumulation of fermentative products in the acidogenesis environment. The results suggest that a relatively fast acidogenic step is avoided when the methanogenic effluent is introduced; the pH did not decreased, allowing the acidogenic reactor itself to reach the methanogenic stage.

Digestion of market waste is in contrast with the results of the food waste experiment. From a technological viewpoint, there are advantages and disadvantages dealing with both one and two-phase operations. It is well known that a one phase system is more simple and easy to operate. But it is sensitive to overloading, which will lead to an accumulation of acid. The two-phase system is more stable and can deal with high peak loading when using a fixed film reactor as a methanogenic phase. For quickly fermentation wastes, a two-stage reactor can have a lower total digestion time than the conventional single stage (Gunaseelan, 1997). The anaerobic pack bed filter used in this study was shown to be efficient for obtaining high methane efficiency. The performance of the digester under single-and two-phase conditions is summarized in Table 4.11. The system was capable of handing OLR of up to a 3.8 g COD/l d. Recycling of the methanogenic effluent reduced alkaline usage to maintain pH in the acidogenic reactor (one phase 0.3 g $\text{NaHCO}_3/\text{gVS}$, two phase 0.1 g $\text{NaHCO}_3/\text{gVS}$). In our study, the application of a two-phase system composed of an acid and a high-rate anaerobic reactor would be more suitable from the energy balance perspective.

Table 4.11 Process performance of one and two-phase treating market waste

Operating conditions and performances	One phase	Two phase
Buffer addition (g $\text{NaHCO}_3/\text{g VS}$)	0.3	0.1
Digestion time (day) ^a	108	37
Acid production rate (g HAc/l d)	0.89	1.38
VS reduction (%)	61	73
Methane yield (l CH_4/gVS)	0.15	0.30

^a minimum requirement

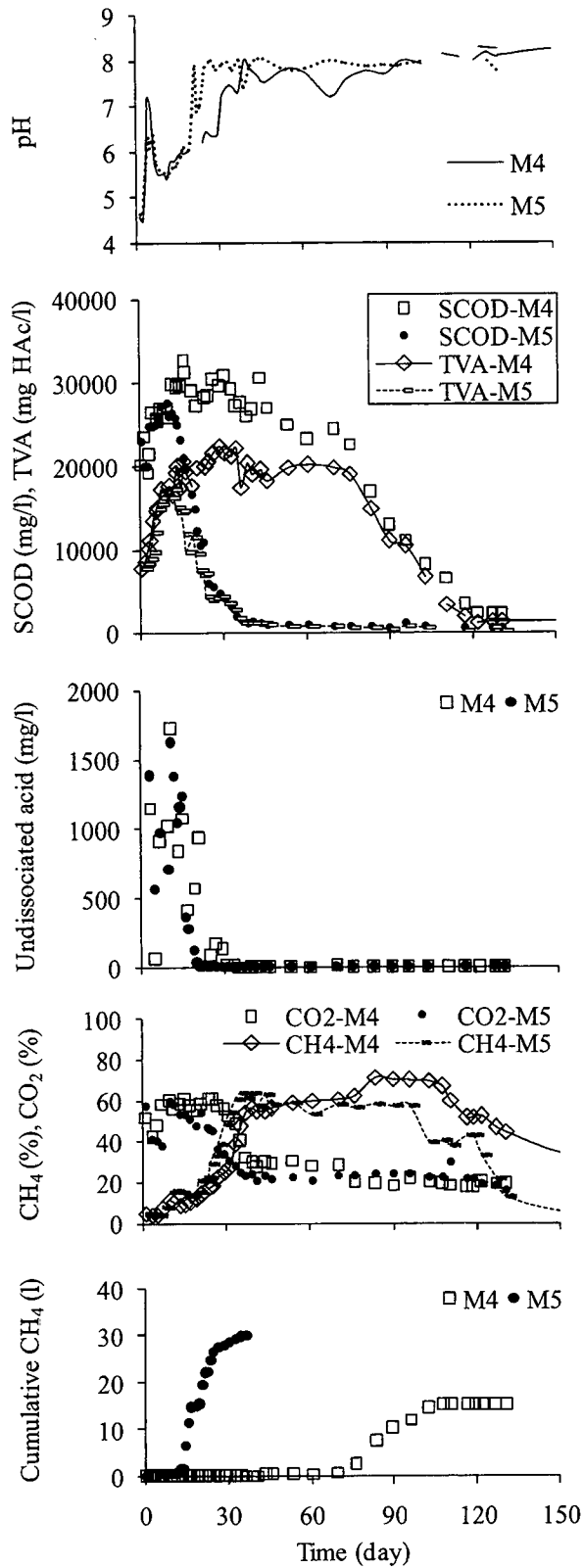


Figure 4.30 Performance comparison of one and two-phase treating market waste

4.4 Summary of Anaerobic Market Waste Digestion

The presence of readily digestible portions in market waste is responsible trend towards acid accumulation inhibition. The pH adjustment at neutral range was the most effective way to improve acidogenesis. Not only pH adjustment enhanced the total VFA production, but their form changed with pH. Compared with pH at 5 and 6, pH 7 provided an optimum working condition for anaerobic digestion of market wastes. At pH 7, the maximum TVA concentration of 19.9 g HAc/l was achieved on the 12 days with yield of 117.2 g HAc/kg DM, following by 90.1 g HAc/kg DM (pH 6) and 76.5 g HAc/kg DM (pH 5), respectively. Neutral pH adjustment was a key to a successful control of the inhibitory undissociated VFA, leading to drop of its level below the inhibition level for acidogenesis-methanogenesis in less time. With the addition of alkalinity to control pH, a substantial increase of TVA concentration from 8.2-11.4 to 42.7-44.3 g HAc/l was found in the scale-up neutral pH control reactors. This condition seriously restricted the methanogenesis onset (max. 15.3%CH₄) under the single-phase condition. The methanogenesis of easily degradable market waste was worsened by neutral pH control. As a result, an attempt was then made to reduce the VFA in the undissociated form in the balance of the total VFA produced under the single-phase system with the stepwise increasing pH technique. An organic matter removal of 61.1% VS reduction was attained, which is lower than the 79.5% VS reduction obtained in the previous study with the initial neutral pH control. However, by the stepwise increasing pH, the acid formation behavior was changed, providing optimal growth condition for initial acidogens and later methanogens under single phase system, resulting in methane yield of 0.15 l CH₄/g VS. It could not be determined whether the low acidogenesis rate and yield resulted from the low dilution degree tested. Nevertheless, applying dilution for solid market waste seems to provide a beneficial effect for methanogenesis (max. 31.8%CH₄) under extreme conditions for methanogens to function (a low pH of 4.39-5.20) and high inhibitory undissociated VFA (343-4378 mg/l).

Phase separation in the two phase system showed a better processing performance over the traditional single phase in handling market waste digestion. The entering into methanogenesis of the acidogenic digester was attained due to the inhibitory products (VFA and undissociated VFA) flushing in the acidogenic digester, intensified with increased OLR. The stepwise increase in pH to neutral also offered the same solution, but a longer time for approaching the final methane process was needed, not less than 108 days.

Separated phase was not only instrumental for the VFA conversion acceleration but also showed better organic solid removal efficiency (73% VS reduction) with the addition of a small amount of buffer (0.10 g NaHCO₃/g VS), or 3-fold less than the one phase reactor with stepwise pH. The current study demonstrated that two-phase anaerobic digestion of market waste provides a high level of energy recovery in the form of methane. Within 37 days, a successive two-phase system generated a methane yield of 0.30 l CH₄/g VS. However, it should be noticed that 37-day was the maximal HRT requirement for natural fermentation because it also took time for determining the OLR effects by the stepwise procedure. The methanogenic fixed film reactor showed the effectiveness to sustain a high organic loading. Under batch operation, with average COD removal of 95%, an organic loading exceeding 3.8 g COD/l d was allowable. Effluent recirculation alleviated the need for alkali additions to the acid digester and played the role of dilution water. Even though the results in the present work did not combine the neutral pH adjustment (the best condition for acid production) and the two phase system, the concept of the pH adjustment either by external buffer addition with one phase reactor or recirculation of effluent by two phase joining with separated phase conversion should be explored to improve market waste treatment.