DRY ANAEROBIC DIGESTION OF MUNICIPAL SOLID WASTE AS PRE-TREATMENT PRIOR TO LANDFILL

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Engineering

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Abstract

The major environmental problem associated with landfilling of municipal solid waste is related to the long-term discharge of the leachate to environment as well as greenhouse gases emissions into atmosphere. Biological pretreatment prior to landfill could be an new and attractive alternative to reduce the environmental impact of this problem. Pre-treatment through anaerobic digestion could help ensure that the residue to landfill is stabilized while producing profitable energy.

The objective of the study was to develop and optimize a combined process with anaerobic dry anaerobic digestion as a basic unit to pre-treat organic fraction of municipal solid waste. The process was carried out in three stages. First stage was flushing and acidification. Second stage was methanization where biogas was produced intensively. Finally, air flushing was practiced to flush out the remaining biogas inside the waste prior to landfills. Batch study was conducted on pilot scale digesters using vegetable waste as feedstock. Optimization of the first two stages was focused.

It was found that flushing fresh waste with additional water (3L/kg waste) for short duration of 5 days was able to wash as much as 30% of volatile solid into leachate, out of which more than half was VFA. Hydrolysis yield was approximately 130 kgDOC/kgTS and acidification yield was about 180 g VFA/kg TS. The removal of VFA prevented their accumulation in the waste bed accompanied by low pH, which is known as inhibitors for biogas production. Application of micro-aeration showed the equivocal result in terms of enhancing hydrolysis and acidification.

In the performance of methanization, biogas production could not be successfully started up without initial pH adjustment accompanied with addition of inoculums. Importantly, the study highlighted the importance of leachate percolation in the enhancement of biogas production shortening the retention time of the process. Micro-aeration during pre-stage appeared to give benefit in biogas production during methanization. After 60 days, 260 L CH_4/kg flushed VS was obtained. Since the methane potential of the waste was 300 L/kg VS, it was implied that 75 % biogas conversion could be achieved in real system. Overall results showed 61% volatile solid destruction. This reduction was contributed by (1) flushing into leachate (30%C of fresh waste) and (2) stabilization through biogas production (25%C of fresh waste).

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List of Abbreviations

AD	Anaerobic Digestion
BF	Biological Fraction of MSW
C	Carbon
C_2H_5COOH	Propionic acid
C_3H_7COOH	Butyric acid
C_4H_9COOH	Valeric acid
$CaCO_3$	Calcium Carbonate
CH_3COOH	Acetic acid
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
GHGs	Greenhouse Gases
Go	Ultimate Biogas Produciton
H_2	Hydrogen
Hac	Acetic acid
Hbu	Butyric acid
Hpr	Propionic acid
Hva	Valeric acid
MC-OFMSW	OFMSW from mechanical sorting
MSW	Municipal Solid Waste
N	Nitrogen
NaOH	Sodium Hydroxide
NH_4-N	Ammonium Nitrogen
NmL	mL in STP
OFMSW	Organic Fraction of Municipal Solid Waste
R1	Reactor 1
R2	Reactor 2
R3	Reactor 3
SCOD	Soluble Chemical Oxygen Demand
SC-OFMSW	OFMSW from separate collection
SC-OFMSW	Source-collected OFMSW
SEBAC	Sequential Batch Anaerobic Composting
SGP	Specific Gas Production
SMP	Specific Methane Production
SS-OFMSW	OFMSW from source sorting
STP	Standard Pressure and Temperature (1 atm, 25^oC)
TCOD	Total Chemical Oxygen Demand
TDS	Total Dissolved Solids
TKN	Total Kdjeldhal Nitrogen
TS	Total Solid
VFA	Volatile Fatty Acids
VS	Volatile Solid
WW	Wet weight

Chapter 1

Introduction

1.1 Background

One of the important environmental issues that we are facing nowadays with the growth of world population is the increasing of municipal solid waste. Even with implementation of waste reduction, recycling, and reuse, disposal of residual solid waste in landfills remains an important component of an integrated solid waste management and it represents the most economical method. However, from an environment point of view, current land filling practices are no longer attractive because of its several disadvantages.

Direct landfilling of municipal solid waste are not definitive solutions, as they generate by-products, which are polluting for a long time. The problem associated with direct landfill are (1) the possibility of water table contamination by the leachate, (2) the low potentiality of biogas utilization, and (3) the difficulty of finding suitable areas near the sites where the waste is being generated. Therefore, there is a need for pre-treatment, especially for organic fraction of municipal solid waste (OFMSW), in terms of volume reduction and stabilization of waste.

Concerning the treatment of solid waste, the anaerobic digestion of solid waste has been studied in recent decades, trying to develop a technology that sum up advantages for volume and mass reduction as well as for energy and resources recovering. Anaerobic digestion, besides aerobic composting, can be an alternative strategy for the reduction of municipal solid waste. Anaerobic digestion has an advantage of using natural method compared to non-biological treatment. In contrast to aerobic composting, anaerobic digestion of solid waste does not require air and produce biogas with high volumetric fraction of methane (50-60%). The potential for energy recovery in anaerobic processes has been promotes as a solution to energy problem. Furthermore, the increasing issue of greenhouse effect makes anaerobic digestion more appealing.

Anaerobic digestion is a natural process in which bacteria convert complex organic matters in the absence of oxygen to simple and stable end products. It produces biogas, a mixture of methane (CH_4) and carbon dioxide (CO_2). The process is complicated and occurs in fours steps: Hydrolysis; Acidogenesis; Acetogenesis and Methanogenesis. Long time is required for methanogens for substrate conversion. Thus, methanogenesis is considered a rate-limitting step. In addition, for particulate substrate it is also well known that hydrolysis is rate-limiting step during hydrolysis/acidification.

Researches have been conducted in anaerobic digestion of solid waste in order to provide an attractiveness of the process. Many types of reactors have been developed so as to treat wastes in an efficient, economical and environmentally acceptable way. The available technologies are varied from (1) wet to dry, (2) from single-phase to multi-phase, (3) from batch to continuous and (4) within a variety of feedstock. The full-scale digesters have met, in some extent, with success and competitive installation. However, the developments are largely limited to developed world.

In high-solid (dry) mode, anaerobic digestion takes place in the solid bed, without addition of water to make slurry as well as without mechanical mixing. This operation is somehow similar to what happen in the landfills. However, in landfill, due to non-optimum conditions, anaerobic digestion normally takes place over long period (for centuries). Controlled anaerobic digestion in digester will help the process takes place in more proper way within shorter time, easily collect by products (leachate and biogas) for latter treatment. Batch and high solid fermentation seems to be the most suitable method as pretreatment of OFMSW prior to landfills with regard to developing world because of low cost and easy operation.

Due to different growth characteristics, it may not possible to use single-phase system to maximize both acdidogenic bacteria and methanogens. Especially, in high solid digestion where substrates are concentrated and VFA produce in high amount inhibiting the growth of methanogens. Therefore, separation of these hydrolysis/acidogenesis and acetogenesis/methanogenesis stages would possibly enhances the whole process. Growth of hydrolytic and acidogenic bacteria will be optimized in the first stage whereas Methanogenesis will be optimized in the second stage. In parallel, it is possible to increase the rate of hydrolysis, which is considered as rate limiting-step in the first stage, by using microaerophilic conditions.

In this study, batch dry fermentation of solid waste was studied as a method of pretreatment of market waste prior to landfill. Phase separation and proper leachate management was taken into account to optimization of the process.

1.2 Objectives of the study

The main objective of the study was to pre-treat municipal solid waste prior to landfill. Here, solid-phase anaerobic digestion was used as the basic unit. Through pre-treatment, solid waste was expected to be stabilized at certain level thus reducing volume and aftercare in landfill.

The pre-treatment technique was the combination of two stages of anaerobic digestion plus an additional stage of aeration. Three stages operate sequentially in batch-mode, in single digester:

(1) Pre-stage: Flushing and Acidification;

(2) Main stage: Methanization;

(3) Final stage: Flushing and control degassing.

This study aimed at optimizations of the individual stages in order to optimizations of the whole process. The specific objectives of the study were:

1. To optimize biogas production;
2. To minimize potential final leachate load and landfill gas;
3. To minimize an after-treatment period (composting).

1.3 Scope of the study

Batch experiments were carried out in pilot-scale digesters in order to pre-treat solid waste from vegetable market prior to landfill. The study mainly focused on the first two stages of the process where complete anaerobic digestion takes place. It covered:

1. Application of different operational conditions in pre-stage in order to optimize hydrolysis and acidogenic yield;
2. Investigation of different strategies in methane phase for maximization of biogas production and minimization of leachate pollutant load;
3. In terms of pretreatment, evaluation the efficiency of anaerobic digestion process by comparison with methane potential of the waste, which was conducted in lab scale.

In addition, the study included examination of the performance of final stage.

Chapter 2

Literature Review

2.1 Introduction

The safe and reliable long-term disposal of solid waste residue is an important component of integrated waste management. Together with the increasing amount of municipal solid waste (MSW), pretreatment of solid waste prior to landfill become more and more important. Taking into consideration the trend of shortage in energy, anaerobic digestion as pretreatment of organic fraction of municipal solid waste (OFMSW) prior to landfill can be considered as the preferable technology, an alternative of aerobic composting and it has an advantages in comparison with non-biological process.

The possibility of using a controlled in-vessel anaerobic digestion has received considerable attention in the research literature since the early 1970s. Before that, anaerobic digestion is the concept mostly applied for low solid substrates. Nowadays, there is an increasing interest in using anaerobic digestion of OFMSW as a mean of reducing the volume, stabilization and biogas production. Although solid waste anaerobic digestion has been applied in full scale with different types of system, researches on anaerobic digestion still continue trying to make the process more enhanced, more stable and cost-effective. Yet, there is the large room for further improvement regarding conditions of developing countries.

This chapter reviews literature on (1) Pre-treatment of OFMSW prior to landfill (2) Fundamental of anaerobic digestion process and (3) High-solid anaerobic digestion of OFMSW.

2.2 Pre-treatment of OFMSW prior to landfill

2.2.1 Problem associated with landfills

Landfills are the physical facilities used for the disposal of residual solid wastes in the surface soils of the earth. Sanitary landfill refers to an engineered facility for the disposal of MSW designed and operated to minimize public health and environment impact. Landfills for the disposal of hazardous waste are called secure landfills.

The waste, which is compacted within a series of cell in sanitary landfill, undergoes a number of simultaneous and interrelated biological, chemical, and physical changes. Consequently, two by-products generated and considered the two important sources of pollution associated with landfill operation are biogas and leachate.

1. The liquid collected at the bottom of a landfill is known as leachate. In generall, leachate is a result of the percolation of precipitation, uncontrolled run off, and irrigation water to landfill. Leachate contains a variety of chemical constituents derived from the solubilization of the materials deposited in the landfill and from the products of the chemical and biochemical reactions occurring in landfill.

2. Landfill gas is the mixture of gases found within a landfill. That is the principal product of the anaerobic decomposition of the biodegradable fraction of the MSW in the landfill. The bulk of landfill gas consists of two major component: methane

(CH_4) and carbon dioxide (CO_2), the others are atmospheric nitrogen and oxygen, ammonia, anaerobic digestion trace organic compound.

Therefore, in landfills, leachate and biogas have to be controlled in order to mitigate impacts on environment. After finishing landfill operation, landfill closure and post-closure care are very important to complete landfill in the future. Unfortunately, this after care must be taken for long time due to the long time stabilization of the waste in landfill. The long-term environmental impact caused by MSW landfilling may last for centuries.

As a result of percolation and transformation process, concern with the landfilling of solid waste related to (Tchobanogolous et al., 1992):

- The uncontrolled release of landfill gases that might migrate off-site and cause odor and other potentially dangerous conditions;
- The impact of the uncontrolled discharge of landfill on the greenhouse effect in the atmosphere;
- The uncontrolled release of leachate that might migrate down to underlying ground water or to surface water;
- Breeding and harboring of disease vectors in improperly managed landfill;
- The health and environmental impacts associated with the release of the trace gases arising from the hazardous materials that were often placed in landfill in the past

2.2.2 Necessity of pretreatment prior to landfills

Landfill problems can be overcome by controlled biological decomposition of the rapidly biodegradable fraction (organic fraction) through aerobic or anaerobic composting. These techniques are subject to pretreatment prior to landfill. Landfilling of resulting residue is odorless, does not attract vermin, does not emit toxic or greenhouse gases or release pollutant into ground water.

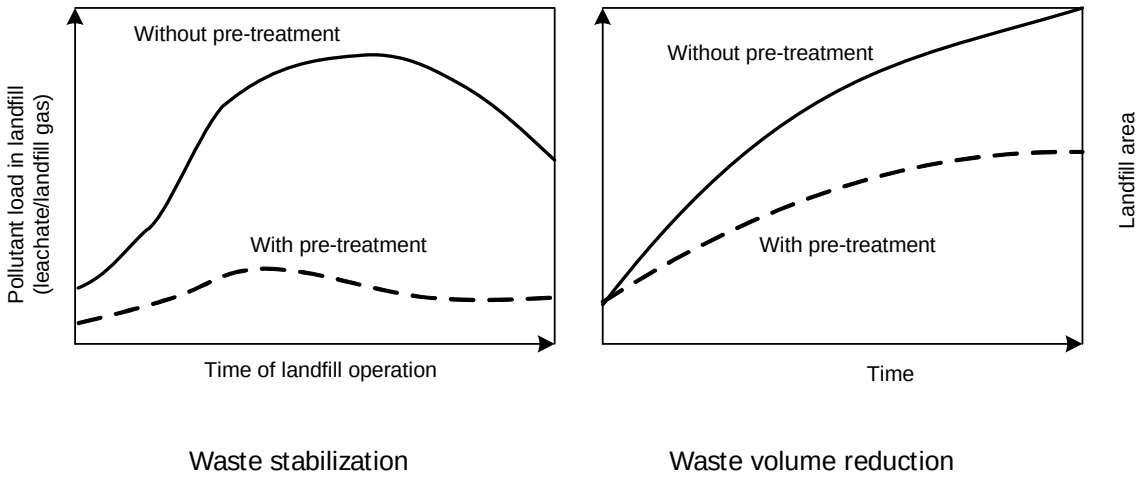


Figure 2.1 Stabilization and volume reduction of waste by pre-treatment prior to landfill

Landfill pretreatment of MSW is a new strategy introduced to the integrated solid waste management system in the last decade and has so far been practiced in very few countries. Pretreatment techniques will help minimize the amount of waste to be landfilled as well as control landfill behavior (biological and physicochemical processes that take place within a

landfill). It is any process that will alter the composition or other characteristic of the waste stream as generated prior to landfilling. Two major objectives of pre-treatment are stabilization of waste and minimization of waste (Figure 2.1).

Stabilization of waste

Stabilization of waste relates to the reduction or elimination of the chemical characteristic of waste that are potentially dangerous for the environment. As the impact of MSW landfill is due to biogas, odor, and leachate production, the processes leading to a drastic reduction of these complications must be considered. When disposed on landfill sites, stabilized waste will have lower polluting emissions. The major advantages are:

- Reduction of global greenhouse effect;
- Improvement of leachate quality;
- Physical stabilization, concerning settlements that would be problematic for landfill;
- Preparation of waste for the fast degradation within landfill conditions.

Minimization of waste

Minimization of waste includes all the techniques that will reduce the amount of waste to be disposed. This includes volume reduction and mass reduction

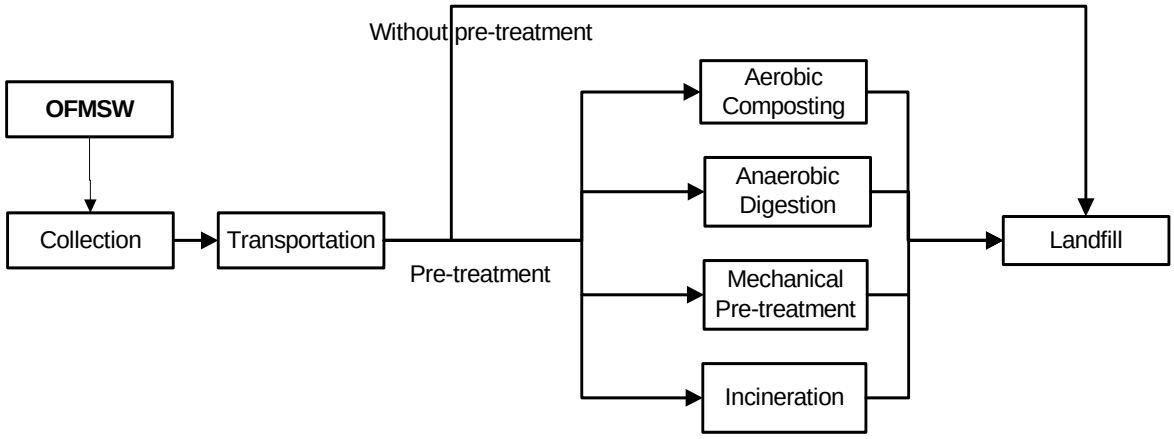


Figure 2.2 Pretreatment of organic fraction of MSW prior to landfill

Figure 2.2 shows various methods of pre-treatment prior to landfill. Currently, mechanical pre-treatment, composting and anaerobic digestion plays the major role in pre-treatment of MSW prior to landfill. The ecology comparisons showed that the biotechnology treatment is generally favorable with respect to incineration in treating biowaste. In addition, the pure composting technology appears to be less ecological than digestion (Edelman et al., 2000).

Anaerobic digestion is now becoming economically attractive in comparison with the conventional practice of treatment of MSW. It is substantially cheaper than incineration and land filling and not as expensive as aerobic composting. Additional advantages are generation of biogas and reduction of CO_2 emission, which are responsible for global warming. All of these factors will be considered in detail in the following sections.

2.2.3 Anaerobic Digestion as Landfill Pre-treatment

1. Controlled anaerobic digestion in digester

In sanitary lanfilling, anaerobic condition is reached within the bulk of the landfilled waste, resulting in the slow, progressive decomposition of the organic material present. As mentioned above the major environmental problem associated with landfill is related to the long-term discharge of the leachate and biogas into the environment.

Controlled anaerobic digestion in digester allows optimization of the operational conditions to increase the production of biogas and to reduce the pollution load of leachate. At the landfill, the impermeability of the material used to cover each cell means that the leachates produced in a cell do not pass through the one immediately below in a uniform manner. This leads to a higher pollution load in the leachate and a lower level of biogas production. If recirculation of leachates is carried out, a beneficial side-effect of this practice is the acceleration of the biodegdradation of the wastes, which leads to a higher rate of biogas production and the organic load of the leachate decreases. During traditional landfilling, biogas is produced at high dry matter contents and degradation is a slow process lasting some 15-20 years. Controlled anaerobic digestion can significantly speed up the degradation process to treatment period of less than 30 days (Chynoweth et al., 1992)

Management of leachate is easier in digester than in landfill. In reactor, better drainage condition is provided for leachate collection. At the same time, leachate pollution load is reduced due to the application of leachate recirculating in the process. Iglesias et al. (2000) conducted a comparative study of the leachate produced by anaerobic digestion in a pilot plant and at a sanitary landfill. Recirculation was carried out in the pilot plant but not in the landfill. It was concluded that the decrease in COD of the leachates with time being slower in the landfill than in the pilot scale plant. The composition of leachate produced in the pilot plant differed depending on the number of digested layer or cells that the leachate had to pass through. Final COD of the leachates produced by anaerobic digestion of the MSW in the pilot plant was lower than the COD of the leachate generated in the landfill

The biogas produced in anaerobic digestion has the great potential of energy sources. In some sanitary landfill, it is collected but cannot be completely collected. This give rise to safety problems, explosions and bad smells as well as environmental concerns related to the greenhouse effect. If the process takes place in control vessel, biogas would be collected fully, minimize the impact.

2. Anaerobic digestion vs. Aerobic composting

Biotechnologies offer sustainable approaches to the problems of OFMSW. Anaerobic digestion particularly has obtained a place among them. The advantages have been proven significantly and are justified even in light of initial higher investment cost in comparison to aerobic composting. An important advantage has been demonstrated to be the high flexibility in treating different types of waste streams, ranging from wet to dry and from clean to grey waste (Baere, 2000). Energy production has remained an important parameter. The greenhouse effect and sustainable development have all contributed to the value of anaerobic digestion. Table 2.1 presents a comparison of the two processes Tchobanoglous (1992).

Table 2.1 Comparison of aerobic composting and anaerobic digestion processes for processing the organic fraction of MSW

Characteristic	Aerobic processes	Anaerobic process
Energy use	Net energy use	Net energy producer
End products	Humus, CO_2, H_2O	Sludge, CO_2, CH_4
Volume reduction	Up to 50%	Up to 50%
Processing time	20 to 30 days	20 to 40 days
Primary goal	Volume reduction	Energy production
Secondary goal	Compost production	Volume reduction, waste stabilization

a) Treatment of high moisture content waste

Wet waste such as OFMSW separated at source is better treated by anaerobic digestion than by composting. Without entering into new energy considerations, composting of such wastes requires a considerable amount of structuring material and its high biodegradability make the final yield very poor (Pavan et al., 2000). Depending on the characteristic of input waste, it can be more suitable to select an anaerobic process for wastes with a higher proportion of nitrogen and lower proportion of carbon (Edelmann and Engeli, 1993). While lignified wastes have to be composted, wet and easily degradable wastes are more suitable for anaerobic digestion. These humid wastes cause odor problems in composting facilities. According to the authors for more than one third of the total potential, digestion is a better solution than composting.

b) Energy recovery

When comparing the different technologies, energy plays a predominant role. Aerobic process is net energy user because oxygen must be supply for waste conversion. On the contrary, anaerobic process offer the benefit of energy recovery in the form of methane gas and thus are net energy user (Tchobanoglous et al., 1992). In composting, very high value fossil and nuclear energy is invested to destroy the renewable energy, which is fixed in the chemical compound of biomass and thus in the biogenic waste. Anaerobic digestion is better than anaerobic from ecological point of view, because they do not need external fossil and electrical energy. In addition, the production of renewable energy has positive consequences because of saving of or compensation of non-renewable energy.

When studying the AD application in Europe, Baere (2000) found that the contribution in renewable energy is not negligible. Anaerobic digestion requires on average an additional 15 kWh per ton of energy in comparison to aerobic composting plants. When this is taken into account, then the biogas generated at the three plants under consideration, yields a surplus energy of 165, 220 and 245 kWh per ton for the plants of Brecht, Salzburg and Bassum respectively. A net energy surplus of 165-145 kWh per ton of waste treated can be generated in the form of electricity. It is clearly that taking consideration the situation of shortage energy in the near future anaerobic digestion has the substantial advantage over aerobic composting.

According to Biey et al. (2003), overall, the investment costs for anaerobic digestion are a factor of 1.2-1.5 higher than for aerobic composting. Nevertheless, the recovery of energy (100-1,500 m^3 biogas per ton of biowaste) is an important factor, particularly in third-world countries.

Besides the above advantages, high flexibility and reduced odors will make anaerobic digestion very attractive in the next millennium (Barae, 2000).

c) Greenhouse gases reduction

In terms of global warming, which is often used as reference value for ecological balance; anaerobic digestion is much better than other options. Theoretically it is not surprising that a considerable amount of methane is emitted while composting. However, in anaerobic digestion in reactor these greenhouse gases (GHGs) will be collected and utilized. Ngnikam et al. (2001) studied a comparison of the GHGs emission from different waste management systems including anaerobic digestion prior to landfill. Figure 2.3 shows the comparison result. Both composting and methanization prior to landfill can help to avoid greenhouse gases from the whole system of waste management. However, in comparison with composting as well as landfill with biogas collection, anaerobic digestion is the most effective way to reduce GHG potential.

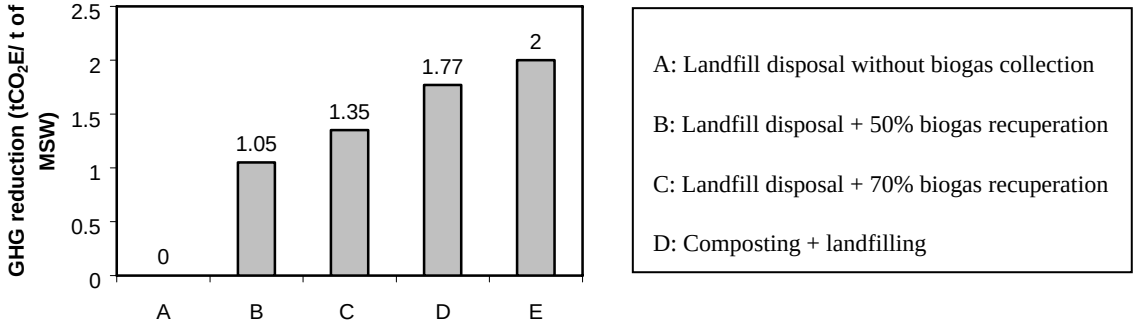


Figure 2.3 Greenhouse gases emission reduction from various treatment of MSW

Table 2.2 presents results of another comparative study conducted by Baldasano and Soriano (2000) on GHGs emissions estimated for different MSW management process. Biogas production, landfilling, composting and incineration were compared with respect to the full cycle of MSW treatment. The results confirmed that pretreatment by AD process prior to landfill have the highest potential in reduce greenhouse effect.

Table 2.2 Greenhouse gases emission factor of various MSW treatment approach

MSW treatment	Emission factor (ton eq. CO_2/tMSW)
Landfill	1.97
Incineration	1.58
Sorting + composting + lanfill	1.61
Sorting + dry biogas production + landfill	1.42

2.3 Characteristics of OFMSW and potential for anaerobic digestion

2.3.1 Organic fraction of Municipal Solid Waste (OFMSW)

Organic fraction of MSW (OFMSW) is the general term for the MSW that are usually obtained in three pathways: the mechanical selection from the unsorted waste, the separate collection, and source sorting. Corresponding to these are three types of OFMSW:

- OFMSW from mechanical sorting (MS-OFMSW),
- OFMSW from separate collection and source sorting (SC-OFMSW and SS-OFMSW)

The MS-OFMSW coming from the unsorted collected waste was probably the earliest category of organic fraction recovered and used for biological process. It is characterized by a high content of dry solids due to inert fraction of the unsorted waste, which is incompletely separable. In fact, the volatile solid TVS value less than 50%. More than 40 % of the substrate is actually unusable as feed for the anaerobic process. Since about 40% of the substrate TVS content comes from the putrescible fraction it is underlined as the other fractions are only partly involved in the biological process (Mata-Alvarez, 2003).

The OFMSW from separate collection can be split into two categories the organic fraction coming from markets, canteens, restaurants, etc (SC-OFMSW) and the organic fraction coming from domestic source sorting (SS-OFMSW).

The organic fraction come from separate collection is normally characterized by a high grade of separation, probably thanks to the information and education of the population done in recent years. The organic fractions from fruit and vegetables markets are very rich in water content, especially substrate coming from a fruit and vegetable markets The volatile solids percentage can be considered in the range of 85-90% for both residues, while the nitrogen content is about 2-3% and phosphorus is negligible (0.2 -0.5%) (Mata-Alvarez, 2003).

2.3.2 Biological characteristic of Solid Waste

The most important biological characteristic of the organic fraction of MSW is that almost all of the organic components can be converted biologically to gases and relatively inert organic and inorganic solids.

a) Biodegradable fraction (BF)

Biodegradable fraction of waste is related to the volatile solid content (VS), which is determined by ignition at 550^{o}C. Volatile solid (VS) or level of ignition (LOI) is usually used for description of solid waste characteristic. However, the use of VS in describing the biodegradability is misleading as some of the organic constituents are highly volatile but low in biodegradability (e.g., new sprint and certain plant trimmings) (Tchobanoglous et al., 1992). Typical biodegradable fractions of some organic constituents in MSW are presents in Table 2.3.

Table 2.3 Biodegradable fraction of the organic constituents in MSW

Organic waste component	Biodegradable fraction, %VS
Food waste	0.82
Newspaper	0.22
Office paper	0.82
Cardboard	0.47
Yard waste	0.72

b) Ultimate Methane Yield (Methane Potential) B_o

Ultimate Methane Yield represents the biological characteristic of the substrate in terms of their response to the anaerobic digestion process.

Ultimate methane yield of the waste is maximum amount of biogas would produce for a given amount of volatile solids (VS). Therefore it is conducted in the prevalence of optimal

condition. This shows the biodegradability of the substrate. For different wastes, even with same volatile solid and biodegradation fraction Methane Potential are different since this parameter taken into account the origin of the waste.

From literature data, the range of ultimate gas productions can be evaluated, both in terms of methane and biogas production. Considering a methane percentage of 55%, these values are the ones reported in Table 2.4 (Mata Alvarez, 2003).

Table 2.4 Ultimate methane and biogas production of OFMSW

Substrate	MS-OFMSW	SC-OFMSW	SS-OFMSW
B_o, m^3 CH4/kg TVS	0.16-0.37	0.45-0.49	0.37-0.40
G_o, m^3 /kg TVS	0.29-0.66	0.81-0.89	0.67-0.72

Go: ultimate biogas production

2.3.3 Characteristic of MSW in Asian countries

MSW from developing countries, are generally high in food and yard wastes, whereas developed countries, have a very high paper and cardboard content (Dhussa et al, 2000).

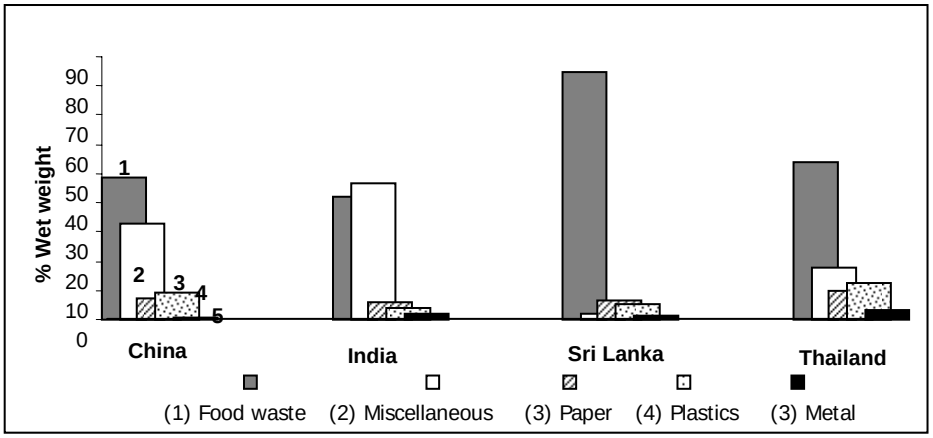


Figure 2.4 MSW composition of some Asian countries

Table 2.5 Characteristics of MSW in Thailand

Municipality	Density (Kg/m^3)	Moisture (%)	C. Value (kJ/kg)	Ash (%)	Ignitable material (%)
Chiang Mai	215	47	5660	27.3	90
Nakhon Ratchasima	200-250	20	3019	-	76.6
Khon Kaen	176	22	4686	-	73.05
Hat Yai	200	57	4799	17.1	90.6
Rayong	244	46.7	2302.25	20.6	67.3
Chonburi	350	59.0	3643	27.4	85.5
Phatum Thani	245	49.0	5329	18.8	94.0
Samut Prakarn	170	65.0	2062	10.2	20.8
Pattaya	207.5	70.0	3830	30.9	93.0
Phuket	260	40.0	4300	6.3	81.6
Udon Thani	204	20.0	4439	-	91.5
Average	227	45.1	4006	19.8	78.5

Source: Vivanathan (2003)

Figure 2.4 presents the composition of MSW in some Asian countries (Visvanathan, 2003) The major portion of the waste generated in the studied countries is dominated by food waste. Therefore, it is very high in biodegradation fraction (Table 2.3). Biological technology would be an appropriate option to pre-treat this type of solid.

Physical characteristic of MSW in Thailand was shown in Table 2.5. Municipal Solid Waste is characterized by high moisture content and very high ignitable material. The waste characteristic shows high potential for biological treatment. The appropriate technology would be anaerobic digestion or aerobic composting.

2.4 Fundamental of Anaerobic Digestion

2.4.1 The process

In the anaerobic decomposition of wastes, various anaerobic organisms work together to bring about the conversion of organic portion of the wastes to stable end products. The metabolic stages involved in the production of methane from waste. The general anaerobic transformation of solid waste can be described by the following equation.

$$\text{Organic matter} + H_2O + \text{nutrients} \xrightarrow{\text{Bacteria}} \text{new cells} + \text{resistant organic matter} + CO_2 + CH_4 + NH_3 + H_2S + \text{heat}$$

The biological conversion of the organic fraction of MSW under anaerobic conditions is thought to occur in fours steps as show in Figure 2.5.

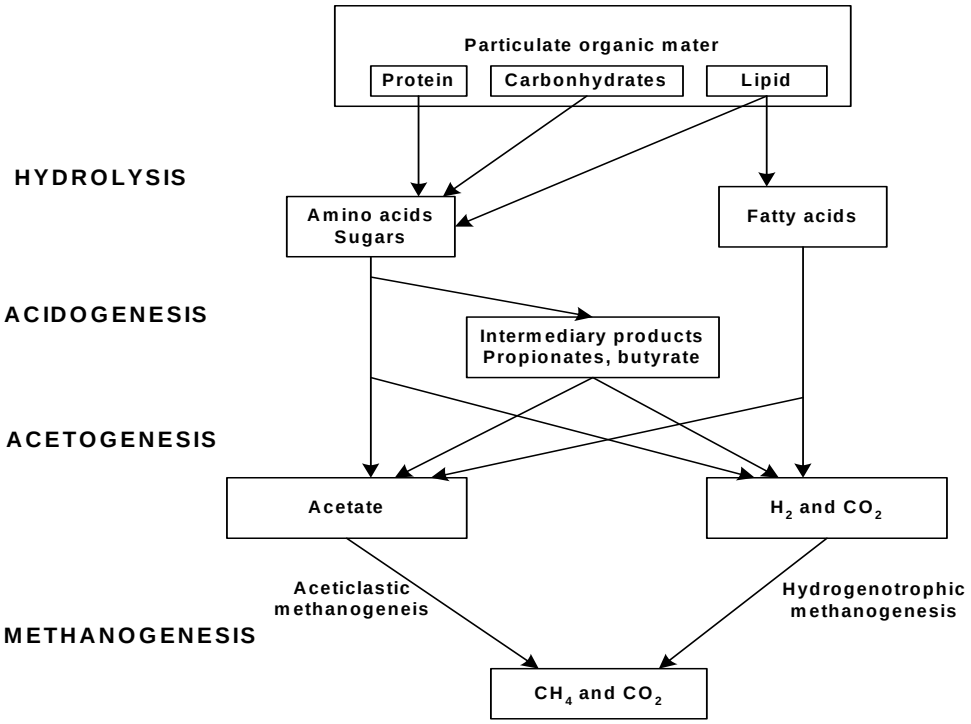


Figure 2.5 A complex diagram for anaerobic digestion considering four simultaneous processes

1. Hydrolysis

The first step in anaerobic biodegradation is the conversion of the complex waste (including particulate and soluble polymer) into soluble products by enzymatic hydrolysis. The stage will be accomplished by the presence of hydrolytic bacteria, which secretes extra cellular enzymes breaking down complex substrates.

Hydrolysis reactions in this stage will convert (1) protein into amino acids, (2) carbohydrate into simple sugars, and (3) fat into long-chain fatty acids. These simple products are organic monomers, which will be further fermented, in the next stage of the process. Liquefaction of cellulose and other complex compounds to simple monomers can be the rate-limiting step in anaerobic digestion. The hydrolysis rate is dependent on substrate and bacterial concentrations, as well as on environmental factors such as pH and temperature.

2. Acidogenesis

The monomers resulted from hydrolysis will be converted to various intermediates, mainly volatile fatty acid (VFA), H_2, and CO_2. Acetic, propionic, butyric and valeric acids were referred as VFA. Ammonia is also produced by the degradation of amino acids.

The group of microorganisms responsible for this biological conversion is described as non-methanogenic, consist of facultative and obligate anaerobic bacteria that are often identified in the literature as “acidogens” or “acid formers”.

3. Acetogenesis

Both long chain fatty acid (hydrolysis products) and volatile fatty acid (acidogenesis products) are degraded by obligate hydrogen producing generating acetic acid, carbon dioxide and hydrogen. Those organic acids having more than 5 atoms of carbon are considered here as LCFA

4. Methanogenesis

Methane is the only reaction product that is not a reactant in the whole process and can, therefore, be considered as an end product. Two processes generate it. The bacteria responsible for these conversions are strict anaerobes, called methanogens, and are identified in the literature as “methanogens” or “methane former”. The methanogens can be classified into two group following two processes to produce methane. Acetoclastic bacteria utilize acetic acid to produce methane whereas hydrogen-utilizing methane bacteria convert H_2 and CO_2 to methane

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO3^- + \text{energy}$$

$$4H_2 + HCO_3 + H^+ \rightarrow CH_4 + 3H_2O + \text{energy}$$

The first mechanisms account for most the CH_4 produced in the overall process

Methanogens have very slow growths rates; as a result, their metabolism is usually considered as rate-limiting in the anaerobic treatment of anaerobic organic waste. Waste stabilization in anaerobic digestion is accomplished when methane and carbon dioxide are produced. Methane gas is insoluble, and its departure from a landfill or solution represents actual waste stabilization

The methane formation is very important in anaerobic digestion because it can produce methane gas and regulates the pH by converting VFA into bicarbonate. Among several kinds of methanogens, it is suggested that the bacteria utilizing propionic and acetic acids are the most important (McCarty cited in Pfeffer, 1979)

2.4.2 Process controlling factors

1. Nutrient requirement

Nutrient is one of the most important environmental factors in biological process in general and anaerobic digestion in particular. Not considering the obvious presence of organic carbon to be degraded, there is a requirement for nitrogen (N) and phosphorus (P); sulfur (S), vitamins and some traces of mineral (K, Mg, Ca, Fe, Na, Cl, Zn, Mn, Mo.). Nutrient, rather than carbon source may at time be the limiting material for microbial cell synthesis and growth. In addition to the inorganic nutrient, some organisms may also need organic nutrient, which is called growth factors. The major growth factors fall into the following three classes: amino acids, purines and pyrimidines, and vitamin. (Tchobanoglous et al., 1992).

Unlike aerobic bacteria, anaerobic microorganism has the low yield of biomass. Considering this factor, the nutrients and microorganism content of organic waste (OFMSW) is usually enough for digestion process. However, it is necessary to specially check the availability of nutrients especially for the two elements N and P.

The relationship between the amount of carbon and nitrogen present in organic materials is expressed in terms of the Carbon/Nitrogen (C/N) ratio. A ratio of 25-30 is considered optimum for an anaerobic digester (Chongrak, 1996). If C/N ratio is higher, there will be not enough nitrogen for bacteria to grow resulting in the remaining of biodegradable carbon and the gas production will be low. If C/N is lower, nitrogen will be liberated and accumulate in the form of ammonia. This will increase pH and consequently cause toxic for methanogens. An average ratio COD/N/P of around 600/7/1 is usually recommended for a subtrate to be anaerobically digested (Mata-Alvarez, 2003).

2. Temperature

Environmental conditions of temperature have an important effect on the survival and growth of microorganism. According to the temperature range in which they function best, bacteria may be classified as psychrophilic, mesophilic, and thermophilic.

Table 2.6 Temperature range for bacteria

	Temperature, ^{o}C	
Type	Range	Optimum
Psychrophilic	-10-30	15
Mesophilic	20-50	35
Thermophilic	45-75	55

In particular, methanogenesis is strongly influenced by this parameter. Degradation rates and yield increases as usual, with temperature. Over this general increase, two optimal ranges with maximum activity have been identified: mesophilic and thermophilic. Figure 2.6 presents a scheme in which the rate of the anaerobic digestion process is represented in front of temperature (Mata-Alvarez, 2003) The implication of this figure is that thermophilic temperatures offer better yield and, consequently, higher biogas production.

However, this surplus of energy should be balanced by the increased need of feed heating. In many cases, this increase energy demand is the as the energy excess.

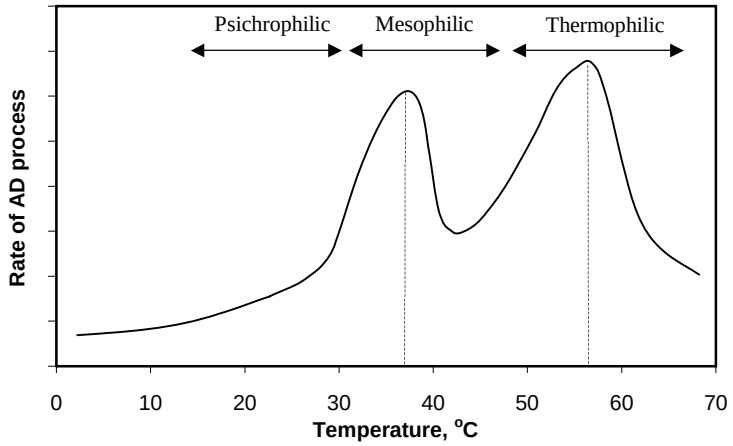


Figure 2.6 Temperature range for anaerobic digestion (Mata Alvarez, 2003)

Pavan et al. (2000) studied a two-phase digester on highly biodegradable OFMSW and identified that the increase of temperature in the hydrolytic phase up to thermophilic level apparently does not improve either yield or kinetic. Thus, unlike methanogens, non-methanogens are not so sensitive to temperature.

In literature, there are references for successful operations at both temperature ranges. Gosh et al. (2000) examined the effect of temperature at 35 ^{o}C, 40 ^{o}C, 55 ^{o}C and 60 ^{o}C and found that thermophilic methane yield from digestion of 1.1-mm-size RDF (refuse-derived fuel) was about 14% higher than that at mesophilic temperature. However, the authors also notified that this modest increase in methane production hardly justified increased energy input for thermophilic operation. Therefore, a mesophilic temperature in many cases is chose. The preference has been accorded to mesophilic conditions also due to the fact that the thermophilic bacteria are more sensitive to temperature fluctuation outside their optimum range and ammonia toxicity is more likely to occur in a themophilic digester than in a mesophilic digester (Biey et al., 2003).

3. pH value

The value of pH, together with temperature, is another most important effect on microorganism. In general, optimal growth occurs within the fairly low range of pH values from 6.5-7.5 although the microorganism may be able to survive within much broader limits. The methanogens are very sensitive to pH value and will not thrive below a value of 6.5. Past studies has showed that methanogenic was favor at a pH between 6.4 and 7.2 (Chugh et al., 1998).

In the initial period of fermentation, large amounts of organic acids are produced and accumulated; the pH values of the mixture can decrease to below 5. This inhibits, or even stops, the digestion and fermentation process. As digestion continues, and the concentration of ammonia increases due to the digestion of nitrogen, the pH value can increase to above 8. Inhibition also occurs, due to ammonia production in the digested material. When the methane gas production has been stabilized, VFA is utilized together. At the same time, production of bicarbonate ion HCO_3^- will buffer the system. The pH will increase and remain between 7.2 and 8.2.

4. Inhibitor and toxic substances

There are substances that at a given concentration inhibit bacterial activity, especially methanogens. There are several common substances that can affect the anaerobic digestion process and which are considered toxic or inhibitory at a given threshold level. VFA, pH, free ammonia and hydrogen sulfur are the most frequent. Others can be salinity or some xenobiotics. Problem of this kind when digesting OFMSW are due to the excess of VFA. Other toxic compounds are rare in this environment if source separation is carried out.

Unionized Volatile Fatty Acid

The VFA are major and important intermediary compounds of the anaerobic digestion of organic matter. The undissociated species have been reported as more toxic because they can more easily diffuse to the inner parts of the cell. Consequently, pH together with the alkalinity level exerts a definite effect on VFA toxicity, and the threshold level will depend on these parameters. Among VFA, propionic and butyric acids have been described as the most inhibitory. According to Boone and Xuni (1987) propionic acid concentration of over 3000 mg/L are definitely toxic and cause digestion failure.

It was concluded by Vavilin et al. (2003) that diffusion and advection of VFA inhibiting both polymer hydrolysis and methanogenesis. Increases of initial hydrolysis rate above a critical value cause an inhibition, first of methanogenesis and then hydrolysis. A decrease of the initial methanogenic rate below a critical value has the same effect. According to Veeken et al. (2000), the accumulation of VFA in the acidogenic pocket will reduce the hydrolysis rate of biowaste due to inhibition VFA.

Ammonia

Ammonium, which is necessary as a nutrient, at some concentrations inhibits methanogenesis. Similarly, pH has also a definite effect on the threshold levels. The reason is the same stage the case of VFA, in which the toxic species is the un-dissociated. For the OFMSW and dry fermentation system at thermophilic temperature, long-term experimental studies at the pilot scale reveal that ammonia inhibition occurs at concentrations of 1200 mg/L (Kayhanian, 1999). To overcome this problem, two methods have been suggested: (1) dilution of digester content with some adequate wastewater and (2) adjustment of feedstock C/N ratio (Mata-Alvarez, 2003).

That high concentration of NH_4^+-N reduces the biogas production rate as was clearly demonstrated during the second stage of biowaste fermentation (Vermeulen et al., 1993). It was confirmed by Lay et al. (1997) that the methanogenic activity was dependent on the level of ammonium, NH_4^+, but not free ammonia, NH_3, indicating that the NH_4^+ was the more significant factor rather than free ammonia in affecting the methanogens of the well.

Metal ions at the trace level are one of the essential nutrients for microorganism. However, the high concentration metal ions in anaerobic environment can act as inhibitor. Concentrations over 1 mg/L for heavy metal or 5-8 g/L for metals group II can be toxic (Mata-Alvarez, 2003). These values are to be considered with cases, as they are dependent on environment factors.

5. Water environment

Water environment is one of the factors contributing to the slow rate of high-solid waste anaerobic degradation. The moisture content of the organic waste to be converted must be known, especially if dry process is to be conducted. In anaerobic digestion, it has been necessary to add water to obtain optimum bacterial activity. The addition of water in anaerobic fermentation processes will depend on the characteristics of the organic waste and the type of anaerobic process that is used.

In anaerobic digestion process, it is most commonly used the solid content to express the water environment. The solid content ranging from 5 to 8% is normally used and considered more suitable since at this value, the agitation and mixing is easier. Nevertheless, the process can be operate well at even higher solid content up to 30 -35 %. This two range of solid content mentioned as dry process and wet process that is further discussed in the section 2.6.

2.4.3 Rate limiting steps

The anaerobic digestion process of complex organic waste can be described by four stages: hydrolysis, acidification, acidogenesis and methanogenesis. Mata-Alvarez (2003) reviewed that during the first step of liquefaction-acidfication reactions, the rate are limited by the hydrolysis of cellulose whereas in the acetogenic and methanogenic stage, the slow microbial growth rate is the rate-limiting step.

1. Hydrolysis: rate-limiting step in liquefaction-acidification phase.

In anaerobic digestion of soluble substrate, methanogenic reaction is usually considered as the rate-limiting step of the overall process. When considering particulate substrate like solid wastes, both accessibility of hydrolytic microorganisms to the solid matter and hydrolysis of complex polymeric components constitute the rate-limiting step (Mata-Alvarez, 2003 cited Eastman and Ferguson, 1981).

OFMSW has high cellulose content (32.9%). Concerning the conversion efficiency, the most important component for the OFMSW is cellulose conversion (74-78%). According to Peer et al. (1992), cellulose conversion is the rate-limiting step in anaerobic digestion of OFMSW. Cellulose solubilization rate depends on its structure, on the associated lignin content, particle size, etc. It was confirmed by Christ et al. (2000) that the major organic waste constituents (carbohydrates, proteins and lipids) which have the low hydrolysis constant. The hydrolysis is the rate-limiting step of the digestion for most substrates.

According to Sanders et al. (2000), the hydrolysis rate is directly related to the amount of substrate surface available and the surface of the particulate substrate is the key factor for the hydrolysis process.

2. Methanogenic: rate-limiting step of acetogenic-methanogenic phase

It is well known that methanogens have very slow growth rate and thus is thought to be the factor deciding the rate of the whole process. Brown and Tanta (1985) found that methanogens have a longer generation time than the acid-forming bacteria. (i.e 2-3 days versus 2-3 h at 36^{o}C, under optimum condition. As results, acid-forming bacteria will

produce volatile fatty acids (VFA) faster than the rate at which the methanogens can utilize.

A balance between the rates of hydrolysis/acidogenesis and methanogenesis is extremely important. In the initial period of fermentation, large amounts of organic acids are produced and accumulated; the pH values of the mixture can decrease to below 5. However, methanogens are very sensitive to pH value and will not thrive below a value of 6.5. This increased level of organic acid will consequently inhibit or even stops, the digestion and fermentation process.

2.4.4 Stability parameters

Some parameters, such as the pH, the VFA concentration, the alkalinity, the VFA: alkalinity ratio, the production and composition of the biogas and the temperatures, are of particular importance in the process control. It is important to underline that all these parameters have to be simultaneously considered for a global approach of process management. The variation of a single parameter is not meaningful to understand the behavior of the process.

pH value

The pH value gives some information about the stability of the medium since its variation depends on the buffer capacity of the medium itself. The pH is an indicator of a complex equilibrium system, where several chemical species are involved. They are bicarbonate concentration (HCO_3), volatile fatty acid (VFA) and ammonia (NH_4-N). Variations in pH are related to variations of these species.

Alkalinity

Alkalinity is the acid-neutralizing capacity of a medium. That is the capacity to resist changes in pH caused by the increase of acids in the medium. It results from the presence of hydroxides, sodium potassium or ammonia. Typical values of alkalinity in anaerobic digesters are in the range 2000-4000 mg $CaCO_3$/L

This parameter is of particular importance in the control of the stability of anaerobic process. Methanogenic microorganism shows a slow growing capacity. The concentration of fatty acids will increase the pH will drop down. So the alkalinity of the system becomes particularly important because it represents the buffer capacity of the system, that is the capability to resist variations in pH. The buffer capacity, in an anaerobic digester, is due to the presence of ammonia, from the degradation of proteins, and bicarbonate, form the carbon dioxide solubilization in the liquid phase.

Volatile fatty acids (VFA)

VFA normally considered stability parameter in anaerobic digestion process. Bolzonella et al. (2003) indicated that VFA concentration is a good parameter to evaluate the variations of the stability conditions. The volatile fatty acids concentration and its indirect measure, alkalinity at pH =4, are the best monitoring parameter. The significant of the stability parameters are VFA concentration, alkalinity (at pH = 4), gas production rate, methane content, alkalinity at pH = 6 and finally pH.

2.5 Efficiency of anaerobic digestion process

2.5.1 Specific gas/methane production (SGP/SMP)

Specific gas production or methane yield is the actual amount of gas produced for a given amount of volatile solid. The higher value SGP is, the higher efficiency process is. However, when evaluating the methane yield in anaerobic digestion of OFMSW, the biodegradability (Ultimate methane yield) of waste should be taken into account. Ultimate methane yields (B_o) at given temperature differentiates the origin of the wastes.

The specific methane production that is obtained in the digester of given waste at the given temperature is not ultimate yield but a function of it and operational condition. Thus, two factors should be taken into account when considering the biogas production efficiency (1) is the biodegradability at a specific temperature that is the ultimate yield and (2) the operating condition of the digester.

The specific methane production (SMP) and the ultimate biogas yield (B_o), both express as m^3 CH_4/ kg VS are related as the following equation (Mata-Alvarez, 2003):

$$SMP = B_o - (1\text{-}f)\, B_o'$$

B_o is the ultimate biogas yield and B_o' is the ultimate biogas yield of the digester effluent
f: fraction of volatile solids biodegraded

It is important to notice that, when values of the specific methane production of a digester operation are reported, a lower value does not necessarily indicate a deficient performance: it can simply be due to a lower biodegradability of the substrate.

2.5.2 Volatile solids destruction

In addition to specific gas production, the net change or loss in volatile matter is a measure of degree of decomposition. The total solid loss can be used but since the destruction is limited to organic matter, volatile solid loss would be more correct in evaluate the stabilization of the waste.

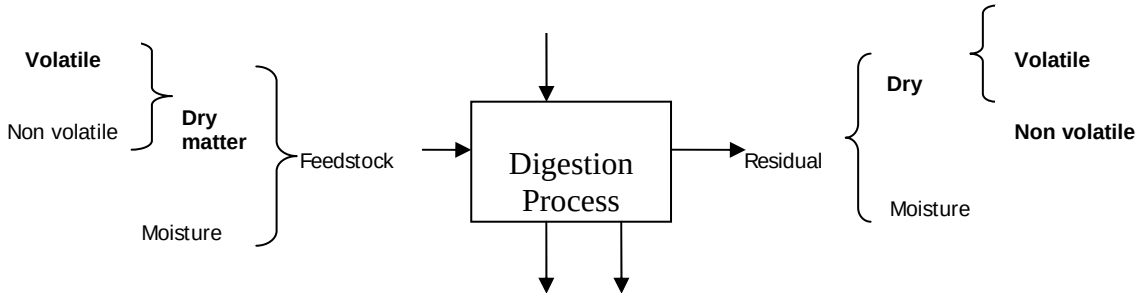


Figure 2.7 Material balance in the process

Figure 2.7 shows material balance in anaerobic digestion process of solid waste. The loss of volatile solid is the different between that in the residual and in the feedstock. It is contributed by the production of biogas and the volatile solid remaining in the leachate. The high efficient process will be the process in which, high volatile acid loss obtained so that the pollutant load in leachate reduce and specific gas is high.

2.6 Anaerobic Digestion Technology

Anaerobic digester of solid waste can be classified into variety of categories based on: (i) Solid content, (ii) Feeding modes, (iii) Stages of operation, and (iv) Types of feedstock.

1. High solids versus low solids

Based on solid content of digestate, digester can be classified into:

- Low-solid anaerobic digestion digester: the feedstock stage is slurred with a large amount of water to provide a dilute feedstock of less than 8%
- Semi solid (semi liquid) anaerobic digestion digester: have the solid content of 7-15%
- High-solid anaerobic digestion digester: the feedstock used as a dry solids content of 20-40%. No water or little water is added.

Conventional anaerobic digestion requires feed material with a total solid content below 10%. Works carried out over the past years on the pilot facilities using different sorted OFMSW in a wide range of different conditions in Italy has demonstrated the feasibility of treating OFMSW at concentrations over 20% (Cecchi et al., 1992). According to Rilling et al. (1996), anaerobic biological treatment of biowaste is possible even with high solid content of solid material of about 45%. Modern concepts accept total solids in the range of 20-80% (Mohee and Ramjeawon, 2003).

The major disadvantages of the low-solids anaerobic digestion process as applied to solid waste is that (1) water must be added to bring the solid content lower than 10-15% and (2) digestate is very diluted and must be dewatered prior to landfill. Mechanical dewatering needs to be applied to achieve 40 % TS. Since the digestate contains less total solids than with dry fermentation, a corresponding amount of water cannot be contained in the dewatered digestate. This will result in a larger amount of wastewater and a smaller amount of compost than in case of dry fermentation. The compost from aerobic composting and dry fermentation contains more inert material whereas the compost from wet fermentation has a higher VS content.

In dry process, only little water has to be added to dry matter content, consequently, the process does not requires costly dewatering of the fermented material. Dry anaerobic digestion also does not include intensive water treatment plant. It is relatively simple in handling and secure in operation and cost effectiveness.

A comparative study of a full-scale dry process (Valorga in La Coruna, Spain) and a wet one (Vagron in Groningen, Spain) was carried out by Luning et al. (2003), with respect to specific gas production). It was concluded that specific gas production of the two systems are practically identical. Wastewater production is obviously higher in wet process. According to Cecchi et al. (1992) dry fermentation allows the reduction of the digester volume and, consequently, the investment cost.

In Europe most of the treatment capacity for solid waste was provided by wet digestion systems at the beginning of the 1990s. However, form 1993 onwards, more dry systems were constructed and in 1998; more than 60% of digestion capacity plants are currently under construction and 44 % by 2000. No clear technology trend can be observed at this moment (Baere, 2000).

2. Batch versus continuous

- In batch process: the reactor vessel is loaded with raw feedstock and inoculated with digestate from another reactor. It is then sealed and left until thorough degradation has occurred. The digester is then emptied and a new batch of organic mixture is added.

- In continuous process: The reactor vessel is fed continuously with digestate material. Fully degraded material is continuously removed form the bottom of the reactor.

The main difference between these two methods is that in the batch process, never a steady state situation is reached, whereas in the continuous process, this is a pre-condition. In the batch set-up, intermediates such as VFA and H_2 can accumulate with time, which changing the process conditions (Mata-Alvarez, 2003).

High-solid batch systems may appear as nothing more than a landfill-in-a-box, they in fact achieve 50 to 100 fold higher biogas production rates than observed in landfills. In a batch system, there is a clear separation between a first phase where acidification proceeds much faster than methanogenic and a second phase where VFA are transformed into biogas.

Table 2.7 Advantages and disadvantages of batch system

Criteria	Advantages	Disadvantages
Technical	- Simple - Low-tech - Robust (no hindrance from bulky agent	- Clogging - Need for bulking agent - Risk explosion during emptying of reactor
Biological	- Reliable process due to niches and use of several reactor	- Poor in biogas yield due to channeling of percolate - Small OLR
Economic and Environmental	- Cheap, applicable to developing countries - Small water consumption	- Very large land acreage required (compared to aerobic composting)

Because batch systems are technically simple, the investment costs are significantly less than those of continuously fed systems (Ten Brummeler, 1992). The land required by batch processes is, however, considerably larger than for continuously-fed dry system. Operational cost, on the other hand, seem comparable to those of other systems.

Table 2.7 shows the advantages and disadvantages of batch system

3. Single-step versus multi-step

- In single-step process all digestion occurs in one reactor vessel

- Multi-step process consists of several reactors, often the organic acid forming stage of the anaerobic digesion process (acetogenesis) is separated from the methane forming stage (methanogenesis).

Table 2.8 and 2.9 present the advantages and disadvantages of one-stage dry system and two-stage system. The detail advantages of multiple phase system will be considered in section 2.7.2.

Table 2.8 Advantages and disadvantages of one-stage dry system

Criteria	Advantages	Disadvantages
Technical	– No moving part inside reactor – Robust – No-short-circuiting	– Wet wastes (< 20 % TS) can not be treated alone
Biological	– Less VS loss in pre-treatment – Larger OLR (high biomass) – Limited dispersion of transient peak concentrations of inhibitors	– Little possibility to dilute inhibitors with fresh water
Economic and Environmental	– Cheaper pre-treatment and smaller reactor – Complete hygienization – Very small water usage – Smaller heat requirement	– More robust and expensive waste handling equipment

Table 2.9 Advantages and disadvantages of two-stage system

Criteria	Advantages	Disadvantages
Technical	– Design flexibility	– Complex
Biological	– More reliable for cellulose –poor chicken waste – Only reliable design for C/N < 20	– Smaller biogas yield (when solid not methanogenized)
Economic and Environmental	– Less heavy metal in compost	– Larger investment

4. Co-digestion / Digestion of MSW alone

– Co-digestion is that the organic fraction of the MSW is mixed with animal manure and/or wastewater sludge. This improves the C/N ratio and improves gas production.

– Digestion of MSW alone is that the feedstock contains the organic fraction of MSW alone or slurred with liquid. No other materials are added.

In cases of separately collected OFMSW, the waste coming from markets, canteens, restaurants, etc, the nutrients and microorganism and moisture content of organic waste (OFMSW) is usually enough for digestion process. Therefore, these types of waste can be digested alone. There is no need of co-digestion.

2.7 High-solid Batch Anaerobic Digestion

High-solids batch systems have up to now not succeed in taking a substantial application. However, specific features of batch process such as simple design and process control, lower investment cost, small water consumption, etc make them particularly attractive for developing countries. According to O'keefe et al. (1993) the limitations of high-solids batch anaerobic composting process is the requirement of heavy inoculation, mixing and possibility of instability and difficulty to overcome instability. To maintain a stable high solids digestion process, the chemical value, pH, volatile fatty acid ammonia and moisture content should be considered as the important environmental factor affecting the efficiency in the high solid waste digestion (Lay et al., 1997). Research are continued to make anaerobic digestion more efficient and enhanced in high-solid batch system.

Previous studies demonstrated that: (i) leachate recycling increases the digestion rate by means of increasing moisture moving through the digestion system and accelerating the stabilization waste, (ii) separating anaerobic process into two phase, i.e., acidification phase and methanogenesis phase, facilitates the optimal growth for non-methanogenic and methanogens.

2.7.1 Leachate recirculation

Water is essential for methane fermentation, as the nutrient for the microorganisms must dissolve in water before they can be assimilated. Leachate recirculation is one of the ways to provide and control moisture content of the waste. In the landfill, where most bio reactions take place to stabilize solid waste, the lack of water sometime is responsible for retarding the degradation of MSW. In addition, the moisture that may be present is seldom uniformly distributed. Then this is achieved primarily by control and management of the liquid flow in the anaerobic digestion process.

The leachate recirculation will enhance degradation since it provides an aqueous environment that facilitates the provision of nutrients and microbes within the landfill cell (Fadel, 1999). Not only the moisture content of but also the moisture movements through the waste affect municipal solid waste decomposition. According to Chugh et al. (1998), the flow of moisture is essential to mobilize nutrients and evenly distribute microorganisms through the waste bed. In addition, the movement of moisture through a waste bed also provides mass transfer, and prevents the development of stagnant zones. These further confirm the role of leachate recirculation.

The moisture content may not only aid in bacteria movement but is also known to influence the mass transport limitation on a high solid bed and the balance between volatile fatty acids production by acidogenic bacteria an the conversion of acids to methane by methanogens (Ghost, 1985).

2.7.2 Phase separation

Conventional single-stage anaerobic digestion of high-solids substrates such as MSW gives rise to unbalanced fermentation. The concentrated substrate in the dry waste bed would increase the possibility of VFA accumulation, especially during the start-up phase of the digestion process, which results in a drop of pH of the media and finally inhibiting methanogens.

In once phase system, microorganism populations are not balanced. The methane-forming microorganisms grow at a rate that is much slower than the acid-formers. It was confirmed by Chugh et al. (1998) that methane-forming microorganism cannot directly consume landfill waste and the acid-former will normally outgrow the methane formers. Consequently, the degradable fraction of landfilled waste will normally become acidic, which slow down microbial activity and inhibits further degradation. Phase separation could possibly over come the problems.

Another rational of two- and multi-step systems is that the overall conversion of waste to biogas is mediated by a sequence of biochemical reaction, which do not necessary share the same optimal environment conditions. Optimizing these reactions separately in different stages or reactors may lead to a larger overall reaction rate and biogas yield. Usually, the organic acid forming stage of the anaerobic digestion process (acetogenesis) is

separated from the methane forming stage (methanogenesis). This results in increased efficiency, as the two microorganisms are separate in terms of nutrient needs, growth capacity and ability to cope with environmental stress. Some multi-stage systems also use a preliminary aerobic stage to raise the temperature and increase the degradation organic material.

Because of these advantages, two-phase treatment is reportedly more rapid and more stable than combined-phase treatment. Besides, two-phase anaerobic fermentation processes are reported, by Peres et al. (1992), presenting good performances since the hydrolytic step occur in more adequate conditions than those of conventional one-phase system

Similarly, O'Keefe et al. (1999) reviewed some advantages of two-phase over combined phase. They were:

- Microorganisms in the two-phase treatment have different growth rates and optima for environmental and nutrient condition, which can be better optimized for improved performance;
- Phase separation provides the opportunity to establish pH and pressure swings needed for methane enrichment of the resulting biogas through enhanced stripping of CO_2 in the first phase;
- Phase separation facilitates localization of the site of methane production and collection in one reactor;
- Phase separation results in improved process stability through maintenance in the methane-phase of active populations of bacteria that can utilize VFA which, if not metabolized, can result in process imbalance.

Advantages of two phase anaerobic digestion process, as demonstrated by pilot-and full scale operations (Ghost et al., 1995) include (1) increase gas yield production rate, (2) enhance volatile solid reduction efficiency, (3) production of higher methane (80-85% mole), (4) lower-sulfide content digested gas, (5) high pathogen kill (6)stabilizing the process. In other hand, Mata-Alvarez (2003) stated that the main advantage of two-stage system is not necessarily higher reaction rate, but rather a greater biological reliability for wastes, which cause unstable performance in one-stage system.

According to Pavan et al. (1996) two-phase approach of the anaerobic digestion process applied to the SS-OFMSW allowed to by-pass the problems connected with the high biodegradability. The higher levels of VFA (17.1 g/L observed in the single-phase process) are reduced to less than 1 g/L in all the operative conditions of the two phase process. The stability of the process also leads to the improvement of yields, obtaining a SGP about three times larger than the one observed in the single phase.

A comparison of one phase and two-phase system was carried out on SS-OFMSW coming mainly from fruit and vegetable markets showed a two-phase system is much more appropriate for the digestion of this kind of highly biodegradable substrate in thermophilic condition Pavan et al. (2000). One phase working in these conditions did not operate successfully. Ghost et al. (2000) found that two-phase process exhibited 18% higher methane yield and 13 % higher methane concentration than the corresponding performance parameters for single-stage digestion.

According to Battistoni et al. (2000), double phase process particularly seems to be the most effective approach in the treatment of the source sorted and separately collected OFMSW. Actually, the phase separation improves process stability due to better working condition of acidogenic and methanogens and reduces significantly over loading.

O'Keefe et al. (1999) reviewed a number of methods of phase separation. They were kinetic and pH control, and sequencing of batch reactors, dialysis membrane separation, and aeration of the effluent…and aeration. They also suggested that aeration of the landfill cell seems to be the most practical option for achieving phase separation in leach-bed reactor and landfill cell.

2.7.3 Sequential batch anaerobic digestion

Sequential batch anaerobic composting (SEBAC) of OFMSW was developed taken into account the two factors: leachate recirculation and phase separation to overcome the limitation of high-solid anaerobic digestion. They are inoculation, mixing and instability problems. SEBAC allowed solid bed anaerobic digestion operates well without addition of seeding materials (Chynoweth et al., 1992). In the first stage of the process, high leachate rate are applied to wash out VFA preventing inhibition of hydrolysis. The leachate then is fed over a reactor, which is already in the second stage of the process. Methanogenis activity is established after VFA is washed out from the reactor. The process diagram is shown in Figure 2.9.

In the process, a bed of feedstock was inoculated by recycle of leachate from a reactor in the final stages of digestion. The leachate supplied water, inoculums, and nutrient needed for optimal digestion. VFA and other fermentation product generated during start up are removed from the new bed and carried to the aged reactor for conversion to methane. This eliminates the possibility of instability that plagues single phase digester. O'Keefe et al. (1993) reported that the process working on OFMSW proved stable, reliable, and effective. It gave the methane yield of 0.19 m3/kg VS after 42 days. The mean VS reduction was 49.7%. Methane content of the biogas stabilized at a mean of 48% from three to two day after start up. The VFA was over 300 mg/L but reduced within a few days to negligible level.

Chugh et al. (1998) demonstrated that with proper leachate management, very rapid decomposition of waste can be accomplished by taking the waste through a series of controlled degradation stages. The process, shown in Figure 2.8, where leachate was exchanged between batches of existing anaerobically degraded waste and a batch of fresh waste, could results in with average yield of 0.18 m^3/CH_4 kg volatile solids in about 2 months. The process overcame the disadvantages of a batch reactor by successfully starting a digester by inoculation with leachate. One conditions are achieved, where the microorganisms are acclimatiezed to the environment in a fresh waste bed, the start-up period is dramatically reduced to just a few days.

Mohee and Ramjeawon, (2003) worked on SEBAC in which, leachate recirculation was done periodically between the two reactors. It was confirmed that the recirculation of leachate was found to be beneficial to the anaerobic digestion process as it considerably reduced the amount of VFA from 140 meq/l to 60 meg/L after 60 days. They found that gas evolution was detected only after leachate recirculation. The best explanation was that the recirculation provided a means of mixing there by displacing the biogas, which was already formed but which was trapped within the feedstock. It was expected that biogas

was accumulated in the reactor itself and leachate recirculation provided the appropriate pressure required helping the biogas come out.

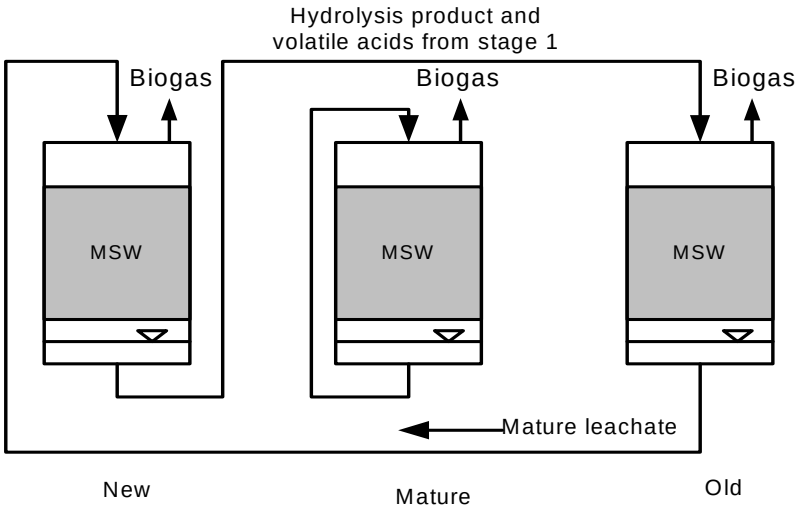


Figure 2.8 Configuration of leachate recycles patterns in different batch system (Chynoweth et al., 1992).

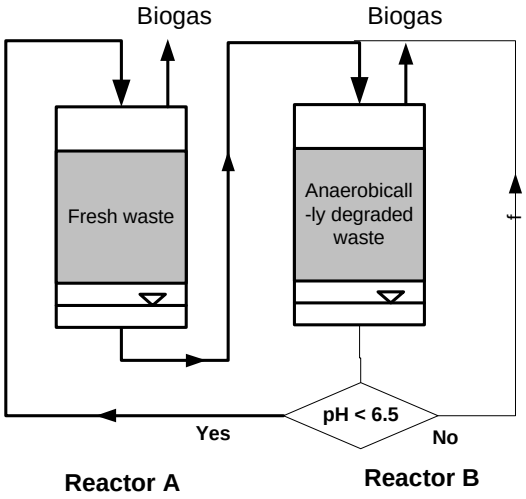


Figure 2.9 Schematic diagram of proposed process by Chugh et al. (1998)

In one hand, leachate recirculation in SEBAC enhanced degradation of waste and gas production. In the other hand, it is also is effective in reducing the overall leachate production load. This offers the two side advantages of SEBAC.

SEBAC has recently been taken into study of solid waste anaerobic digestion as a strategy for dry process. As discussed above, researchers have successfully studied the scheme with different type of wastes. Due to various advantages provide, SEBAC has been showing good performance in terms of biogas production, volatile solid destruction and volume reduction as well.

Chapter 3

Methodology

In the combined process of pre-treatment three stages were carried out. The overall objective was to enhance waste stabilization and biogas production. At the first stage, flushing with tap water along with the practice of micro-aeration was applied to accelerate hydrolysis/acidification and partly remove the intermediate products from the waste bed. Following this initial stage, methanogenic phase was optimized in the reactor, where the intermediate product of VFA was no longer inhibitor. Finally, air flushing completed the process of pre-treatment before waste was unloaded from the digester and landfilled.

The waste was loaded in batch mode. In a single digester, solid waste was brought into various stage of the combined process. They are (1) Flushing and Acidification (2) Methanization (3) Air Flushing. The major operational conditions, which were controlled to optimize individual stages, are (i) oxygen condition and (ii) leachate recirculation scheme (iii) inoculums and (iii) temperature.

3.1 Introduction

3.1.1 Concept of the combined process

Figure 3.1 illustrates the digester operation through different stages. Anaerobic digestion is separated into flushing (hydrolysis and acidification) and methanization stages. The process arrangement and leachate recirculation scheme serves the following purposes:

1. Firstly, in pre-stage, the volatile fatty acid (VFA) as well as other dissolve organic compounds produced by the fresh waste is flushed out into the leachate. This leachate is acidified.

2. Starting up of methane phase follows pre-stage by seeding. The purpose of seeding is to enrich the waste bed, which was partly hydrolyzed, with active methanogens.

3. When the reactor switches on mature methane phase, the acidified leachate is then gently fed into the waste bed. This allows methanogens to utilize VFA from the first stage without shock loading.

4. Finally, air flushing is provided to wash out the biogas available in the digester. At the same time, composting starts, oxidizing the non-digested material in the residue before landfilling.

It is noted that leachate recirculation was done during anaerobic digestion, both in flushing where large amount of water and high flushing rate are applied and in methane phase where very small rate (percolation) is done. It is to provide enough moisture; evenly distribute bacteria, nutrient, enzymes, and avoid locally shock loading.

Detail operations of individual stages are described in the following sections.

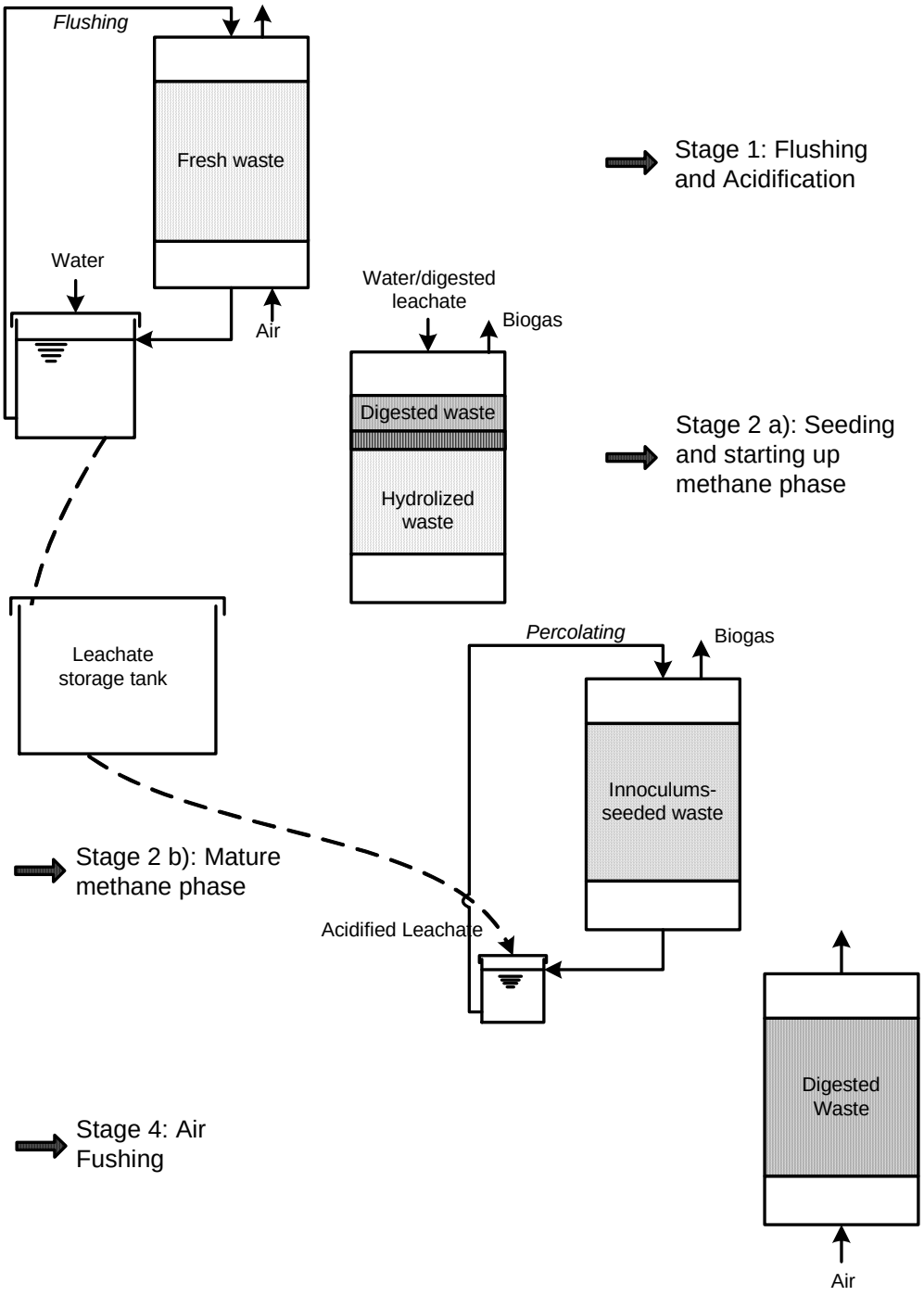


Figure 3.1 Concept of the combined process

3.1.2 Feedstock preparation

Vegetable market waste was the substrate for the process. This type of waste is classified as separately collected municipal solid waste (SC-MSW) with high moisture content, organic fraction and it is easily biodegradable. In this study, Rangsit market waste was collected for experiments. The waste had the moisture content of around 85-95 % and volatile solid of 75-85 %.

This biowaste for anaerobic digestion was prepared in the following maner:

1. Solid waste taken from the market was manually segregated to remove any potential hazardous, plastic, and bulky as well as non-degradable material.

2. After segregating, the sorted waste was reduced the size to less than 6 mm by being passed through a pulverizer. Size reduction could enhance hydrolysis, by creating more contact surface area.

3. Finally, together with bulking agents, solid waste was compacted into the digester to required density. Alternately, one layer of waste and one layer of bulking agent (totally 10% of compact area) were loaded. The rationale of adding bulking agent was to create void space for gas and liquid flow to pass through. In one hand, it was very important to avoid local blocking especially when flushing progresses. In another hand it ensured biogas in the methane phase to easily escape from the waste bed. Two types of bulking agent were used in the study. In the first two run, PVC cutlets was used. In the last run, the agent was bamboo cutlets, with diameter of around 2-4 cm diameter and 5-6 cm length,

3.1.3 Pre-stage: leaching and acidification

The first stage of anaerobic digestion was hydrolysis following acidification. The specific purpose of this pre-stage was to provide optimum condition to make solid waste to be hydrolyzed/acifified quickly. At the same time, it partly removed hydrolyzed products (mainly VFA) from the waste bed into leachate. As a result, the waste bed after being flushed would not be high in organic acids, which can, itself or through pH drop, inhibit methanogenic activities. The stage also targeted at highly acidified leachate in order to provide sufficient feed for the following methanization stage.

These purposes would probably be accomplished by two means. Firstly, it was the application of aeration into the waste bed. Microaerophilic was thought to possibly increase the rate of hydrolysis, which is the limiting factor for cellulose. Aeration was controlled so that aerobic composting would not happen. Since thermophilic temperature is practically considered as an indicator of the growth phase in aerobic composting, it was avoided. The second was the use additional water with high recirculation rate to wash out the soluble organic, mainly volatile fatty acid. It is known as flushing stage. Large amount of water was also to dilute inhibitor, provide water environment to enhance hydrolysis of the waste.

The stage was conducted at ambient temperature. Tap water was applied at the ratio of 4:3 or 5:3 (weight based) to flush the waste bed during short time of 5 days. This operation was based one the results of lab-scale leaching experiment of the same waste carried out by Dayanthi (2003).

3.1.4 Main stage: methanization

The main stage of the anaerobic digestion process to produce biogas is methanization. Methanization was separated from hydrolysis/acidification by stopping flushing, aeration, and gently starting up methanogenic activities. Temperature was controlled at optimum mesophilic range for methanogens (37± 2 ^{o}C).

1. Start up methanization

Seeding materials such as digested solid waste, anaerobic sludge from biogas plant and cow dung have high methanogens population. These materials were added to the waste bed which had already finished flushing and acidification. There were two ways of seeding: either loading into the vessel by opening or mixing with water then provides percolation. It is well known that methanogens have slow growth rate. Thus, the advantage of seeding was to supply waste bed with high population of inoculums, and consequently shorten the lag phase time. Leachate percolation was practice initially to distribute methannogens throughout the waste bed and then the vessel was incubated for start up.

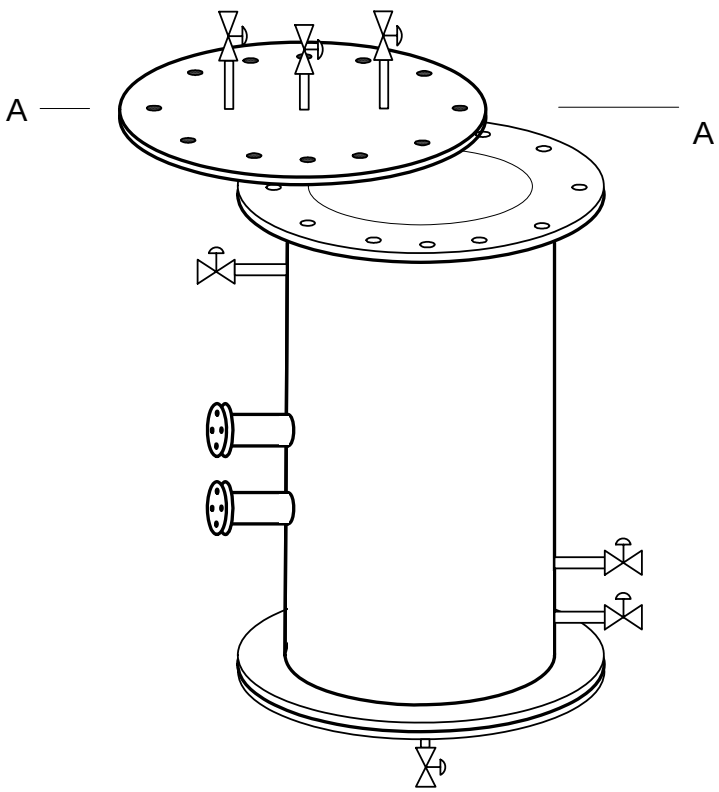
2. Methanization

After start up phase, leachate percolation was done in order to accelerate biogas production. This percolation was thought to give benefit by even distribution of bacteria, nutrient as well as local shock loading prevention. Low rate of recirculation (percolation) was provided. The reduction in VFA concentration in the leachate as well as the methane production rate served as two major parameters to examine the efficiency of this mature phase.

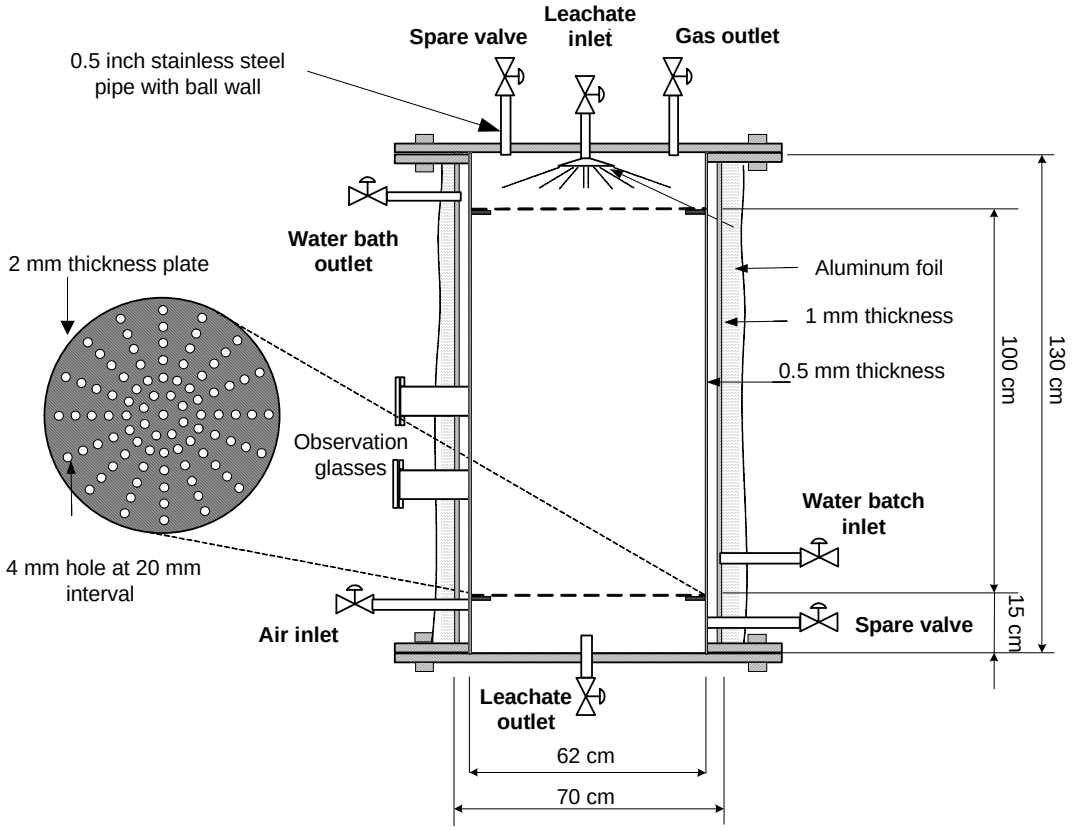
When the mature methane phase reached could be the appropriate time to supply more substrates for methanogens. Available substrates, VFA, were early extracted in pre-stage leachate. This acidified leachate was fed back into digester in batch mode. Since the waste bed was in the mature phase, producing HCO_3^- having pH-buffering capacity, the pH adjustment of leachate might not be necessary.

3.1.5 Final stage: air flushing

In the final stage of the whole process where aeration was applied, a double target had to be achieved: reduction of methane content in order to reduce the risk of explosion and re-starting aerobic degradation. It was expected that the anaerobically digested residue would be further stabilized in anaerobic condition. The remaining leachate was drained. The stage was conducted at ambient temperature.



Opened digester in 3-D



A - A section

Figure 3.2 Reactor design

3.2 Experimental set up

Experimental runs were conducted in pilot scale digesters. There were three digesters, which were operated in parallel. Operational conditions were changed among different digesters to optimize different stages of the process.

3.2.1 Reactor design

Pilot-scale reactors were tightly closed vessels made of stainless steel. Each reactor had a total volume of 390 L with the waste compaction area of 300 L. Reactor height was 130 cm and its out side diameter was 70 cm. Figure 3.2 depicts reactor design. Reactor was designed with double wall and top removable cover. The thickness of inside wall and outside wall were 1 and 0.5 mm respectively. The inside diameter of the reactor was only 62 cm giving the gap between the two walls which was called water jacket. This water coat had the role of holding hot water/cool water in order to regulate the temperature of the digester content. Reactor was insulated by a layer of thermo foil cover. In addition, there were two thermocouple injected into the biowaste in order to monitor the temperature of the digester content.

Reactor was equipped with removable cover. For each batch of digestion, solid waste was loaded and unloaded from the top by opening this cover. When closing the digester, a rubber buffer ring was put in between the cover and the digester so that they could fit well each other without air leakages.

Solid waste was compacted in the middle area between two percolating plates. They were the 2 mm thick plate with holes arranged at 20 cm interval along radiuses. The bottom one was located at 15 cm above the bottom acting as a support for solid waste. The evenly distributed holes were for leachate to trickle down. The bottom floor was designed with a small slope in order to direct the leachate to leachate outlet which is connected to leachate collecting tank. In latter runs, a gavel layer was placed on this bottom space to provide better drainage. The upper space was 15 cm high for installation the leachate sprinkler and for biogas collection before going to gas outlet. The water sprayer is designed so as to distribute recirculated leachate homogeneously throughout the waste bed.

There were two sampling holes installed in the middle of reactor. Inspection glasses are equipped for observation of reactor content.

3.2.2 Digestion system

Main accessories in the digestion system included leachate tanks and leachate pumps; air pump to provide aeration; wet gas meter for biogas flow rate measurement; hot water tank an pumps to provide hot water maintaining the temperature in side.

Each reactor had two leachate tanks. The bigger one, lechate tank 1, with the volume of 200 L was used for first stage where large amount of water were apply for daily flushing The tank had removable cover to in order to do water replacement. Centrifugal pump was equipped pumping water/leachate form this tank through flushing line to the leachate sprinkler. On the flushing line was a flow meter. Flow rate was controlled by adjust the valve on the pipeline.

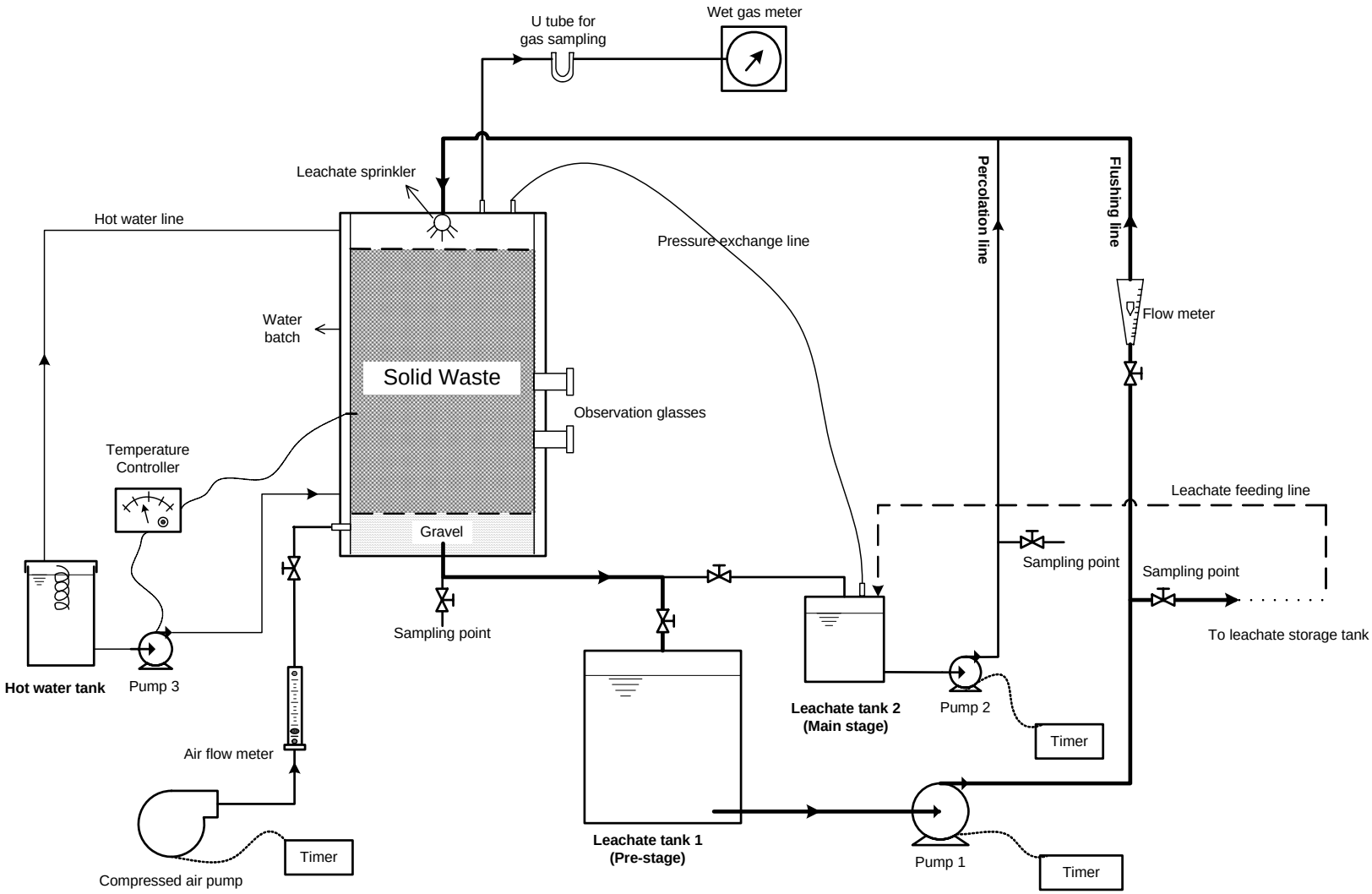


Figure 3.3 Anaerobic Digestion System

In the methane phase, another tank was used to stored leachate. That was lechate tank 2 with the volume of 60 L. It was noted that, during percolation, the tank was tightly closed to make sure no leakage happened. Master flex pump, which operate in lower flow rate range were equipped on percolation line in order to percolate leachate from this tank to digester.

Compressed air pump were installed for aeration, in the first stage as well as in the final stages. On the airline was the air flow meter to control the air flow rate. Air will be pumped through bottom space where it was distributed throughout the waste bed and coming out at the top outlet. It should be noted that, two leachate pumps and air pumps was connected to timers. They automatically operated or stopped according to the time set on these timers.

Biogas produced from the process was directed to "U" tubes before going to the wet gas meter to measure gas flow rate. This is to ensure that biogas sample which was taken at U tubes would not be affected by water in the wet gas meter. Another equipment for gas flow rate measurement was Gas counter. In this counter, biogas is collected in the basket put in the water bath. The air pocket in the basket makes the air basket turning and the turning number is proportional to the gas flow rate.

Hot water for water jacket was supplied from hot water tank. In the tank, water was heated by coil. One pump was connected to pump this water. The pump was linked to temperature controller where there is a dectector to measure the temperature inside digester. According to this controller, hot water would automatically be pumped when the temperature of the waste bed did not reach $37 \pm 2^{o}C$ in methane phase. The cool water going out from the jacket was collected back and heated up before pumping.

During methane phase, the system was tightly closed. One pipe was connected between the digester and small leachate tank so that pressure can exchange between digester and leachate tank while leachate was pumping into/ draining out of digester. In order to ensure anaerobic condition in reactors, a leakage test were provided with soap solution while applying a pressure of one bar in the empty, closed reactor.

3.3 Experimental Runs

The overall experimental procedure followed the specific objective of the study: optimizations of individual stages, which resulted in optimization of the whole process. Totally, three runs were conducted. In first run, only pre-stage was carried out. In run 2, pre-stage was followed by start up methane phase. In the final run, where complete anaerobic digestion was investigated, methane phase was focused to be optimized. Final run also was an examination of air flushing stage.

For each run, there were there reactors running in parallel. Operational condition was changed among these reactors to find out the best performance. Thus, the following run would have at least one reactor follow optimum condition of the previous run.

Figure 3.4 shows overall pilot scale experimental work. Detail operational conditions of each stage as well as each run are presented in the following sections.

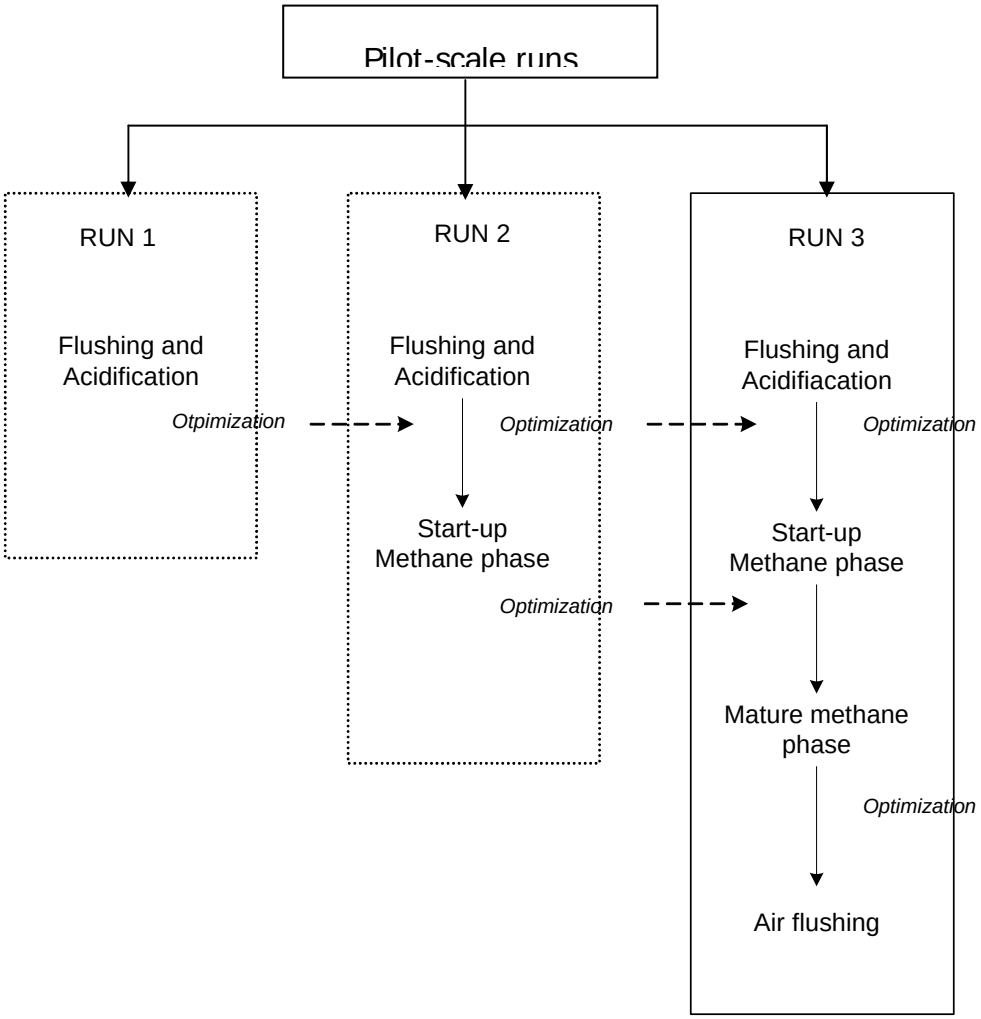


Figure 3.4 Pilot - scale experiment study

3.3.1 Optimization of pre-stage (Run 1, Run 2, Run 3)

The stage was optimized in three runs as shown in Figure 3.4. In this first stage of anaerobic digestion, non-aerated run and aerated run with different duration and aeration rate were compared in order to examine the effect of aerobic/microaerophilic condition in term of enhancing hydrolysis and acidification. Especially in run 3, semi-continuous waste feeding was applied, amount of flushing water were reduced, and partly limestoned gravel was employed to optimize the performance of the whole process.

The stage was conducted at ambient temperature. Using tap water, flushing was carried out during every 4 hours, at flow rate of 5L/min (18 m^3/m^3 waste. day), following every 4 hours stop. In aerated-run, aeration was provided during period of flushing interval.

Table 3.1 presents the variable in the experimental run. Figure 3.5 and 3.6 illustrate the detail of variables in each reactor. Detail operational conditions are as following.

Table 3.1 Variable conditions in Pre-stage

	Feeding	Reactor 1	Reactor 2	Reactor 3
Run 1	One time; 400kg/m^3	Daily water replacement		
		No gravel support		
		Non-aerated	3 days aerated	7 day aerated
Run 2	One time; 400kg/m^3	Daily water replacement		
		Gravel support	No gravel	No gravel
		Non-aerated	Non-aerated	2 day aerated
Run 3	Two-day-interval feeding; 500 kg/m^3	Daily water replacement	Every-two-day water replacement	Every-two-day water replacement
		Gravel support		
		Non-aerated	Non-aerated	Aerated

Run 1. One-time solid waste feeding; effect of aeration duration on hydrolysis/acidification yield

An amount of 120 kg biowaste, together with bulking agent, was initially loaded into the digester. Bulking agents, which was different size of PVC pipe cutlets, was accounted for 10% of the compacted volume. Thus, not taking into account this bulking agent, compaction density of the waste was approximately 450 kg/m^3.

For this first trial, the stage was conducted at 7 days. A daily amount of 200 L of tap water was supplied in each leachate tanks to flush the waste so that a Liquid: Solid ratio of 5:3 could be obtained (Figure 3.5). Leached water was drained into the same tank. Every day, the acifified leachate was removed and was replaced by 200L of tap water.

Reactor 1 was non-areated run without any aeration. In reactor 2, aeration was applied during the first 3 days whereas 7-day aeration was completed in reactor 3 (Figure 3.5). It was noted that aeration was accomplished during 4 hours of flushing interval at the rate of 3L/min (1.5L/kg.h) (Figure 3.6).

Run 2. One-time solid waste feeding; effect of gravel layer on pH and acidification yield; effect of intermittent aeration

In this run, amount of solid waste fed and tap water applied were similar in run 1. However, the duration of the stage was shortened to 5 days (Figure 3.5).

One gravel layer was supported at the bottom of reactor 1. This gravel made the pH of the leachate higher and consequently the effect of it on the efficiency of hydrolysis and acidification was considered. In reactor 2 and 3, no gravel was added.

Reactor 3 was aerated run. In this reactor, flushing was conducted during the first day. In second day and third day, flushing was stopped, only aeration was provided at 4 hrs run/4 hrs stop. During, the last two day, flushing was again applied.

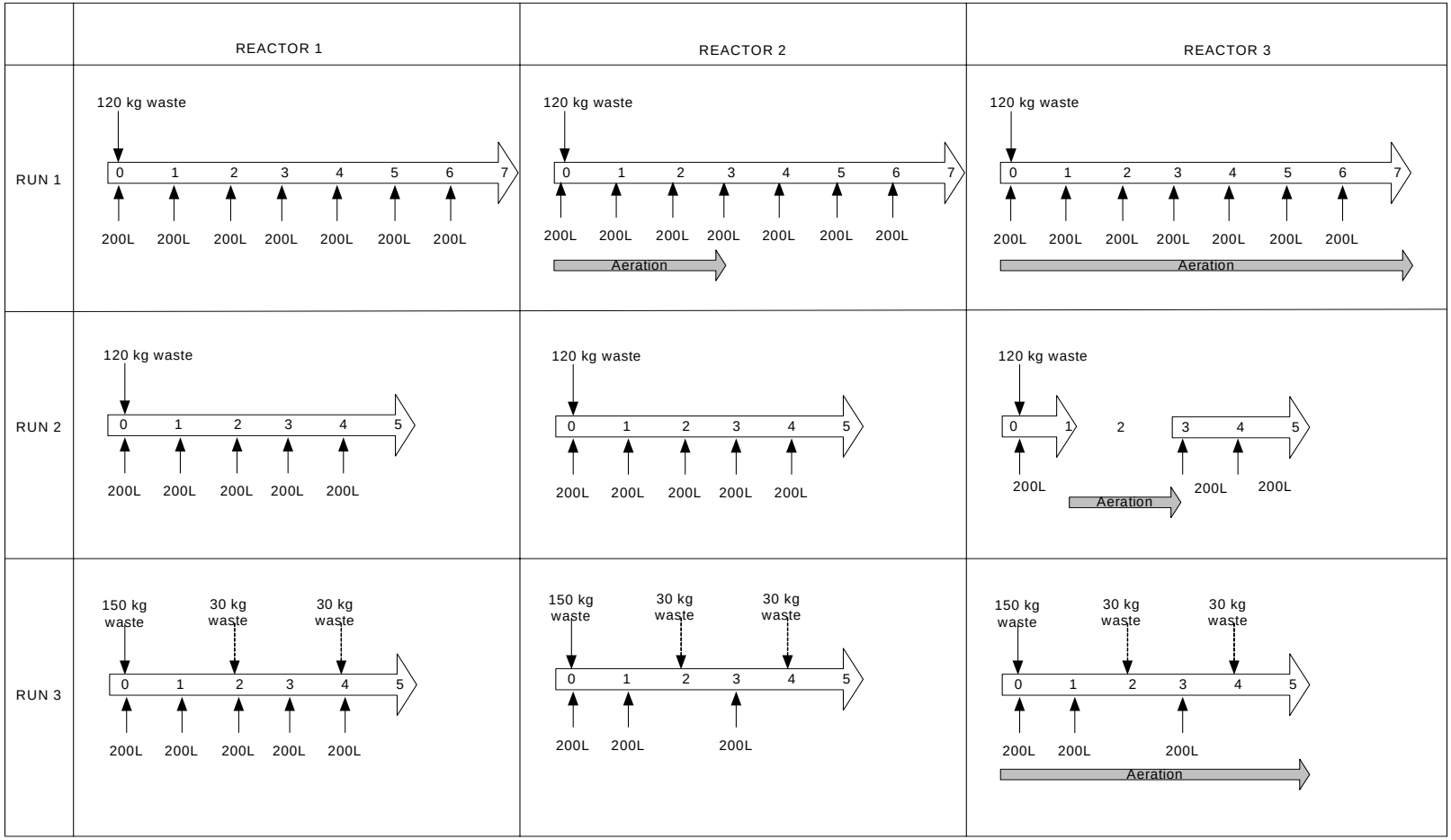


Figure 3.5 Detail of variable parameter during optimization of pre-stage

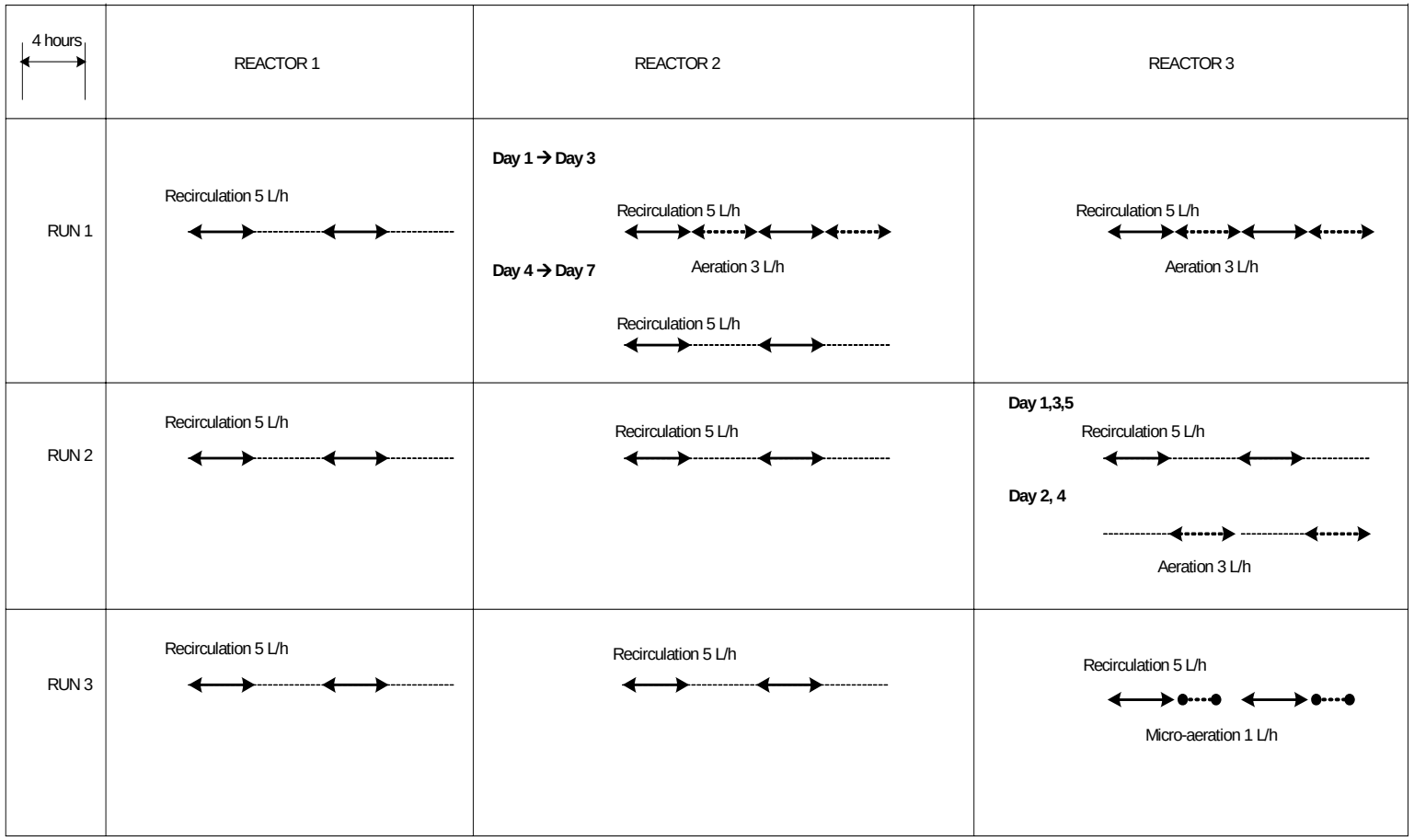


Figure 3.6 Recirculation and Aeration Rate and Interval in different Runs

Run 3. Solid waste feeding with certain interval; effect of microaerophillic on hydrolysis and acidification yield

Since the previous runs showed the significant settlement after flushing and there fore, in order to utilize this space the waste was fed into reactors with two-day interval (Figure 3.5). Initially, 150 kg waste was fully loaded in 300L vessel at compaction density of 500 kg/m^3 with 10% of bamboo chip. After two days, vessels were opened and 30 kg fresh waste (20 % of initial waste) was filled into the headspace of each reactors. Another 30kg biowaste was added after 4 days of flushing. This additional amount of fresh waste corresponded to the available space so that 500 kg/m^3 compaction density was maintained in the new layer of fresh waste, ensuring optimum flushing. The stage was accomplished during 5 days.

Daily water replacement was conducted in reactor 1 whereas reactor 2 and 3 water was replaced after first day and every two days after (Figure 3.5). This objected to reducing amount of water use as well as concentrating the dissolve matter, VFA, in acidified leachate.

In reactor 3, aeration was provided during 5 days to obtain microaerophilic condition. It was noted that microaerophilic is the condition of low oxygen concentration (2-10%) (..). There fore, during 4 hours flushing interval, only 2 hour was spend for low rate of aeration (1 L/min ~ 0.4 L/kg.h) (Figure 3.6). It was expected that during this time, microorganism consumed thus reducing oxygen contrentration and consequently create microaerophilic condition.

3.3.2 Starting up methanization (Run 2)

Run 2 was a trial to find out quickly start-up of methane phase of the waste bed which had already passed flushing and acidification. It was noted that, for this run, one reactor was supported by limestone-gravel thus, affecting pH of the system not only in the first stage but also in the methane phase.

After pre-stage, three reactors were tightly closed, kept in anaerobic condition without flushing. Temperature was maintained at 35-37^{o}C. No seeding material was added. Percolation was done with the rate of 1L/d during 2 hrs/day. Since pH environment is very important during methane phase, it was monitored.

The effect of pH on methanogenic activity was observed through this run .After first 5 days, methanogenic activity was expected to work, rising up the pH of the system. Depending on the leachate pH as well as relative gas composition; if the inhibition occurred, the system with pH of less than 6 was adjusted by using sodium hydroxide.

3.3.3 Optimization of methanization (Run 3)

Complete digestion process was conducted in run 3. Pre-stage was carried out, as mentioned in section 1.3.1, with gravel support so as to partly buffer pH of the system. Waste was added during flushing (Figure 3.5) thus no significant space was available in digester during methane phase.

The overall procedure for this run is illustrated in Figure 3.7.

After flushing and acidification, one day was spent for pH adjustment to provide optimum pH in the waste bed for methnogenic bacteria. Sodium hydroxide was added to acidified leachate to adjust the pH of the leachate to 7.5. Recirculation was done with this pH-adjusted leachate. This pH adjustment and recirculation was carried out until the leachate in the tank stable at pH of more than 6.5 within 2 hours.

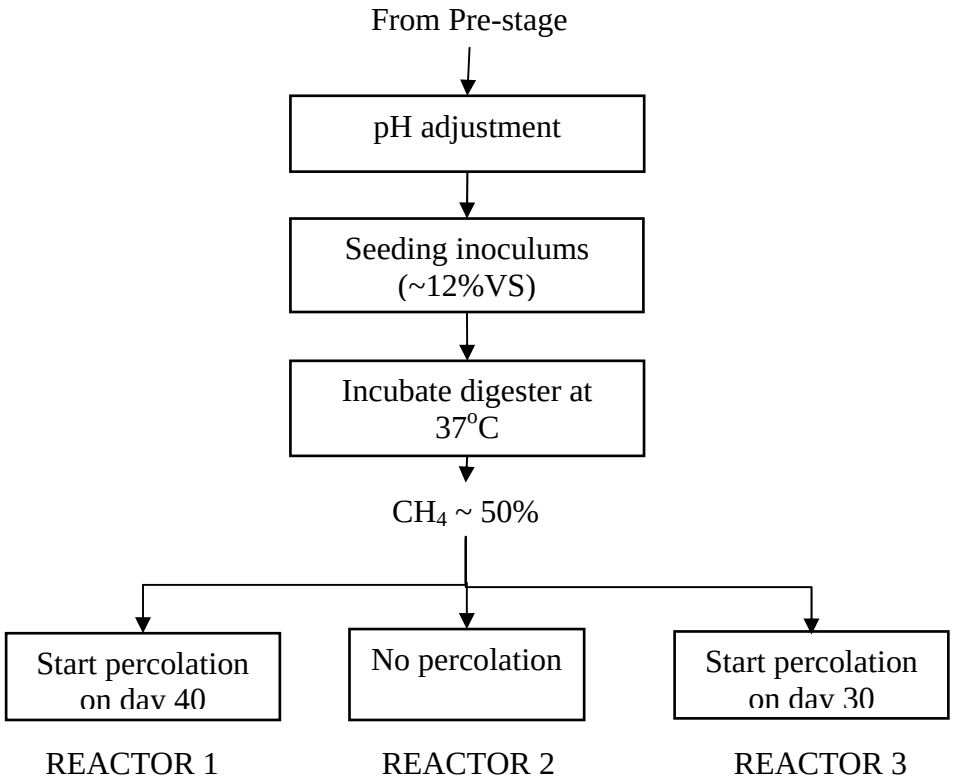


Figure 3.7 Optimization of methanization (Run 3)

Following one day of pH adjustment, three reactors were seeded with inoculums. Three vessels were opened and seeded on top of the hydrolyzed waste bed with one layer of sludge (3 L, 4%TS, 80%VS); one layer of mature waste (20 kg, 18%TS, 0.8 %VS); one layer of cow dung (5 kg, 10%TS, 0.1 VS). Totally, volatile solid added was 15% of the initial VS of the system.

Percolation was carried out for two days after adding seeding material at the rate of 0.2 L/min. With this percolation, inoculums in the top layer of reactor were spread throughout the waste bed. Then all the valves were closed and the digesters were incubated with inoculums at 35-37^{o}C without leachate percolation until methane gas reached 50% in biogas.

When methanogenesis was started (50% methane in biogas), three strategies were applied for three digesters. While in reactor 2, only solid phase of the waste continue digestion, in reactor 2 and 3, leachate percolation was practiced. Reactor 3 started leachate percolation right after methane content reached 50% (on day 30) whereas in reactor 1, leachate percolation was applied 10 days latter. Leachate was supplied and/or replaced in batch mode in the small leachate tanks. It should be noted that, leachate was fill fully in the leachate tanks so that no atmospheric air could disturb the system. Percolation was done at the rate of 0.2L/min and the interval of 4hrs run/4hrs stop.

3.3.4 Final stage examination (Run 3)

Two digesters coming from main stage of methanization were allowed to operate at final stage before unloading the waste. Aeration were applied at the rate of 3 L/h for short duration of 2 days. One day after that, no further aeration was applied and if biogas production were less significant, the digesters were stopped. Solid waste was unloaded for characterization.

3.3.5 Lab scale run: biological methane potential test

The study included lab-scale experiment for determination of methane potential of the waste. The procedure followed the method of Hansen et al. (2003), which has been applied for measuring methane potentials of organic solid waste. Triplicate lab-scale reactors with 10 gram of volatile solids were incubated at 37^{o}C with 400 ml of mesophilic inoculums. Methane potential was followed over 50-day period by regular measurement of methane composition.

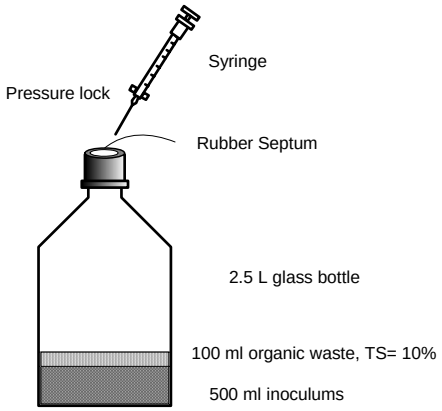


Figure 3.8 Illustration of lab-scale reactor and gas sampling

Figure 3.8 illustrates reactor and gas sampling whereas Figure 3.9 presents the procedure of the test. It was noted that the procedure involved triplicate blank control. By subtracting the methane produced by inoculums itself (the result from blank sample), the result presented the methane potential of the waste.

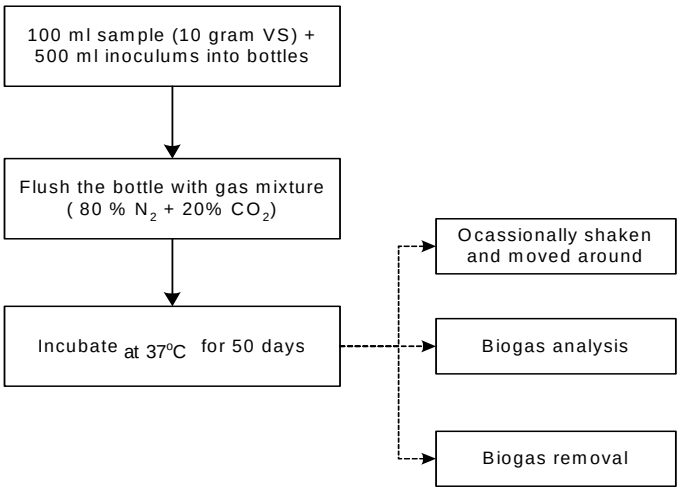


Figure 3.9 Lab scale experimental procedure

3.4 Sampling and Analysis

Figure 3.10 shows the parameters were analyzed during the process as well as frequency of analysis. Detail sampling and analysis are presented in the following sections.

Table 3.2 Analyzed parameters in different stages of the process

	Gas	Leachate	Solid waste
Pre-stage		Daily analysis: pH, Conductivity, ORP, DOC, COD, VFA, TKN, NH_4-N, TDS, Akalinity	Fresh waste, acid-flushed waste: Moisture content (MC), Volatile solid (VS), Dry matter (DM)
Main-stage	Daily analysis: Composition, gas production	Daily analysis: pH, VFA	
Final stage	Daily analysis: Composition		Digested waste: Moisture content (MC), Volatile solid (VS), Dry matter (DM)

3.4.1 Solid waste analysis

Waste characteristic will be examined in order to calculate the mass reduction and volume reduction for each operational stage. Fresh solid waste, partly hydrolyzed waste (from pre-stage) as well as digested residue after biogas production was determined in term of composition, moisture content (MC), dry matter (DM).

Figure 3.11 shows different physical fractions of solid sample and analysis methods.

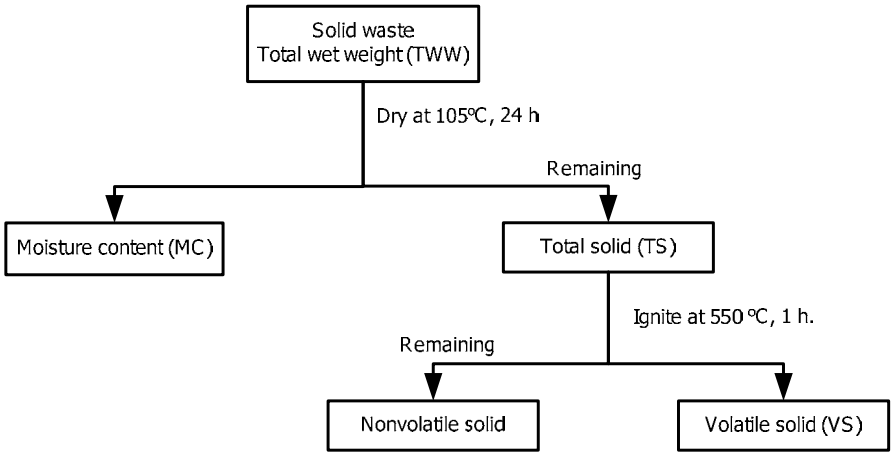


Figure 3.10 Different physical fractions of solid waste sample

Grabbed sample of solid waste was collected and parameters was analyzed based on the methods in ASTN (1996) and ASTN (1992)

- Determination of moisture content

Solid sample will be filled in several aluminum trays with the amount of 1 kg for each tray. The trays then were dried in the oven at 100 ^{o} C. After 24 hours, the weight losses were obtained. Drying was repeated until the difference of weight loss is less than 3%. Then the moisture content and total solid for each tray was calculated using equation 3.1 and 3.2. The final value was the average values of all analyzed samples.

$$\%MC = \frac{1000 - w_0}{1000} \times 100\% \qquad \text{Eq. 3.1}$$

$$\%TS = 100\% - \%MC \qquad \text{Eq. 3.2}$$

- Determination of Volatile solids

The sample after being dried was grinded into a powder using a shredder. Then, it was mixed well. Several grabbed samples each of size 2 g was put in evaporating dishes, which had been ignited at 550^{o}C for one hour in a muffle furnace. The empty dishes was weighed immediately before ignited. Initially, the solid samples were evaporated to dryness in an oven at 103-105^{o}C for at least one hour. Then the samples will be cooled in desiccators and weighed on an analytical balance. The cycle of drying, cooling, desiccating and weighing was repeated until a constant weight obtained. The volatile solid of each dish will be calculated using Eq. 3.3. Final results will be the average value of all analyzed samples.

$$\%VS = \frac{w_0 - w_f}{w_0 - w_e} \times 100\% \qquad \text{Eq. 3.3}$$

- Calculation of %TS and %VS loss.

The Figure 2.7 illustrates the material balance of reactor. Feedstock fed into reactor has total weight of TWW_o and dry weight M_o. After being digested residual will have total weight TWW_1 dry weight M_1 which are less than TWW_0 and M_o respectively.

The following equations will be used to obtain percentage total solid loss (%TS loss) and percentage volatile solid loss (%VS loss)

$$\%TSloss = \frac{M_0 - M_1}{M_0} \times 100\% \qquad \text{Eq. 3.3}$$

M_o: dry weight of feedstock going in reactor, g

$$M_o = TWW_o \times TS_o \qquad \text{Eq. 3.4}$$

TWW_o: wet weight of solid waste going in reactor, g

TS_o: % total solid of feedstock (%TWW)

M_1: dry weight residual going out reactor, g

$$M_1 = TWW_1 \times TS_1 \qquad \text{Eq. 3.5}$$

TWW_1: wet weight of residual going out reactor, g

TS_1: % total solid of residual (%TWW)

$$\%VSloss = \frac{N_0 - N_1}{N_0} \times 100\% \quad \text{Eq. 3.6}$$

N_o: weight of volatile fraction of feedstock going in reactor, g

$$N_o = M_o \text{ x } VS_o \quad \text{Eq. 3.7}$$

VS_o: % volatile solid of feedstock (%TS)

N_1: weight of volatile fraction of residual going in reactor, g

$$N_1 = M_1 \text{ x } VS_1 \quad \text{Eq. 3.8}$$

VS_o: % volatile solid of residual (%TS)

3.4.2 Pre-stage analysis

The stage focused on the hydrolysis and acidification yield of the solid into soluble matter in leachate. Gas characteristic was negligible and not taken into account in this first stage.

Leachate sample were taken every day from the leachate tank (sampling point in the recirculation line in Figure 3.3). One-line parameters including conductivity, pH, ORP were measured in the field at the time sample was taken. Parameters were analyzed were:

1. Total dissolve organic matter: DOC and/or COD;
2. Volatile fatty acids: acetic acid (Hac), propionic acid (Hpro), butyric acid (Hbu) and valeric acid (Hva);
3. Dissolve nitrogenous compounds: NH_4-N, TKN;
4. Solid content: TDS; and Alkalinity

Leachate parameters will be analysed according to the standard method for examination of water and wastewater (APHA et al., 1995). Well-mixed leachate sample were filtered through glass-fibre filter disks (GF/C) with the aid of a vacuum filtration apparatus and filtrates will be used to obtain soluble fraction of leachate. Table 3.2 summarizes the analytical methods including the application range, the interferences and as well as precautions during sampling and analysis.

3.4.3 Main-stage analysis

In methane phase, during start-up, by inserting gas syringe into U tubes, biogas sample were taken daily. Gas was analyzed in volumetric composition (CO_2, CH_4, O_2, N_2) by Gas Chromatograph

Daily gas flow rate was noted from wet gas meter and gas counters. Gas flow rate and composition is required for calculation of specific gas production (SGP) and gas production rate (GPR).

Acidified leachate was taken before and after each batch of percolation. Parameters analyzed were: pH, DOC and VFA.

Table 3.3 Analysis of leachate characteristics

Parameter	Method / Instrumentation	Unit	Applicable range and Accuracy	Interferences	Precaution during sampling and analysis
Flow rate	Flow meter	m^3/d			
pH	pH meter			- Sodium if pH >10 - Temperature	- Using "low sodium error" electrodes - Equipped with temperature compensator
Conductivity	Conductivity meter	µS/cm			
COD	Closed reflux method	MgO_2/L	For COD > 50mg/L	- Halides - Nitrite (NO_2^-) - Reduced organic species (Fe^{2+}, S^{2-}, Mn^{2+}…)	- Add $HgSO_4$ to eliminate Cl-. Do not use the test if Cl^- >2000mg/L - Add sulfamic acid to remove NO_2^-
TOC	TOC analyzer	mg/L			
TDS	Filtration and Evaporation	mg/L	Standard deviation: 13 mg/L	- High Ca, Mg, Cl^-, SO_4^{2-} - High carbonate	- Prolong drying, proper desiccation, and rapid weighing
VFA	Gas Chromatograph	mg/L	Accuracy of about 95%	- Eluting organic acids and some synthetic detergents…	
Alkalinity	Titration method	mg/L as $CaCO_3$	Standard deviation: 5 mg/ L Bias (lower than true value): 9 mg/L	- Soap, oily matter, suspended solids, precipitates	- Allow additional time between titrant additions - Do not filter, dilute, concentrate sample
TKN	Macro Kjeldhal method	mg/L	Accuracy even with Organic N <5 mg/ L		- Fresh sample is preferable - Storage: adding H_2SO_4 for pH 1.5-2 and store at 4^oC

Chapter 4

Results and Discussions

This section exhibits and analyzes the results of the study, mostly in pilot scale experiments. The characteristics of feedstock of all runs are presented. The results of pilot scale experiment are described in two parts in accordance with two main stages of the digestion process: 4.2 Optimization of pre-stage and 4.3 Optimization of methanization. In addition to pilot scale, lab scale experiment results on biodegradability of the substrate also are presented giving the basis for evaluation the overall digestion process in the pilot scale experiment.

4.1 Feedstock characteristics

Solid waste was of the wet type with high moisture content and ignitable fraction. Characteristics of the waste used in experiments were presented in Table 4.1

Table 4.1 Characteristic of solid waste in experiments

	Moisture content (%WW)	Total solid (%WW)	Volatile solid (%TS)
Run 1	90.11	9.89	79.45
Run 2	90.27	9.73	80.59
Run 3	89.02	10.98	79.15

It is noted from the table that characteristics of solid waste were almost similar for three runs. Therefore, it was satisfied the attempt to have similar characteristics for easy comparison. Physically, the waste was characterized by high fraction of fruit peels and vegetable straps. It is the reason for the waste to have very high moisture content and high organic fraction (volatile solid). Preparation of the feedstock for digestion experiment was described in the previous chapter.

However, the presented parameters could not exactly reflex the potential of the waste in anaerobic digestion process. Methane potential would be more valuable to examine the response of the waste to anaerobic digestion. The biological methane potential test was conducted in lab scale is described in section 4.3.3.

4.2 Optimization of pre-stage

The stage was optimized in three runs. Despite identical characteristics of the waste presented, for conservative approach, evaluation and comparison is mostly carried on for individual run in which a bulk of solid waste taken is mixed and load into three reactors.

Pre-stage assessment is largely based on the characteristic of the leachate. The following results show the characteristic of daily leachate in terms of carbonaceous and nitrogenous materials. Since VFA is the major product in acidogenesis it was also specially analyzed. Consequently, organic pollutant (soluble fraction) loads in cumulative leachate per kg of total solid was calculated as function of run time. Attention was paid in these yields in order to evaluate the efficiency of hydrolysis and acidification during this short time of flushing (5-7 days). Fresh waste and flushed waste characteristics also serve as another factor contributing to analysis of the stage.

4.2.1 Performance of pre-stage and effect of aeration duration (Run 1)

In this first run, oxygen condition was varied in there digesters. Reactor 1 was flushed without aeration. In reactor 2, aeration applied in 3 days, whereas reactor 3 aeration were applied throughout 7 days of this pre-stage. Everyday, same amount of 200L water were applied and removed. Aeration and flushing (recirculation) was conducted alternately.

1. Hydrolysis of carbonaceous materials

Figure 4.1 presents the variation of TCOD, SCOD and DOC in daily leachate as well as cumulative leachate. The result shows that COD concentration in daily leachate reduced with run time. The same trends were observed for DOC. As depicted in this figure, no significant difference in the overall trends could be found in three reactors.

Reactor 1, under anaerobic condition, brings the highest load both in terms of soluble and insoluble organic load. From the variation of DOC, SCOD, TCOD, it seems that the organic load in leachate reduces with level of aeration. In aerated run, aerobic metabolism of the hydrolyzed product in the leachate could be the possible reason to reduce organic load. There was no positive effect of aeration on hydrolysis enhancement.

In all three digesters, highest concentrations of DOC and COD were noted in the first days of flushing, as high as 8000 mg/L SCOD (equivalent to 3500 mg/L DOC). With time, the concentration of DOC reduced sharply. From day 5, concentration was low of less than 2000 mg/L in COD (1000mg/L in DOC). Thus, the cumulative load did not show significant increase. The organic carbon reduction in daily leachate was thought to be due to two reasons. They are the early extraction of hydrolyzed materials and the dilution of solid bed by flushing.

Looking into total COD and soluble COD, it is seen that soluble organic account for the major fraction of total organic that could be extracted from the waste bed and particulate organic was less in leachate. Since Soluble COD and DOC exhibit the same trends, DOC could be a meaningful parameter in evaluation and it is considered as parameter of important instead of COD.

The low DOC concentration in the leachate from the day 5 did not imply that hydrolysis of the waste bed were stop or inhibited. Among the various factors thought to be inhibitor of hydrolysis are low pH and high VFA. According to Wheatley (1990), concentrations up to 3000 mg/L do not cause inhibition assuming pH is above 6.8. Since low concentration of less than 2000 mg/L VFA (Figure 4.4) and pH higher than 5.5 (Figure 4.8) were observed in day 5, they are not the reasons to cause the cease. Low DOC concentration gives the hint that the solid bed is excess diluted and flushing is less significant from day 5.

Considering the factor for hydrolysis, it is well known that the liquefaction of organic solid waste is limited by hydrolysis of particulate material (Eastman and Ferguson, 1981). Since substrate in the waste includes both soluble and insoluble biodegradation materials, it is not necessary that the entire soluble fraction in leachate only represent the hydrolysed product of particulate substrate. Within such a short time of 7 days, it is likely that only the soluble and easily materials in the solid waste bed were extracted into leachate and hydrolysis of particle substrate was less significant. The observation demonstrates the importance of the short duration needed for rapid flushing of organic portion for the solid waste. Here, after 5 days of initial flushing no further significant addition of organic removal was noticed.

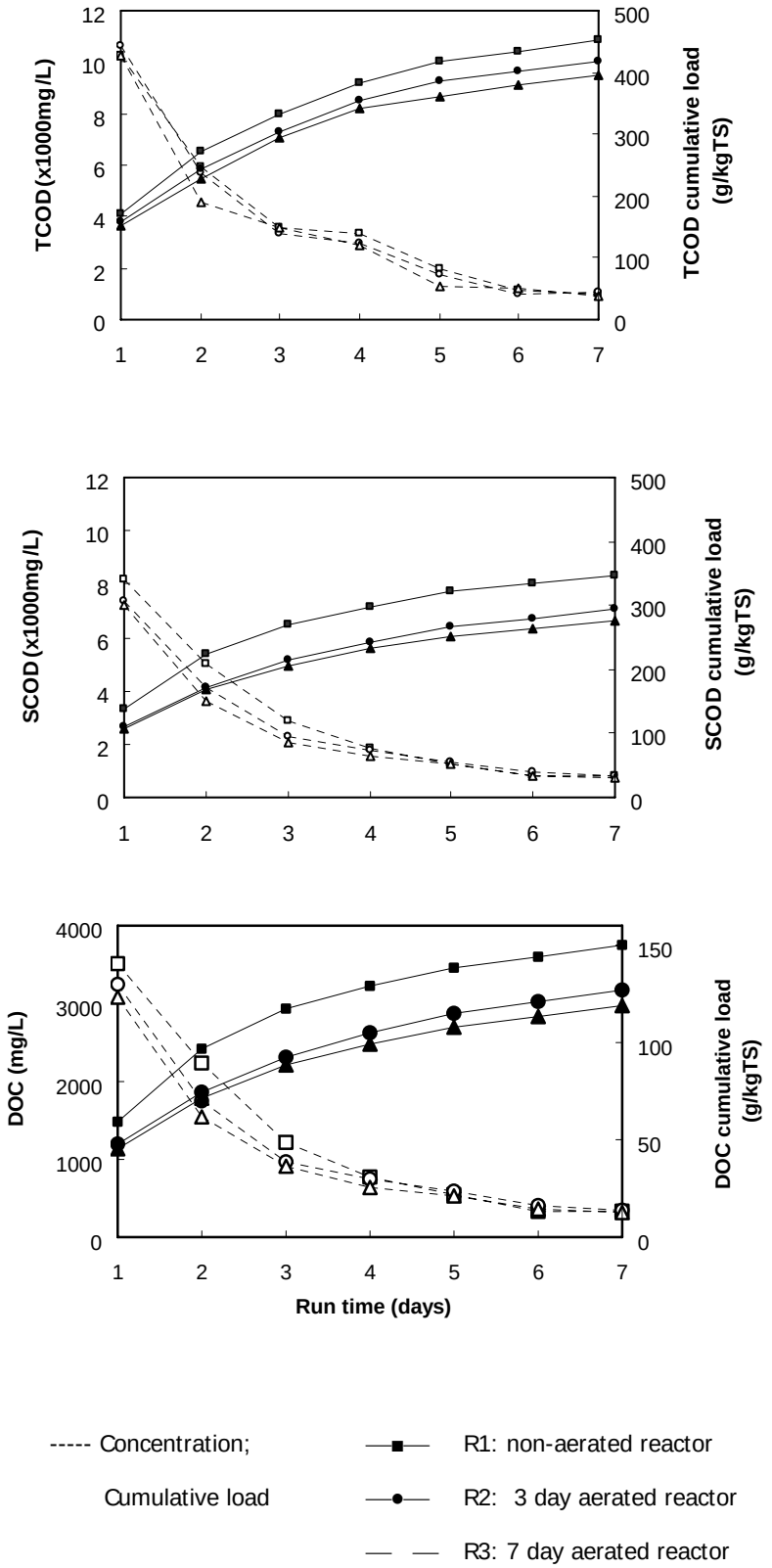


Figure 4.1 Variation of Total COD, Soluble COD and DOC in leachate (Run1)

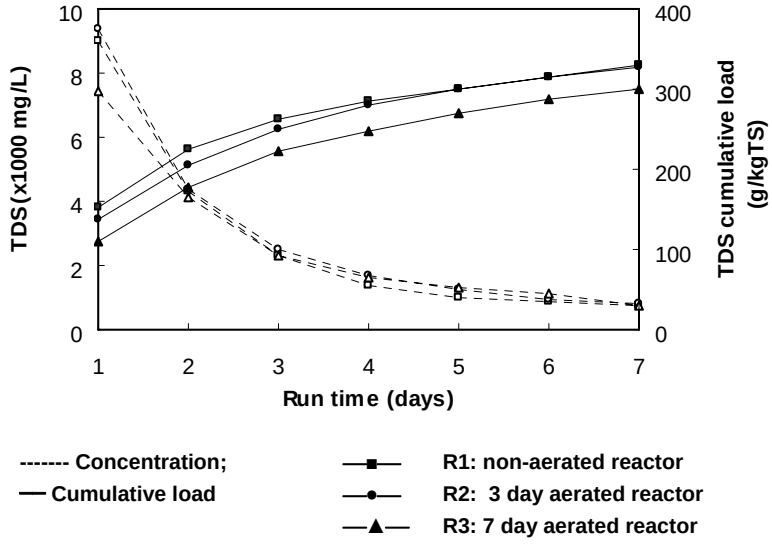


Figure 4.2 Variation of TDS in leachate (Run 1)

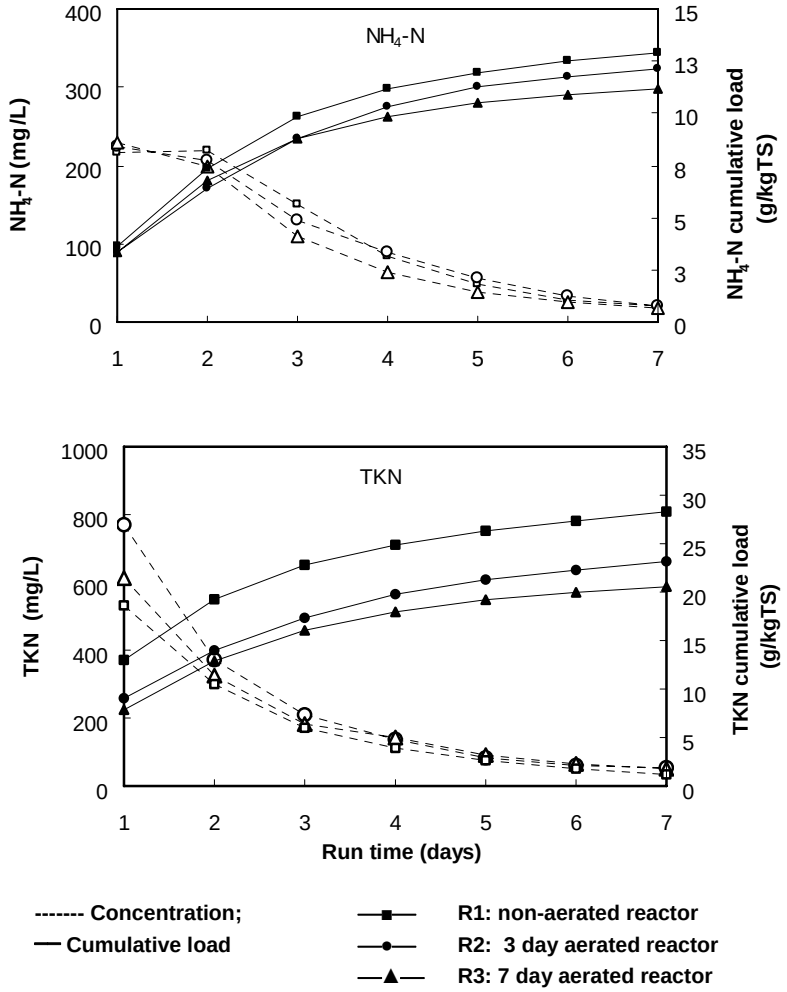


Figure 4.3 Variation of NH_4-N, TKN and NH_4-N : TKN ratio (Run1)

Total dissolve solid (TDS) concentration and cumulative load in leachate of three reactors bring the same trends (Figure 4.2). Dissolve solids representing for the hydrolysis product of particulate substrate in all reactors were very high initially then were in the decreasing phase with time until day 5. The trends are in correlation with DOC, and COD of leached confirming the early biodegradability of the waste.

The overall results suggest that major portion of easily biodegradation substrate was quickly lechate out. For each kg of dry waste, nearly 150 mg of Carbon and 320 mg/kgTS dissolve solid was extracted into soluble fraction of leachate within 7 days. For 5 days, the productions was approximate this value (Table C-5). Since the objective of the stage is to partly remove organic fraction for the preparation of methane phase, 5 days retention time could be the good enough time for this pre-stage.

2. Hydrolysis of nitrogenous material

Ammonia is an end product in anaerobic degradation of nitrogeneous material. Protein first converted to amino acid in hydrolysis stage then further degraded anaerobically in acidification stage producing ammonia. However, it is not nessessary, for the waste at this initial stage, that the concentration of soluble nitrogenous material totally reflex the hydrolysis of nitrogenous materials. The dissolution of readily solubilized fraction of N material in the fresh waste also contributes to the concentration of the leachate.

Figure 4.3 presents the concentration of total soluble nitrogen and ammonia nitrogen in daily leachate and the load in cumulative leachate. It could be seen that same configuration as carbonaceous materials was depicted. There was no difference in behavior of hydrolysis for carbonaceous and nitrogenous organic. Initially, high concentration of both TKN and NH_4-N was noticed. The concentration in leachate reduced sharply during first five day, form the 600-800 mg/L in the first day for TKN down to less than 100 mg/L after day 5. The initially higher concentration of TKN might be largely contributed by readily solubized fraction. Finally, 20-30 gTKN was extracted from 1 kg of TS after 7 days. It should be noted that non-aerated condition could bring into the leachate higher TKN load.

Looking into NH_4-N profile in three digesters, there is a reasonable effect of aeration on anaerobic degradation of protein. Regardless the level of TKN, ammonia nitrogen is higher in non-aerated run. It is reasonable since under aerobic condition, organic nitrogen would be converted more to oxidized form of nitrogen rather than the reduced form of NH_4-N. Aeration totally did not show reduction degradation of protein since both TKN and NH_4-N in aerated run is lower as compared to non-arerated reactors.

The ratio NH_4-N: TKN of around 0.4 (Table C-3) is obtaind in three reactor, indicating significant anaerobic activity of microorganism to degrade protein. The amonnia concentration reduce from 200 mg/L to very low of less than 50 mg/L in the day 7. Ammonia concentration is partly cause the variation of pH. The low concentration of ammonia could possibly results in the low alkalinity that cannot buffer high concentration of VFA. As an effect, the pH of acidified leachate cannot be higher than 6. (Figure 4.8).

3. Acid production

Fermentation of monomers, which are produced from hydrolysis, results in production volatile fatty acids (VFA). Among the main component of biodegradation matter, namely,

carbohydrates, lipids and proteins, carbohydrates are known to be easily and rapidly converted via hydrolysis to simple sugars and subsequently fermented to VFA. Lipids are hydrolyzed to long chain fatty acids, and then oxidized to acetic acid or propionic acid. Proteins are hydrolyzed to amino acids (in hydrolysis) which are further degraded to VFA.

In this pre-stage, it was anticipated to get high SCOD/DOC in leachate, which represents the hydrolyzed products from the fresh waste. At the same time, VFA, the product of acidogenesis/hydrolysis, was also the other important target. Figure 4.4 shows the concentration and cumulative load of total VFA in three reactors. It appears that the variation trends were quite similar in three reactors in terms of concentration, thus cumulative load of total VFA.

The highest concentration of total VFA occurred at the first day leachate with value of 4.3, 3.0, 3.6 g/L in reactor 1, 2, 3 respectively. For many author, the peak VFA concentration may reach to the range of 10 g/L or more than (De Baere, 1995; Ghosh 1984). In order to compare the concentration with previous studies, it is important to know the liquid to solid ratio. More additional water, of course, results in the lower concentration in leachate. According to Cho & Park (1995), who coducted hydrolysis and acidogenesis of fruit and vegetable waste in solid bed, at Liquid: Solid ratio of 0.25-0.5 (recirculation flow rate of 1-2 L/d), the peak concentration was found at around 10 g/L. Considering this factor, the concentration of VFA leahcate in this results is comparable since higher Liquid: Solid ratio of 4: 3 was applied.

The acid concentrations were lowered significantly within several days. The concentrations decrease to less than 1000 mg/L in day 5. It was due to the excessive flushing of digested solid. Although, the flushing water can enhance acid production, it diluted acids produced from the digester too early. The low concentration of VFA in the final stage suggests that strictly separation of acidogenic and methanogenic fermentation might not be maintained at the end of flushing. Therefore, as soon as the VFA concentration was so low that it would no longer be inhibitor of methanogenesis, it would be the appropriate time for the waste bed to switch to methane phase. Here, the low concentration reached at day 4 or 5 suggests that it is not necessary to use further additional water or flushing was no more meaningful.

As a whole, for all three reactors, the VFA produced rapidly at the initial stage of fermentation indicating that acidification occurred strongly at the early flushing. This is because acidogenic bacteria are fast-growing bacteria. If hydrolysis is not rate limiting then, acid will produced quickly. According to (Sans et al., 1994), with minimum doubling times of around 30 min, acidogenic bacteria are capable of fermenting part of the soluble fraction of the organic refuse to produce a mixture of VFA in a short interval time.

The first stage in anaerobic biodegradation is the conversion of the complex waste including both particulate substrate and soluble polymers (dissolve polymeric substrate). Products from this hydrolysis stage are organic monomers, i.e., amino acids, long chain fatty acid and sugars. It is well known that in hydrolysis/acidification of solid waste, hydrolysis of particulate, especially cellulose, to be the rate-limiting factors. This may not be the case where the solid taken from fruit and vegetable waste, which containing high soluble fraction. Thus, these soluble monomers were quickly fermented to acidogenesis products, which can be observed by high concentration of VFA at the first day leachate (Figure 4.4). This proves the significance of flushing for this kind of substrate. However, it appeared that the more hardly biodegradation such as cellulose still remain in the partially

digested material represent the fraction making hydrolysis the limiting step. However, in terms of pretreatment, flushing within the short time seems to be effective.

At the end of flushing, a maximum VFA yield of around 180gVFA/kgTS was achieved in reactor 1. Aeration did not cause significant effects in the production of total VFA except for slightly reducing it. Lower acid yield of 160 gVFA/kgTS was observed in reactor 2 and 3. It is also important to note that the yield reducing with duration of aeration.

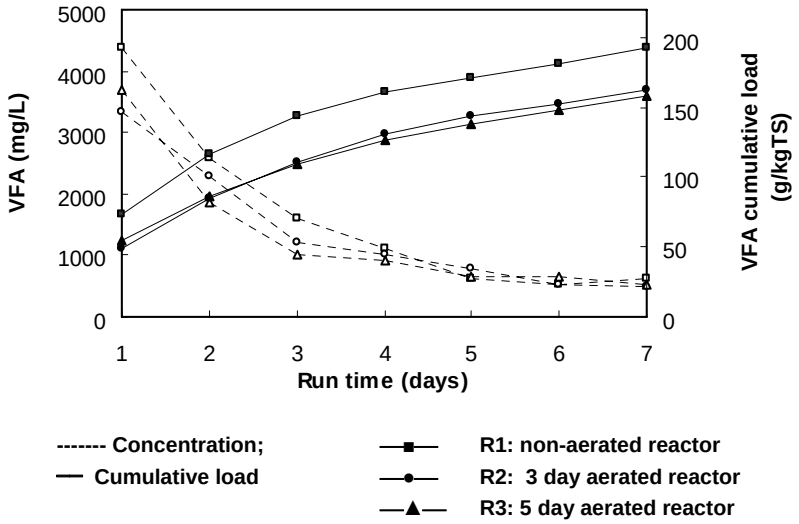
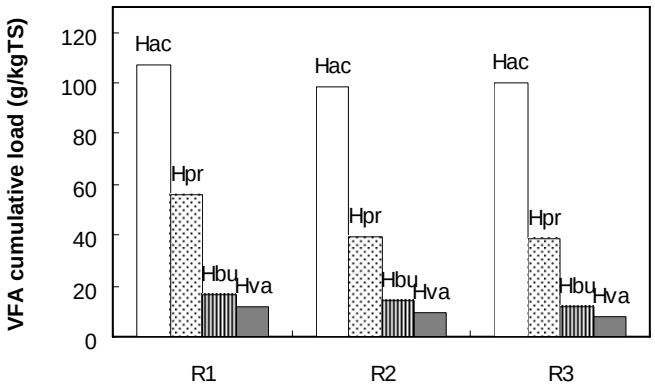
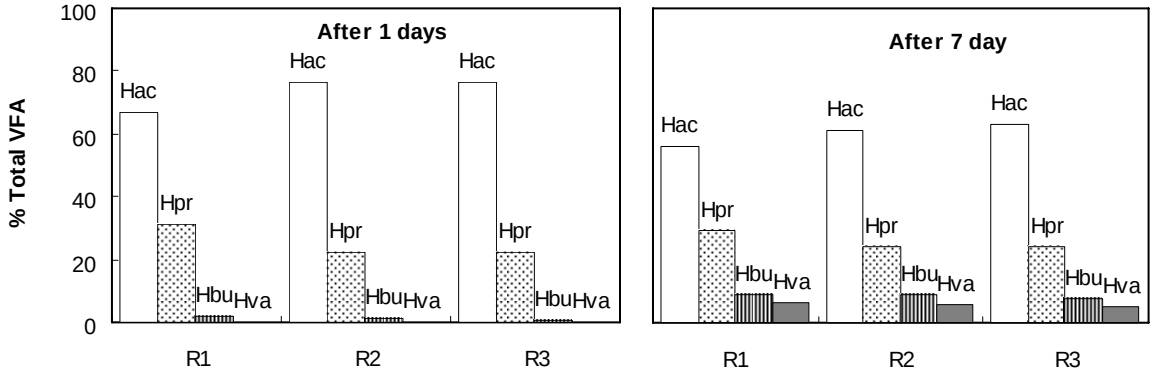


Figure 4.4 Variation of total VFA concentration and cumulative load (Run1)



a) Individual VFA load in total leachate



b) Individual VFA percentage in Total VFA in cumulative leachate (after 1 day and 7 days)

Figure 4.5 Individual VFA in leachate (Run1)

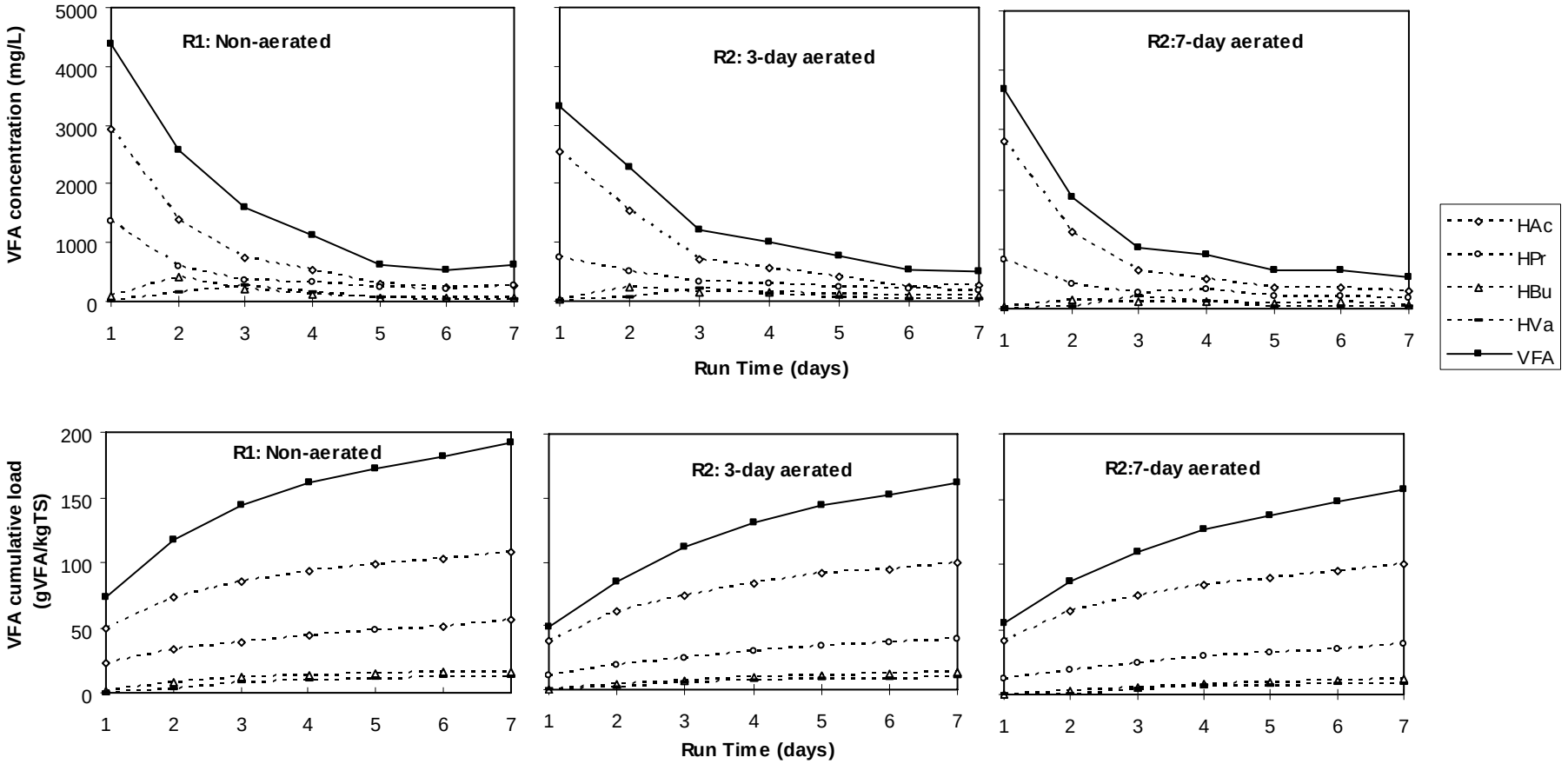


Figure 4.6 Variation of individual VFA concentration and cumulative load (Run1)

4. Individual VFA distribution

In addition to total yield and concentration of total VFA, it is necessary to look into single VFA distribution in the leachate. VFA mentions the main acidogenesis products including the organic acids with carbon atom number from 2 to 5. They are acetic acid (Hac), propionic acid (Hpr), butyric acid (Hbu) and valeric acid (Hva). Figure 4.6 shows the concentration and cumulative load of individual acids, whereas Figure 4.5 presents the loads as well as percentages of each acid in total leachate.

Considering the result presented, with short time of flushing, the favored product was mainly acetic acid. Initially it reached concentration of which around 2.2-2.9 g/L, and as and totally in cumulative leachate acetic acid accounted for more than half of total VFA (Figure 4.5a). Next to acetic acid was propionic acid. The concentration of longer chain VFA reduced with the number of carbon atom. Among various VFA, acetic acid is the desired intermediate since it is the direct substrate for methanogenesis. It is well known that acetic acid is the most important intermediate since approximately 70% of methane produced from acetic acid (Polprasert, 1996). Figure 4.5 b) give a hint that for longer retention time, the contribution of longer chain VFA among total VFA increased significantly.

The results here is in good agreement with some researchers studying on hydrolysis and acidification of MSW including Sans et al. (1994, 1995), Cho and Park (1995) and Mtz-Virtura et al. (1994). According to Sans et al. (1994) acetic acid tended to be the major product of the acidogenic process within short retention time, and low concentration of propionic and butyric acids were observed. It was seen by Cho and Park (1995) that acetic acid concentration is predominantly higher than those of others up until 70 days. Vieitez and Gosh (1998) found that acetic acid was the major acid produced in the first stage. In accordance with the authors, this initial burst of acetic acid production may be attributed to metabolism of readily fermentable substrate such as sugars. Same hypothesis could be applied for this case.

Since acetic acid is the direct substrate for methanogens, its higher concentration compared with longer-chain fatty acid (propionic, butyric, valeric acids) indicates that methanogenic activity did not occur. The concentration in daily leachate of those acids also were different. Acetic acid reached peak concentration at the first day (Figure 4.6). Butyric acid reached highest concentration at the second-day leachate and valeric acid concentration peak was found in third-day leachate.

It is not clear to evaluate the effect of aeration on the behavior of acidification, not only in terms of total VFA but also in terms of single VFA distribution, if not to say that aeration cause negative effect. The only difference that could be realized from this figure is that, the non-aerated run offered higher-acid leachate, especially for acid with more than two-carbon atoms: propionic acid, butyric acid and valeric acid.

5. Acidogenesis versus hydrolysis

A comparison of DOC and DOC equivalent of total VFA gives an interesting point. It is depicted from the Figure 4.7 that more than half of soluble organic carbon in the total leachate in pre-stage, was acidified into VFA. Since DOC includes VFA and hydrolyzed material that is still not acidified, the difference between these two parameters represents un-acidified hydrolysates. Here unacidifed hydrolysates fraction was small part of less than

50 %. This information may be interpreted to means that not only hydrolysis but also acidification reaction was dominant during the first stage of anaerobic digestion within such a short time of 7 days and acidification were strong over hydrolysis. However, different observation was noticed in the study of Vieitez and Gosh (1998).The author found that, for simulated Indian municipal solid waste, hydrolysis was the predominant reaction during the first two-months since COD concentration during these period were much higher than COD equivalent of VFA.

It has been found that high-solid batch system give rise in unstable anaerobic digestion due to concentrated substrate (Mata-Alvarez, 2003)The reason causing instability is in the start up period where acid is produced too much that possibly cause inhibition throughout the waste bed. High fraction of organic acids in leachate observed here gives a hint that the situation seemed to agree with this constraint since acidification occurred strongly in early stage of digestion process. Then, it could be concluded that flushing was significant not only for hydrolyzed products but also for acidified product. Consequently, it prevented the waste bed from shock loading in the coming stage of methanogenesis. The high fraction of VFA in the leachate would favor the proposal of feeding this leachate back into digester in next stage where methanogens are in active phase.

6. pH, alkalinity and VFA

Figure 4.8 indicates that pH of leachate in all reactors varied in a short range (pH 5-6), during 7-day flushing period. The pH values in all three reactors were low initially in the first day corresponding with the high concentration of volatile fatty acids observed. The variations of pH were minor and the trends were same for all leachates. The highest value was around 6, reached at the second and third day leachates and tended to gradually decrease with run time.

In comparison among the three reactors, it appears that the pH were lowest in non-aerated reactor. In the reactor 3 where aeration was applied for the whole period, pH was highest and more stable. The effect of aeration is confirmed when looking at the pH curve in reactor 2. In this reactor, pH dropped lower when aeration were stopped after day 3.

In order to evaluate the cause of pH variation, VFA and alkalinity play the two main important parameters. That the concentration of VFA and alkalinity together decreased with the run time in all three reactors bears the evident why the pH curves are quite stable. There was no significant different in alkalinity of three digesters. However, that VFA concentration was highest in non-aerated run must be the reason for lowest pH in this reactor.

7. Stabilization of waste

The total solid loss and volatile solid loss in this first stage of leaching and acidification were high for all reactors. Surprisingly, within such a short time of 7 days, more than 50% volatile and total solid destructions could be obtained in all reactors (Figure 4.10). This results even better than the value of 40% obtained in smaller pilot-sclale reactors in previous research on leaching of the same waste (Dayanthi, 2003). This figure depicted that aeration did not result in positive effect in terms of TS/VS loss and that TS/VS loss reduced with the level of aeration.

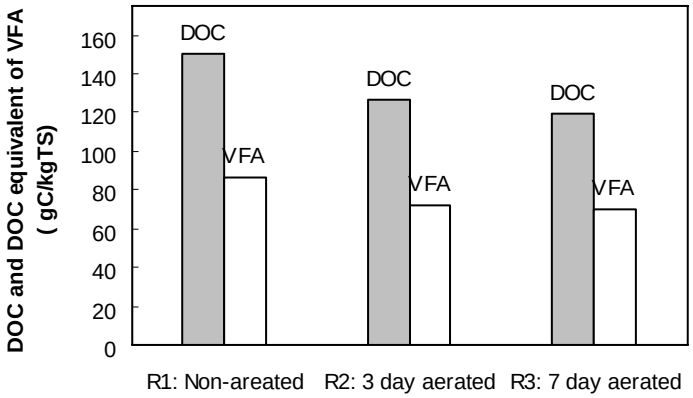


Figure 4.7 Load of DOC and DOC equivalent of Total VFA in Total leachate (Run 1)

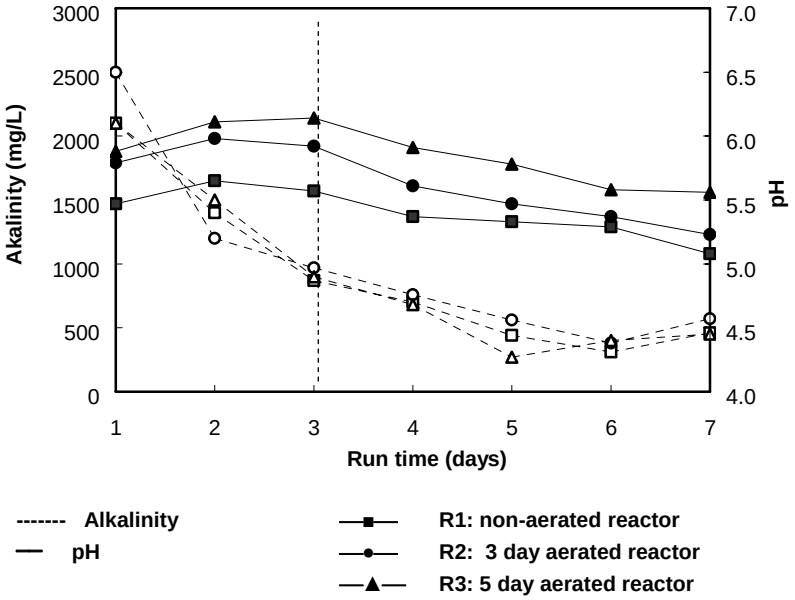


Figure 4.8 Variation of Alkalinity and pH in daily leachate (Run 1)

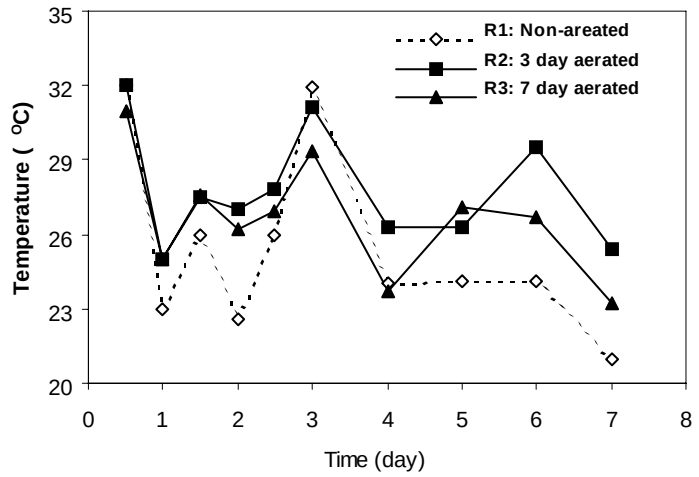


Figure 4.9 Variation of temperature (Run 1)

It should be noted that the destruction was mostly due to flushing in which volatile solid in the waste bed was extracted into soluble and particle organic fraction of the leachate as well. In addition to liquefraction, gasification could be another cause contributing to the VS destruction. According to Dayanthi (2003), during 7 days period of flushing, biogas production could be neglected. However, since aeration was applied here in leaching, it is important to look at gasification of the waste bed.

For better evaluation of the process, liquefraction, volatile solid destruction and gasification should be taken account, in order to understand the effect of aeration on early stage of degradation. For this purpose, carbon basis was applied.

It could be derived, from the total Carbon in solid and liquid phases (flushed waste and leachate), the Carbon in the gas phase. 100% of carbons in fresh waste after after pre-stage were divided into 3 part: in the residue (solid form), in the leachate (soluble) and in the gas. It could be seen from Figure 4.11 that, in reactor 2 and 3, the lower carbon load in leachate were almost compensated by the higher volatile solid in the residues. Therefore, the remaining fraction, gasified fraction, were almost equal but not completely equal. It appears that, with level of aeration, this total amount of carbon reduce thus, the gasified carbon increased. The results give a hint that at the end of flushing, more carbon in the gas phase in these two reactors favoring the hypothesis that, aeration enhance aerobic metabolism of waste into carbon dioxide (CO_2) and water (H_2O). Carbon distribution in biogas is increasing with level of aeration. There is no doubt that it was due to the aerobic metabolism of the waste.

There are two possible reasons for lower, solid/C destruction of the fresh waste (higher solid/C remaining in the residue). First is the lower hydrolysis yield to transform the solid into soluble fraction of leachate. The second is due to the lower gasification process. Again, it should be mentioned that gasification is negligible during this early period of degradation process. However, this figure depicted that despite higher fraction of C in gas phase, the solid destruction still low in reactor 2 and 3. Then it would be concluded that the reason for low solid destruction is definitely due to the low hydrolysis process not because of low gasification process.

Regarding the effect of aeration in organic load in leachate, the result is in good agreement with some studies. The common point was that aeration always bring lower leachate load as compared to non-aerated run. However, the reason here, as discussed above is in different point view was found by (O'Keef et al., 1999). According to the author, the reason could possibly be the aerobic metabolism occurred to leachate reducing organic load in the leachate. It also possibly happened in this study, since carbon distribution in leachate were less in aerobic run. Carbon transferred into leachate is reducing with the level of aeration, highest in anaerobic run. That aeration reduces the leachate load both in terms of DOC as well as VFA is possibly due to: (1) the aerobic conversion of carbon in leachate and/or waste into CO_2 (2) The lower bioconversion of carbon from the waste into leachate. The latter reason is still questionable.

As a consequence, the carbon fractions in digested waste of three reactors were quite incomparable. If the difference is more significant, thus it can be concluded that aeration in this case seems to give negative effect on biodegradation of the waste. However, in this case the effect of aeration on biodegradion (either aerobic or anaerobic) seems to be unclear.

In terms of not enhancing hydrolysis, the results seem to be in agreement with O'Keef et al. (1999). It was concluded by the authors that the effect of aeration on hydrolysis is equivocal, neither clearly positive nor negative. Nowadays, there is the way to apply aeration to achieve (1) quicker reduction of COD the leachate into carbon dioxide (2) reduction of lightly degradable material in order to reduce the formation of VFA in landfill. In this sense, aeration with small flow rate and short time in our case seem to be not suitable but it not the objective.

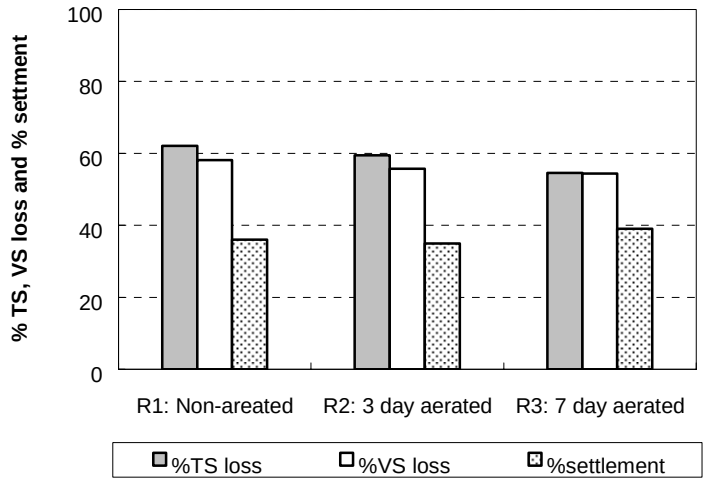


Figure 4.10 % TS loss, % VS loss, and % Settlement after pre-stage (Run 1)

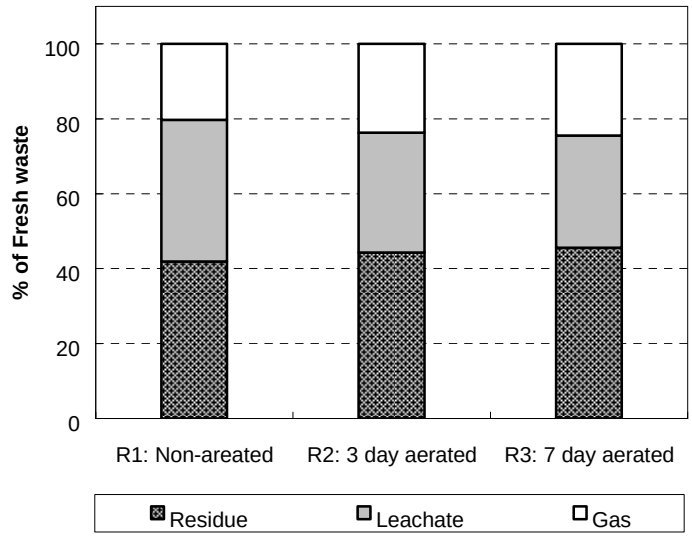


Figure 4.11 Distribution of carbon after pre-stage (Run 1)

Fluctuation of temperature could be considered as an indicator in the aerobic activity. The aeration was provided with the purpose to enhance hydrolysis and acidification so that increasing of temperature (like in case of aerobic composting) was not expected. It should be noted that only relative comparison is valuable since the stage was conducted in ambient temperature thus, it fluctuated. Since flushing occurred right after intermittent aeration, the heat if produced would be loss significantly. According to the Figure 4.9 there

is an increase of temperature in aerated reactors as compared to non aerated reactor, however, the difference was not significant. As a whole, temperature in reactor 1 where no aeration was applied, were a little bit lower than other. Aeration, as expected, increased the temperature but slightly. That temperature increase with aeration is small showing that aerobic metabolism did not strongly occur.

It is important to note that significant volume reductions were observed after 7 days of flushing. Approximately 40% volume reduction was noted in three reactors (Figure4.10). The bulking agent applied in reactor 2 and 3 as well as the level of aeration doesn't seem to affect much on the volume reduction. Then it should be concluded that in terms of pre-treatment for volume reduction and VS reduction, the flushing period was significant.

4.2.2 Effect of pH on hydrolysis and acidification (Run 2)

According to the previous study on leaching (Dayanthi, 2003), the initial stage of anaerobic leaching was inhibited by low pH and pH of around 6 could promote leaching SCOD and NH_4-N to some extent. Since the inherent pH of raw solid used for the previous study was around 6, no pH adjustment was necessary.

However, in current experimental runs (Run 1), it was observed that pH dropped less than 5.5 on day five and further decreased to less than 5. The Baronbsky (1984) pointed out that acid production ceased at pH 5. The effect of pH on liquefaction/acidogenesis was observed in run 2 as discussed below.

1. pH and the buffering role of limestone

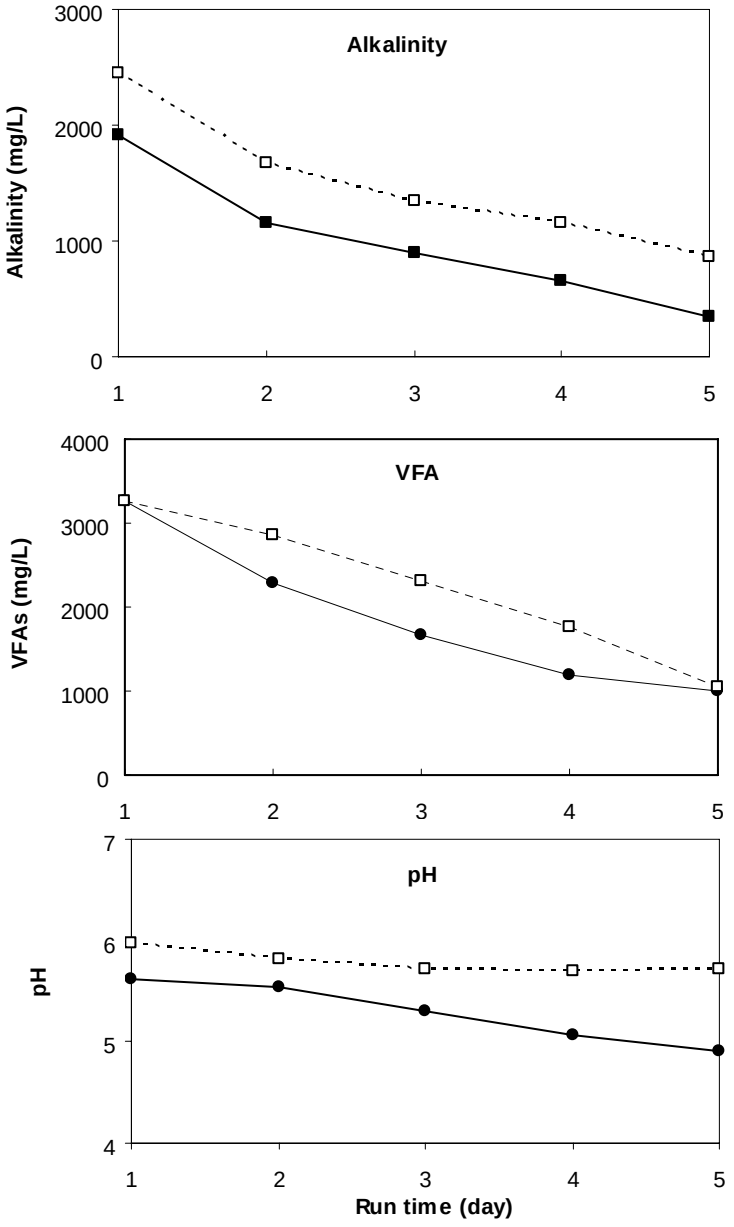
In anaerobic process, pH is controlled by the interaction of the weak and strong acid-base systems. These acids and bases are either present in the waste or released during digestion process. Weak acid-base system present in most processes are carbonic, orthophophoric, hydrosulfuric, long chain fatty acids, volatile fatty acids, ammonia and metal salt (Carpri and Marais, 1973; Hobson, 1981). If these forms of acid and alkaline tend to neutralize each other, the pH will be optimum for methanogenesis. In the case where, the digester content contains very high concentration of VFA without the pH being adversely affected, the buffering action is due to alkalinity (Hobson, 1981). According to Mata-Alvarez (2003), pH value is strongly affected by the buffer capacity of the system and bicarbonate, VFA, and ammonia are the main process controllers in terms of buffering capacity.

In experimental run 2, a layer of partial-limestone gravel layer was supported at the bottom of reactor 1, while in reactor 2 and 3, no limestone was added. The initial objective of gravel layer is to provide better drainage and prevent block in the digester. In addition, limestone can act as alkalinity buffering the pH of the leachate going through the layer.

Figure 4.12 presents the pH, alkalinity and total VFA profiles of the 5-day flushing and acidification period. In pH-uncontrolled run, reactor 2 and 3, pH were low initially of less than 6 then reduced significantly to the value of lower than 5 at the end of flushing period. The low pH level encountered initially was largely due to high VFA concentration and low buffering capacity (alkalinity) of the wastes (hence of the leachate). With the run time, VFA concentration reduced but lower alkalinity produced by the substrate could not buffer the system. Leaching with large amount of water might lead to earlier extraction of mineral from the biomass substrate. It is depicted by the sharply reducing curve of alkalinity

concentration. Same argument was found by Chanakya et al. (1992) with two-phase anaerobic digestion of water hyacinth or urban waste.

Different from reactor 2 and 3, pH of leachate from limestone-buffered reactor was quite stable with time at a value of nearly 6. Initially, same VFA concentration of around 3000mg/L was observed in both cases, with and without limestone support. However, that alkalinity value of around 2500 mg/L was in reactor 1 whereas lower values of 2000 mg/L were found in pH-uncontrolled reactors could be the reason for pH in the former to be higher. This give the role of limestone layer in buffering. With the run time, the limestone kept on providing alkalinity buffering the system. Consequently, the pH value was stable at 5.7 from day 3, 4 and 5 (Table C-2).



---- R1: Limestone buffered reactor

R2: pH uncontrolled reactor

Figure 4.12 Variation of pH, VFA and Alkalinity in daily lecchate (Run 2)

In one hand, low pH value found in acidogenic-phase leachate would favor phase separation. There is the well-established principle that low pH (6.0) is an effective inhibitor of methanogenesis (O'Keefe and Chynoweth, 1999). This has been demonstrated for dry digestion of organic waste (Jewell et al., 1982; Cecchi et al., 1990). In another hand, low pH could be the reason for low liquefaction/acidogenesis, specially for solid waste substrate.

2. Hydrolysis of carbonaceous and nitrogenous material

DOC and TDS profiles in run 2 showed the same trends, concentrations reduced with time and cumulative load increased as found in the first run (Figure 4.13).

It is known that the conversion of bio-degradation particulate volatile solid into VFA is limited by hydrolysis of the substrate. However, previous study on leaching as well as the first run favored assumption that, during earlier stage, hydrolysis is not the rate-limiting step for this kind of easily degradable substrates. It confirmed the role of early flushing. In addition, it is important to note that hydrolysis can be described by first order kinetic models whose constant is pH dependent (Chaplin and Bruckle, 1990)

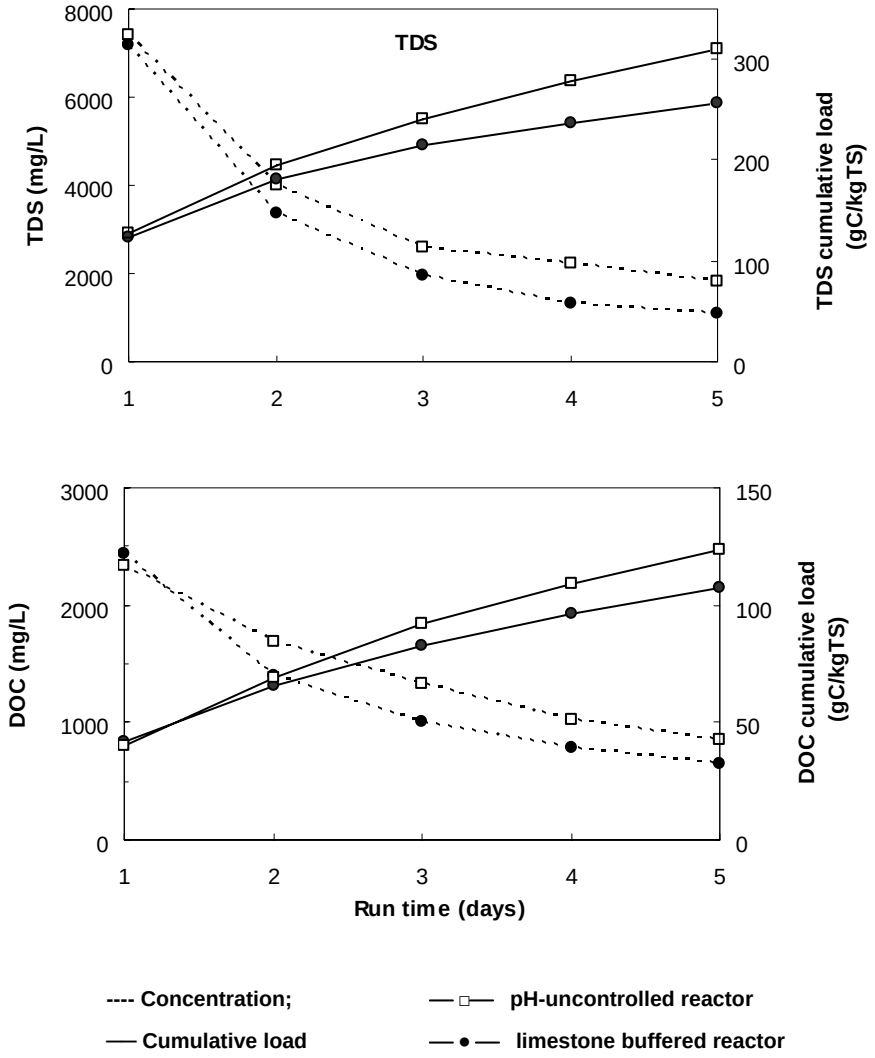


Figure 4.13 Variation of DOC and VFA concentration and cumulative load (Run 2)

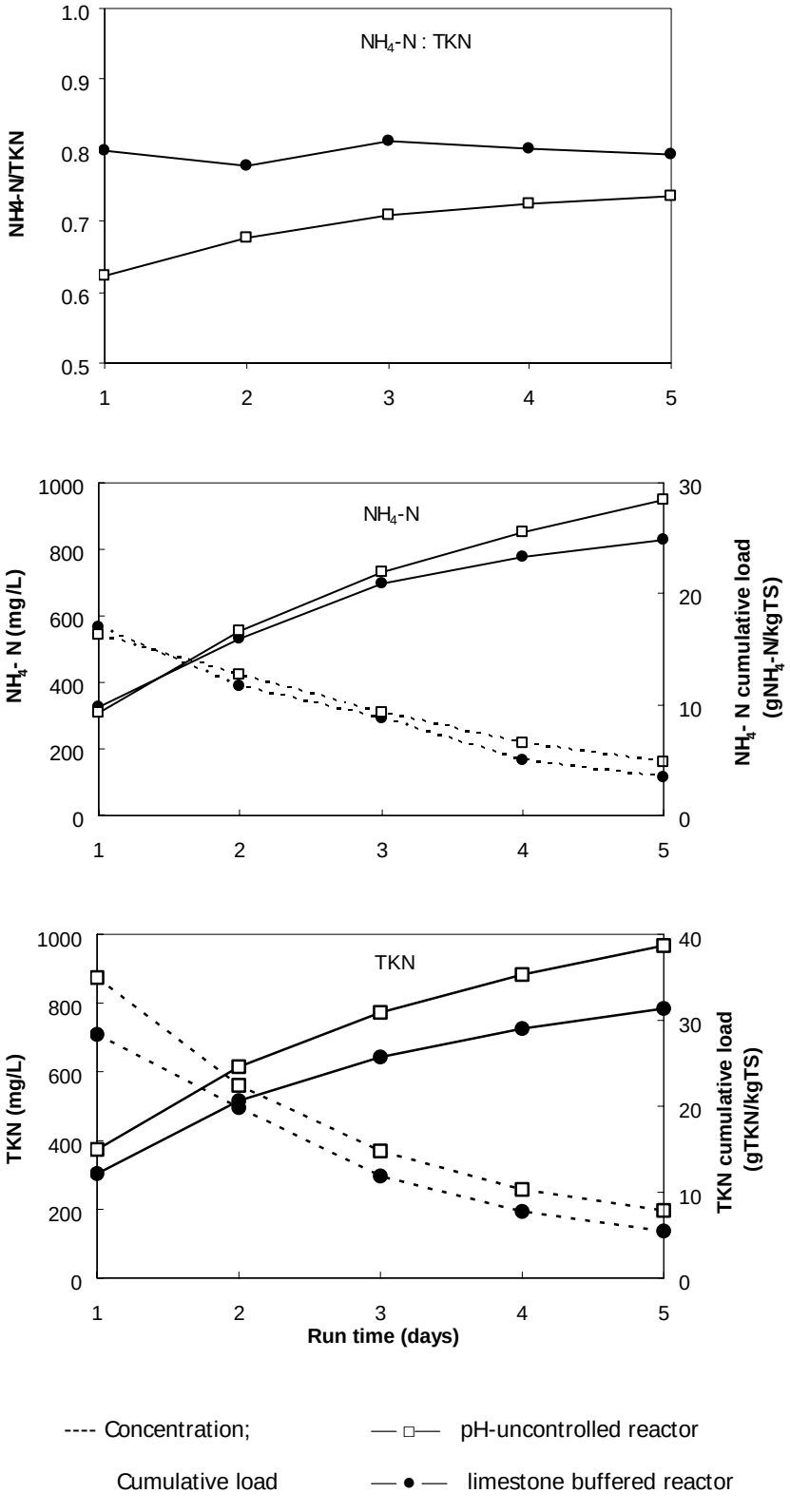


Figure 4.14 Variation of NH_4-N, TKN and NH_4-N : TKN ratio (Run2)

The effect of pH on hydrolysis could be observed in run 2. Limestone-buffered reactor, reactor 1, exhibited higher DOC and TDS in concentration of daily leachate thus the cumulative load in the total leachate. It favors the hypothesis that higher pH of around 6 would favor hydrolysis over lower value of around 5 and is in good agreement with some authors who found that low pH suppress proper hydrolysis. According to Verrier et al. (1987), an aerobic liquefaction of vegetable wastes was not satisfactorily achieved without control of the pH above 6.5. It was pointed out earlier by Le Ruyet (1984) that in spite of improved cellulose activity under slightly acid conditions, pH value lower than 6 may strongly decrease the growth rate of hydrolytic bacteria (cited in Verrier et al., 1987).

Degradation of proteins, which was evaluated based on the concentration and cumulative load of soluble TKN and NH_4-N, is depicted in Figure 4.14. As compared to the pH-uncontrolled run, the limestone-buffered reactor produced higher concentration of TKN in all daily leachate. It would give a hint that higher pH enhance hydrolysis not only of hydrocarbon but also of proteins. While TKN was significantly higher with higher pH, NH_4-N did not show the significant increase with pH. As consequent, the NH_4-N ratio was higher in pH-uncontrolled run. However, anaerobic degradation of protein is slight increase with run time in limestone-buffered run. As a whole, degradation of protein were high in both runs showing the easily degradability of the nitrogenous substrate. A fraction of around 0.6-0.8 of soluble nitrogen was in the reduced forms.

As a whole, in reactor 1, there was a better yield in hydrolysis of not only carbonaceous but also nitrogenous material. The results demonstrated the fact that higher pH range of 5.7-6.0 (Reactor 1) favored hydrolysis over the lower pH range of 4.9-5.6 (Reactor 2).

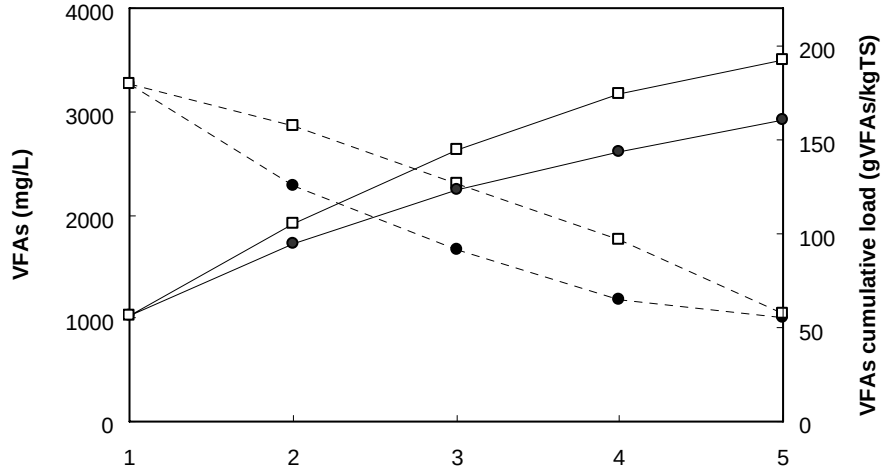
The effect of pH on hydrolysis presented is in good agreement with earlier researches. It was reported that the biodegradability of both nitrogeneous and carbohydrate compounds is positively effect by the increase of pH from 5 to 7. Eastman and Ferguson (1981) found that degradation of nitrogenous components was very fast at pH 5.17 and followed first-order kinetics. The “bell shaped” curve of the relation between enzyme activity and pH during hydrolysis established by Chaplin and Bruckle (1990) showed the optimum pH at 6.5 for both the total COD and the proteineous COD According to Boon (1994) the hydrolysis constant is slightly increases with increasing pH for both proteins and total COD.

3. Acid production

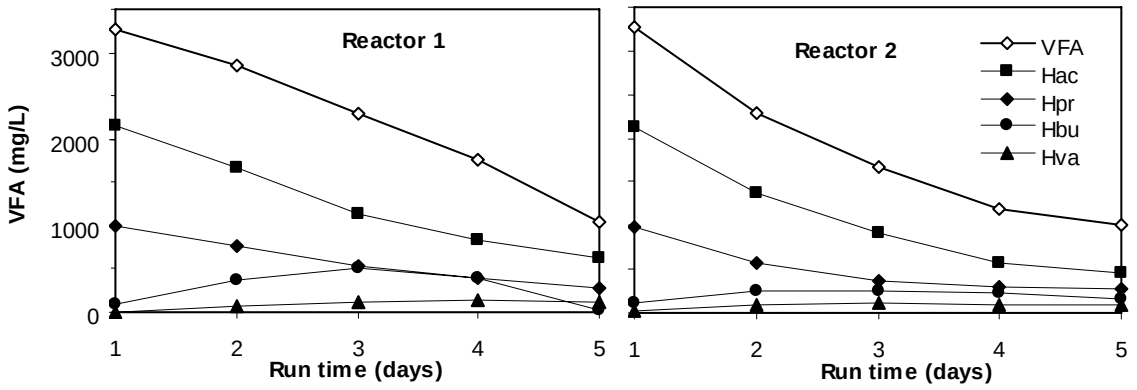
Higher pH value had the positive effect not only to hydrolysis but also to acidification of soluble and hydrolyzed products. This is clearly presented by the VFA curves in Figure 4.15. That VFA cumulative load increased with run time were observed in three reactors but with different rates in two pH range of leachate. In the reactor 1, where the pH value was higher, the VFA load at the end of this period was 192 g/L while lower values of 162 mg/L and 158 mg/L were observed in reactor 2 (Table C-6). It suggested that pH value of around 6 favored acidogenesis over lower pH.

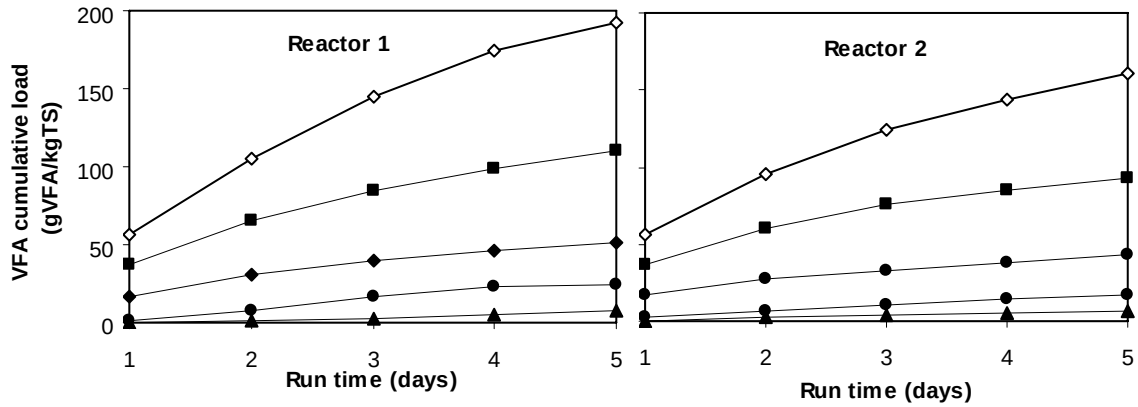
The results reported by Verrier et al. (1987) showed that both productivity and quality of the liquefaction products are very dependent on the parameter such as pH and temperature. At pH of 4.0, fermentation yield was very low whereas, at pH 5.5, the fermentation yield were about 40% and when the pH was controlled at 7, or 6.5, the fermentation yield was increased to more than 50%. Then the author concluded a minimal pH of 6 is necessary to obtain the satisfactory fermentation yields with the polymerized wastes. This is in good

agreement with the results published by Arntz et al. (1985) on anaerobic hydrolysis of beet pulps.



a) Total VFA





b) Individual VFA

Figure 4.15 Variation of VFA concentration and cumulative load (Run 2)

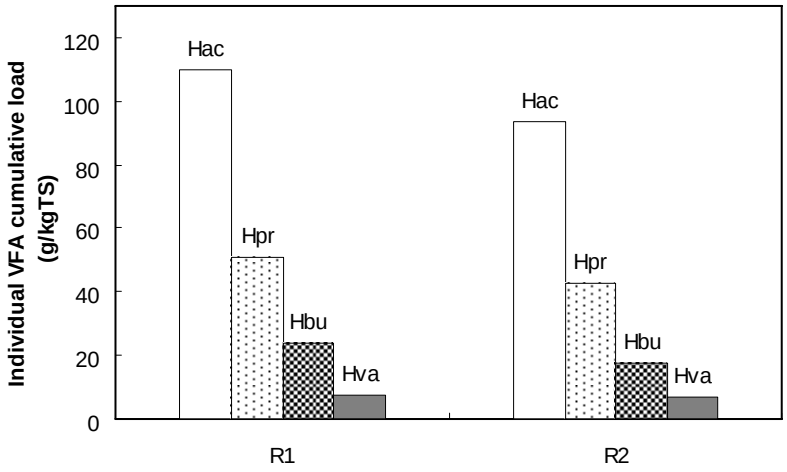


Figure 4.16 Individual VFA load in total leachate (Run 2)

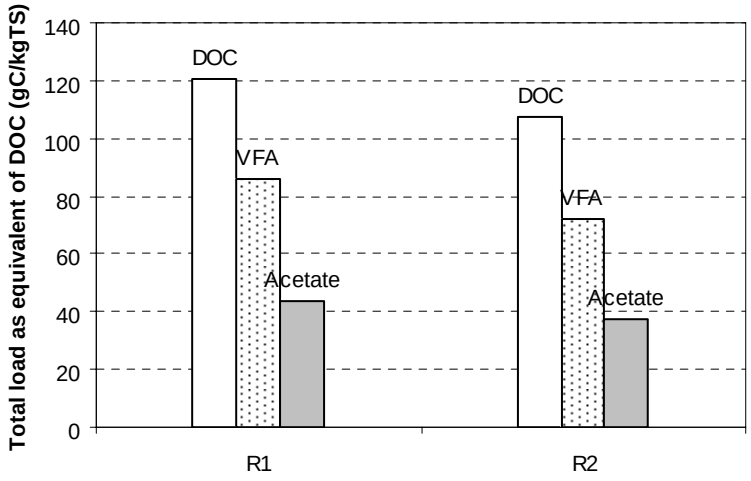


Figure 4.17 DOC, VFA and Acetic acid load in total leachate (Run 2)

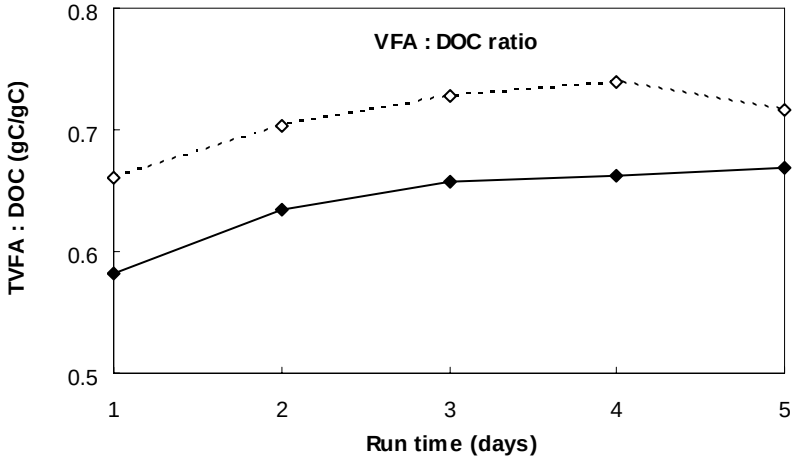


Figure 4.18 VFA: DOC and Acetic acid: VFA ratio (Run 2)

One possible reason is laid on the dependence of VFA dissociation on pH. Lower pH prevents VFA from ionization. The un-inonized acidic species have been reported as more toxic because they can more easily diffuse to the inner parts of the cell (Andrews, 1969, Pohland and Martin, 1969). In accordance with D'Addario et al. (1993), the resulting high level of non-inonized acids contributes also to the inhibition of acetogenesis. A critical role is played by the pH and consequently by the concentration of non-ionized acids. Replicated experiments carried out under pH maintained at 6.5 by continuous addition of sodium hydroxide, showed in fact a remarkable increase of acids concentration and yields. Under pH controlled at 6.5, the batch system gave better performance both in terms of Total VFA concentration and conversion yield.

According to Anderson et al. (1982), to identify the cause of inhibition or define suitable condition for acidogenesis/methanogenesis, both VFA and pH must be considered. Wang and Wang (1983) pointed out that both ionized and un-ionized acid could cause inhibition. Ionized VFA is thought to be inhibitor at pH higher than 6 whereas, at pH lower than 6, inhibition is due to non-inonized one. However, unionized VFA is much more inhibitory than the ionized ion.

Ghosh and Klass (1978) found that the optimum pH for the fermentative acidification stage of their small-scale two-stage digestion of sewage sludge or glucose was 5.7-5.9. Cohen et al (1979) ran the acidification stage of a two-stage digester using glucose at a pH of 6.0. Zoetemeyer et al. (1982) confirmed an optimal growth rate on acidogenic dissimilation of glucose achieved at pH 6.0. In addition, stable operation of the acidogenesis of carbohydrates in a single as well as two-stage anaerobic process is hardly possible in the pH range of 6.0 –8.0. The authors suggested that running the acid reactor in the pH range of 5.7-6.0 offered a stable and most favorable substrate for the methane reactor.

4. Acidogenesis vs. hydrolysis

Total dissolve carbon (DOC) includes VFA and unacidfied hydrolysate. Out of VFA, acetic acid is the desired intermediate for methane formation. Other VFA must be converted to acetic acid before forming biogas, the process called acetogenesis. The variation of concentrations and cumulative loads of three important soluble products: DOC, VFA and acetic acid in leachate were presented in Figure 4.17.

As discussed above, higher pH would favor hydrolysis and acidogenesis since the DOC yield and VFA yield is higher. Additionally, when looking at the ratio of VFA: COD, it could be seen that in limestone-buffered run, the ratio is significantly higher. Then it could be concluded that pH range of 5.7-6 could result in higher conversion of hydrolysate into organic acid. In other words, higher pH favored both acidogenic and liquefaction but more with acidogenic. In limestone-buffered run, a yield of up to 70 % of DOC was acidified after 5 day in comparison to the value than 65 % in pH-uncontrolled run. This ratio increased with run time indicating the improvement of acidogenesis over the time.

Distribution of VFA reflexes the same situation as observed in Run 1. Acetic acid is still the predominant component in total VFA produced in daily leachate (Figure 4.16). Around 60% of acetic acid in total VFA was produced initially in both cases. It appeared that the acetogenic step occurred early as the digestion take place. There was no effect of pH on the distribution of acetic acid in total VFA .

Individual VFA concentrations in daily leachate as well as cumulative loads in total leachate were graphed in Figure 4.15. The figure exhibited the same trends of individual VFA as previous run. With time, the fraction of longer-chain VFA out of total VFA in daily leachate seemed to increase. The main difference can be extracted on the figure is the behavior of propionic acid which is in higher concentration in high pH reactor.

5. Effect of pH on flushing and acidification: comparison of Run 1 and Run 2

Figure 4.19 presents the total pollutant loads of important parameters of 5 days of flushing for three different pH ranges. The leaching results of run 2 with limestone buffering reactor(pH 5.7-6.0) as well as pH-uncontrolled reactor (pH 4.9-5.6) are compared with that of non-aerated reactor in run 1 in which pH was not controlled (pH 5.3-5.7). No matter pH was controlled or not, the effect of pH was clearly depicted.

The figure depicts that, for almost parameters, higher pH resulted in higher pollutant loads in acidified leachate. The highest pH range from 5.7-6.0 in limestone buffered reactor resulted in the highest pollutants loads extracted from the solid bed, except for DOC. pH-uncontrolled run 1, which had higher pH range (5.3-5.7) compared with pH-uncontrolled run 2 (4.9-5.6), also showed the higher pollutant loads of all parameters except for TKN. Therefore, it strengthens the assumption that higher pH could favor the transfer of fresh biomass into hydrolysate and acidified products.

In conclusion, the results show the possibility to enhance acid production by providing the gravel support. There is a possibility of further improvement of hydrolysis/acidogenesis in higher pH than 6. However, in the concept of phase separation in these process, the pH of around 6 or a little bit lower seemed to be the optimum value for flushing and acidification since it not only causes the higher yield on hydrolysis and acidogenesis but also is able to suppress the methanogenic activity. In addition, adjusting pH from the lower value to 6 or, in other words, providing buffering capacity, is a preparation step for the solid bed to easily switch to methane phase, which require neutral pH.

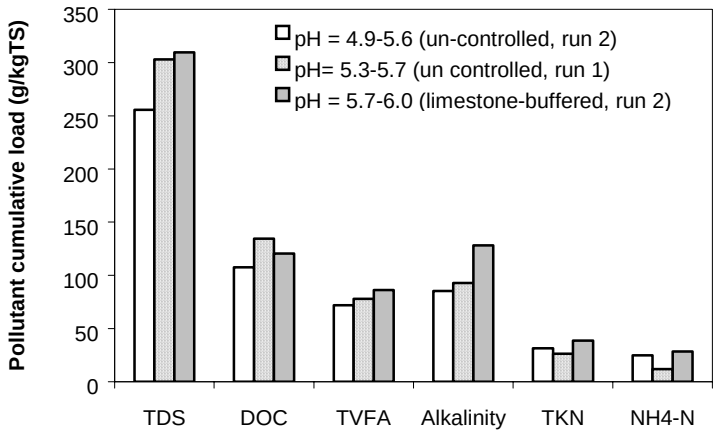


Figure 4.19 Effect of different pH range on 5-day flushing and acidification (Run 1 & Run 2)

4.2.3 Effect of intermittent aeration (Run 2)

In run 2, aeration was applied by different means from previous run. In previous run, aeration was done alternately with leaching with interval of 4 h run/4 h stop. However, aeration may be interfered with leaching with this mode of operation. Therefore, in reactor 3 (run 2), after two days of flushing, aeration was applied during day 3 and 4, without leaching and at the same interval. The last day was spent for leaching. Thus leaching was carried on totally in three days. Operation conditions for non-aerated run and aerated run were same for the first two days.

Pollutant cumulative loads after 5 days (third day of flushing) in aerated run were compared with that of after 3 days and 5 days in anaerobic run (Figure 4.20). Compared with 5-day flushing results, pollutants loads in aerated run were much smaller for all parameters analyzed. In comparison with 3-day flushing result, the results did not show significant difference. DOC and VFA were quite similar, TDS was a little bit smaller, and TKN was a little higher. It seemed that aeration and leaching scheme applied in reactor 3 did not favor leaching and acidification in pre-stage.

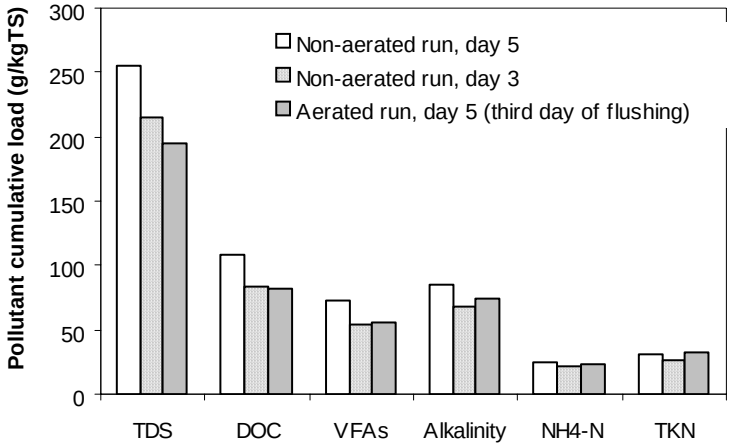


Figure 4.20 Effect of aeration on flushing and acidification (Run 2)

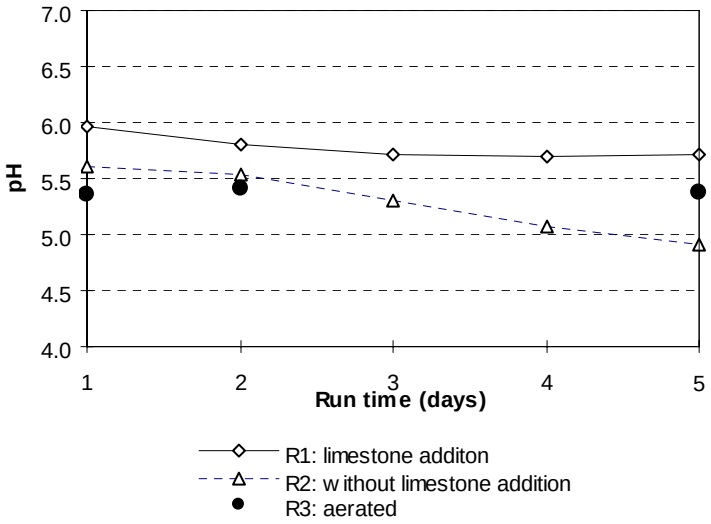


Figure 4.21 Effect of aeration on pH (Run 2)

Figure 4.21 shows the pH variation in leachate from three reactors in run 2. It was noted, from the first run, that aeration increased pH. This was possibly due to higher carbon dioxide produced during aerobic metabolism which acted as alkalinity buffering pH. In run 2, there was also the effect of aeration. It seemed that aeration caused a slight rise in pH. The pH value in the aerated run, despite the lower initial value (pH 5.4), could remain unchanged until the end of flushing period whereas pH reduced sharply in other pH-uncontrolled runs. This pH value of 5.4 was a little bit higher than 3th day leachates in non-aerated reactor 2 (pH 5.3) (Table C-2) and much higher than pH 4.9 of 5th day leachate same. Higher pH value at the end of pre-stage would favor methanogenic activity of next stage and require less chemical to neutral solid bed.

4.2.4 Effect of amount of flushing water (Run 3)

According to previous study on leaching (Dayathi, 2003), periodic leachate removal seemed to be a better option in the viewpoint of enhanced leaching. Following this result, in run 1, 2, every day new 200L of tap water was applied. In one hand, larger addition of water could improves the possibilities for potentially soluble material to dissolve. Since accumulation of VFA is the cause for inhibition of hydrolysis process, it is possible for digester, at low VFA concentration, to produce more acids. In another hand, additional water might cause unnecessary dilution as well as flushing of hydrolytic bacteria probably resulting in low acids production. Wheatley (1990) reported that concentrations up to 3000 mg/L did not cause inhibition. Since VFA concentration observed in leachate is low, of less than 2000 mg/L (Table C-4) on day 3, it is possible to reduce the amount of water use Low dilution water can reduce water applied, concentrate VFA in the leachate for next methane phase. In Run 3, instead of 1000 L used for flushing in 5 days, the case of reactor 1, in reactor 2, and 3 only 600 L was applied.

Comparison is based on reactor 1 and 2, where no aeration were provided. At the first day, the same amount of 200 L tap water were applied for reactor 2 and 3, thus same concentration and cumulative load were observed. In reactor 2, the leachate resulting from day 2 was keep for recirculating in the day 3. Therefore, the concentration of leachate is higher. Similarly the concentration of pollutants in day 5 is higher in reactor 2 than reactor 1 since leachate in day 4 were used for flushing of day 5. The load in cumulative leachate gives better evaluation.

As depicted in Figure 4.22 for DOC and VFA, there was no significant change in cumulative load of DOC and VFA. Instead of 1000 L tap water used in reactor, only 600 L of water was applied in the reactor 2 but the same pollutant loads of DOC and VFA could be obtained. It indicated that high VFA concentration of 5000 mg/L observed in 3 day leachate in reactor 2 (as compared with 3000 mg/L in reactor 1) and 4000 mg/L in 5 day leachate (as compared to 2500mg/L) did not show any inhibition of VFA on hydrolysis and acidification. This offered the possibility to save the water, as well as concentrate the pollutant in leachate without any adverse effect. With concentrated substrate, it would be easier to finish the acidified leachate in the methane phase.

4.2.5 Effect of micro-aeration on flushing and acidification (Run 3)

In reactor 3, small rate and short time aeration was applied to create the microaerophilic condition. To evaluate the effect of microaerophilic on hydrolysis and acidification, reactor 3 was compared with reactor 2. Within such a short time of flushing period, there is no

interesting point in microaerophilic since it did not cause either lower or higher load in VFA and DOC as compared with non-aerated reactor 2.

4.2.6 Intermittent solid waste feeding (Run 3)

Intermittent solid waste feeding was applied in three reactor of run 3, whereas in previous run, solid was fed once initially. Total 220 kg of waste could be loaded in run 3, compared with 120 kg in run 1 and 2. The result shows no significant different in terms of pollutant load that could be extracted from the waste bed into leachate. Optimum compaction density of 500 kg/m^3 provide for the new waste layer could be the reason for the comparison yield.

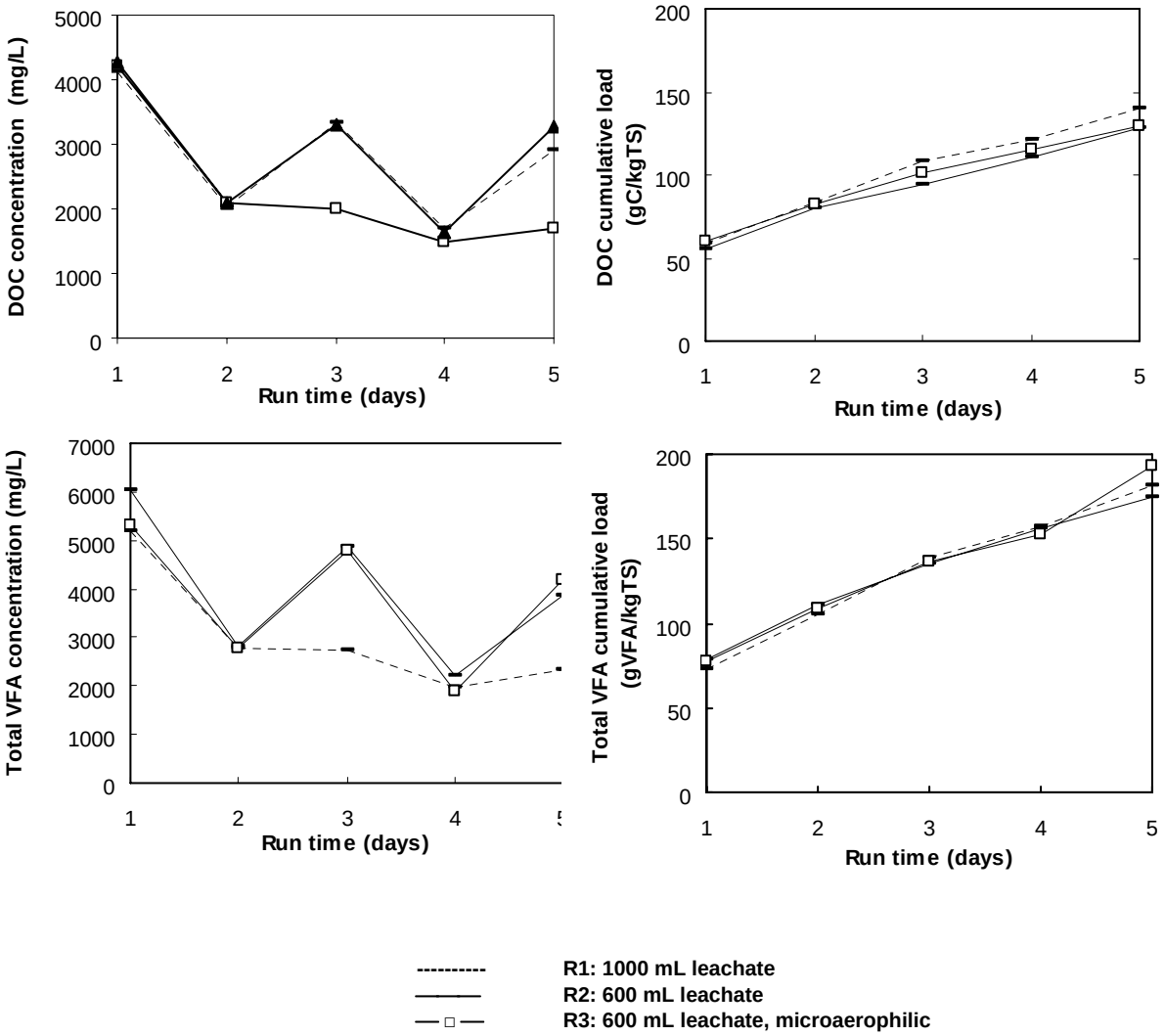


Figure 4.22 Variation of DOC and VFA cumulative load (Run 3)

Considering the higher amount of waste that is loaded into the reactor as well as the lower water consumption for flushing, overall, in this run, same hydrolysis yield and acidification yield was obtained as compared to run 1 and run 2. (130 mgDOC/kg TS as compared to 140 gDOC/kgTS in Run 1 and 123 kgDOC/kgTS in Run 2). Acidification did not show any different from previous run; distribution of organic was predominant by acetic acid and total organic acid accounted for more than half of organic load (Figure 4.24, 4.26).

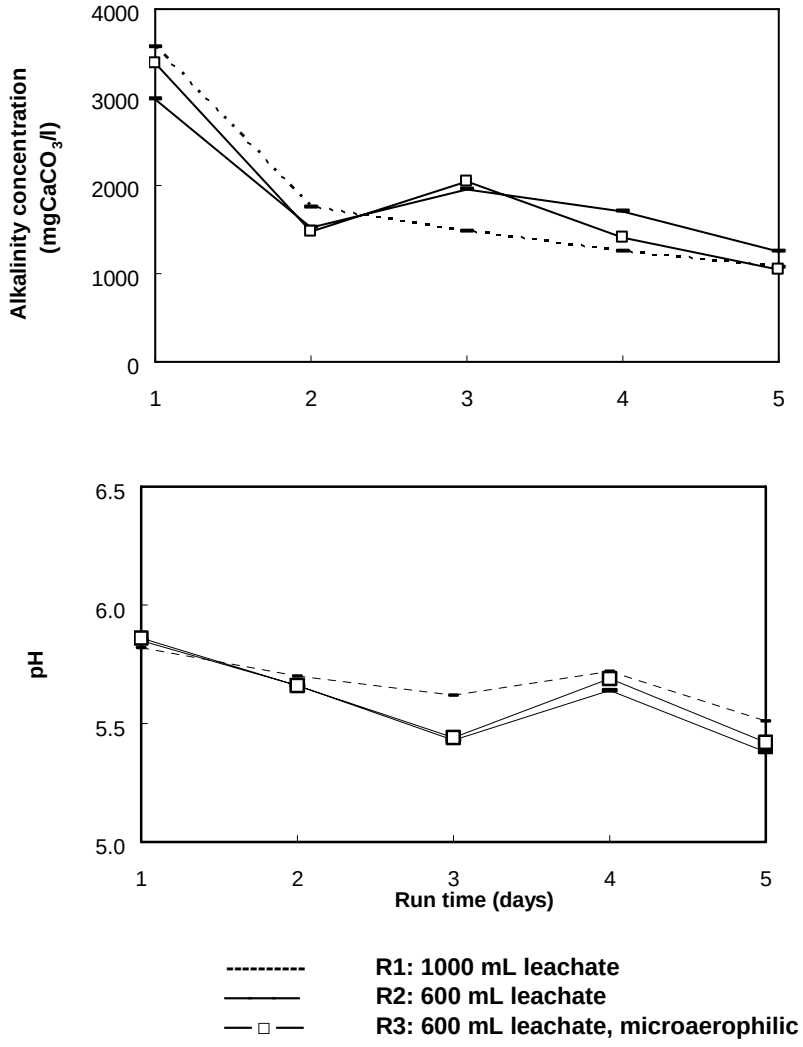


Figure 4.23 Variation of VFA and pH in daily leachate (Run 3)

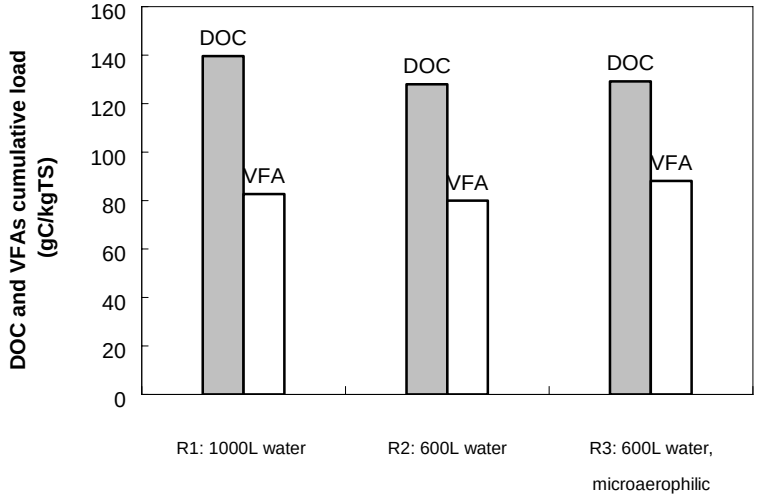


Figure 4.24 DOC and total VFA load in total leachate (Run 3)

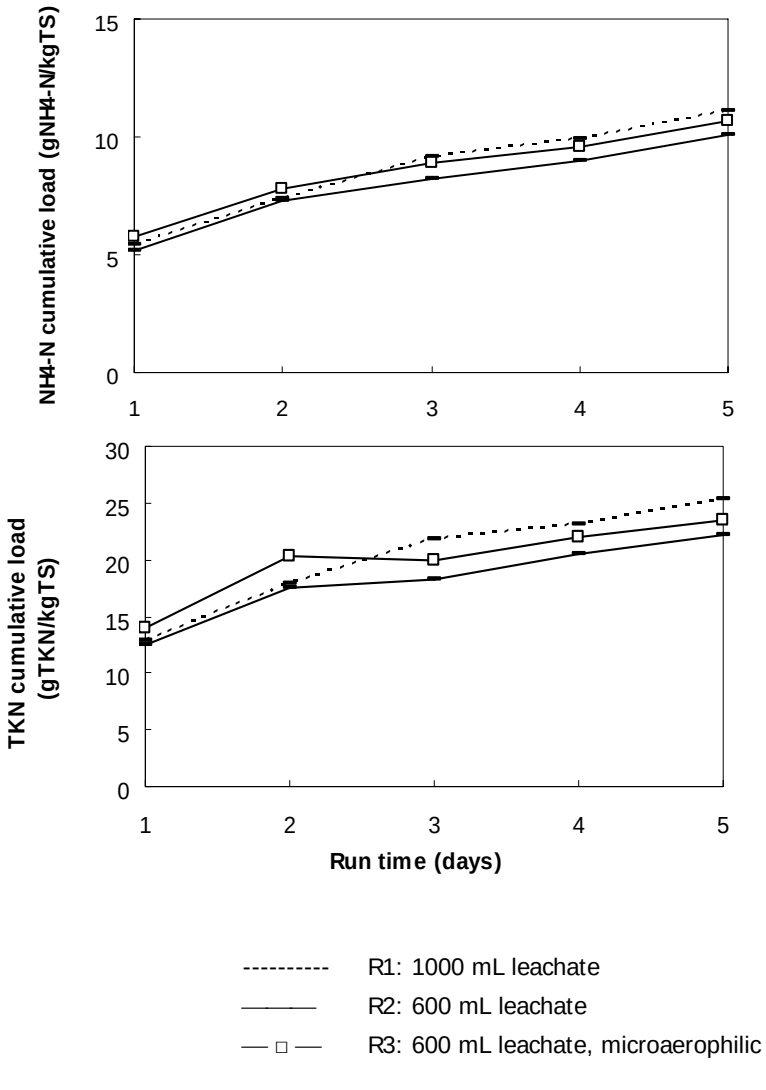


Figure 4.25 Variation of TKN and NH_4-N load (Run 3)

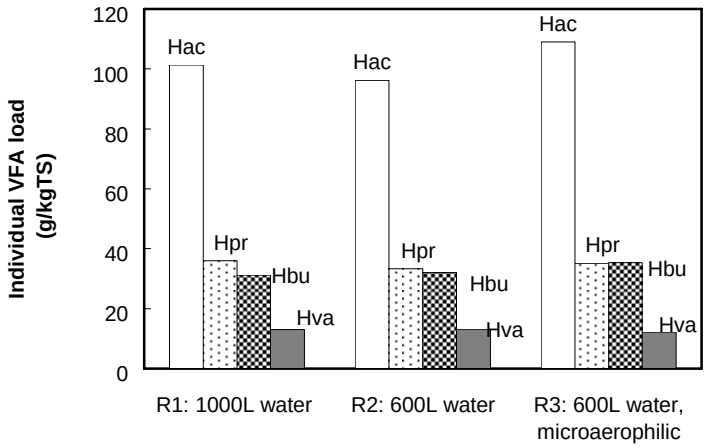


Figure 4.26 Individual VFA load in total leachate (Run 3)

4.2.7 Overall assessment of flushing and acidification

The hydrolysis and acidification yield (gram pollutant/kgTS) of all runs were presented in Table 4.2 and Table 4.4. In non-aerated reactor, reactor 1 the highest yield of from 120-140 kgC/kg TS was obtained. This yield is equivalent to approximately 30% of carbon that could be extracted from the waste bed into leachate. During such a short time of flushing, 30% of organic carbon could be extracted from the waste, showing the good results (Table 4.3). Hydrolysis appeared to be very high in this early stage since it is likely that readily soluble material could contribute the large fraction. In addition, suspended solid fraction leachate would also contribute to TS loss of the waste of more than 50% (data in run 1). The results exhibit the importance of early flushing in reducing the load from the waste bed, which is the major constraint in the high-solid anaerobic digestion.

Table 4.2 Hydrolysis yield (gC/kgTS)

	Run 1	Run 2	Run 3
Reactor 1	138.42	123.86	139.59
Reactor 2	114.88	107.63	128.06
Reactor 3	107.85	82.52	129.17

Table 4.3 % C removal into leachate

	Run 1	Run 2	Run 3
Reactor 1	31.36	27.66	31.75
Reactor 2	26.03	24.04	29.12
Reactor 3	24.43	18.43	29.38

Anaerobic reactors also exhibited the highest acification yield (Table 4.4. Reactor 1, Run 1, Run 2, Run 3). After 5 day of flushing (in run 1 and run 2) and 7 day (in run 3) a approximate yield of 0.18gVFA/g TS (correspondent to 0.225 g/gVS). This yield much higher to value 0.12 g/gVS (Vieitez and Ghosh, 1997) in pH range of 5 and comparable to the value of 0.22g/gVS at more favorable pH value of 6.5 (D'Addario et al, 1993).

Table 4.4 Acidification yield (gVFA/kgTS)

	Run 1	Run 2	Run 3
Reactor 1	171.74	182.67	181.53
Reactor 2	144.25	160.11	174.67
Reactor 3	137.75	119.98	193.23

With respect to effect of aeration on leaching enhancement, it could be seen, from the Table 4.4, that aeration (Reactor 2-Run 1, Reactor 3-Run 1), did not cause in improvement of neither hydrolysis nor acidification. Microaerophilic condition in Reactor 3-Run 3 could bring a little bit higher acidification yield as compare with others. However, the result were still equivocal.

Acidogenesis occurred early since more than half of carbonaceous hydrolysate was convereted to VFA. Considering short solid retention time, among the various type of VFA, acetic acid was the major product. In one hand, the accumulation of VFA inhibit the hydrolysis of polymer and acetogenesis of higher VFA to acetic acid (Angelidaki, 1992). In another hand, inhibiting levels of fatty acids may also occur during overloads with substrates for which methanogenesis rather than hydrolysis is the limiting step. Therefore,

it could be concluded that early production/flushing of VFA from the waste bed would certainly lessen the possibility of inhibition caused by VFA accumulation both in hydrolysis and in methane phase. The result also bears out the significant of short time flushing of 5 days since further flushing seemed not to be effective.

According to Daynathi (2003), Liquid: Solid ratio of 2: 1 was the optimum value for leaching. However, the result here showed that it is not necessary to use that much water. In run 3, only 600L of water was used to flush 200 kg of waste during 5 days without reducing the organic load in leachate. Therefore, average Liquid: Solid ratio of 0.5:1 daily basis could be applied. pH value have major effect on hydrolysis and acidification. By supporting partly limestone gravel in the bottom of the reactor, the pH of leachate could increase significantly consequently raise up the pollutant load in the leachate.

Flushing resulted in significant settlement of the waste bed with 40% volume reduction Intermittent solid waste feeding during flushing provides the benefit to utilize the headspace of the reactor. At the final, total compaction density of 750 kg/L was obtained while the optimum density for flushing still was maintained in new layer of fresh waste.

4.3 Optimization of main stage

4.3.1 Starting-up methanization (Run 2)

Starting-up methane phase is claimed to be inhibited by the accumulation of VFA accompanied by the low pH (Ghost et al, 1987, Kisaalita et al., 1987). This is because methanogens, different from hydrolytic and acidogenic bacteria, are especially sensitive with pH environment. To solve this constraint, acidified products was washed out into leachate during pre-stage, as discussed earlier. It was expected that partial removal of VFA from its site of formation would raise the pH of the waste bed in methane phase.

Based on this rational, after 5 days of flushing, the system was incubated in anaerobic condition without any actions. Since methaongenic bacteria have very slow growth rate, it would certainly take a lag phase for them to get acclimatize the waste bed. During start up period, methane content in biogas as well as daily gas production would be increasing. Due to very slow biogas production in all reactors, the measurement of daily gas production could not be obtained. Biogas composition of 50% CH_4 was used as an indicator for success start of methanogenesis.

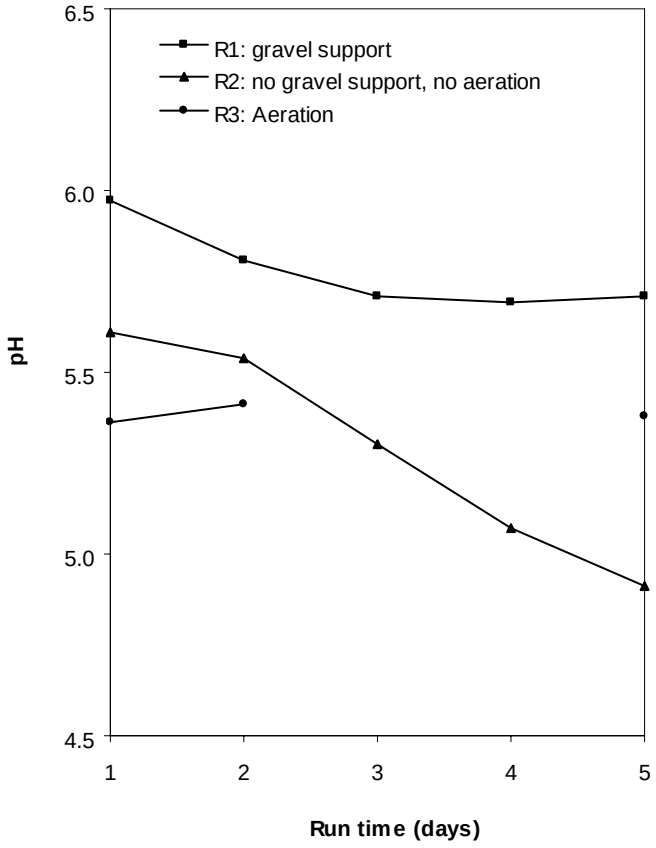
Figure 4.27 depicts the variation of pH in flushing and acidification stage as well as methane content in biogas during start up methanization. It could be seen that the reactor 1 showed much better results in start up methanogenesis. The methane content increased significantly in growing trend as compared with reactor 2 and 3. The reason could possibly be in the higher pH at the end of flushing period, which can be easily observed in this figure.

Until day 22, no pH adjustment was conducted in all three reactors. During this period, methane composition in reactor 2 and 3 were very low of less than 10%. A comparison of composition between these two reactors shows a little bit higher methane composition in reactor 2. Again, it could be explained by the effect of pH on methanogens. In reactor 2, due to effect of aeration, consequently higher pH, a better performance of methanogenesis was noticed.

Right after pH adjustment was done in reactor 2 and 3 (day 22), the trend in gas composition changed positively. The adjustment was based on the target pH of higher than 6.5 in effluent leachate, using NaOH. In reactor 2, pH of the leachate was adjusted daily for 5 days to show the better performance as compared with reactor 3 where pH was adjusted for only one day. Here, with pH adjustment, methane composition was 25% at day 36 whereas less than 10% still observed in reactor without daily pH adjustment.

The results reveal the fact that, without adjustment of pH, it would take long time for the system of low pH to reach methane phase (30 days for reactor 2 to reach 40%). Even with the earlier extraction of VFA from the waste bed, the pH of the system was still low. Low pH might be due to low buffering capacity of the waste together with high VFA concentration. After flushing, VFA might reduce in load but high in concentration because of no additional water. Consequently, the pH in the waste bed seems not to be able to rise naturally to the neutral level. In addition to that, one possible reason resulting in the long time start up is the lack of high population of methanogens and lack of mixing moisture content.

→ a) Flushing and Acidification



→ b) Starting up methanization

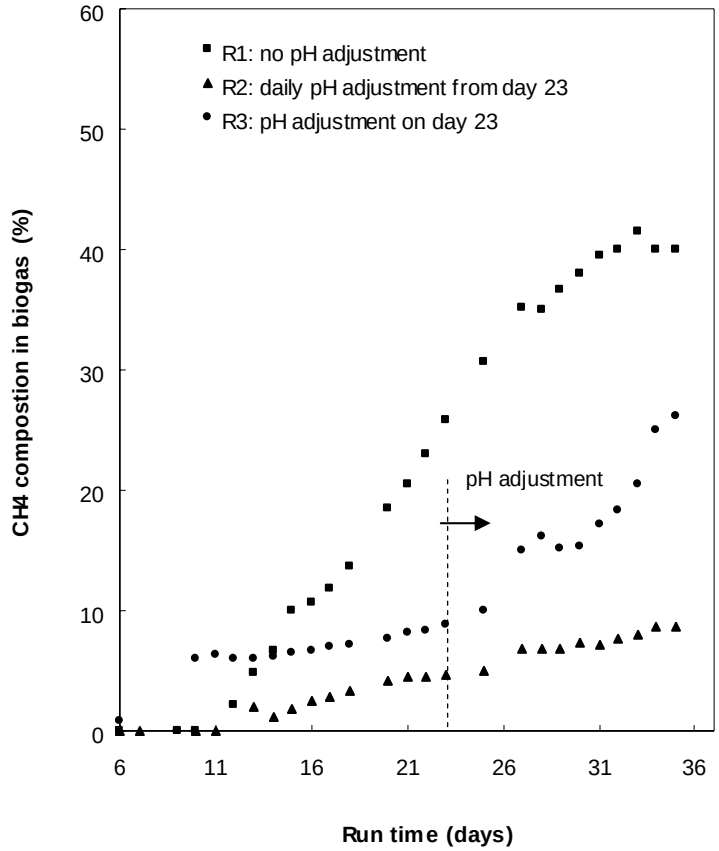


Figure 4.27 Performance of Start up methane phase following Flushing and Acidification (Run 2)

The necessity of pH adjustment in low buffering capacity waste was also reported by earlier researchers. When starting anaerobic digestion of solid waste, care should be taken to provide buffering media (Biey et al., 2003). In the study of Chugh et al. (1998), the leachate was recirculated back over the waste after adjusting its pH and the commencement of indirect recirculation of leachate was carried out until the pH of effluent leachate from the fresh-waste reached a value ≥ 6.5. Mohee et al. (2003) conducted SEBAC for organic waste. According to the authors, the pH of the system was very low, reactor was unstable, and to avoid the risk of the reactor souring, alkalinity was added to increase the buffering capacity of the feedstock.

Finally, even with the adjustment of pH and significant increase in methane content, gas production was low. In this case, we could not measure daily gas production. It reveals that even with pH adjustment, methanogenesis still was delayed. It may due to the low population of methanogens in the waste. This trial run not only signified the importance of pH adjustment but also offered the need of inoculums addition.

4.3.2 Methanization stage (Run 3).

1. Performance of digester in methanization (reactor 3)

The successful and typical performance of methanization was observed in reactor 3. The behavior of methanogenesis in this reactor is described as following.

Lag phase (starting up)

The first period of methanogenesis is the time for methanogens to acclimatize in the digester and start producing biogas with increasing methane content. Figure 4.28 depicted that it took around 25 days for the methane content in biogas to reach composition of 50% in all three reactors. In anaerobic system, the predominance of CO_2 in gas production indicates the strong activity of hydrolysis over methanogenesis. On the other hand, higher CH_4 implies strong activity of methanogens. Methane content gradually increased until day 25 to the value of 50% then quickly rose and stabilized to normal biogas of 60% CH_4. The system was successfully started up.

It was noted, by Chynoweth (1993), that first time start up of the first reactor required heavy inoculums (active digester effluent equivalent to 25% of the feed volatile solids), pH control and longer retention time for completion. Additionally Bae et al (1998) found that pH of 6 was not a limiting factor for methane production and that the number of active methanogens was the most important factor affecting methane production from solid waste.

Here systems were started by two means: controlling pH and providing inoculums. pH of system was adjusted until it reached stable value of higher than 6.5 on day 1 after flushing. Once pH was stable, layers of inoculums were added on top of waste bed then distributed throughout digester by water percolation. Total addition of around 12 % VS might be an insufficient amount of inoculums, as compared with SEBAC (25%). This could be the reason contributing to the relative long start up time of the system. In reactor 3, the lag phase took nearly half of the digestion time (25 days compared with 60 days to finish the process). Of course, longer time was required for this first batch of digestion as pointed out by Chynoweth. (2003).

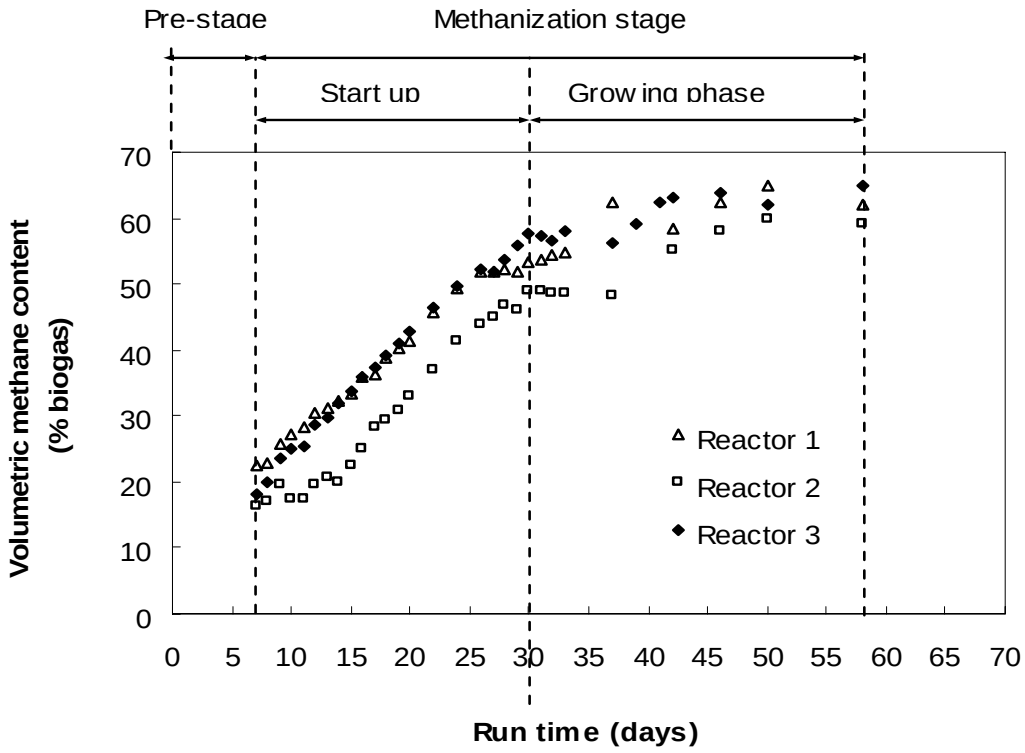


Figure 4.28 Biogas composition (Run 3)

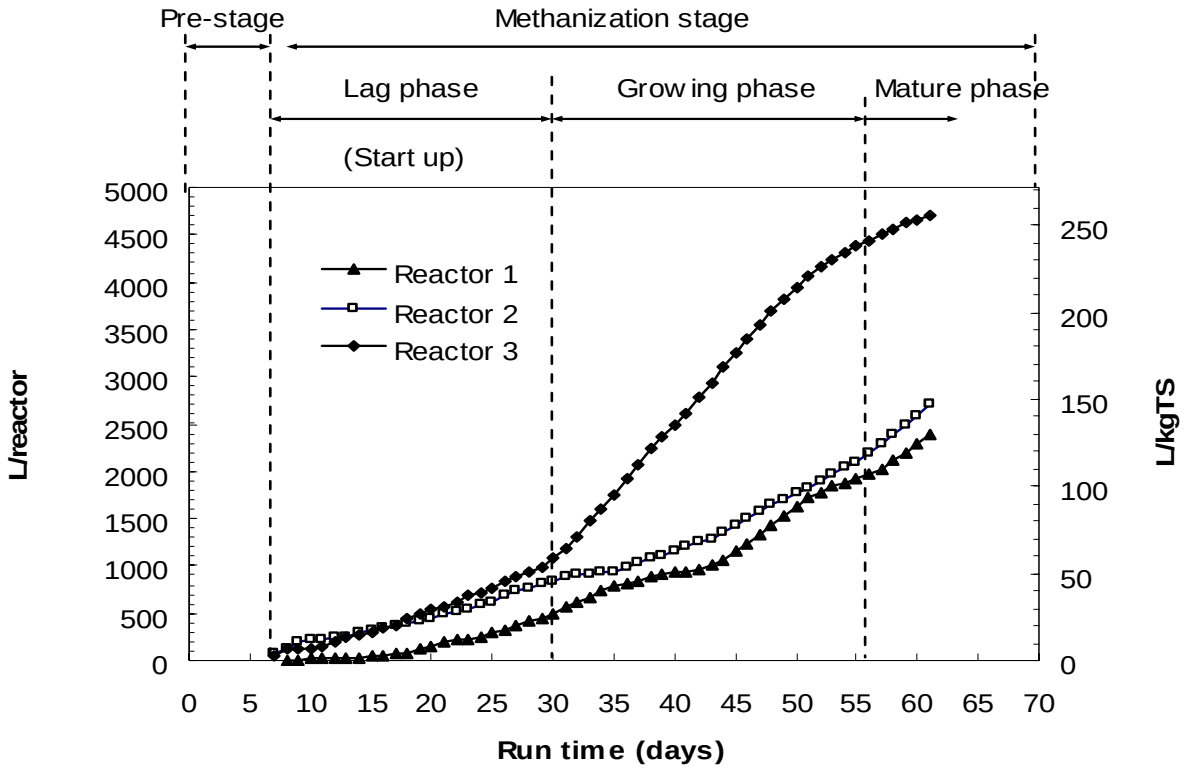


Figure 4.29 Cumulative gas production (Run 3)

Possible reason for the reactor 3 to have higher gas production rate during starting up might be due to earlier aeration. The microaerophilic condition may result in better hydrolysis/acidification during starting up of methanogenesis, offering better performance in lag phase.

The growing phase

Cumulative gas production increased suddenly after lag phase, when methane composition was stable and leachate percolation was practiced (Figure 4.29). It indicated the growing phase. The curve implied that the waste bed was sufficiently well inoculated and buffered so that methanogens worked intensively. Once escaping from starting up, the cumulative gas sharply raised.

Biogas production increased but there was no notable change in VFA of reactor 3. (Figure 4.33, leachate batch 1) The good explanation is the continuous production of volatile fatty acid from the waste bed. Thus, based on this hypothesis, the phase was still the mixture of acidic and methanogenic phase. Of course, strict phase separation could be never obtained in batch system. Here it is possible that the hardly biodegradable materials, which were still not acidified during short time of flushing, were degraded in longer solid retention time. Therefore, VFA kept producing providing substrate for methanogens. The accumulative methane yield and methane gas content rapidly increased, occasionally up to 65% in this period, indicating development of balanced methane fermentation.

Mature phase

Mature phase was characterized by long-term reduction of daily biogas production. Reducion in gas production rate was accompanied by the decrease of organic content in the leachate (Figure 4.30 and Figure 4.33). Hydrolyzed and acidified product were almost utilized in growing phase. To this period, not much further available substrates for methanogens.

In reactor 3, cumulative methane yield leveled off at about 60 days (Figure 4.29) showing that conversion was more or less completed. It is likely that only slowly-hydrolyzed compounds still remained resulting in a long-term low-level biogas production. In term of pre-treatment, the process could be stopped at this point where the cumulative gas increased slowly and the rate was less considerable.

2. Effect of leachate percolation

There were two modes of leachate recirculation, direct leachate recirculation and indirect leachate recirculation. According to literature, both modes have the objective of providing moisture content and mixing the system. The latter, in another hand, bring another objective of supplying VFA from the first stage as the substrate for methanogens.

Leachate percolation was practiced in three reactors, but started at different time. Right after escaping from lag phase, on day 30, reactor 3 was provided with percolation. In reactor 1, percolation was applied 10 days latter and reactors 2 were kept without recirculation until day 60.

In reactor 3, at the commencement of the first batch of percolation, the daily gas production was increasing very high and quite stable at the rate of 150 L/day. Recirculation

proves the means of mixing, both of bacteria and of substrate, in the waste bed. Water is essential for methane fermentation, as the nutrients for the microorganisms must dissolve in water before they can be assimilated (Foster and Wase, 1989). The moisture content may not only aid in bacteria movement, but is also known to influence the mass transportation in high solids (Gosh et al., 1985).

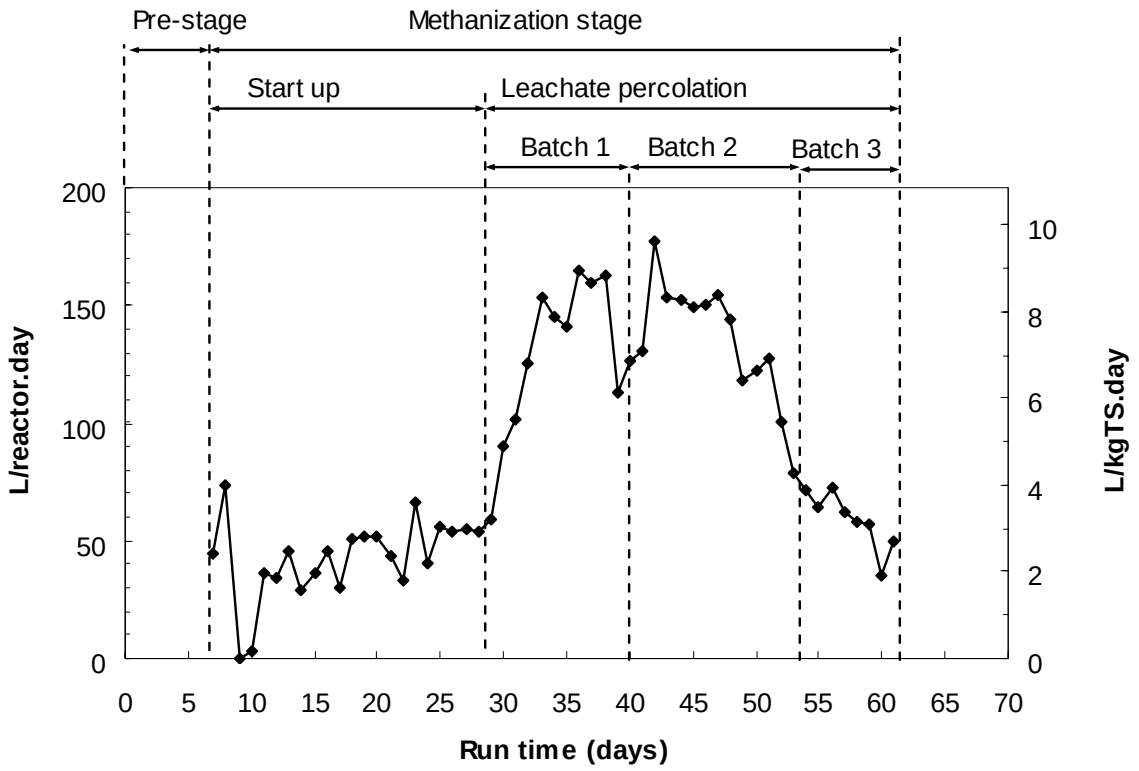


Figure 4.30 Daily gas production in digester 3 (Run 3)

During the first batch of percolation, the biogas were stable for certain period of 9 days and then suddenly reduced. However, the drop in biogas production was not accompanied by the reduction of VFA in the leachate. Concentration of propionic acid in leachate keep on increasing up to 6 mg/L. Propionic acid was thought to be the major inhibitor during methane phase (Inanc et al., 1996; Gourdon et al., 1987 Mawson et al., 1991; Pullammanappallil et al., 2001). It may be a good explanation for biogas production to reduce suddenly on day 40.

New batch of leachate was fed into the leachate tank for percolation. Interestingly, the daily gas production increased back to the level of 150L/day. Since the concentration of propionic acid in new leachate was very low, it favors the hypothesis that high propionic acid in old leachate caused inhibition.

In second batch of leachate percolation, daily gas production was stable for around 1 week then started to decrease. This time, the drop in biogas production was along with reduction of VFA concentration in the leachate. This indicated that inhibition of VFA was no longer the reason. Initially, acetic acid concentration was low. In order to produce substrate for methanogens, propionic acid was converted to acetic acid in the step called acedogenesis. This was clearly depicted by the reducing trend in propionic acid concentration in Figure 4.33.

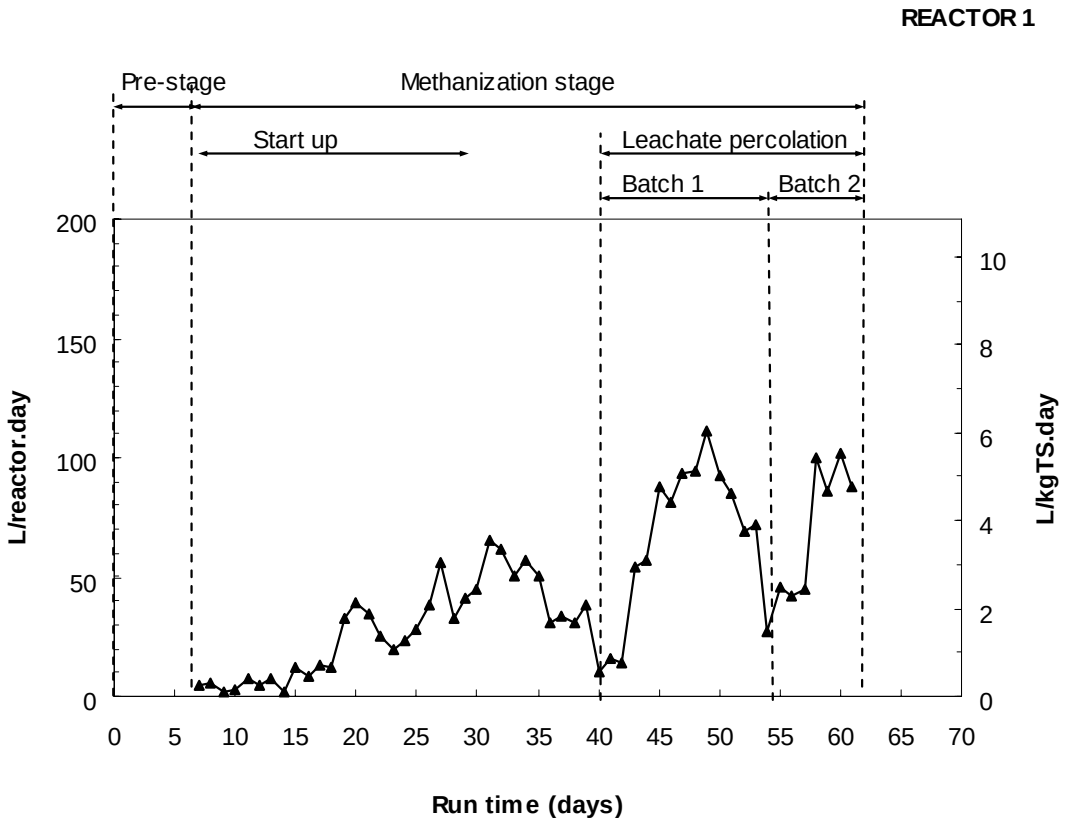


Figure 4.31 Daily gas production in digester 1 (Run 3)

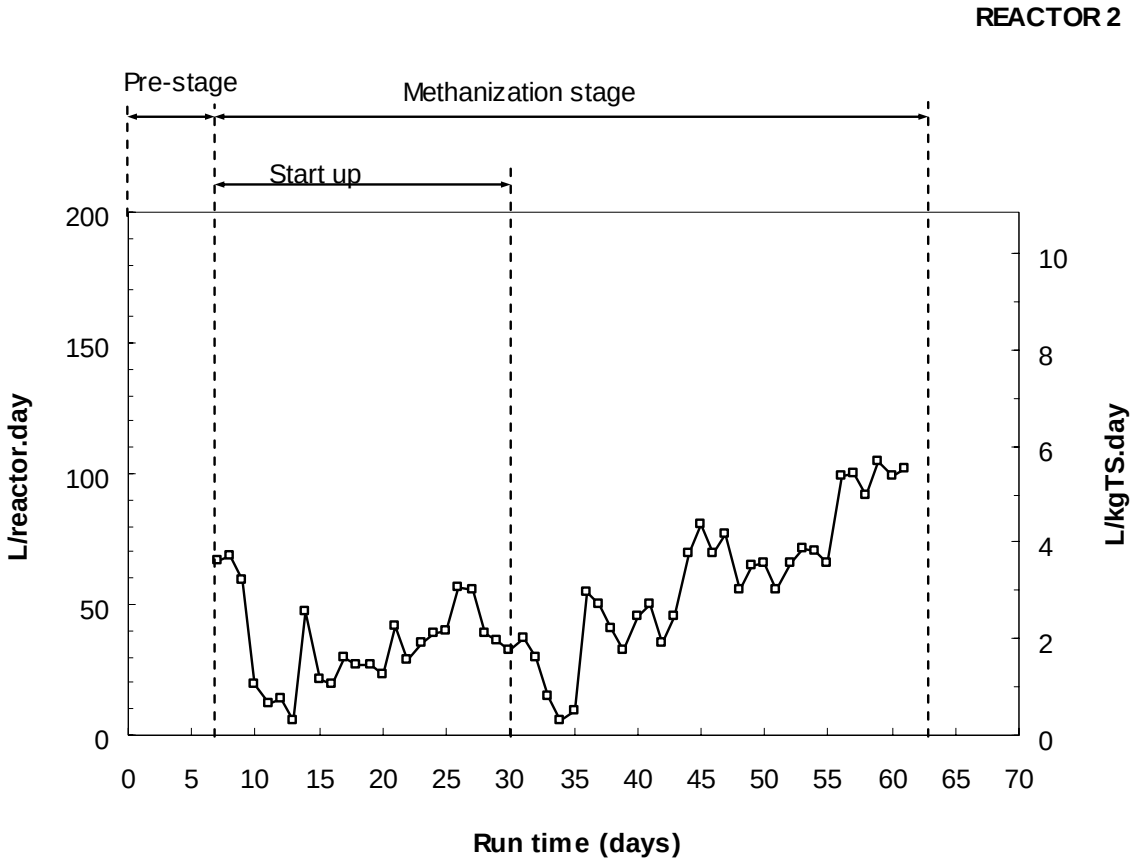


Figure 4.32 Daily gas production in digester 2 (Run 3)

Biogas production dropped at the time when all VFA concentrations were low. Here, the reduction of VFA, direct substrate for methanogens was the reason for biogas production to decrease.

A third batch of leachate was replaced, in order to supply VFA for digester. Unfortunately, the fresh acidified leachate could not be obtained. Due to long time storage with improper cover, VFA concentration reduced significantly as compared to the fresh acidified leachate. As a consequence, it was not able to provide the waste bed with high concentration of intermediate product. The system kept on producing biogas but not the high rate as observed before and the rate was slowly reducing. Long-term going down line of biogas production was observed showing that more or less the waste bed was stabilized and biogas production was less significant.

Recirculation was thought to enhance biogas production in many ways. It has been found that the digester became more stable through leachate recirculation and the degradation was faster. Most of authors agreed leachate recirculation as means to provide moisture content and means mixing (O'Keefe et al., 1993; Chanakya et al., 1992; Wang and Banks et al., 1999) Additional benefits were pointed out in literature. In SEBAC, leachate was exchange between two reactors to provide VFA from the fresh waste to mature waste and to utilize buffering capacity from the old reactor to the new one. In addition to that, the recirculation of leachate was found to be beneficial since it provided the appropriate pressure required to help the biogas come out (Mohee et al., 2003). The author argued that leachate recirculation gave a means of mixing thereby displacing the biogas which was already formed but trapped within the feed stock. On another hand, Chan et al. (2001) demonstrated that leachate recirculation was not only effective in enhancing the degradation rate of the waste and gas production but also give reduction of the overall leachate loading.

Here the results were in good agreement with those findings. The first peak of daily biogas production in Figure 4.30 signified the importance of supplying moisture content and mixing. The second peak was due to the removal of the old leachate, which is possible cause inhibition and percolation of the new fresh leachate. Finally, percolation by fresh leachate (acidified leachate) provided VFA to the waste bed where it reached mature phase. This could bring the system to further production of biogas while reducing VFA concentration in the fresh leachate.

In reactor 1, same behavior of biogas production was depicted, (Figure 4.31). At the commencement of leachate recirculation, daily biogas production from a waste, where inoculums was provide with high bacteria, increased rapid. Since leachate percolation was practiced late in comparison with reactor 3, the peak of was detected late. As a result, biogas production was in slowly increasing phase. Second peak also observed with new batch of leachate addition and percolation. The inhibition of propionic acid also was the possible reason for the biogas reduction in old batch of leachate percolation.

Regarding the cumulative gas production, reactor 3 reached the plateau after around 60 days. The stable cumulative gas was signal for the digester to be in mature phase. In reactor 2, short-term plateau could be seen from the day 25 to 35. Instead of exhibiting gas stabilization it showed the inhibition. This was overcome by the practice of leachate recirculation.

In reactor 2, where no recirculation was practiced, no peak in daily gas production was observed (Figure 4.32). Gas production rate increased slowly. Until day 60, the rate was 100 L/day. That rate was obtained at day 50 in reactor 2, and day 32 in reactor 1.

As compared with reactor 1 and 2, reactor 3 give a much better results in overall pattern in biogas production. It would favor the finding that early leachate recirculation with proper leachate management can significantly shorten the period of digestion process, quickly stabilize the waste in anaerobic biogas production.

3. Fate of VFA in leachate and pH value

During start up period, leachate recirculation was not practiced, thus VFA was not analyzed. When leachate recirculation was done, analysis of VFA in the leachate could, in some extent, explain reactors operation.

As discussed earlier, during short solid retention time of 5 days, acetic acid was the major component. Different from pre-stage, in the growing phase of methanogensis, propionic acid was highest accumulated in the systems (Figure 4.33, 4.34). Propionic acid reached the level of 4 g/L as compared to 2 g/L of acetic acid. Butyric and valeric acids were two acids accumulated with very small concentration. According to Chugh et al. (1998), butyric acid is a major acid formed by the hydrolysis of lipids. Thus its low concentration of might be due to low lipid fraction in the waste. The observation about the concentration of VFA in methane phase is in good agreement with Rees (1980). The author reported that the leachate generated from freshly placed MSW contained mainly acetic acid. Due to favorable environment condition for the acid former, mainly high pH, other acids start to appear.

pH value was stable in the range of 7.3-7.8, despite VFA concentration of as high as 6 mg/L. Thus, the change of pH and VFA seemed not to be related to each other. Chan et al (2001) found that in the methanogenic digester, pH value gradually roes to about 8 but did not appear to be related to VFA concentration. Since digester was operating in balanced phase, the observation signified the buffering capacity of carbonate HCO_3^- produced by CO_2 producing in biogas. In accordance with Lay et al. (1997), the rate of methane production at moisture contends of 90-96% functioned in a pH range between 6.6 and 7.8, but optimally at pH 6.8 and the process may fail if the pH value was lower than 6.1 or higher than 8.3. Then it could be concluded that pH range here is the optimum value for methanogenesis.

Since the pH did not drop less than 7, VFA remained in the ionized form (Chugh et al., 1998). According to WPCF (1997), if the total acids can not be changed, changing the pH and thus changing the un-ionized concentration can be a useful way of preventing toxicity. Therefore, the toxicity caused by unionized forms was prevented.

In the growing phase, acetic acid concentration in leachate showed little change. It indicated the balance between the rate of consumption and production. In one hand, propionic and other acids were kept on producing; it also converted to acetic acid consequently to methane and carbon dioxide. For many authors propionic acid, next to acetic acid, was the last acid to disappeared (Chugh et al., 1998). Similar observation was noted here. In accordance with Mtz-Viturtia et al., 1994, the lower acetic acid concentration compared with that of the propionic acid indicates high methanogenesis activity.

The relative low concentrations of valeric and butyric acids were not only due two the inherent low productions of them in acidogenics phase, but also due to high acetogenic activity. In mature phase, all four acids started to decrease revealing that the system had stabilized and the leachate was mature. At low VFA level in the leachate, most of the gas production was likely to occur form the biomass bed itself.

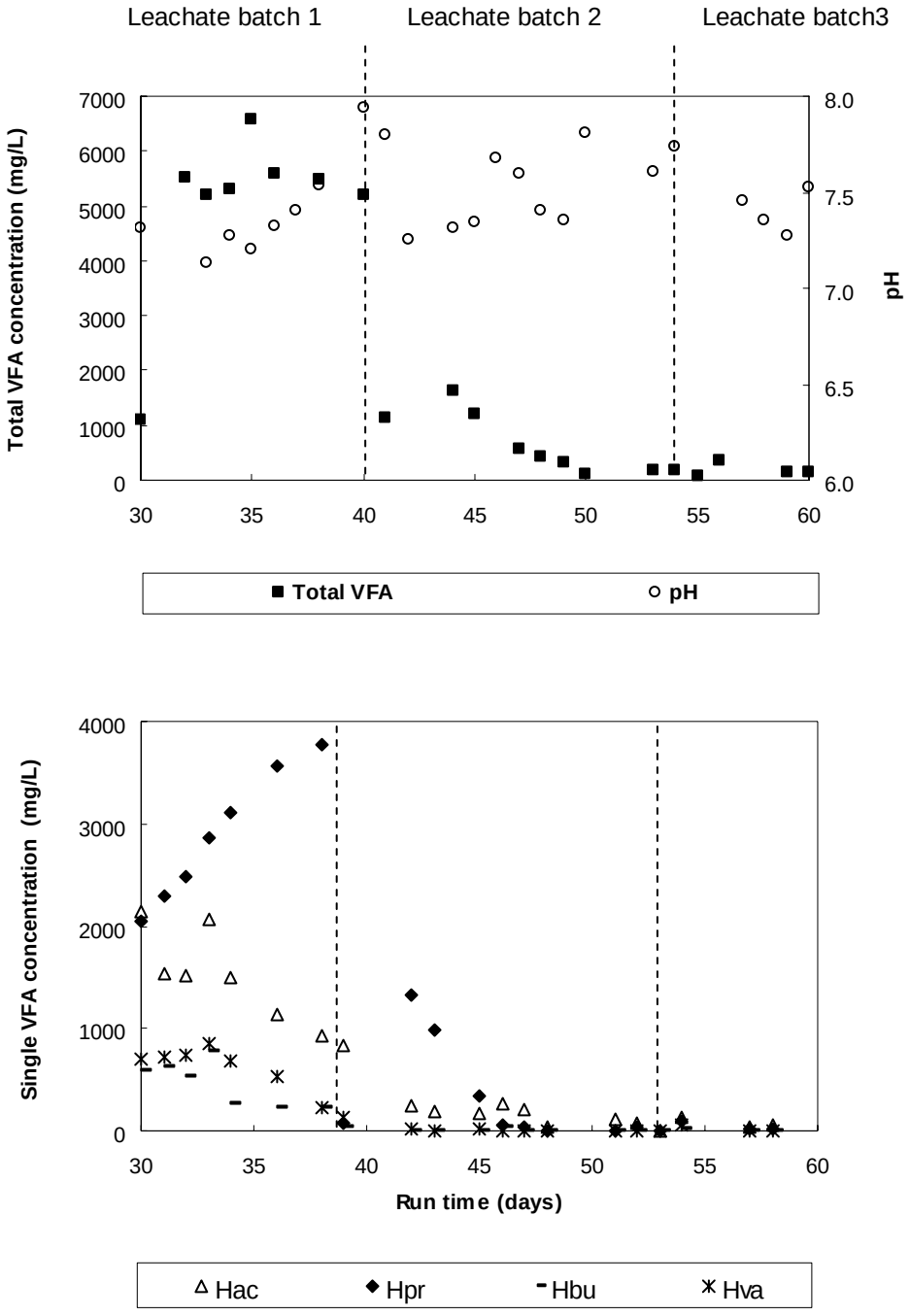


Figure 4.33 Variation of VFA in leachate during methanization (reactor 3) (Run 3)

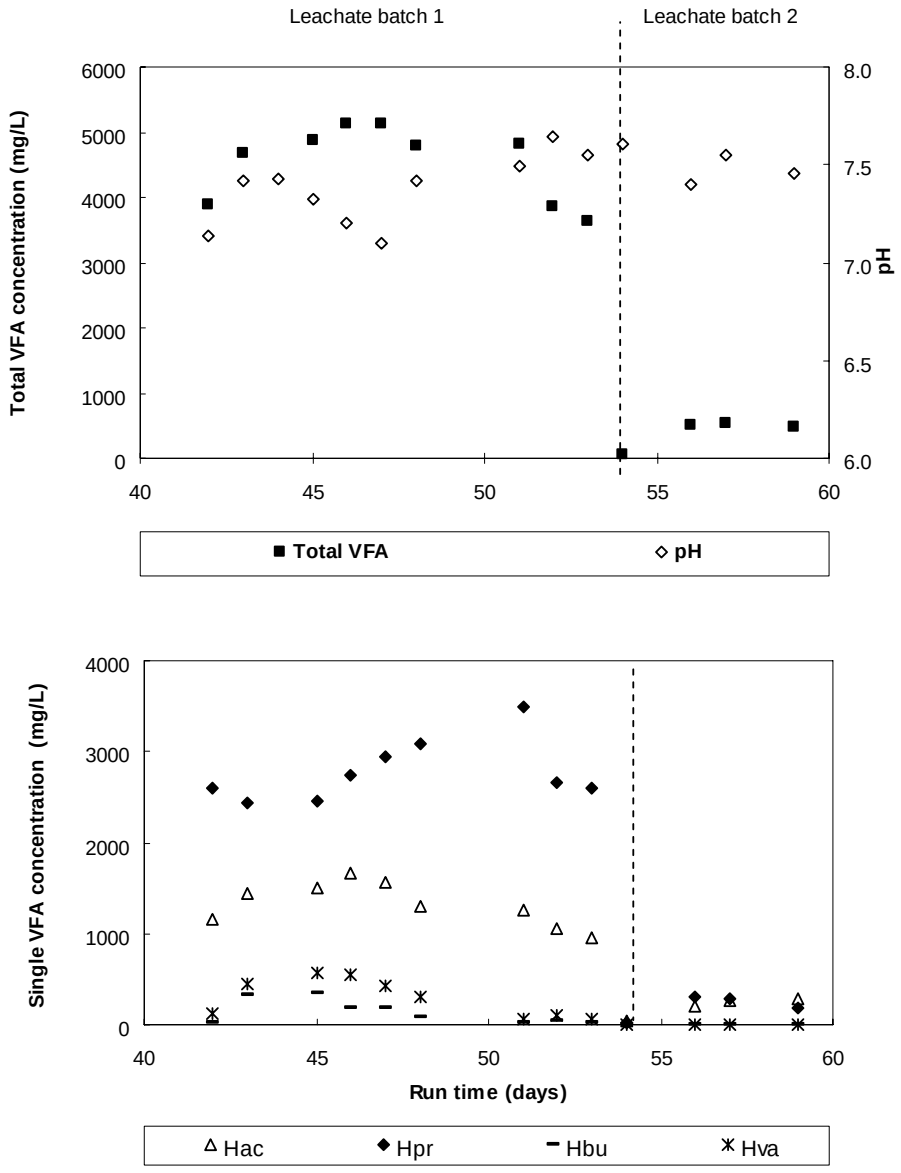


Figure 4.34 Variation of VFA in leachate during methanization (reactor 1) (Run 3)

4. Gas production

During lag phase, a stable rate of around 3 L/kgTS.day was noted in all three reactors. Corresponding to that was the slow increase of cumulative biogas.

As discussed earlier, the sharp increase in daily gas production in reactor 3 was a due to the practice of leachate recirculation. The growing phase can be easily seen in Figure 4.29 from day 25. The high rate, together with steady increase in cumulative gas, shows that when the system in active period, the methanogenic activity worked very well.

In the steadily increasing period, daily biogas production was quite stable. An average rate could be observed in reactor 3 was 12 L/kg flushed TS.day, about four time higher than in lag phase. Daily gas production, equivalent of 9 L/kg flushed VS.day was positively comparable with SEBAC in the fully started up system. According to Silvey et al. (2000), the daily methane yield was less than 0.1 L/kgVS.day from day 1 and peaked at 5.1 L/kgVS.day on day 25. Here, the peak happened at the same but with higher rate. It revealed the high decomposition waste.

In reactor 3, almost gas production was produced in such shot time of 30 days of growing phase. This was due to the successful start up of the system as well as the practice of leachate recirculation in well-acclimatized waste bed. Cumulative gas production was obtained as

4.4 Efficiency of main stage and overall performance of combined process

4.4.1 Methane potential of fresh waste (lab-scale run)

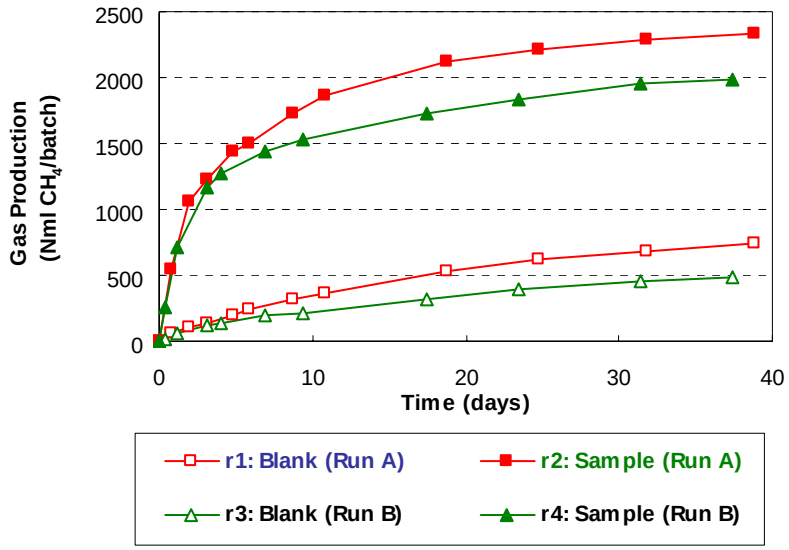


Figure 4.35 Cumulative methane production (lab scale runs)

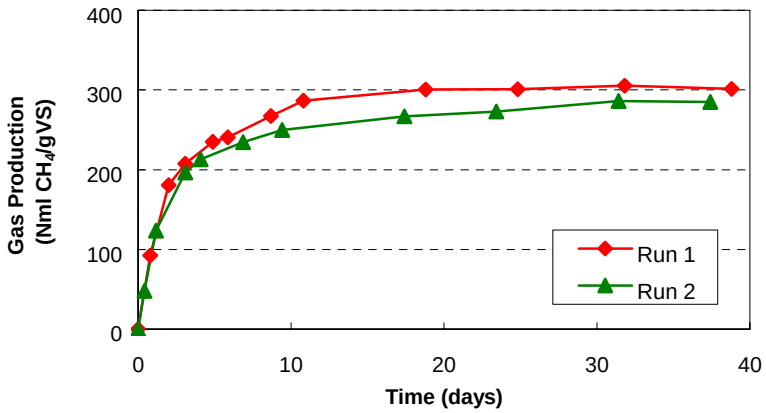


Figure 4.36 Corrected cumulative methane production (lab scale runs)

The methane yield is limited by the biodegradability of the feedstock, which is independent of digester design. This parameter for different type of solid waste are different, showing the response of different type of waste to anaerobic digestion.

The BMP test incorporated favorable environmental condition for the microorganisms such as pH, and temperature. Therefore, it were used to determine the maximum methane could be obtained for the certain amount of volatile solid. The methane potential represents a guide to the target results. Of course, it would have never been achievable in a reasonable time frame in practical systems.

Here, the test were followed the method of Hansen et al. (2003). It should be noted that, in lab-scale reactor only around 2gVS was diluted to 100 ml solution. This dilution was suitable to avoid excess acidification accompanied with low pH. In addition to that, after set up, the reactors was flushed for 2 minutes with anaerobic gas containing 80% N_2 and 20% CO_2 to ensure anaerobic condition. The mixed gas was used to prevent pH change in the water phase due to removal of CO_2 from the heads space of reactors.

Figure 4.35 presents the gas production from 4 lab-scale reactors, duplicate blank reactors and duplicate waste reactors. The blank sample indicated the gas production from the inoculums itself. By subtracting methane production from the inoculums, the methane production was obtained as depicted in Figure 4.36.

In waste reactor, reactor 2 & 4, most of the gas was produced in the first week of incubation. No lag phase was found. The long time operation of reactor was followed to make sure bioconversion of hardly-biodegradable material. As time went by, the cumulative gas was stable. The slightly increasing in both blank and sample reactors shows the self-decay of inoculums to biogas.

The final results after 40 days of mesophilic incubation showed that for each kg VS of the fresh waste, around 300 L of methane could be produced. This value represents very high biodegradability of the waste as compared with general MSW. According to Owens et al. (1993), the methane yield of MSW was estimated to be as high as 0.2 m^3/kg VS added, which indicates that more than 50% of volatile solid in MSW can be destroyed in anaerobic processing. However, for the source-separated organic household waste, a methane potential of 495 mL CH_4/gVS was found at thermophilic range.

4.4.2 Actual methane yield (reactor 3, run 3)

In reactor 3, methanization was stopped after 60 days, 6 days for flushing and acidification, 25 day of lag phase in methanogenesis and 30 days during that gas production was highest. After 60 days, approximately 5 m^3 (4706 L) biogas obtained in reactor 3 where 205 kg fresh waste were loaded, with the average methane content of 55 %. This corresponding to a gas yield of 260 L biogas/kg TS equivalent to 130L CH_4/kg TS added or 162 LCH_4/ kg fresh VS.

Due to the decomposition of pre-stage leachate during one-month period storage, this acidified leachate could not be used to recirculate back to digesters. It is very important to mention here the fraction of volatile solid in acidified leachate. After pre-stage, approximately 30% of the easily biodegradable waste extracted into leachate, did not participate in biogas production. Therefore, only flushed waste, with maximum 70 % of initial VS, was left in digester participate in biogas production (Figure 4.37). Taken into

account this consideration, the actual methane yield would be 230 L CH_4/kg flushed VS not 162 L CH_4/kg fresh waste VS.

The actual methane yield of 230 L CH_4/kg flushed VS as compared to 300 L CH_4/kg fresh waste in lab scale highlighted that almost 75 % methane conversion was obtained in the pilot scale system at mesophilic condition. That was not taken into account the different natures of the fresh waste and flushed waste. The methane test is for fresh waste, but what was stabilized in the system was not the fresh waste, but the flushed waste. Of course, flushed waste contain more hardly biodegradable fraction, compared with fresh waste, for the same amount of volatile solid. Therefore, a number of 75% biogas conversion achieved here show a high value.

4.4.3 Waste stabilization and carbon balance after main-stage

After a combined treatment period of 60 days, volatile solid destruction of 61% was obtained in reactor 3 (Table D-7). This high volatile solid destruction was comparable with literature. The mean volatile solid reduction in SEBAC system was reported by O'Keefe et al. (1992) as 49.7 % for 42 days period. A 40-60% of VS destruction occured with most biomass feedstock at residence time of 20-30 days (Chanakya). Mohee and Ramjeawon (2003) reported the volatile solid destruction of 72 % for the retention time of 142 days.

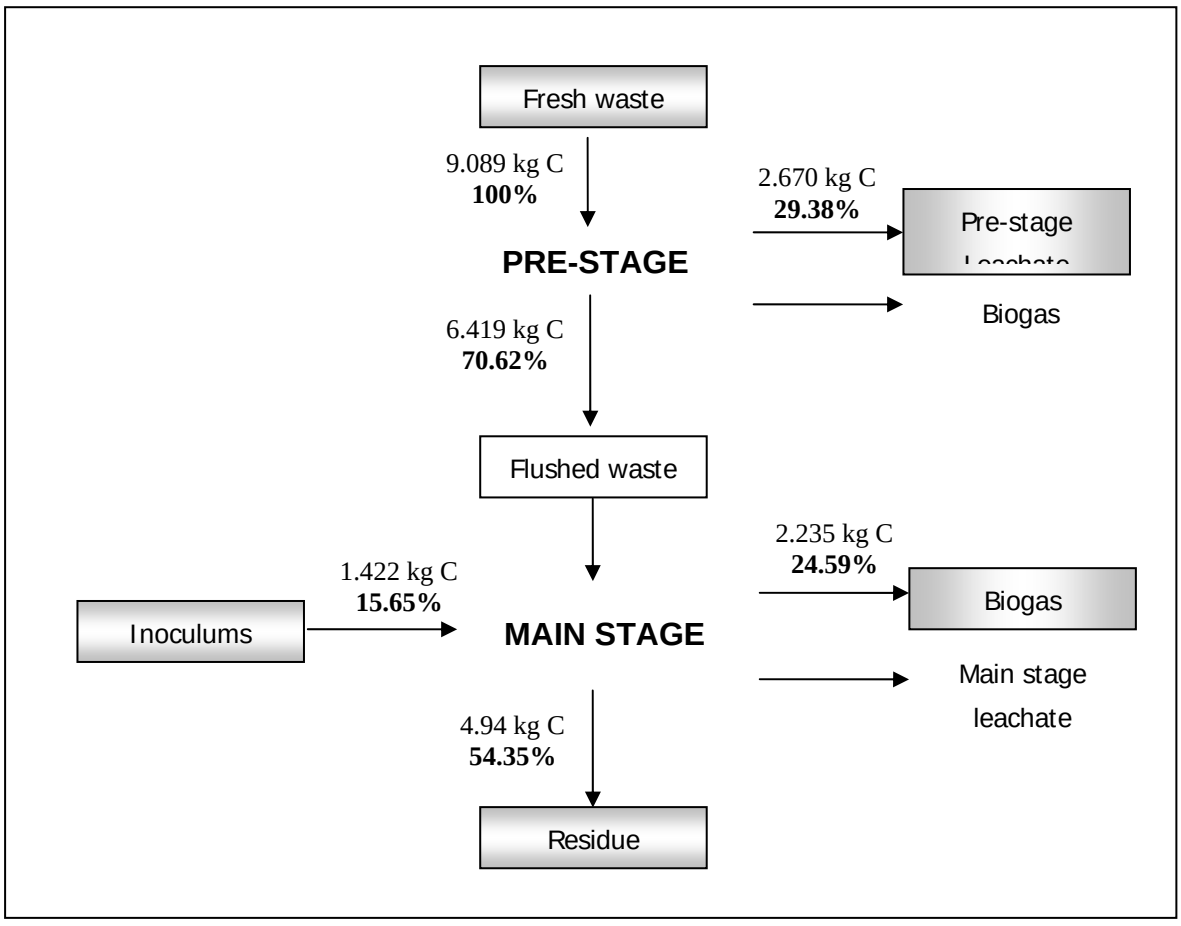


Figure 4.37 Carbon balance in pre-stage and main stage

It is very important not that volatile solid/carbon destruction of the waste bed was contributed by two main factors. First, it was the early flushing of soluble material into pre-stage leachate. Second was the stabilization of the "flushed" waste bed into biogas. As depicted in Figure 4.37, after two stage treatment, carbon in fresh waste was distributed into three main fractions (1) acidified leachate (2) biogas and (3) residue. Of course, the destruction of volatile solid in the waste also was contributed by the biogas coming from the pre-stage as well as the leachate of main stage. However, it was neglected from the calculation.

In reactor 3, after five days of pre-stage, a hydrolysis yield of 129 gC/kg TS were obtained in acidified leachate. This was interpreted to 30% C of the fresh waste, as reported in section 2.4.7 and again depicted in Figure 4.37.

The following 55 days was spent for stabilization of "flushed" waste. This period is main stage in which carbon content in the digester was converted to that in biogas. A gas yield of 4705 L (Table D-4) is equivalent to 2.679 kg C or 25% C of fresh waste (with an assumption that biogas was produced at 1atm and 35^{o} C).

Consequently, according to the carbon balance, a carbon destruction of 55% should be obtained or approximately 45% carbon content should be left in the residue. Analysis of volatile solid in the residue gave 54% C of the fresh waste. However, it is important to note that this fraction included 15.65 % of inoculums added in main-stage. Considering this VS addition, the result is reasonable.

Taking into account the fraction of carbon in pre-stage biogas and main stage leachate, the carbon destruction must be higher than 55% then it might be similar to 61% VS destruction obtained. It could be concluded that the process showed consistent result for solid reduction of the waste, leachate load and gas yield.

For a digestion period of 74 days, Chugh et al. (1998) reported a VS reduction of 67.4% corresponding to the yield of $0.17 m^3$ CH_4/kgVS. Here, the same solid destruction could be obtained with similar methane yield of 0.16 m^3/kg VS. However, the potential of 30% volatile solid of fresh waste in pre-stage leachate (Figure 4.37), in which more thane half VFA, was not utilized to produce biogas. If this acidified leachate would be converted into biogas in methanogenic phase (either in separate methane digester or incorporated in the solid bed methane phase) the total potential of biogas production would be much higher than 0.16 m^3/kg fresh TS. In addition, it is possible for each gram of volatile solid in leachate to get higher specific methane yield. That is because volatile solid in leachate is easier biodegradation part as compared to the solid remaining after flushing.

4.5 Final stage

Final stage was allowed to operate in reactor 2 and 3 before waste was unloaded from reactors. As depicted in Figure 4.38, haft days after aeration was practiced, almost biogas in the waste was flushed out. Methane and carbon dioxide contents in the gas were very low of less than 5%. Carbon dioxide content was higher than methane content indicating that aerobic metabolism has occurred. However, no significant change in composition during aeration was noticed in both reactors.

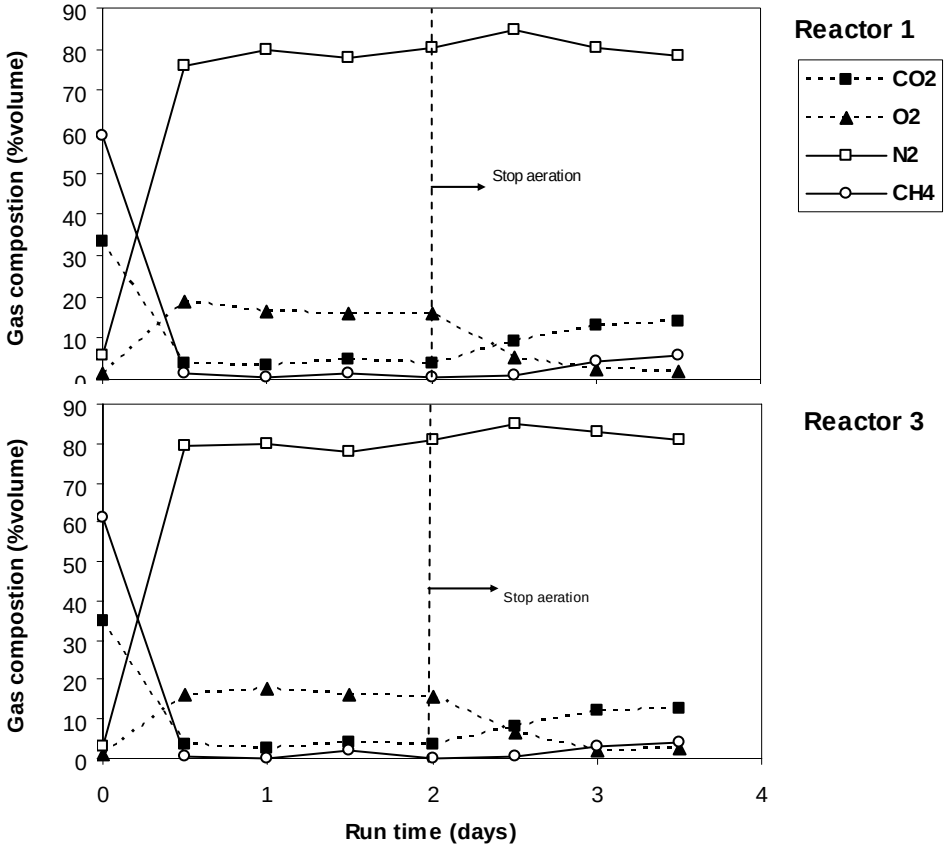


Figure 4.38 Gas composition in final stage (run 3)

After two days, no further aeration were applied. Gas production was observed in both reactor with small rate of about 15 L/day.reactor. The decreasing line of oxygen and increasing line of carbon dioxide reveal the fact that aerobic metabolism has occurred in which oxygen was consumed in aerobic stabilization of the waste producing carbon dioxide. Methane content also increased showing that some anaerobic digestion still happenned. However, the small contents of around 3 % (reactor 3) and 5 % (reactor 1) (Table D-6) were negligible. Since reactor 3 has already reached mature methane phase, methane production was less than that in reactor 3 where biogas production was in increasing phase.

Overall results suggested that in order to flush out the biogas content in the waste bed prior to landfill, one day aeration might be sufficient. In another hand, for further stabilization of waste, aeration could be practiced further to bring the digester to composting period in which the hardly biodegradable in the waste could be stabilized.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The study worked on a biological method to pre-treat MSW prior to landfill. An attempt was taken to develop a combined process with anaerobic dry fermentation as a basic unit to treat market waste. Experiments were conducted in pilot scale reactors. Combined process includes three stages: pre-stage of flushing and acidification, main stage of methanogenesis, and last stage of air flushing. Optimization of was focused on pre-stage and main-stage. The following conclusion may be drawn based on the observed results.

1. Pre-stage: Flushing and Acidification

In pre-stage, additional water was used to flush the waste producing leachate. The stage was conducted at ambient temperature, with or without aeration/micro-aeration. The optimization of flushing stage gives the following results:

1. Flushing, during such a short time of 5 days, was able to remove as much as 30% of carbon content in the fresh waste into hydrolysates in leachate. The hydrolysis yields were around 130 kgC/kg TS.

2. Acidogenesis occurred early with acidification yield of 180 gVFA/kgTS. This value is equivalent to 60% of dissolve organic carbon washed out. In short retention time, acetic acid was predominant.

3. Aeration with rate of 15 L/kgTS.h did not give rise in hydrolysis/acidification yield as compared with non-aerated run. Micro-aeration showed the equivocal results in terms of enhancing short-term hydrolysis and acidification.

4. Higher pH of around 6 had significant effect on hydrolysis/acidification yield. By supporting a layer of partly limestone gravel in the bottom, it could, in one hand, buffer the waste bed and in another hand provide better drainage condition.

5. It is not necessary to use Liquid: Solid (L: S) ratio of 2:1 (2L/kgTS every day). Reducing the tap water to 600 L, instead of 2000L, for 200 kg waste did not aversely affect the efficiency of flushing (3L/kgTS for 5 days).

6. Substantial waste stabilization and volume reduction could be obtained after 5 days flushing. Approximately 50% of TS and VS reduction was achieved. Interestingly, flushing resulted in early settlement of the waste (40% volume reduction). Thus, intermittent solid waste feeding during pre-stage provided benefit to utilize the headspace of reactor.

Finally, the optimum conditions for pre-stage were: (1) Feeding the waste intermittently at compaction density of the new layer of 500 kg/m^3 with bulking agent and gravel support at bottom. (2) Flushing the waste with 3L/kgTS for 5 days, at recirculation rate of 5 L/h (4 hr run/ 4 hrs stop) and (2) Application of microaerophilic condition alternately with flushing.

2. Methanization stage

Following flushing and acidification, digester was allowed to work as solid phase methanogenic digester. At mesophilic temperature, methanization stage was optimized in the waste bed where the intermediate products of VFA were no longer inhibitor. It could be concluded that

a. The waste had low buffering capacity. Despite significant VFA removal in pre-stage, pH of system was as low as 5 inhibiting the methanogenic activity. Biogas production could not be successfully started without initial pH adjustment (pH > 6.5) accompanied with addition of inoculums, which were cow dung, digested waste, and anaerobic sludge.

b. During start-up period, microbial ecosystem needs time to adapt itself to the new substrates. Lag phase of around 1 month was required for methanogens to acclimatize the waste.

c. The study signified the benefit of leachate percolation in the enhancement of biogas production. Leachate percolation could double gas production from 5 L/gTS day to 10 L/gTS day. It provided the moisture content to the waste, provided means of mixing and accelerated methanogenesis. In addition, periodic leachate removal/replacement could possibly remove inhibitors and provide new substrate for methanogens. Without leachate recirculation, it would take double time for digester to reach mature phase.

d. Aeration in pre-stage did not seem to be beneficial to short time hydrolysis/acidification. However, that early micro-aeration may bring to latter benefit in methane phase since aerated digester performed best in term of biogas production.

e. A period of totally 60 days was sufficient for waste stabilization and biogas production. For 18 kg fresh VS, approximately 5 m^3 of biogas with average methane content of 55% could be obtained. Since methane potential of the waste was 300 L CH_4/kg VS, the actual yield of 260 LCH_4/kg flushed VS indicated that 75 % biogas conversion was achieved.

3. Overall system performance

The idea of flushing following methanization in high-solid digester was successful in solid waste stabilization as well as biogas production for reasonable period of 60 days.

First it was highlighted the importance of early flushing with micro-aeration in reducing VFA load from the waste bed, which is the major constraints in high-solid anaerobic digestion. Early flushing could remove 30% carbon; more than haft of them were VFA.

70 % of carbon remaining in the waste was well stabilized with gas production of 260 L CH_4/kg flushed TS. High gas production was due to the early removal of VFA, earlier aeration, pH adjustment, inoculums supply and leachate recirculation. Here solid phase methanization escapes several common problems encountered during biogas production form solid biomass substrates in conventional digester such as inoculation, mixing and instability. At the final stage, air flushing during short time of one day was sufficient to remove biogas in the residue before being transported and landfilled.

Overall results show volatile solid destruction of 61%. This reduction was contributed by (1) the flushing of solid waste (30%C of fresh waste) and stabilization through biogas production (25%C of fresh waste).

5.2 Recommendations

Based on the results, the following recommendations are made for future works:

Pre-stage

1. Optimization of L: S with flushing time

In the study, lower L: S ratio than recommended value from Dayanthi (2003) did now show negative effect on flushing. Reducing L: S ratio with flushing time could concentrate the intermediate products in leachate and save tap water. Concentrated leachate may be better to be treated in methanogenic reactor than diluted leachate.

2. Flushing the waste with mature leachate instead of fresh water

Mature leachate, in which substrates for methanogens were utilized, has high buffering capacity and contains inoculums. Therefore, flushing fresh waste with mature leachate would bring to various benefits: saving water, buffering low pH of fresh waste, providing inoculums. Since the study was the first run for methane phase, mature leachate was not available.

Main stage

3. Optimization of leachate percolation in methane phase

The rate and duration of leachate percolation was not varied in the Main-stage of the study. The effect of the rate of leachate recirculation as well as duration of percolation on gas production should be further examined to optimize methane stage.

4. Investigation of methanization stage at thermophilic temperature

Thermophilic temperature can maximize methanogenic activity consequently improving biogas production and waste stabilization. However, the possible better gas yield (surplus) energy) should be higher than increased need of feed heating. This offers the need for examination.

Further stabilization of the whole system (additional stages)

5. Composting of residue for further stabilization of waste

Even with high biogas conversion, it is likely that only easily degradable waste was stabilized during anaerobic digestion. Such a fraction of hardly decomposable waste as lignin is more suitable to be composted. Therefore, composting following anaerobic digestion can served as the complete method for waste stabilization.

6. Treatment of acidified leachate in separate methane digester

Since it took long time, more than 2 months, for digester to reach mature, the treatment of acidified leachate by passing it through mature reactor may extend the time of pre-treatment. A separate leachate treatment could be an alternative for leachate stabilization and biogas production. In parallel with solid digester, treatment of this acid-rich leachate in an UASB (up-flow anaerobic sludge blanket) digester could be examined.

7. Regarding bulking agent materials

Bamboo cutlet was the good bulking agent and it is almost inert to anaerobic digestion. However, after pre-treatment, it needs to be sorted out from digested residue before landfilling. Further study also can be focused on this matter to find a cheap and degradable material so that there would not be a need to sort out this bulking agent.

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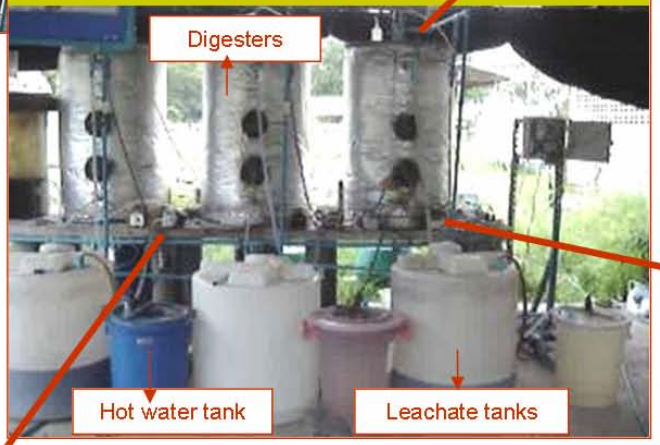
Appendix A: Photographs

Anaerobic digestion system

Opened digester for unloading waste

THE SYSTEM



Wet gas meter

Temperature controller and pumps

Sampling biogas

Appendix B: Specimen Calculations

1. Calculation of DOC load (pilot scale Run 1, reactor 1)

Day 1

DOC concentration C = 3509 mg/L Table C-3
Leachate removal V = 200 L Table C-1
Dry weigh of the waste TS = 11.863188 (kg) Table C-7

→ DOC load (day 1) $= \frac{C*V}{TS} = \frac{3509(mg/L)*200(L)}{11.8632(kg)}$

= 59.16 *10^3mgDOC/kg TS
=59.16 gDOC/kgTS

→ DOC cumulative load (day i) = $\sum_{i=0}^{i} DOCload_1$

→ DOC cumulative load (day1)
=DOC cumulative load (day i-1) + DOC load (day i)
=DOC cumulative load (day 0) + DOC load (day 1)
= 0 + 59.16
= 59.16gDOC/kgTS Table C-5

Day 2, Similarly

DOC load (day 2) $= \frac{C*V}{TS} = \frac{2234(mg/L)*200(L)}{11.8632}$
=37.66 (gDOC/kgTS)

→ DOC cumulative load (day 2)
= DOC cumulative load day 1 + DOC load day 2
= 56.16 + 37.66
= 93.82 gDOC/kg TS Table C-5

Day 7 Similarly

DOC load (day 7) $= \frac{C*V}{TS} = \frac{334(mg/L)*215(L)}{11.8632(kg)}$
= 6.05 gDOC/kgTS

DOC cumulative load (day 6) = 143.97 gDOC/kgTS Table C-5

→ DOC cumulative load (day7)
= DOC cumulative load (day 6) + DOC load (day 7)
= 143.97 + 6.05
=150.02 gDOC/kgTS Table C-5

2. Calculation of %TS loss, %VS loss (pilot scale) (Table C-7)

	Fresh waste	Flushed waste
Total wet weight	WW =120.0 kg	WW = 85.50 kg
%TS	TS =9.89% WW	TS = 5.26 %WW
→ Dry weight of loaded into reactor:		
kgTS = WW*TS	=120 kg*9.89/100	=85.50 *5.26/100
	= 11.86 kgTS	= 4.50 kg TS
%VS	VS = 79.45 %TS	VS = 87.88 %TS

→ Volatile solid loaded into reactor:

= kgTS *VS	= 11.86*79.45/100	=4.50*87.88/1000
	= 9.43 kg VS	= 3.95 kgVS

→ %TS loss = $\frac{kgTSfreahwaste - kgTSflushedwaste}{kgTSfreashwaste}$

$= \frac{11.86 - 4.50}{11.86} * 100\% = 62.10\%$

→ %VS loss = $\frac{kgTVSfreahwaste - kgVSflushedwaste}{kgVSfreashwaste}$

$= \frac{9.43 - 3.95}{9.43} = 58.08\ \%$

3. Calculation of Carbon distribution in pre-stage (pilot scale)

Carbon balance in pre-stage:
C (fresh waste) = C (flushed waste) + C (leachate) + C (biogas)

Calculation of carbon in solid phase (Carbon (fresh waste) and Carbon (flushed waste)):

	Fresh waste	Flushed waste
kgVS	= 9.43 kg VS	= 3.95 kgVS
kgC = kgVS/ 1.8	= 9.43/1.8	= 3.95/1.8
	=5.23 6 (kg)	=2.195 (kg)

Calculation of Carbon in leachate:
= DOC cumulative load (7days) *kgTS
=150.02 gDOC/kgTS*11.8632 kg TS * 1.1
= 1.977 kgC

Carbon (Gas) = Carbon (fresh waste) – Carbon (flushed waste)- Carbon (leachate)
= 5.236 -2.195-1.977
= 1.064 (kgC)

4. Calculation of methane production in lab-scale reactor (Reactor 3 Table ..)

Step 1: Determination of mass of CH_4 in 0.2 mL sample

Standard curve for determination of CH_4 mass in sample ;
Mass CH_4 (g) = Area (CH_4 peak in chromatogram) * K
K = constant = 1.7759*10-10
$Area_{0.42}$ (before removal) = 6,247 (0.42: run time (days))
→ Mass of CH_4 in sample :
$m(sample)_{0.42}$ = 86,247*1.7759*10-10 = 15.317 ug

Step 2: Determination of CH_4 mass in reactor (before and after removal)

Volume of headspace in reactor V= 2095 mL
→ Mass of CH_4 in reactor

$m_{0.42}$ (reactor) = $\frac{V}{0.2}$ *m $(sample)_{0.42}$

$m_{0.42}$ (reactor, before removal) = $\frac{V}{0.2}$ *m (sample)

$$= \frac{2095}{0.2} * 15.317 \mu g$$

$$= 0.16044 \text{ (g)}$$

$m_{0.42}$ (reactor, after removal) = $\frac{V}{0.2}$ *m (sample)

$$= \frac{2095}{0.2} * 13.39 \mu g$$

$$= 0.14\ 026 \text{ (g)}$$

Step 3: Determination of amount removal

m_i (removal) = m_i (before removal) - m_i (after removal)

m_i (cumulative removal) = m_i (removal) + m_{i-1} (cumulative removal)

i=3.08

→ $m_{3.08}$ (removal) =0.27229 - 0.17864 = 0.09365 (g)

Step4: Determination of cumulative gas production (g)

Cumulative gas production (day i)

m_i = m (before removal)$_i$ + m (cumulative removal)$_{i-1}$

i= 4.08

→ $m_{4.08}$ = 0.24285 + 0.52794= 0.77080(g)

Step5: Determination of cumulative gas production (L in STP)

Gas Law Equation

PV = $\frac{m}{M}$RT

P: standard pressure (1 atm)

V: CH_4 production in volume (L in STP)

m: CH_4 production in mass (g)

M: molecular weight of methane (dvC)

R: Universal Gas constant = $8.2057*10^{-2}$ ($L.atm.mol^{-1}K^{-1}$)

T: standard temperature ($25^oC = 298^oK$)

→ V = $\frac{m}{M}$PRT

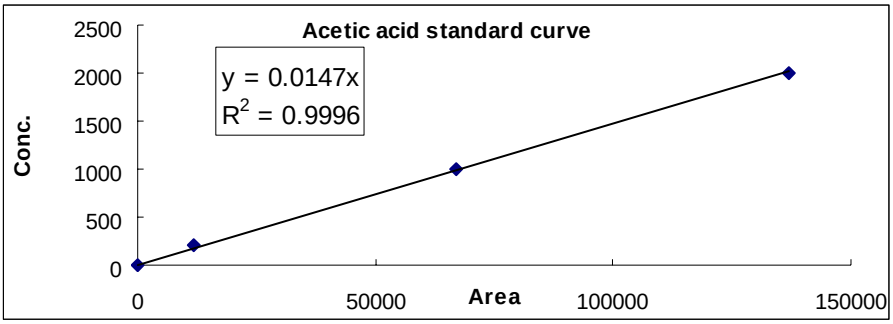
→ $V_{4.08}$ = $\frac{0.77080}{16}$ *1*$8.2057*10^{-2}$* 298 = 1.178 (NL) = 1178 (NmL)

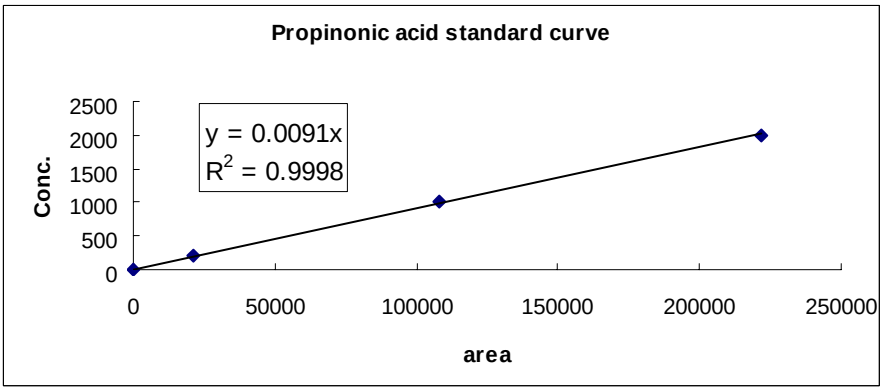
5. Calculation of methane potential

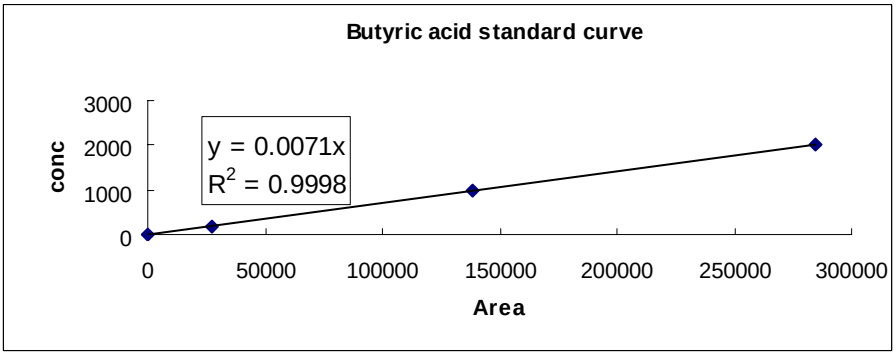
Methane potential (NmL) = $\frac{Methaneproduciton(sample) - Methaneproduciton(bank)}{kgVSinreactor}$

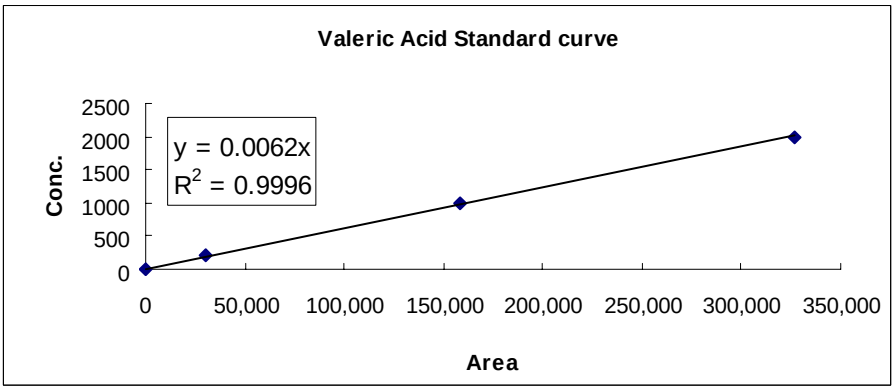
$$= \frac{Methaneproduciton(sample) - Methaneproduciton(bank)}{kgVSinreactor}$$

VFA standard curve









Appendix C: Pilot scale experimental run - Pre-stage

Table C-1 Daily leachate removal in pre-stage (L)

Run time (days)	Run 1			Run 2			Run 3		
1	200	175	175	205	200	192	210	195	217
2	200	180	200	200	210	215	203	200	195
3	200	220	220	200	205	195	215	205	215
4	180	200	200	205	195	205	187	195	178
5	205	200	195	200	200	200	218	210	200
6	200	180	180						
7	215	205	210						

Table C-2 Online parameters in daily leachate

Run time (days)	Run 1			Run 2			Run 3		
	R1	R2	R3	R1	R2	R3	R1	R2	R3
pH									
1	5.47	5.79	5.88	5.97	5.61	5.36	5.82	5.85	5.86
2	5.65	5.98	6.11	5.81	5.54	5.41	5.70	5.66	5.66
3	5.57	5.92	6.14	5.71	5.30		5.62	5.43	5.44
4	5.37	5.61	5.91	5.69	5.07		5.72	5.64	5.69
5	5.33	5.47	5.78	5.71	4.91	5.38	5.51	5.38	5.42
6	5.29	5.37	5.58						
7	5.08	5.23	5.56						
Conductivity (mS/cm)									
1	7.65	8.16	7.68	6.94	6.98	5.12	10.42	10.38	10.32
2	4.91	5.01	4.68	4.98	4.11	3.88	5.23	5.24	5.33
3	2.99	2.98	2.73	3.80	2.59		4.85	7.34	7.85
4	1.89	2.06	1.87	2.72	1.89		4.21	4.18	4.59
5	1.21	1.41	1.32	2.16	1.52	3.84	4.11	6.07	6.27
6	1.13	1.00	1.05						
7	0.80	0.80	0.85						
ORP (V)									
1				-301	-313	-305	-311	-297	-304
2				-302	-253	-232	-169	-192	-207
3	-302	-345	-354	-225	-184		-180	-218	-230
4	-248	-285	-326	-243	-191		-153	-234	-254
5	-203	-292	-316	-214	-124	-221	-203	-250	-229
6	-153	-222	-247						
7	-146	-194	-248						

Table C-3 Pollutants concentrations in daily leachate (g/kgTS)

Time (days)	Run 1			Run 2			Run 3		
	R1	R2	R3	R1	R2	R3	R1	R2	R3
DOC									
1	3509	3246	3080	2336	2433	1846	4227	4279	4134
2	2234	1750	1545	1680	1399	1289	2097	2085	2044
3	1215	966	913	1335	1011		2000	3315	3340
4	771	745	639	1031	790		1480	1644	1700
5	544	590	528	847	648	1680	1695	3280	2905
6	330	405	361						
7	334	344	318						
NH_4-N									
1	216	224	230	543	566	543	386.4	400	400.4
2	218	207	199	426	370	330	170.8	179	179.2
3	151	129	109	308	286		145.6	258	254.8
4	84	88	63	218	140		81.2	78	75.6
5	49	56	39	162	91	440	114.8	179	182.0
6	29	32	26						
7	21	20	17						
TKN									
1	770	613	532	874	708	846	591	616	618.8
2	372	325	300	560	496	459	242	246	316.4
3	210	182	171	370	297		196	316	319.2
4	137	143	112	258	193		78	126	123.2
5	83	91	76	196	137	549	137	246	232.4
6	60	65	51						
7	53	50	34						
Alkalinity as CaCO3									
1	2100	2500	2100	2440	1920	1960	3560	2980	3380
2	1400	1200	1500	1680	1160	1200	1740	1520	1480
3	870	970	900	1340	900		1480	1960	2040
4	700	760	680	1160	650		1260	1700	1420
5	440	560	270	860	350	1160	1060	1240	1040
6	310	380	400						
7	460	570	450						
TDS									
1	8988	9344	7416	7418	7165	4960			
2	4308	4384	4096	3992	3382	3310			
3	2332	2492	2312	2585	1954				
4	1368	1700	1616	2246	1318				
5	980	1260	1304	1829	1098	3144			
6	864	936	1108						
7	756	812	780						
TCOD	Run 1			SCOD	Run 1				
	R1	R2	R3		R1	R2	R3		
1	10230	10623	10230		8179	6754	7234		
2	5902	5705	4525		5027	4150	3587		
3	3541	3344	3541		2839	2248	2070		
4	3344	2951	2852		1845	1744	1553		
5	1967	1770	1279		1283	1328	1216		
6	1102	1023	1220		775	947	811		

7	1023	1062	905		781	790	724		

Table C-4 VFA concentrations in daily leachate (mg/L)

	Run 1			Run 2			Run 3		
Time (days)	R1	R2	R3	R1	R2	R3	R1	R2	R3
Acetic Acid									
1	2917	2276	2819	2162	2130	1651	3109	3519	3207
2	1404	1544	1297	1660	1362	1243	1542	1494	1617
3	730	713	657	1134	922		1475	2593	2699
4	540	561	483	829	564		959	1118	960
5	288	421	344	627	469	616	1228	1956	2169
6	241	239	344						
7	278	261	289						
Propionic Acid									
1	1360	734	833	1002	992	906	1198	1336	1124
2	591	511	411	77	579	612	538	507	496
3	367	329	251	538	368		468	822	791
4	320	297	307	385	299		367	401	330
5	226	247	203	286	271	582	367	620	642
6	206	193	192						
7	261	165	168						
Butyric Acid									
1	81	43	34	100	116	61	631	840	724
2	416	238	154	361	243	281	487	530	481
3	221	157	117	518	260		565	1010	935
4	120	142	125	396	139		445	487	412
5	61	115	101	24	169	555	533	906	1000
6	47	86	104						
7	49	79	68						
Valeric acid									
1	12	9	2	6	30	20	254	321	272
2	163	70	36	67	97	129	212	288	201
3	277	218	192	112	108		233	438	376
4	144	129	124	142	136		208	222	184
5	47	49	36	234	88	347	209	373	374
6	42	36	31						
7	40	35	25						
Total VFA									
1	4370	3062	3688	3270	3269	2638	5192	6016	5326
2	2574	2363	1899	2165	2281	2264	2779	2819	2795
3	1595	1416	1217	2302	1659		2742	4863	4801
4	1124	1129	1039	1752	1138		1979	2228	1886
5	621	832	685	1170	996	2099	2338	3856	4184
6	536	555	671						
7	629	540	550						

Table C-5 Pollutants loads in commutative leachate (g/kgTS)

Time	Run 1			Run 2			Run 3		
(days)	R1	R2	R3	R1	R2	R3	R1	R2	R3
TOC									
1	59.16	47.89	45.43	40.03	41.69	31.64	59.18	55.63	59.80
2	96.83	74.44	71.48	68.82	65.67	53.74	83.50	79.45	82.57
3	117.32	92.36	88.40	91.69	83.00	53.74	108.07	94.46	100.83
4	129.01	104.93	99.18	109.35	96.53	53.74	121.57	110.10	115.60
5	138.42	114.88	107.85	123.86	107.63	82.52	139.59	128.06	129.17
6	143.97	121.02	113.32						
7	150.02	126.97	118.95						
NH_4-N									
1	3.63	3.30	3.39	9.69	9.31	9.31	5.41	5.21	5.79
2	7.32	6.45	6.74	16.03	16.60	14.97	7.39	7.25	7.79
3	9.87	8.84	8.76	20.92	21.88	14.97	9.18	8.22	8.92
4	11.14	10.32	9.83	23.32	25.62	14.97	9.92	8.97	9.58
5	11.99	11.27	10.47	24.88	28.41	22.50	11.14	10.06	10.70
6	12.48	11.75	10.86						
7	12.86	12.09	11.16						
TKN									
1	12.98	9.05	7.85	14.97	12.14	14.49	9.19	8.90	9.95
2	19.26	13.97	12.90	24.57	20.63	22.36	12.83	12.55	14.52
3	22.80	17.35	16.07	30.90	25.72		15.51	13.02	14.30
4	24.88	19.76	17.95	35.32	29.03		16.44	14.58	15.70
5	26.31	21.29	19.20	38.67	31.38	31.77	18.06	15.82	16.82
6	27.32	22.28	19.97						
7	28.28	23.15	20.57						
Alkalinity as CaCO3									
1	35.40	36.88	30.98	41.81	32.90	33.59	49.84	38.74	48.90
2	59.01	55.09	56.27	70.60	52.78	54.15	70.02	56.11	65.39
3	73.67	73.07	72.96	93.57	68.21		88.21	61.70	73.96
4	84.29	85.89	84.42	113.45	79.34		99.70	77.87	86.29
5	91.90	95.33	88.86	128.19	85.34	74.03	110.97	74.40	84.11
6	97.12	101.09	94.93						
7	105.46	110.94	102.89						
TDS									
1	151.53	137.84	109.40	127.13	122.79	85.00			
2	224.16	204.36	178.45	195.55	180.74	141.72			
3	263.47	250.57	221.33	239.84	214.23				
4	284.23	279.23	248.57	278.34	236.82				
5	301.16	300.47	270.00	309.68	255.63	195.60			
6	315.73	314.67	286.82						
7	329.43	328.71	300.62						
TCOD				SCOD		Run 1			
	R1	R2	R3		R1	R2	R3		
1	172.46	156.70	150.90		137.90	99.63	106.72		
2	271.95	243.27	227.18		222.65	162.59	167.19		
3	331.65	305.28	292.85		270.52	204.27	205.58		
4	382.39	355.03	340.94		298.51	233.68	231.76		
5	416.39	384.88	361.95		320.68	256.06	251.76		
6	434.96	400.40	380.46		333.74	270.43	264.06		
7	453.50	418.76	396.48		347.89	284.09	276.88		

Table C-6 VFA loads in cumulative leachate (g/kgTS)

Time	Run 1			Run 2			Run 3		
(days)	R1	R2	R3	R1	R2	R3	R1	R2	R3
Acetic Acid									
1	49.18	37.48	41.58	37.05	36.51	28.29	43.53	45.74	46.39
2	72.85	60.91	63.45	65.50	59.85	49.59	61.42	62.81	64.41
3	85.16	74.12	75.63	84.93	75.65		79.55	76.12	79.54
4	93.36	83.59	83.78	99.14	85.31		88.29	86.75	87.88
5	98.33	90.69	89.42	109.89	93.34	60.15	101.35	96.15	109.04
6	102.40	94.32	94.65						
7	107.44	98.83	99.77						
Propionic Acid									
1	22.92	10.82	12.28	17.17	17.00	15.52	16.77	17.36	16.26
2	32.89	18.58	19.21	18.48	26.92	26.01	23.01	23.16	21.79
3	39.08	24.67	23.87	27.71	33.24		28.77	27.00	25.97
4	43.93	29.69	29.05	34.30	38.37		32.12	30.81	28.84
5	47.84	33.85	32.40	39.19	43.02	35.98	36.02	33.35	35.10
6	51.30	36.78	35.30						
7	56.04	39.63	38.28						
Butyric Acid									
1	1.36	0.64	0.51	1.71	1.99	1.05	8.83	10.93	10.47
2	8.37	4.24	3.11	7.90	6.15	5.86	14.47	16.98	15.82
3	12.09	7.16	5.27	16.78	10.62		21.42	22.76	21.96
4	13.90	9.55	7.37	23.56	13.01		25.48	27.40	25.54
5	14.95	11.48	9.03	23.96	15.89	15.37	31.15	32.04	35.29
6	15.75	12.79	10.61						
7	16.63	14.15	11.81						
Valeric acid									
1	0.21	0.13	0.04	0.10	0.52	0.34	3.56	4.18	3.94
2	2.95	1.20	0.65	1.26	2.18	2.55	6.01	7.47	6.18
3	7.62	5.23	4.21	3.17	4.04		8.88	9.30	8.56
4	9.82	7.40	6.29	5.61	6.36		10.78	11.41	10.16
5	10.62	8.23	6.89	9.62	7.86	8.49	13.00	13.13	12.21
6	11.34	8.78	7.36						
7	12.07	9.38	7.80						
Total VFA									
1	73.67	49.07	54.41	56.03	56.02	45.21	72.69	78.21	77.06
2	117.06	84.93	86.42	93.14	95.10	84.01	104.92	110.43	108.20
3	143.95	111.19	108.98	132.59	123.54		138.61	135.18	136.04
4	161.01	130.23	126.49	162.61	143.04		156.67	156.37	152.41
5	171.74	144.25	137.75	182.67	160.11	119.98	181.53	174.67	193.23
6	180.78	152.67	147.92						
7	192.18	162.00	157.66						
DOC equivalent of Total VFA									
	31.69	20.68	22.91	24.17	24.27	19.64	32.48	35.16	34.49
	51.44	36.42	36.80	40.24	41.68	37.19	47.20	50.05	48.63
	64.15	48.64	47.22	58.47	54.59		62.72	61.47	61.47
	72.07	57.44	55.37	72.49	63.62		71.18	71.35	69.09
	77.01	63.85	60.51	81.75	71.56	54.94	82.70	79.89	88.06
	81.17	67.76	65.15						
	86.41	72.05	69.56						

Table C-7 Solid waste characteristics

		Fresh waste			Flushed waste		
		Run 1	Run 2	Run 3	Run1 Reactor 1	Run1 Reactor 2	Run1 Reactor 3
MC	(%WW)	90.11	90.27	91.02	94.74	93.45	93.45
TS	(%WW)	9.89	9.73	8.98	5.26	6.55	8.23
VS	(%TS)	79.45	80.59	77.15	87.88	86.78	79.74
Total wet weight	kg	120.00	120.00	205.00	85.50	73.50	65.50
Dry weight	kg	11.86	11.67	20.50	4.50	4.81	5.39
Volatile weight	kg	9.43	9.40	15.82	3.95	4.18	4.30
% TS loss	%				62.10	59.43	54.57
% VS loss	%				58.08	55.69	54.40
Settlement	%				36	35	39

Table C-8 Carbon distribution after pre-stage (Run 1)

		Reactor 1		Reactor 2		Reactor 3	
		kg	%fresh waste	kg	%fresh waste	kg	% fresh waste
In	Fresh waste	5.236	100.0	5.236	100.0	5.236	100.0
Out	Flushed waste	2.195	41.9	2.320	44.3	2.388	45.6
	Acidified leachate	1.977	37.8	1.674	32.0	1.568	29.9
	Biogas	1.064	20.3	1.242	23.7	1.281	24.5

Appendix D: Pilot scale experimental run - Main stage and Final stage

Table D-1. Biogas composition in Start up main stage (Run 2)

Run time (days after pre-stage)	Reactor 1	Reactor 3	Reactor 3
0	0.00	0.00	0.75
1			
2			
3	0.00	0.00	0.00
4	0.04	0.00	5.97
5			6.42
6	2.13	1.96	6.04
7	4.77	1.20	5.96
8	6.75	1.79	6.12
9	10.06	2.42	6.50
10	10.60	2.85	6.70
11	11.91	3.37	6.94
12	13.69		7.11
13		4.20	
14	18.58	4.51	7.72
15	20.47	4.53	8.21
16	22.97	4.69	8.39
17	25.79		8.85
18		4.98	
19	30.59		9.96
20			
21			
22		6.86	
23	35.25	6.89	14.99
24	34.94	6.89	16.09
25	36.62	7.35	15.11
26	37.93	7.21	15.29
27	39.52	7.71	17.24
28	40.02	8.03	18.31
29	41.54	8.63	20.58
30	40.00	8.67	25.06

Table D-2. Biogas production and composition in reactor 1 (Run 3)

Run time (days)	Gas Production Rate	Cumulative Gas Production	Specific Gas Production Rate	Specific Gas Production	Gas Composition		Note
					CO_2	CH_4	
	L/day	L	L/kgTS.day	L/kgTS	%	%	
7	4.40	4.40	0.24	0.24	77.55	22.45	
8	5.56	9.96	0.30	0.54	77.24	22.76	
9	2.04	11.99	0.11	0.65	74.33	25.67	
10	2.42	14.41	0.13	0.78	72.65	27.35	
11	7.10	21.51	0.39	1.17	71.58	28.42	
12	4.35	25.85	0.24	1.40	69.38	30.62	
13	7.92	33.77	0.43	1.83	68.84	31.16	
14	1.76	35.53	0.10	1.93	67.68	32.32	
15	12.32	47.85	0.67	2.60	66.50	33.50	
16	8.80	56.65	0.48	3.08	64.09	35.91	
17	13.37	70.02	0.73	3.80	63.58	36.42	
18	12.21	82.23	0.66	4.47	61.14	38.86	
19	32.50	114.73	1.77	6.23	59.85	40.15	
20	39.00	153.73	2.12	8.35	58.55	41.45	
21	35.00	188.73	1.90	10.25			
22	25.00	213.73	1.36	11.61	54.43	45.57	
23	19.20	232.92	1.04	12.65			
24	23.16	256.08	1.26	13.91	50.51	49.49	
25	28.44	284.51	1.54	15.45			
26	37.90	322.41	2.06	17.51	48.15	51.85	
27	55.88	378.29	3.04	20.55	48.24	51.76	
28	33.06	411.34	1.80	22.34	47.80	52.20	
29	40.70	452.04	2.21	24.56	48.22	51.78	
30	44.94	496.98	2.44	27.00	46.86	53.14	
31	65.67	562.65	3.57	30.56	46.50	53.50	
32	61.55	624.19	3.34	33.91	45.54	54.46	
33	50.44	674.63	2.74	36.65	45.34	54.66	
34	57.15	731.77	3.10	39.75			
35	50.49	782.26	2.74	42.49			
36	31.30	813.56	1.70	44.19			
37	33.83	847.38	1.84	46.03			
38	30.91	878.29	1.68	47.71	37.67	62.33	
39	38.23	916.52	2.08	49.79			
40	10.34	926.86	0.56	50.35			
41	15.46	942.31	0.84	51.19			
42	13.75	956.06	0.75	51.93			
43	53.79	1009.85	2.92	54.86	41.78	58.22	Start leachate percolation, batch 1
44	56.98	1066.83	3.10	57.95			
45	87.84	1154.67	4.77	62.72			
46	81.73	1236.40	4.44	67.16			
47	93.78	1330.17	5.09	72.26	37.56	62.44	
48	94.77	1424.94	5.15	77.40			
49	111.21	1536.15	6.04	83.45			
50	92.24	1628.38	5.01	88.46			
51	85.36	1713.74	4.64	93.09	35.00	65.00	
52	68.86	1782.60	3.74	96.83			
53	71.83	1854.43	3.90	100.73			
54	27.28	1881.71	1.48	102.22			
55	45.43	1927.14	2.47	104.68			Start leachate percolation, batch 2
56	42.35	1969.49	2.30	106.99			
57	45.00	2014.49	2.44	109.43			
58	99.88	2114.37	5.43	114.86			
59	86.41	2200.78	4.69	119.55	38.00	62.00	
60	102.14	2302.91	5.55	125.10			
61	87.62	2390.53	4.76	129.86			

Table D-3. Biogas production and composition in reactor 2 (Run 3)

Run time (days)	Gas Production Rate	Cumulative Gas Production	Specific Gas Production Rate	Specific Gas Production	Gas Composition		Notes
					CO_2	CH_4	
	L/day	L	L/kgTS.day	L/kgTS	%	%	
7	66.33	66.33	3.60	3.60	84	16	
8	68.59	134.92	3.73	7.33	83	17	
9	59.18	194.10	3.21	10.54	80	20	
10	19.69	213.79	1.07	11.61	82	18	
11	11.94	225.72	0.65	12.26	82	18	
12	13.53	239.25	0.73	13.00	80	20	
13	5.45	244.70	0.30	13.29	79	21	
14	47.20	291.90	2.56	15.86	80	20	
15	21.70	313.60	1.18	17.04	77	23	
16	19.60	333.20	1.06	18.10	75	25	
17	29.90	363.10	1.62	19.72	72	28	
18	27.00	390.10	1.47	21.19	71	29	
19	27.00	417.10	1.47	22.66	69	31	
20	22.72	439.82	1.23	23.89	67	33	
21	41.50	481.32	2.25	26.15			
22	28.40	509.72	1.54	27.69	63	37	
23	35.00	544.72	1.90	29.59			
24	39.30	584.02	2.13	31.72	59	41	
25	39.50	623.52	2.15	33.87			
26	56.10	679.62	3.05	36.92	56	44	
27	55.50	735.12	3.01	39.93	55	45	
28	39.00	774.12	2.12	42.05	53	47	
29	35.75	809.87	1.94	43.99	54	46	
30	32.00	841.87	1.74	45.73	51	49	
31	36.74	878.61	2.00	47.73	51	49	
32	29.48	908.09	1.60	49.33	51	49	
33	14.69	922.77	0.80	50.13	51	49	
34	5.67	928.44	0.31	50.43			
35	8.97	937.40	0.49	50.92			
36	54.51	991.91	2.96	53.88			
37	50.00	1041.91	2.72	56.60	52	48	
38	41.00	1082.91	2.23	58.82			
39	32.00	1114.91	1.74	60.56			
40	45.00	1159.91	2.44	63.01			
41	50.00	1209.91	2.72	65.72			
42	35.00	1244.91	1.90	67.62	45	55	
43	45.00	1289.91	2.44	70.07			
44	69.80	1359.70	3.79	73.86			
45	80.47	1440.17	4.37	78.23			
46	69.00	1509.17	3.75	81.98	42	58	
47	77.28	1586.44	4.20	86.18			
48	55.55	1641.99	3.02	89.19			
49	65.00	1706.99	3.53	92.73			
50	66.00	1772.99	3.59	96.31	40	60	

51	56.00	1828.99	3.04	99.35			
52	66.00	1894.99	3.59	102.94			
53	71.72	1966.71	3.90	106.83			
54	70.24	2036.95	3.82	110.65			
55	65.84	2102.78	3.58	114.23			
56	99.00	2201.78	5.38	119.60			
57	100.16	2301.94	5.44	125.04			
58	91.47	2393.40	4.97	130.01	41	59	
59	104.72	2498.12	5.69	135.70			
60	98.80	2596.92	5.37	141.07			
61	102.02	2698.94	5.54	146.61			

Table D-4. Biogas production and composition in reactor 3 (Run 3)

Run time (days)	Gas Production Rate	Cumulative Gas Production	Specific Gas Production Rate	Specific Gas Production	Biogas composition		Note
					CO_2	CH_4	
	L/day	L	L/kgTS.day	L/kgTS	%	%	
7	44.88	44.88	2.44	2.44	81.79	18.21	
8	73.54	118.42	3.99	6.43	80.03	19.97	
9	0.05	118.47	0.00	6.44	76.41	23.59	
10	3.36	121.83	0.18	6.62	75.09	24.91	
11	36.74	158.57	2.00	8.61	74.54	25.46	
12	34.65	193.22	1.88	10.50	71.24	28.76	
13	45.65	238.86	2.48	12.98	70.35	29.65	
14	29.39	268.25	1.60	14.57	68.05	31.95	
15	36.47	304.71	1.98	16.55	66.27	33.73	
16	45.98	350.69	2.50	19.05	64.18	35.82	
17	30.25	380.94	1.64	20.69	62.58	37.42	
18	50.77	431.71	2.76	23.45	60.65	39.35	
19	52.00	483.71	2.82	26.28	59.14	40.86	
20	51.87	535.57	2.82	29.09	57.14	42.86	
21	43.23	578.80	2.35	31.44			
22	33.06	611.86	1.80	33.24	53.57	46.43	
23	66.10	677.96	3.59	36.83			
24	39.99	717.94	2.17	39.00	50.22	49.78	
25	55.83	773.77	3.03	42.03			
26	54.00	827.77	2.93	44.97	47.91	52.09	
27	54.95	882.71	2.98	47.95	48.13	51.87	
28	54.01	936.72	2.93	50.88	46.46	53.54	Leachate percolation, batch 1
29	58.90	995.62	3.20	54.08	44.15	55.85	
30	90.50	1086.12	4.92	59.00	42.44	57.56	
31	102.00	1188.12	5.54	64.54	42.60	57.40	
32	125.00	1313.12	6.79	71.33	43.60	56.40	
33	153.00	1466.12	8.31	79.64	41.79	58.21	
34	145.30	1611.42	7.89	87.53	0.00	0.00	
35	141.20	1752.62	7.67	95.20	0.00	0.00	
36	165.10	1917.72	8.97	104.17	0.00	0.00	
37	160.00	2077.72	8.69	112.86	43.88	56.12	
38	163.10	2240.82	8.86	121.72			
39	112.80	2353.62	6.13	127.85	40.77	59.23	Leachate percolation, batch 2
40	126.40	2480.02	6.87	134.72			
41	130.60	2610.62	7.09	141.81	37.60	62.40	
42	177.00	2787.62	9.61	151.43	36.77	63.23	
43	153.00	2940.62	8.31	159.74			
44	152.00	3092.62	8.26	168.00			
45	149.60	3242.22	8.13	176.12			
46	150.40	3392.62	8.17	184.29	36.28	63.72	
47	154.00	3546.62	8.37	192.66			

48	143.60	3690.22	7.80	200.46			
49	118.50	3808.72	6.44	206.89			
50	121.90	3930.62	6.62	213.52	38.00	62.00	
51	127.40	4058.02	6.92	220.44			
52	100.20	4158.22	5.44	225.88			
53	78.40	4236.62	4.26	230.14			
54	72.00	4308.62	3.91	234.05			Leachate percolation, batch
55	64.00	4372.62	3.48	237.53			
56	73.00	4445.62	3.97	241.49			
57	62.00	4507.62	3.37	244.86			
58	57.70	4565.32	3.13	247.99	35.00	65.00	
59	56.70	4622.02	3.08	251.07			
60	35.20	4657.22	1.91	252.99			
61	49.32	4706.54	2.68	255.67			

Table D-5. VFA and pH in main stage leachate (Run 3)

Run time (days)	Reactor 3						Reactor 1					
	Hac	Hpr	Hbu	Hva	Total VFA	pH	Hac	Hpr	Hbu	Hva	Total VFA	pH
28	831.8	81.7	44.2	125.9	1083.7	7.31						
30	2138.9	2055.5	596.7	701.5	5492.6							
31	1539.4	2299.3	617.3	718.8	5174.9	7.13						
32	1522.7	2492.0	528.8	741.0	5284.5	7.27						
33	2064.4	2859.2	768.9	846.1	6538.6	7.2						
34	1497.1	3109.2	264.7	687.2	5558.3	7.32						
37												
38	930.8	3776.8	229.6	236.7	5173.9	7.94						
39	831.8	81.7	44.2	125.9	1083.7	7.8						
42	243.6	1321.6	3.1	27.4	1595.7	7.31	1166.3	2594.0	20.2	116.4	3896.9	7.14
43	183.4	976.6	2.7	7.9	1170.5	7.34	1448.6	2446.2	332.7	439.0	4666.4	7.42
44						7.68						7.43
45	163.9	345.7	4.9	11.5	526.0	7.6	1506.8	2456.5	339.1	568.1	4870.5	7.32
46	260.5	55.8	45.8	3.2	365	7.4	1656.7	2737.4	190.1	548.6	5132.8	7.20
47	211.4	43.7	2.9	1.0	259	7.4	1556.4	2953.2	191.3	435.9	5136.8	7.10
48	43.0	0.8	0.0	0.0	44	7.8	1301.8	3092.6	88.7	300.5	4783.6	7.42
49												
50												
51	118.5	1.4	0.0	0.0	120	7.6	1250.5	3495.4	20.7	52.3	4818.9	7.49
52	79.0	42.2	0.0	0.0	121	7.7	1065.1	2667.4	31.0	99.2	3862.7	7.64
53	2.9	9.2	0.0	0.0	12		962.2	2594.1	16.8	64.0	3637.2	7.55
54	138.8	90.5	13.4	47.6	290		50.0	19.1	0.0	0.0	69.1	7.61
55						7.5						
56						7.4	205.3	294.6	6.6	0.2	506.7	7.40
57	46.3	9.8	6.9	7.9	71	7.3	264.7	275.0	2.5	6.6	548.9	7.55
58	55.4	16.8	9.1	8.3	90	7.5						
59							280.8	191.3	2.5	7.9	485.3	7.46

Table D-6. Gas composition in final stage (Run 3)

Run time (days)			Reactor 1				Reactor 3			
			CO_2	O_2	N_2	CH_4	CO_2	O_2	N_2	CH_4
0	Before aeration		33.5184	1.6858	5.8342	58.9616	34.9752	0.8859	3.1124	61.0263
0.5	Aeration	rate 3L/min	3.6382	19.0246	75.8656	1.4716	3.6093	16.2508	79.6178	0.522
1	Aeration	rate 3L/min	3.535	16.2184	79.8349	0.4117	2.401	17.5287	79.9561	0.1142
1.5	Aeration	rate 3L/min	4.664	15.836	78.0606	1.4394	3.9619	16.1708	77.7487	2.1187
2	Aeration	rate 3L/min	3.678	15.7393	80.2882	0.2944	3.6254	15.5581	80.6682	0.1483
2.5	No aeration		9.1821	5.2094	84.4402	1.1683	7.9618	6.3214	85.0585	0.6583
3	No aeration		12.9386	2.2842	80.4792	4.298	12.0682	2.0395	83.0313	2.8609
3.5	No aeration	15 L/days	14.051	2.0754	78.1934	5.6803	12.6641	2.3902	81.1391	3.8065

Table D-7. Waste characteristics (Run 3)

Parameter	Unit						
		Fresh waste		Seeding material		Digested waste	
		Reactor 1	Reactor 3	Reactor 1	Reactor 3	Reactor 1	Reactor 3
MC	(%WW)	89.02	89.02			81.36	82.53
TS	(%WW)	10.08	10.08			18.64	17.47
VS	(%TS)	79.15	79.15			69.75	68.83
Total wet weight	kg	205	205			74.8	73.9
Dry weight	kg	20.67	20.67	3.2	3.2	13.94	12.91
Volatile weight	kg	16.36	16.36	2.56	2.56	9.72	8.89
Carbon	kg	9.089	9.089	1.422	1.422	5.40	4.94
% TS loss	%					48.04	53.02
% VS loss	%					56.23	61.30
Settlement	%			0	0	26	26

Appendix E: Lab-scale experimental data

Table E-1. Lab-scale reactors data (Run A)

Sample No.	Run time (days)	Chromatographic area of CH4		Mass of CH4 (µg) in 0.2mL		Mass of CH_4 per reactor (g)		Removal (g)	Cumulative mass removal (g)	Cumulative mass production (g)	Cumulative volume production (NmL/reactor)
		Before removal	After removal	Before removal	After removal	Before removal	After removal				
Run A, reactor 2 (r2)											
0	0.00	0	0	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
1	0.79	205,067	93,549	36.418	16.614	0.3582	0.1634	0.1948	0.1948	0.3582	547.40
2	2.00	285,659	194,475	50.731	34.537	0.4989	0.3397	0.1593	0.3540	0.6937	1060.21
3	3.08	259,459	259,459	46.078	46.078	0.4532	0.4532	0.0000	0.3540	0.8072	1233.68
4	4.88	336,574	228,602	59.773	40.598	0.5879	0.3993	0.1886	0.5426	0.9419	1439.53
5	5.88	253,800	253,800	45.073	45.073	0.4433	0.4433	0.0000	0.5426	0.9859	1506.79
6	8.69	333,573	333,573	59.240	59.240	0.5826	0.5826	0.0000	0.5426	1.1252	1719.73
7	10.81	388,938	286,511	69.072	50.882	0.6793	0.5004	0.1789	0.7215	1.2220	1867.52
8	18.81	380,127	380,127	67.507	67.507	0.6639	0.6639	0.0000	0.7215	1.3855	2117.42
9	24.81	413,717	413,717	73.473	73.473	0.7226	0.7226	0.0000	0.7215	1.4441	2207.08
10	31.81	445,230	445,230	79.069	79.069	0.7776	0.7776	0.0000	0.7215	1.4992	2291.20
11	38.81	460,123	460,123	81.714	81.714	0.8037	0.8037	0.0000	0.7215	1.5252	2330.96
Run A, reactor 1 (r1)											
0	0.00	0	0	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
1	0.79	23,348	23,348	4.146	4.146	0.0408	0.0408	0.0000	0.0000	0.0408	62.32
2	2.00	42,438	42,438	7.537	7.537	0.0741	0.0741	0.0000	0.0000	0.0741	113.28
3	3.08	54,312	54,312	9.645	9.645	0.0949	0.0949	0.0000	0.0000	0.0949	144.98
4	4.88	78,110	78,110	13.872	13.872	0.1364	0.1364	0.0000	0.0000	0.1364	208.50
5	5.88	92,873	92,873	16.493	16.493	0.1622	0.1622	0.0000	0.0000	0.1622	247.91
6	8.69	121,031	121,031	21.494	21.494	0.2114	0.2114	0.0000	0.0000	0.2114	323.08
7	10.81	138,954	106,559	24.677	18.924	0.2427	0.1861	0.0566	0.0566	0.2427	370.92
8	18.81	174,515	174,386	30.992	30.969	0.3048	0.3046	0.0002	0.0568	0.3614	552.32
9	24.81	208,299	208,299	36.992	36.992	0.3638	0.3638	0.0000	0.0568	0.4206	642.85
10	31.81	232,312	232,312	41.257	41.257	0.4058	0.4058	0.0000	0.0568	0.4626	706.94
11	38.81	255,781	255,781	45.425	45.425	0.4468	0.4468	0.0000	0.0568	0.5036	769.59

Table E-2. Lab-scale reactors data (Run B)

Sample No.	Run time (days)	Chromatographic area of CH4		Mass of CH4 (µg) in 0.2mL		Mass of CH4 per reactor (g)		Removal (g)	Cumulative mass removal (g)	Cumulative mass production (g)	Cumulative volume production (mL/reactor)
		Before removal	After removal	Before removal	After removal	Before removal	After removal				
Run B, reactor 4 (r4)											
0	0.00	0	0	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
1	0.42	86,247	75,397	15.317	13.390	0.1723	0.1506	0.0217	0.0217	0.1723	263.35
2	1.17	222,606	0	39.533	0.000	0.4447	0.0000	0.4447	0.4664	0.4664	712.84
3	3.08	146,373	96,029	25.995	17.054	0.2924	0.1919	0.1006	0.5670	0.7589	1159.78
4	4.08	130,546	130,546	23.184	23.184	0.2608	0.2608	0.0000	0.5670	0.8278	1265.17
5	6.88	185,326	185,326	32.912	32.912	0.3703	0.3703	0.0000	0.5670	0.9373	1432.44
6	9.42	218,698	175,028	38.839	31.083	0.4369	0.3497	0.0872	0.6543	1.0039	1534.34
7	17.42	237,560	237,560	42.189	42.189	0.4746	0.4746	0.0000	0.6543	1.1289	1725.27
8	23.42	272,168	272,168	48.335	48.335	0.5438	0.5438	0.0000	0.6543	1.1980	1830.95
9	31.42	314,562	314,562	55.864	55.864	0.6285	0.6285	0.0000	0.6543	1.2827	1960.39
10	37.42	322,819	322,819	57.330	57.330	0.6450	0.6450	0.0000	0.6543	1.2992	1985.61
Run B, reactor 3 (r3)											
0	0.00	0	0	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
1	0.42	4,008	4,008	0.712	0.712	0.0080	0.0080	0.0000	0.0000	0.0080	12.24
2	1.17	22,025	22,025	3.911	3.911	0.0440	0.0440	0.0000	0.0000	0.0440	67.25
3	3.08	43,639	43,639	7.750	7.750	0.0872	0.0872	0.0000	0.0000	0.0872	133.25
4	4.08	50,515	50,515	8.971	8.971	0.1009	0.1009	0.0000	0.0000	0.1009	154.24
5	6.88	69,440	69,440	12.332	12.332	0.1387	0.1387	0.0000	0.0000	0.1387	212.03
6	9.42	76,921	76,921	13.661	13.661	0.1537	0.1537	0.0000	0.0000	0.1537	234.87
7	17.42	108,932	108,932	19.345	19.345	0.2176	0.2176	0.0000	0.0000	0.2176	332.62
8	23.42	135,538	135,538	24.070	24.070	0.2708	0.2708	0.0000	0.0000	0.2708	413.85
9	31.42	156,371	156,371	27.770	27.770	0.3124	0.3124	0.0000	0.0000	0.3124	477.47
10	37.42	167,596	167,596	29.764	29.764	0.3348	0.3348	0.0000	0.0000	0.3348	511.74

Table E-3. Corrected methane production and BMP

Run A					Run B				
Run time (days)	r2	r1	BMP		Run time (days)	r4	r3	BMP	
	Sample + Innoculums	Innoculums				Sample + Innoculums	Innoculums		
	mL/reactor	mL/reactor	mL/batch	Nm3/kg VS		mL/reactor	mL/reactor	mL/batch	Nm3/kg VS
0.0	0	0	0	0	0.0	0	0	0	0
0.4	263	12	251	48	0.8	547	62	485	92
1.2	713	67	646	123	2.0	1060	113	947	180
3.1	1160	133	1027	195	3.1	1234	145	1089	207
4.1	1265	154	1111	211	4.9	1440	209	1231	234
6.9	1432	212	1220	232	5.9	1507	248	1259	239
9.4	1534	235	1299	247	8.7	1720	323	1397	265
17.4	1725	333	1393	264	10.8	1868	371	1497	284
23.4	1831	414	1417	269	18.8	2117	552	1565	297
31.4	1960	477	1483	281	24.8	2207	643	1564	297
37.4	1986	512	1474	280	31.8	2291	707	1584	301

Dry Anaerobic Digestion of Municipal Solid Waste as Pre-treatment prior to Landfills

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Content of Presentation

- Introduction
- Methodology
- Results and Discussions
- Conclusions and Recommendations

Objectives

→ To develop and optimize a combined process of solid waste pre-treatment prior to landfill with dry-anaerobic digestion stage as a basic unit.

- Pre-stage: Flushing and Acidification
- Main stage: Methanization
- Final stage: Air Flushing

→ Scope of the Study → to treat vegetable market waste

1. Application of different operational conditions in **Pre-stage** in order to optimize hydrolysis and acidogenic yield
2. Investigation of different strategies in **Main-stage** for maximization of biogas production and waste stabilization
3. Evaluation of the efficiency of anaerobic digestion by comparison with **methane potential** of the waste

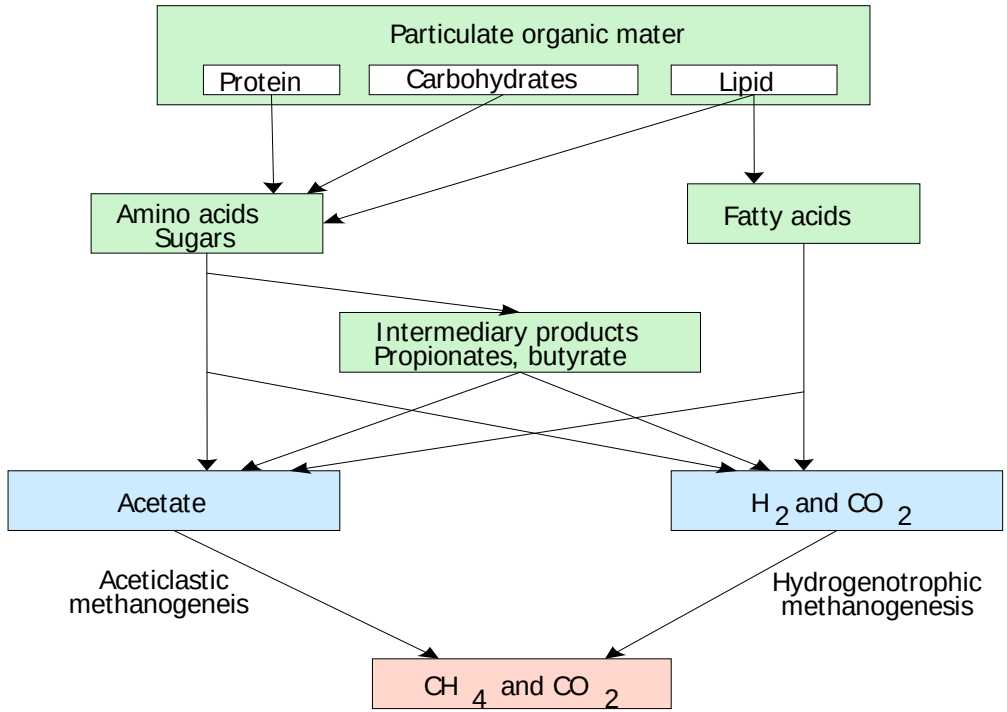
Anaerobic Digestion Process

HYDROLYSIS

ACIDOGENESIS

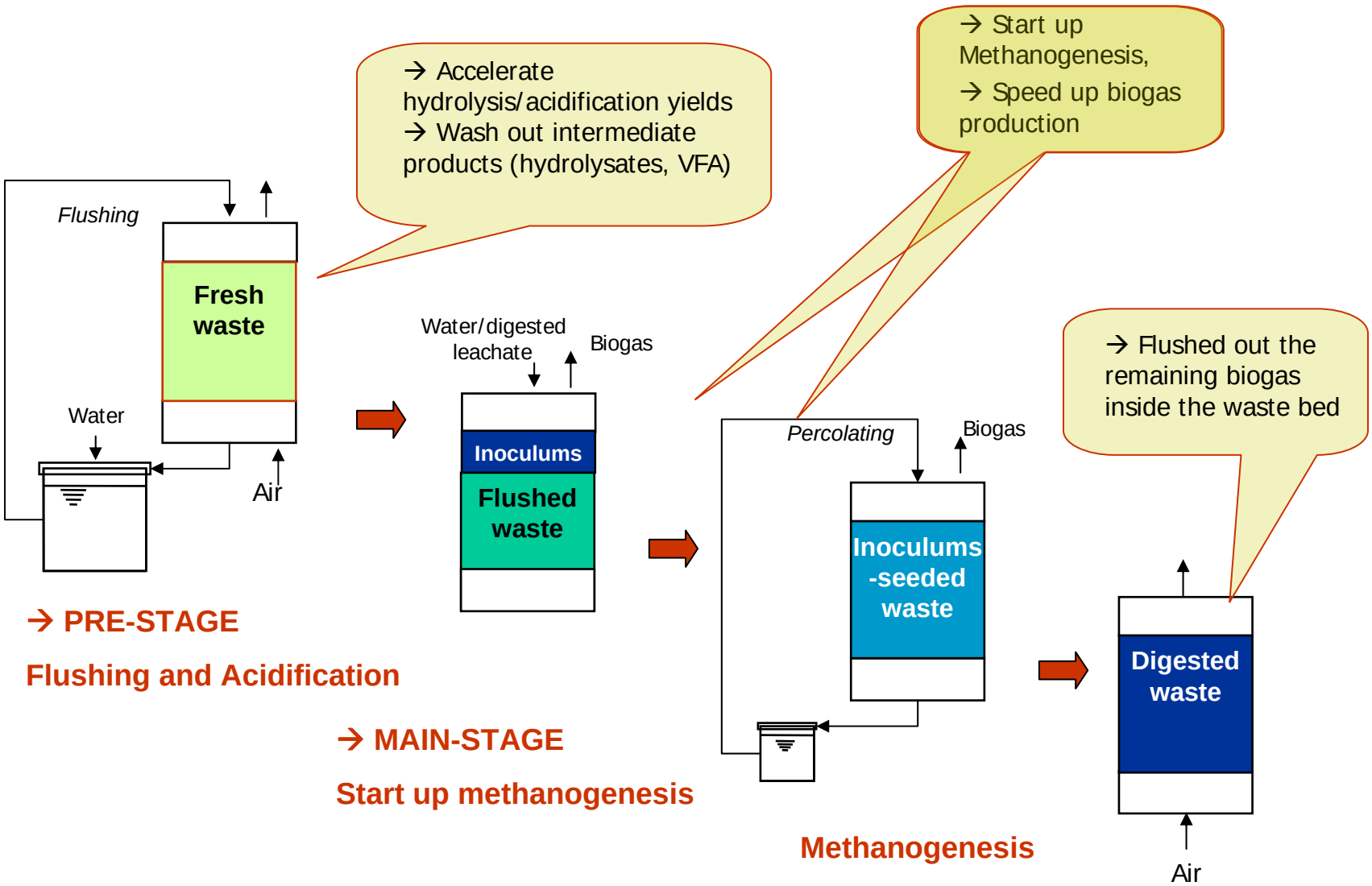
ACETOGENESIS

METHANOGENESIS

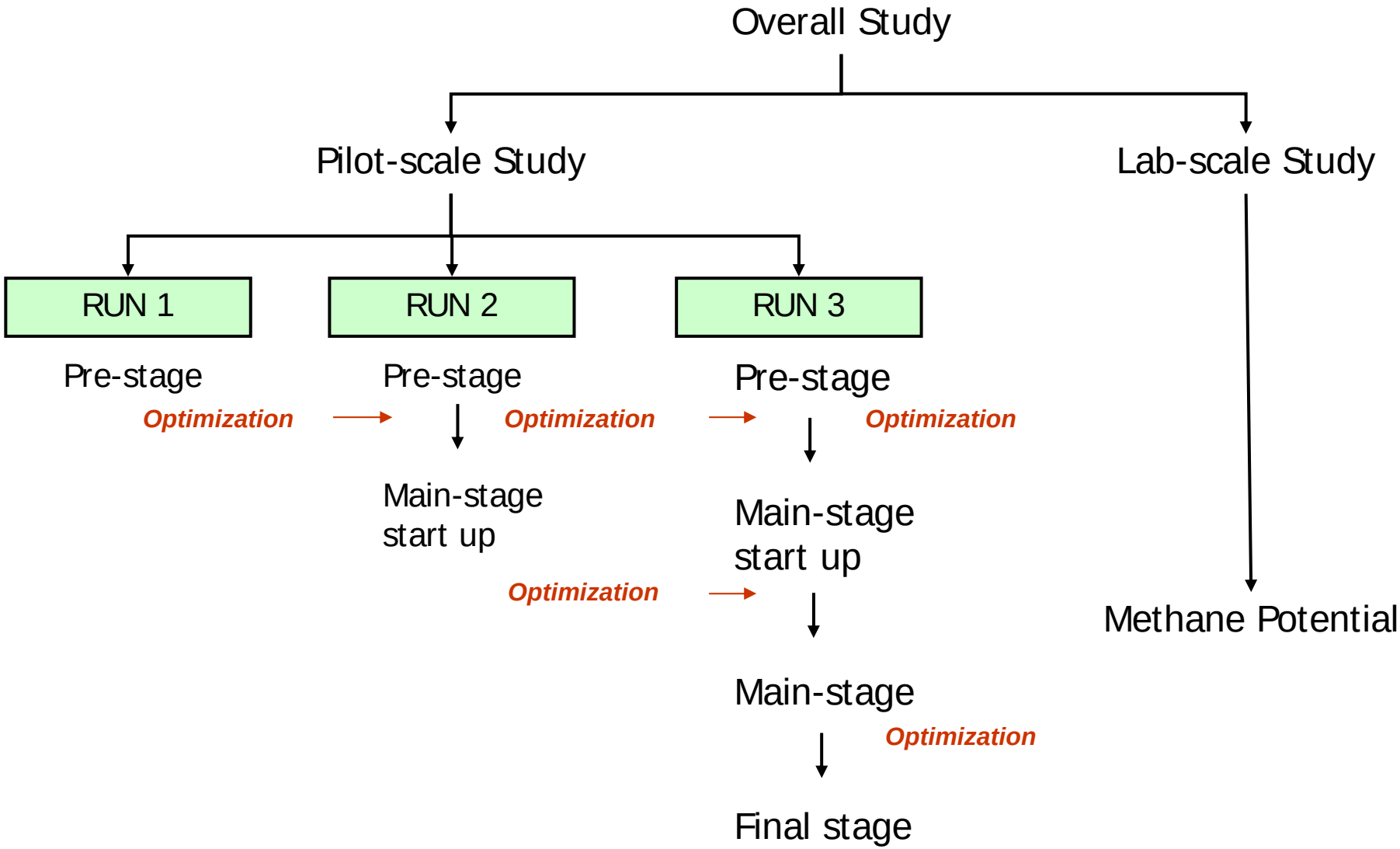


Problems in high solid anaerobic digestion:
→Methanogenesis is rate-limiting step → accumulation of VFA → inhibiting process
→Hydrolysis of particulate material is rate-limiting step

Concept of Combined Process

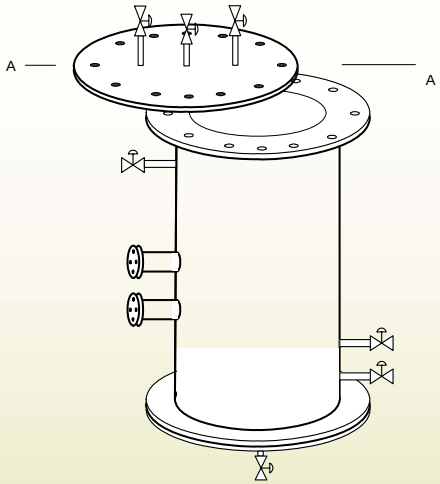


Overall study



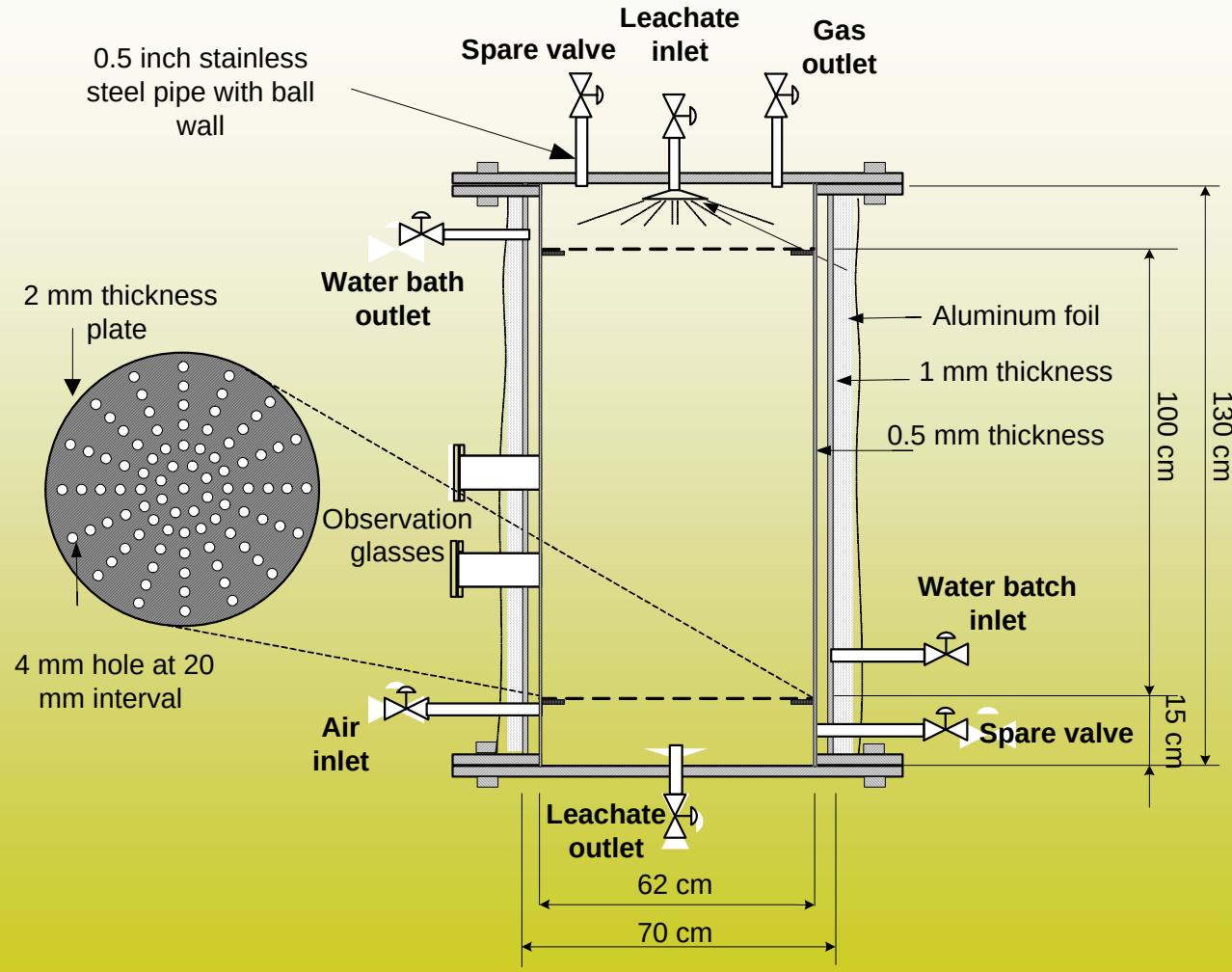
Pilot-scale digestion system

Digester design



Opening reactor in 3D

A-A Section



Feedstock and preparation

Fresh vegetable market waste → segregated

Pulverized

Weighted

Loaded into reactor with bamboo cutlet (bulking agent) to about 500 kg/m^3

Waste characteristics			
	MC, %WW	TS, %ww	VS, %TS
Run 1	90.11	9.89	79.45
Run 2	90.27	9.73	80.59
Run 3	91.02	8.98	77.15

Operational condition of digesters

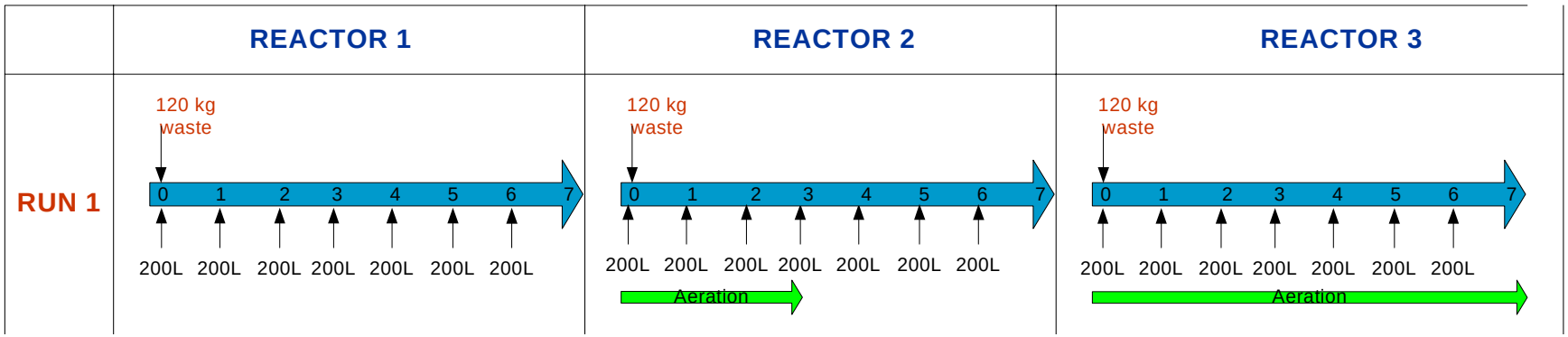
	Flushing and Acidification	Methanogenesis	Air Flushing
Oxygen condition	Anaerobic / Microaerophilic (1L/min ~0.4 L/kg.h)	Strict Anaerobic	Aerobic (10 L/min ~ 4L/kg.h)
Temperature	Ambient	Mesophilic <37^{0}C>	Ambient
Leachate management	Flushing (high rate) (5L/min ~ 18 m^3/m^3 waste/day) 4hrs run/ 4hrs stop	Percolation (rainfall simulation) (0.2L/min ~ 720L/m^3waste/days) 4 hrs run/4 hrs stop	No percolation / recirculation
	Tap water	Available leachate	

Analysis

	Bio gas	Leachate	Solid waste
Pre-stage		pH, Conductivity, ORP, DOC, COD, VFA, TKN, NH_4-N, TDS, Alkalinity	Fresh waste, acid-flushed waste: Moisture content (MC), Volatile solid (VS), Dry matter (DM)
Main-stage	Composition Gas production	pH, VFA	
Final stage	Composition		Digested waste: Moisture content (MC), Volatile solid (VS), Dry matter (DM)

1. Pre-stage Optimization (pilot scale study)

→ Objective: high hydrolysis and acidification yield

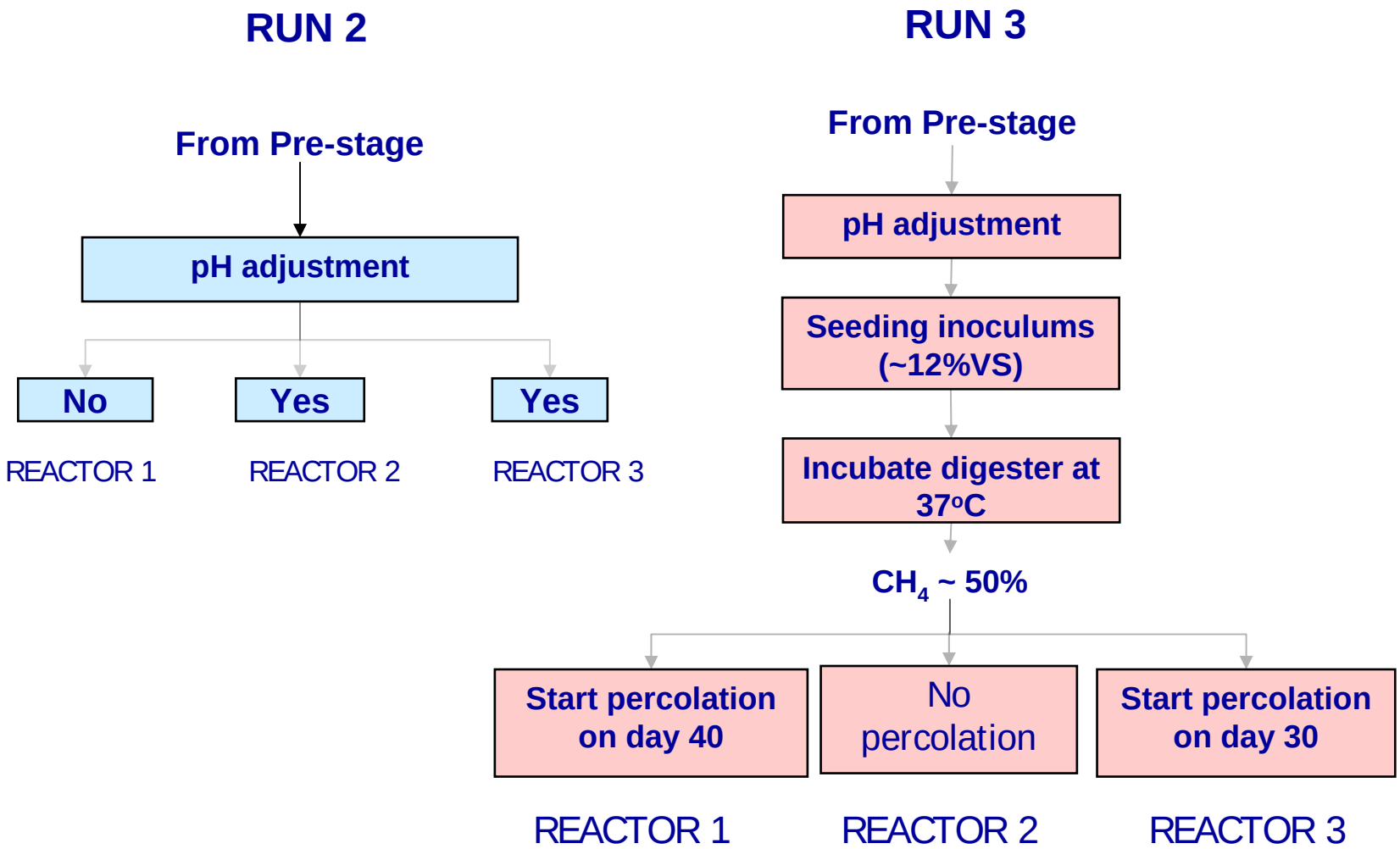


2. Main stage Optimization (pilot scale study)

→ Objective: high biogas production

Start up methanogenesis

Methanogenesis



3. BMP Test (Lab-scale experiment)

BMP: Biological Methane Potential (Ultimate Methane Yield): maximum amount of methane obtained at given temperature and optimal condition.

Method <Hansen et al., 2003>

100 mL sample + 500 mL inoculums

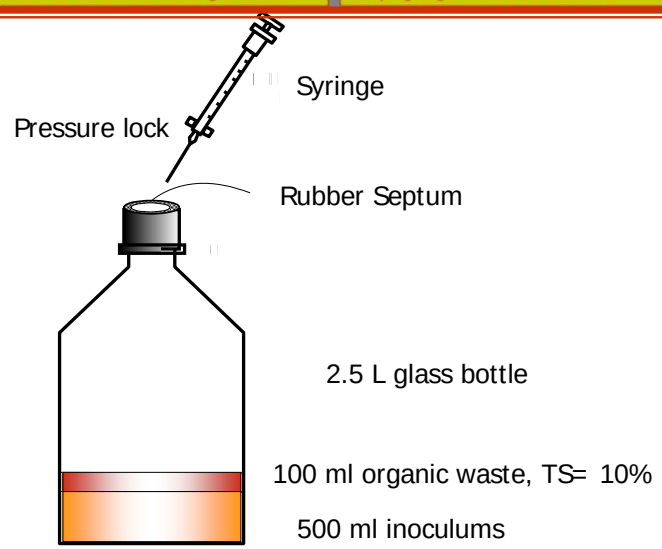
Flushed with gas mixture (20% CO_2 + 80% N_2)

Incubate at 37^{0}C for 40 days

Occasionally shaken and moved around

Biogas analysis *Mass-based*

Biogas removal



Results and Discussions

- Part I: Pre-stage Optimization
- Part II: Main-stage Optimization
- Part III: Process Evaluation

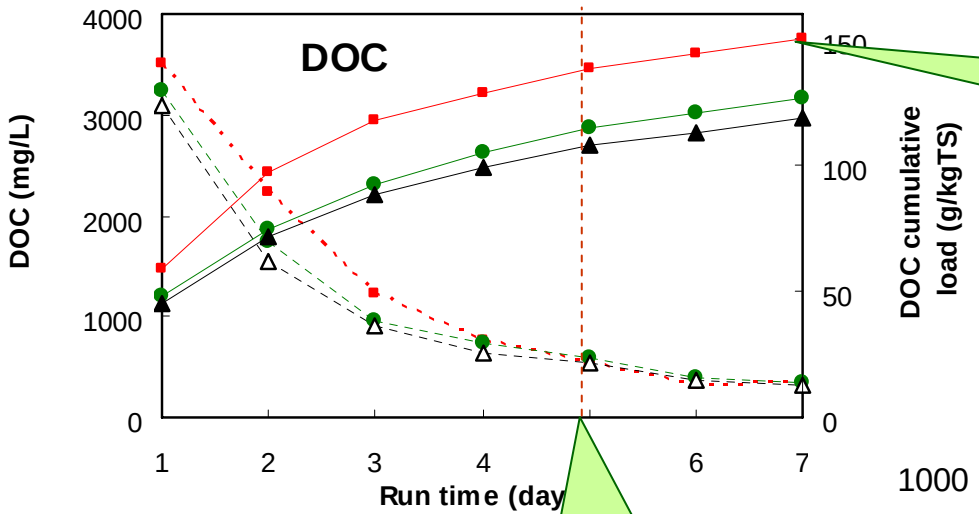
Part I: Pre-stage optimization

1. Hydrolysis (Run 1)

---- Concentration;
—— Cumulative load

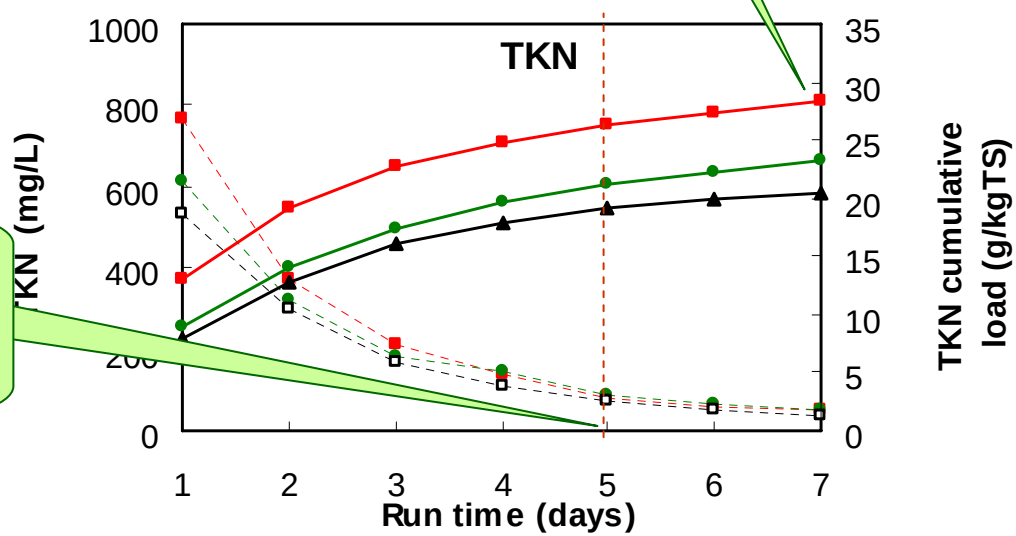
R1: non-aerated reactor
R2: 3 day aerated reactor
R3: 7 day aerated reactor

Hydrolysis of carbonaceous materials



Optimum retention time for Pre-stage was 5 days

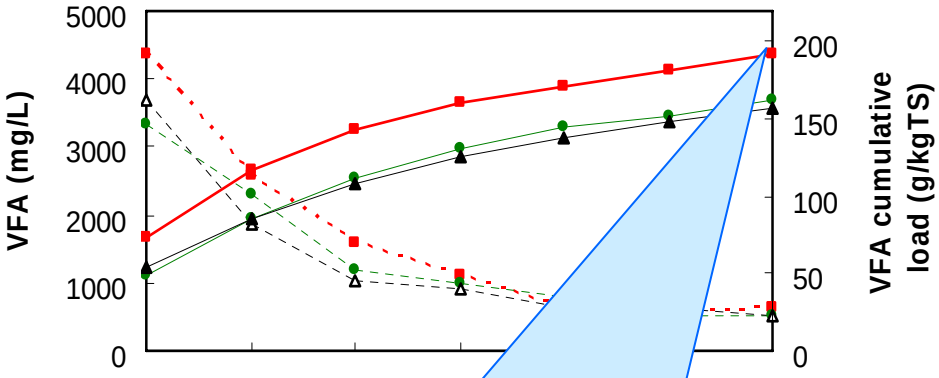
Hydrolysis of nitrogenous materials



Non-aerated reactors result in highest hydrolysis yield
→ aeration did not enhance flushing

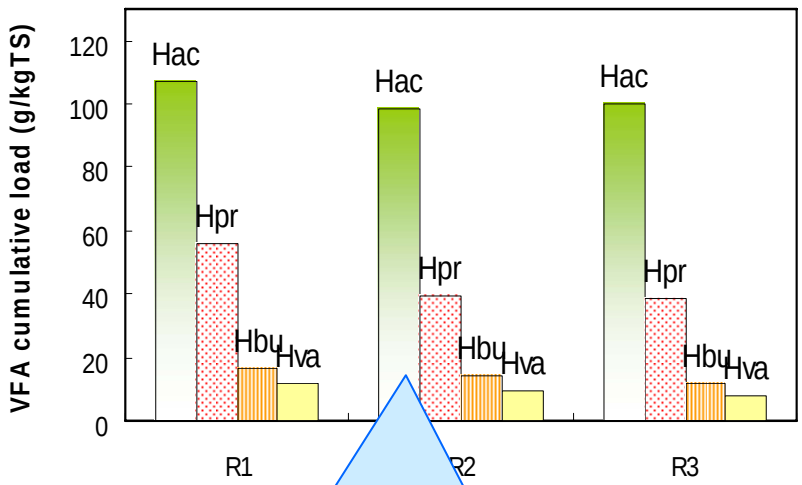
2. Acidification (Run 1)

Variation of total VFA



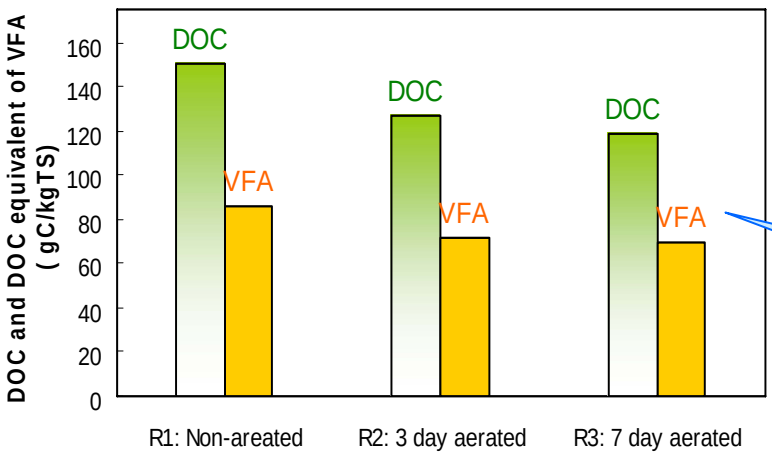
High acidification yield ~0.18 gVFA/kg TS compared with Vieitez and Gosh 1987 D'Addario et al., 1993.

Individual VFA distribution



Acetic acid was predominant Similarly to Sans et al., 1994; Cho and Park, 1995; Mtz Virtura et al., 1994)

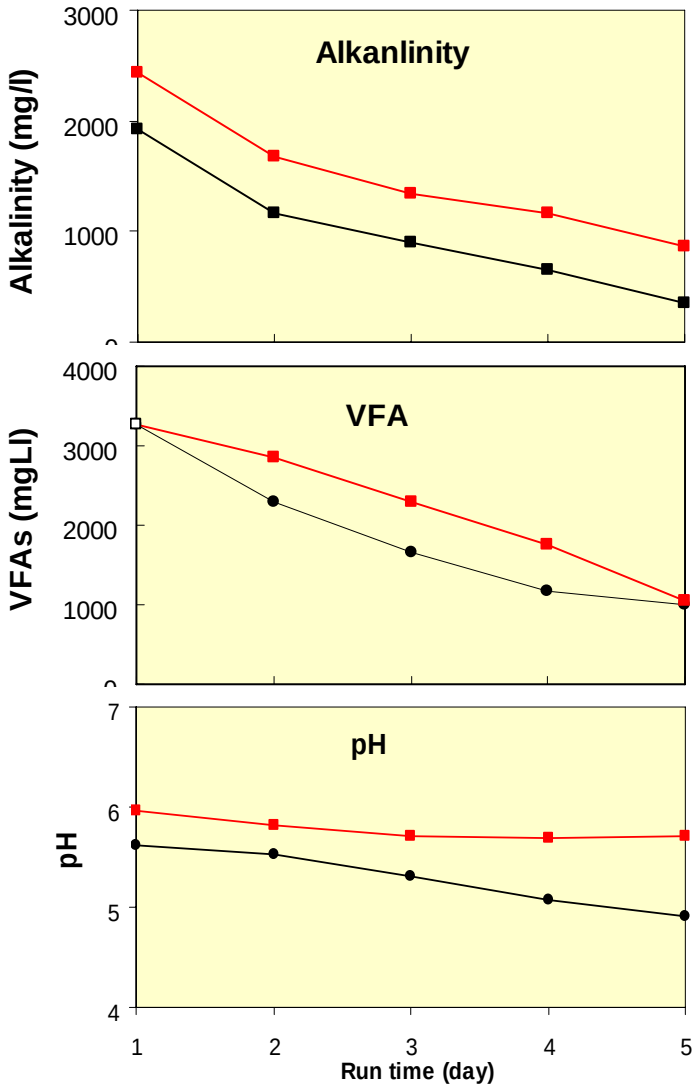
Acidificaiion yield vs. hydrolysis yield

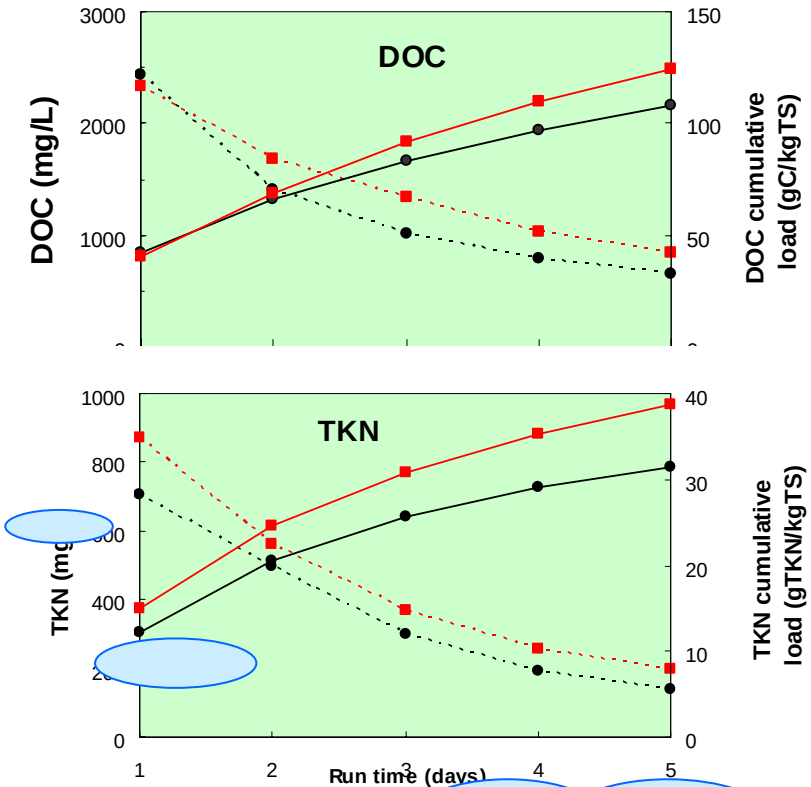


More than 50% of hydrolysate was acidified

3. Effect of pH (Run 2)

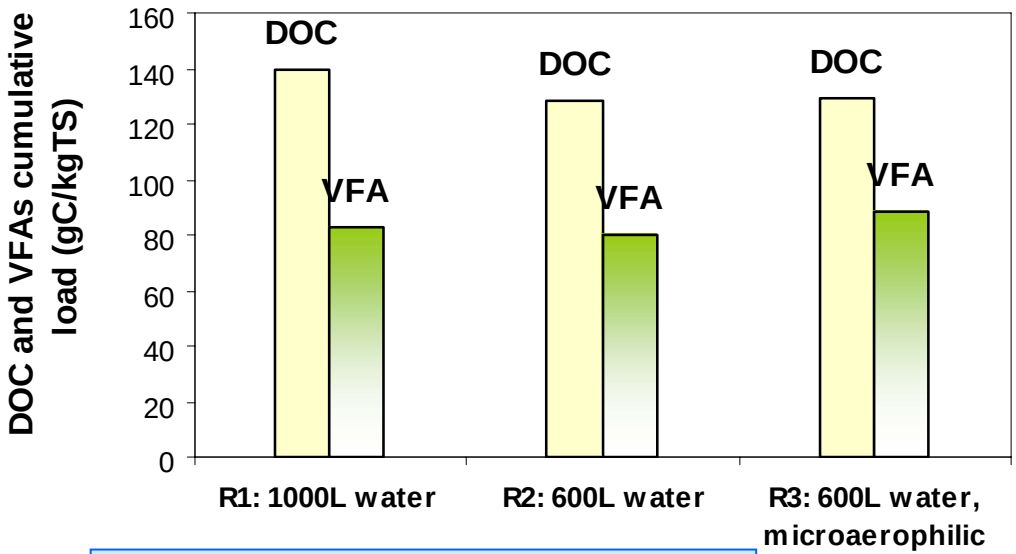
---- limestone buffered reactor
---- pH uncontrolled reactor





Lime-stone support could raise pH
→enhance leaching and acidification

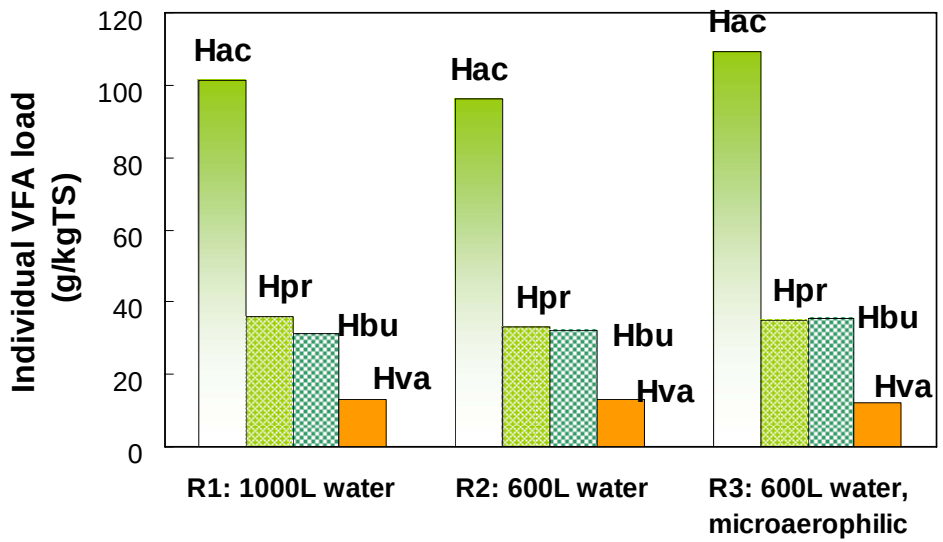
4. Effect of - Flushing water/ Micro-aeration/ Intermittent waste loading (Run 3)



1. Reduce water from 1000 to 600 (5L/kg → 3L/kg) did not significantly reduce flushing efficiency

2. Micro-aeration exhibited the equivocal results in enhance acidification

3. Intermittent solid waste loading result in overall loading rate of 700 kg/m^3 while maintaining approximate yeild (130 g/kgTS) as compared with Run 1,2 (400 kg/m^3)



5. Overall results

	Feeding		Reactor 1	Reactor 2	Reactor 3
Run 1	One time (120kg)	1000 L water	Non-aerated	3 days aerated	7 day aerated
Run 2	One time (120kg)	1000 L water	Non-aerated-Gravel support	Non-aerated	2 day aerated
Run 3	Three time feeding (200kg)	Gravel support	1000 L water	600 L water	600 L waste
			Non-aerated	Non-aerated	Micro-aeration

Hydrolysis yield (% C in leachate)			
	Reactor 1	Reactor 2	Reactor 3
Run 1	31.36	26.03	24.43
Run 2	27.66	24.04	18.43
Run 3	32.57	29.88	30.14

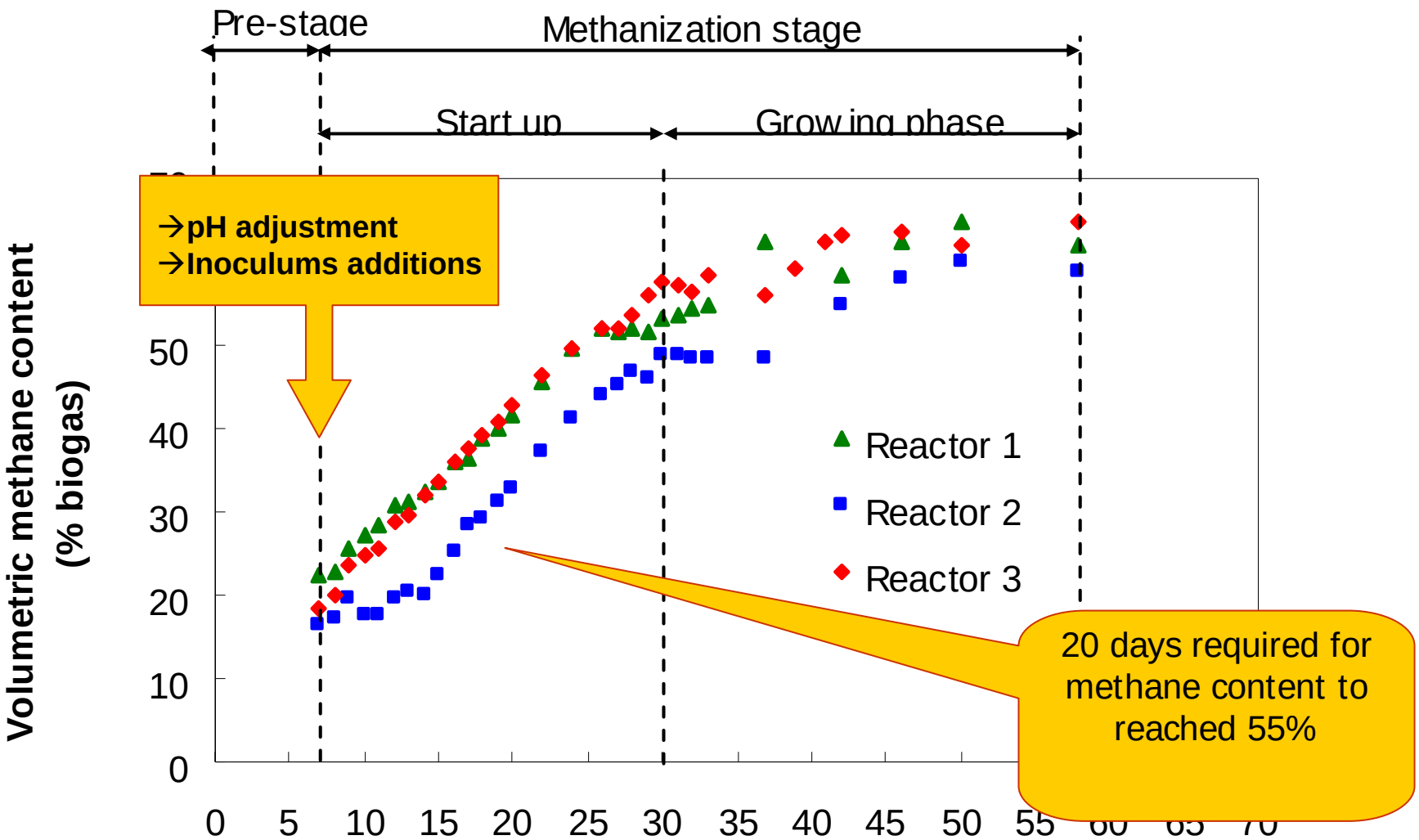
cation yeilds (gVFA/kgTS)		
ctor 1	Reactor 2	Reactor 3
171.74	144.25	137.75
182.67	160.11	119.98
	174.67	193.23

Optimized operation was reactor 2, 3 (Run 3)

- **Intermittent waste loading- every two day (500kg/m^3)**
- **Duration 5 days; tap water feeding 3L/kg**
- **Without aeration or with micro-aeration**

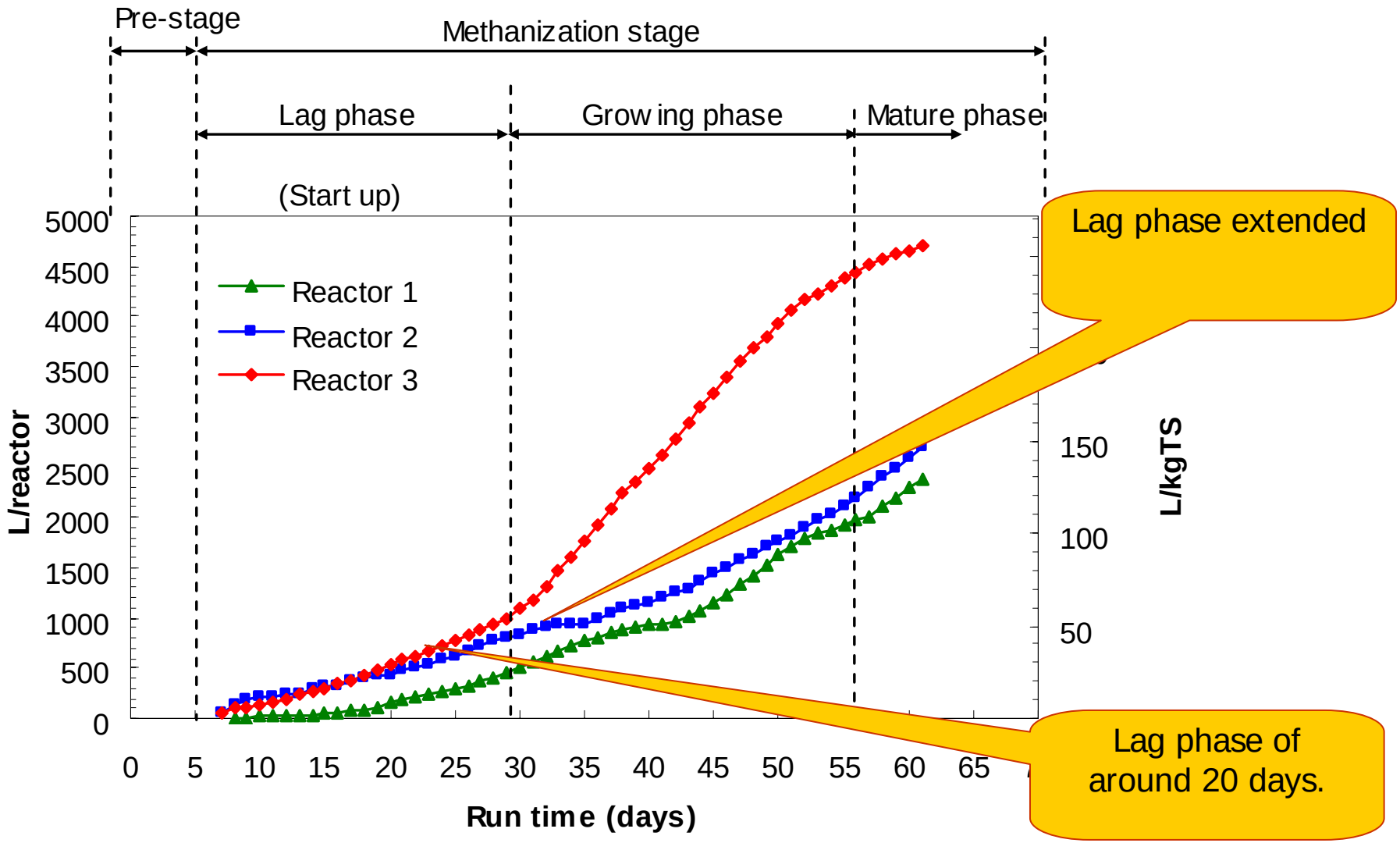
Part II: Main stage optimization

1. Biogas composition (Run 3)



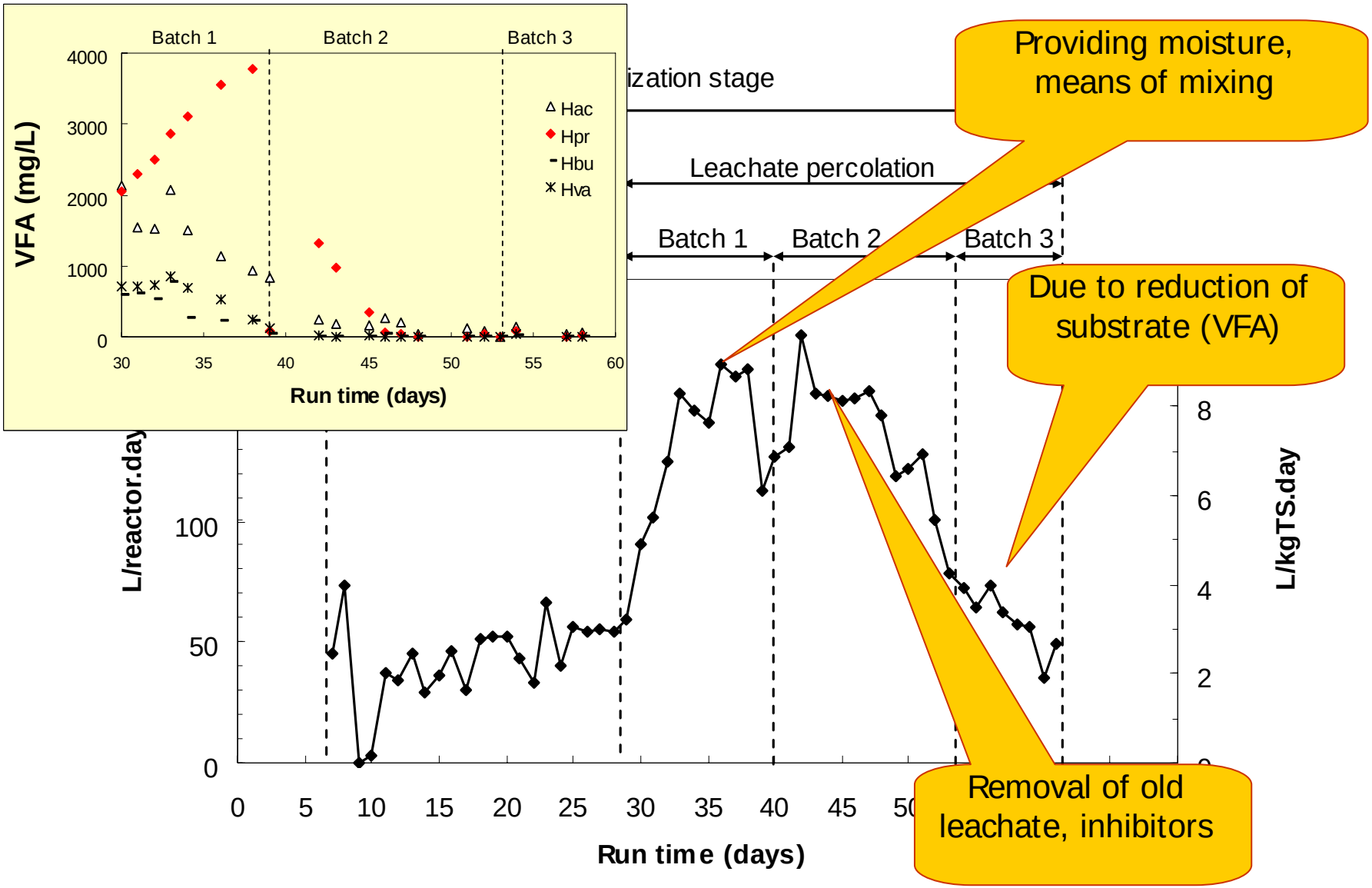
<Figure 4.28>

2. Cumulative gas production (Run 3)



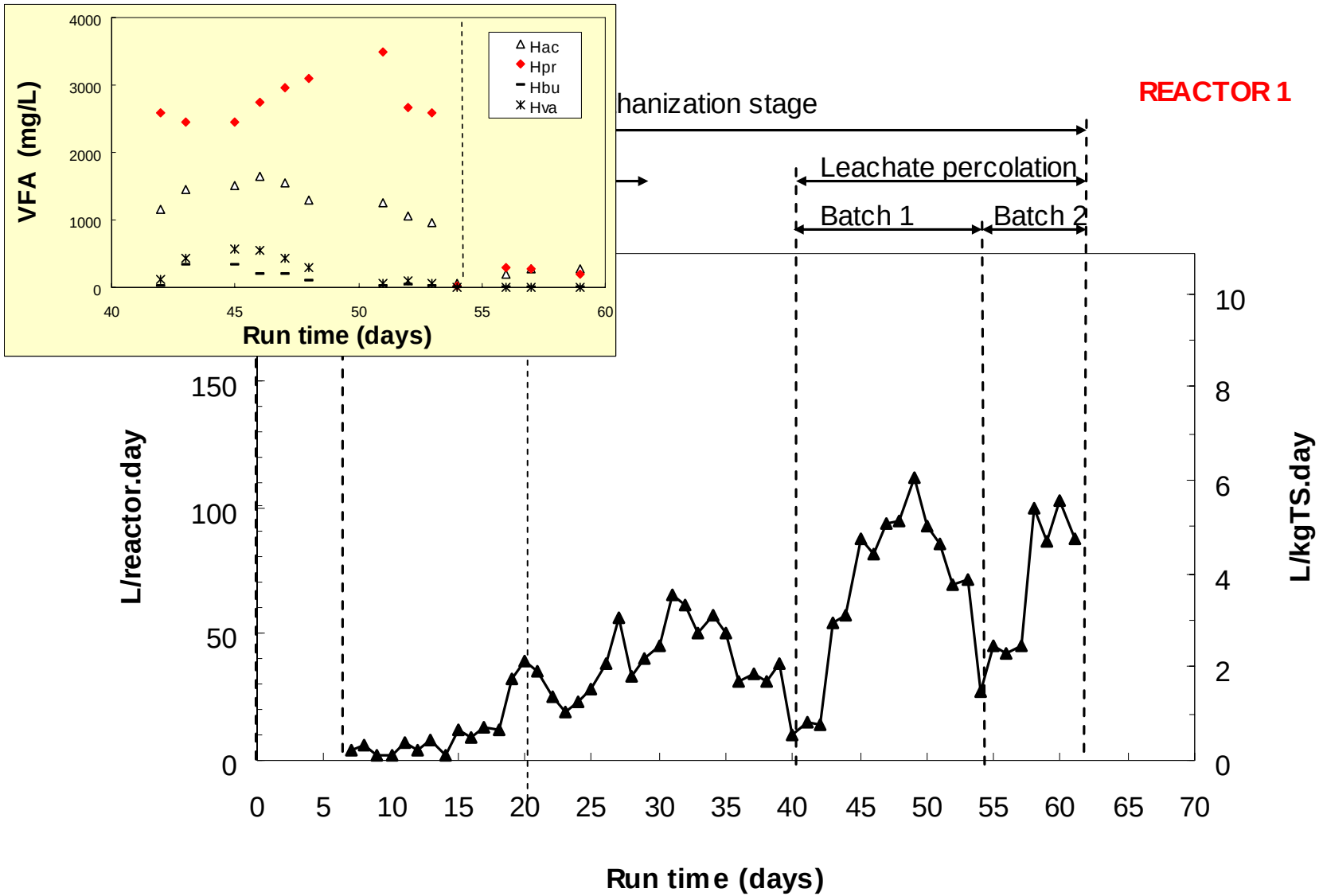
<Figure 4.29>

3. Daily gas production (Reactor 3)



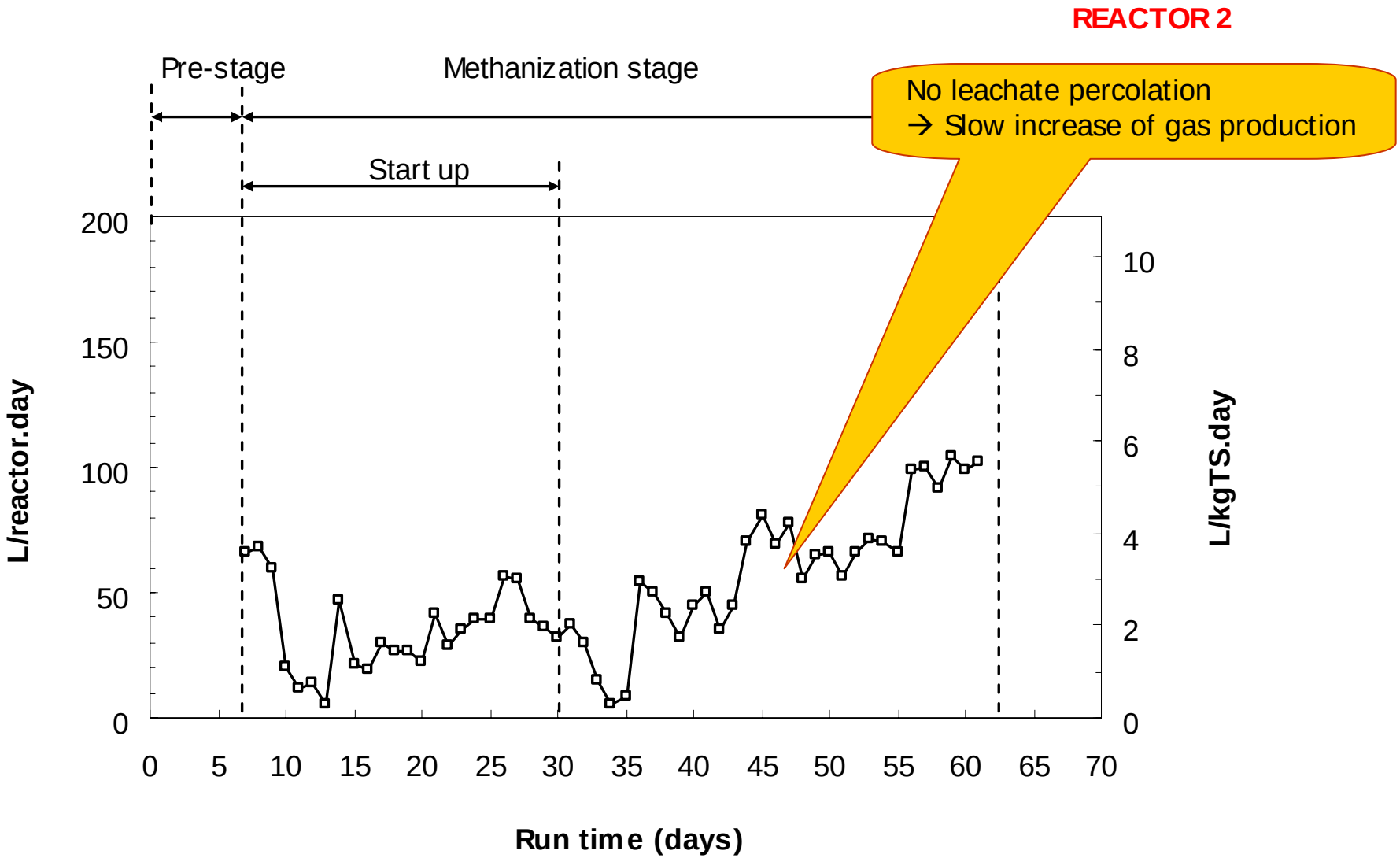
<Figure 4.32>

4. Daily gas production (Reactor 1)



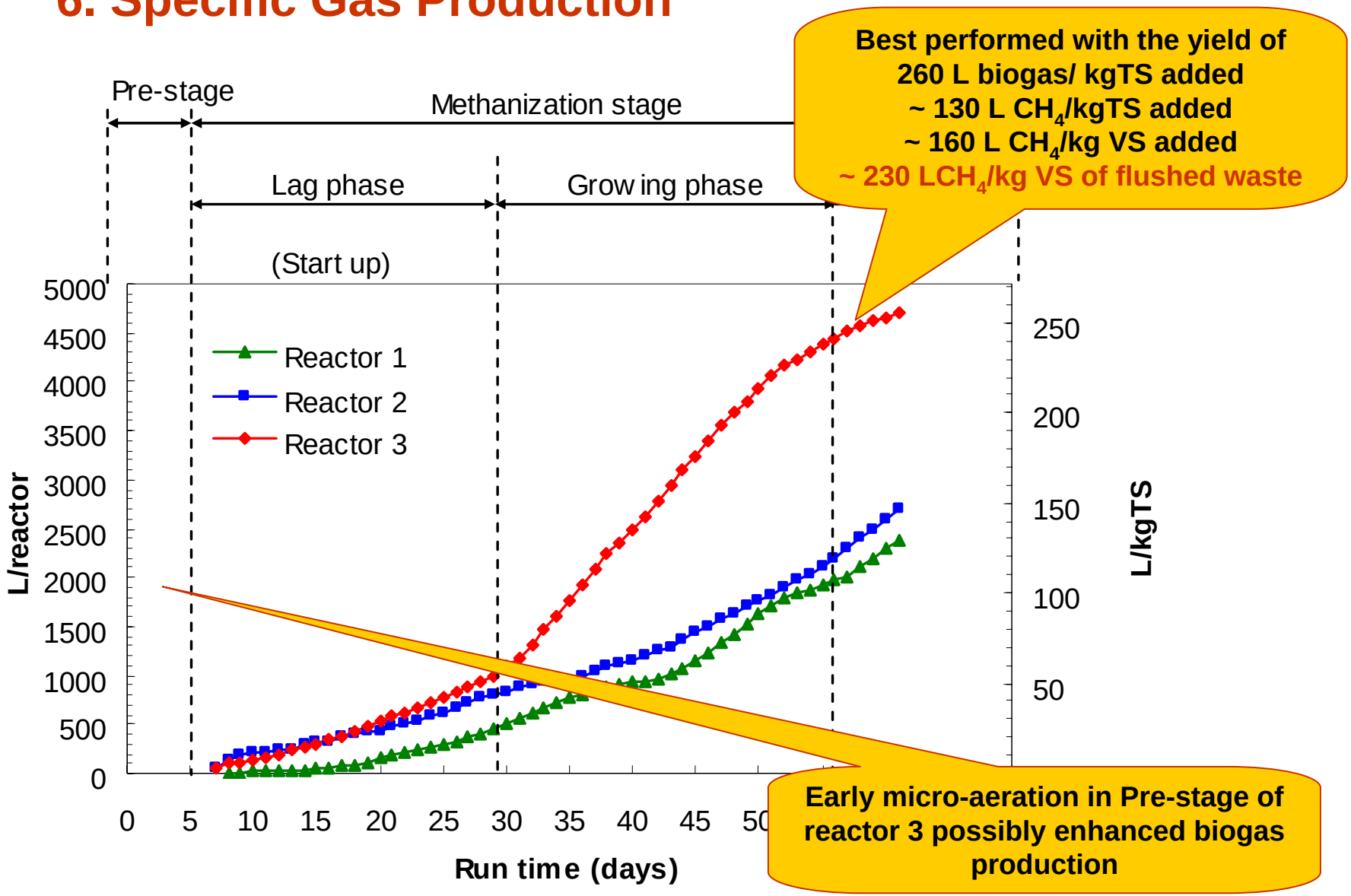
<Figure 4.31>

5. Daily gas production (Reactor 2)



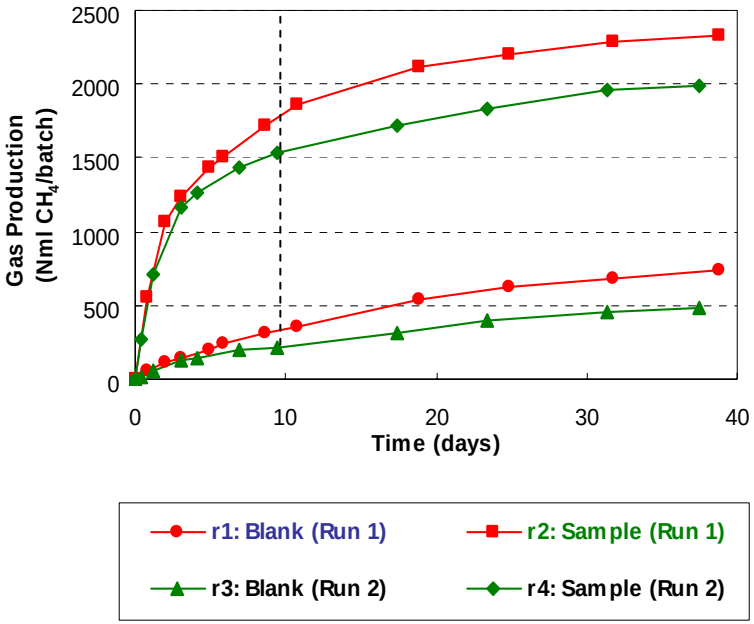
<Figure 4.31>

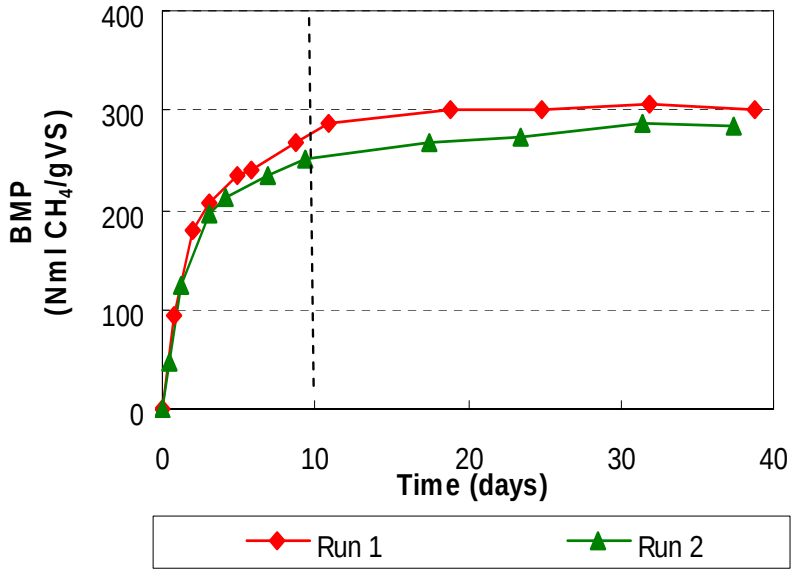
6. Specific Gas Production



<Figure 4.29>

7. Methane Potential Test





Efficiency of methanization stage

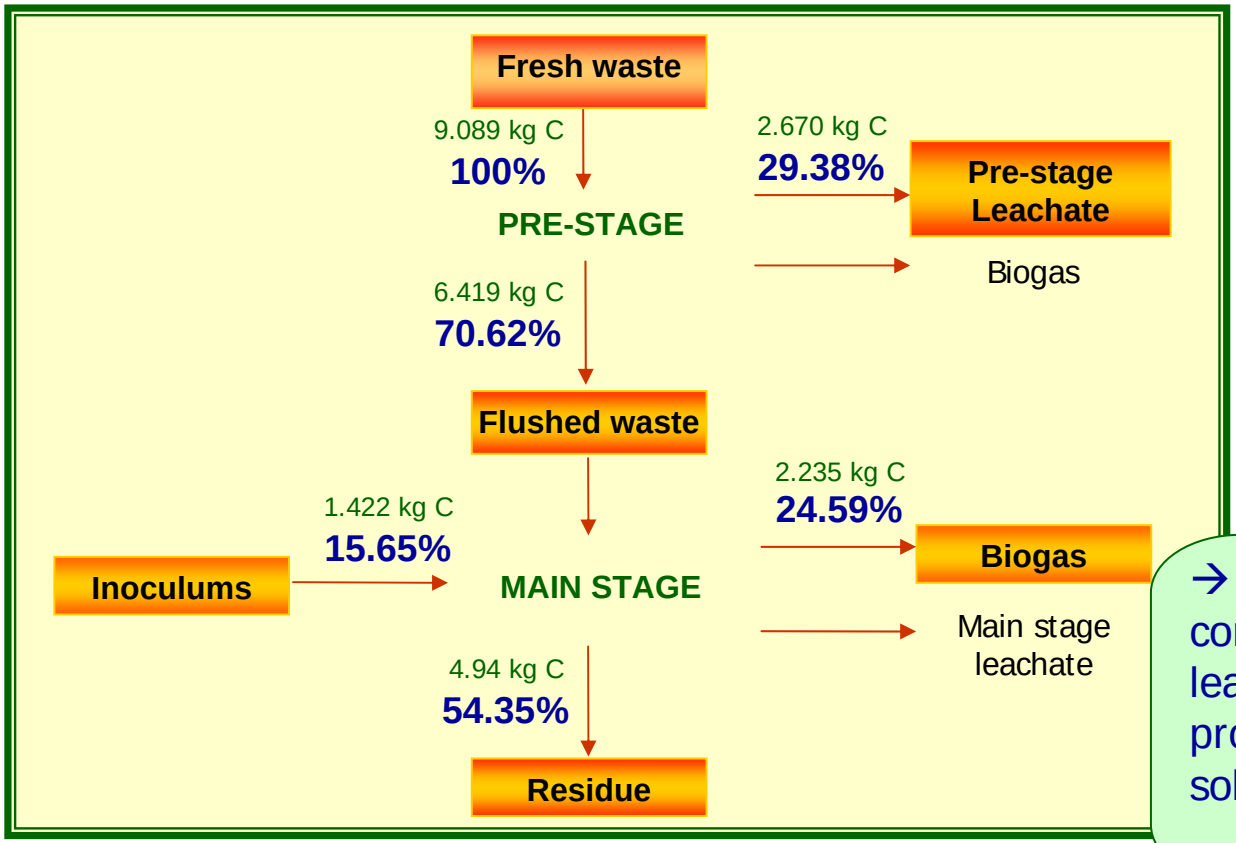
BMP
~ 300 L/kgVS

Actual yield
~ 230 LCH_4/kg VS

75 % biogas conversion achieved in the reactor of flushed waste

Part III: Process Evaluation

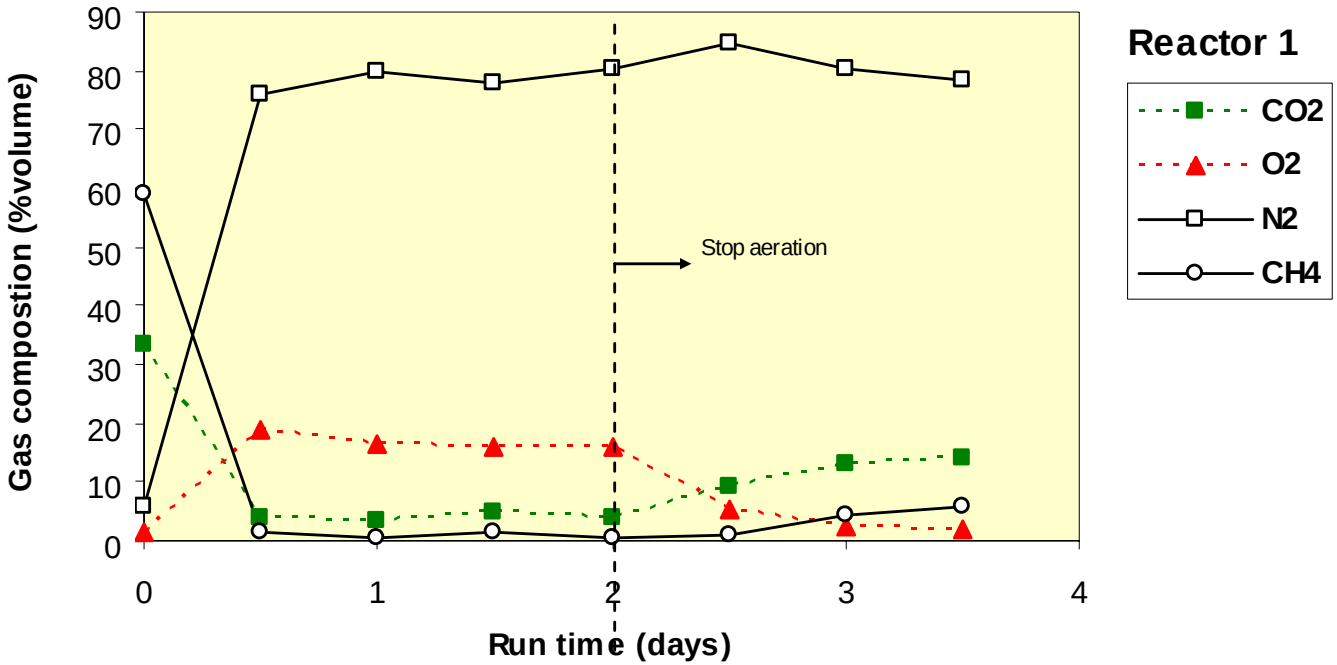
Volatile solid destruction and carbon balance



→ Process show consistent result in leachate load, biogas production, and volatile solid destruction

- ❑ 130 gC/kgTS in pre-stage leachate ~ 29.38 %C (leachate)
- ❑ 4700 L biogas in main stage ~ 24.59 % C (biogas)
- ❑ volatile solid destruction of 61% ~ 39 % C (residue) ≅ 54% -15%

Final stage: air flushing



→ One day aeration was sufficient for biogas removal

Conclusions and Recommendations

Conclusion

Optimization of Flushing and Acidification

- Flushing, during 5 days, was able to remove 30% of carbon content in the fresh waste (hydrolysis yield ~ 130gC/kgTS)
- Acidogenesis occurred early with acidification yield of 180 gVFA/kgTS (equivalent to 60% of DOC). In short retention time, acetic acid was predominant.
- Micro-aeration showed the equivocal results in terms of enhancing short-term hydrolysis and acidification.
- Supporting a of partly limestone gravel could bring higher hydrolysis/acidification yield due to favorable higher pH of around 6
- Optimum flushing water was 3 L/kg for 5 days flushing
- Flushing resulted in early settlement of the waste (40% volume reduction). Thus, in order to utilized the headspace of reactor, intermittent solid waste feeding during Pre-stage could be feasible

Conclusions (cont')

Optimization of methane phase

1. The waste had low buffering capacity. Methanogenesis could not be quickly started without initial pH adjustment (pH > 6.5) accompanied with addition of inoculums. Lag phase were 20 days.

2. Leachate percolation could enhance biogas production, shortening solid retention time to finish the process, due to: moisture addition; improving bacteria movement, mass transportation, inhibition removal.

3. Early micro-aeration, during Pre-stage, could possibly bring to higher biogas production in methane phase as well as better waste stabilization

4. Two month period was sufficient for waste stabilization

5. Methane potential of the waste was 300 LCH4/kg TS, the actual yield of 260 LCH4/kg flushed TS indicated that 75 % biogas conversion was achieved.

6. The process resulted in 61% VS destruction, it was partly contributed by flushing into leachate (30%) and partly by stabilization into biogas (25%)

Recommendations

Pre-stage

- Optimization of L: S over flushing time, for saving water and more concentrated acidified leachate.
- Flushing fresh waste with mature leachate instead of fresh water, for saving water, providing buffering capacity and inoculums from the mature leachate

Main stage

- Optimization of leachate percolation (rate and duration) in methane phase
- Investigation of methanization stage at thermophilic temperature

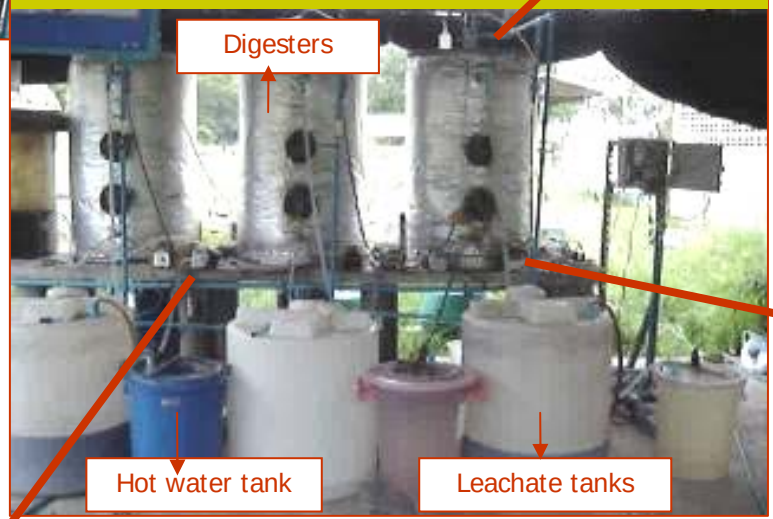
Additional stages

- Composting of residue for stabilization of hardly anaerobically-digested materials
- Treatment of acidified leachate in separate methane digester → Reduce the need to extend the system for long mature phase

Anaerobic digestion system

Opened digester for unloading waste

THE SYSTEM

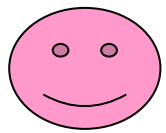


Wet gas meter

Temperature controller and pumps

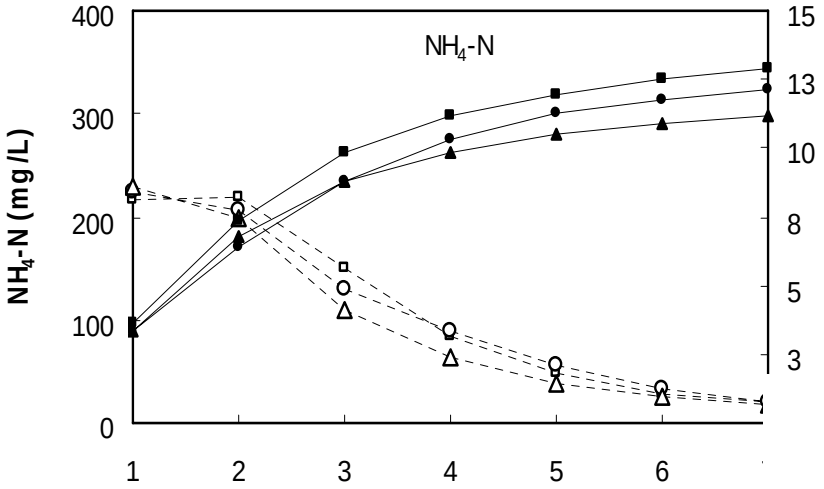
Sampling biogas

Thank you !



Ammonia and pH

Run 1



→Ammonia concentration were low (200mg/l) → low alkalinity → low pH

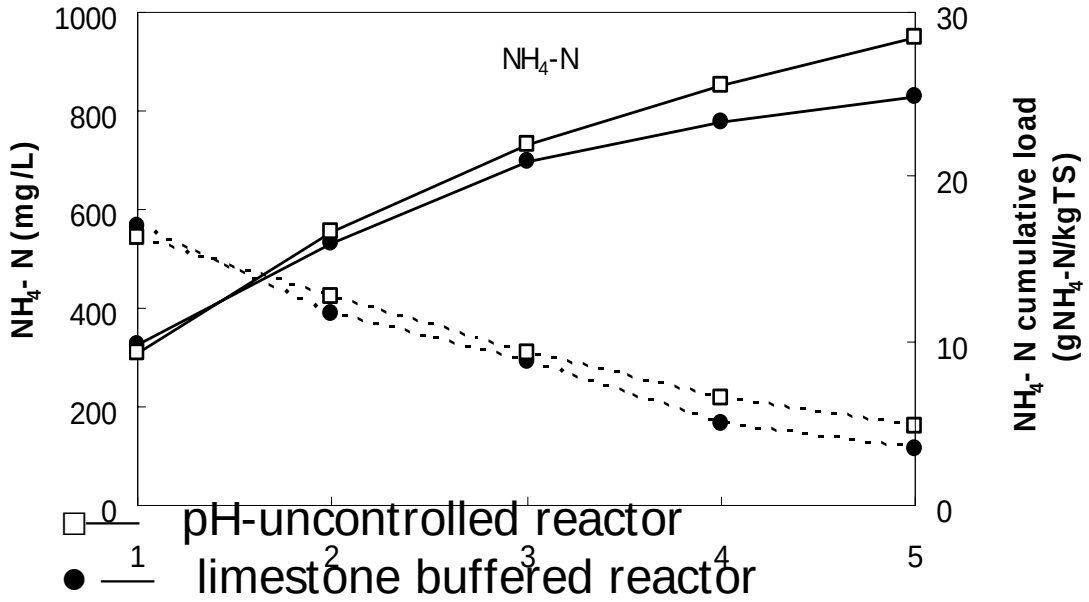
In limestone buffer reactor

Higher pH → lower NH_4^+, due to

$NH_3 + H^+ \rightarrow NH_4^+$

Higher pH → less H^+ → balance is from right to left.

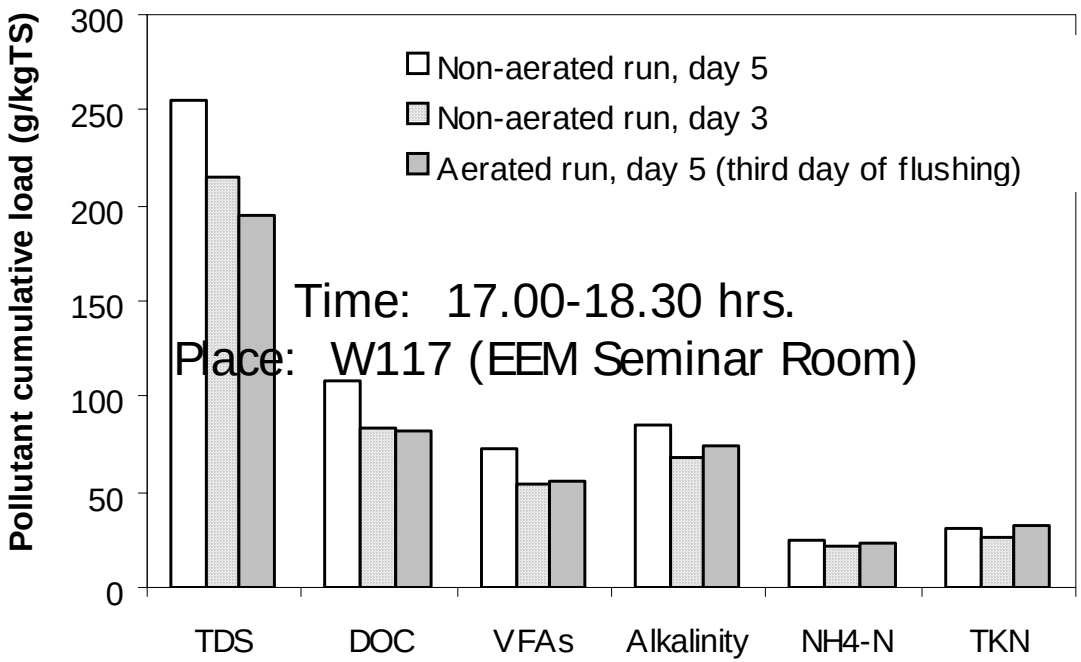
Run 2



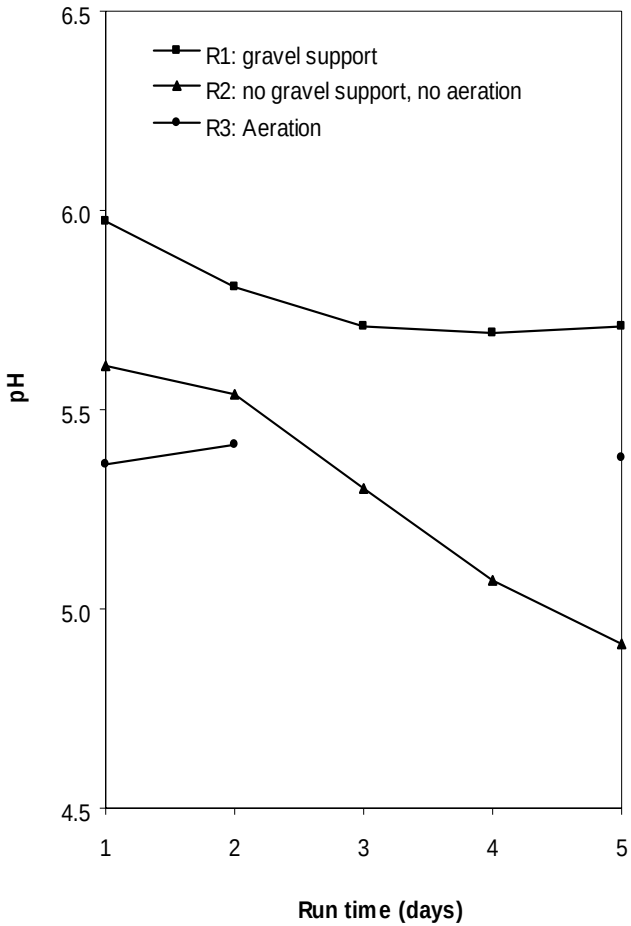
Ammonia inhibition

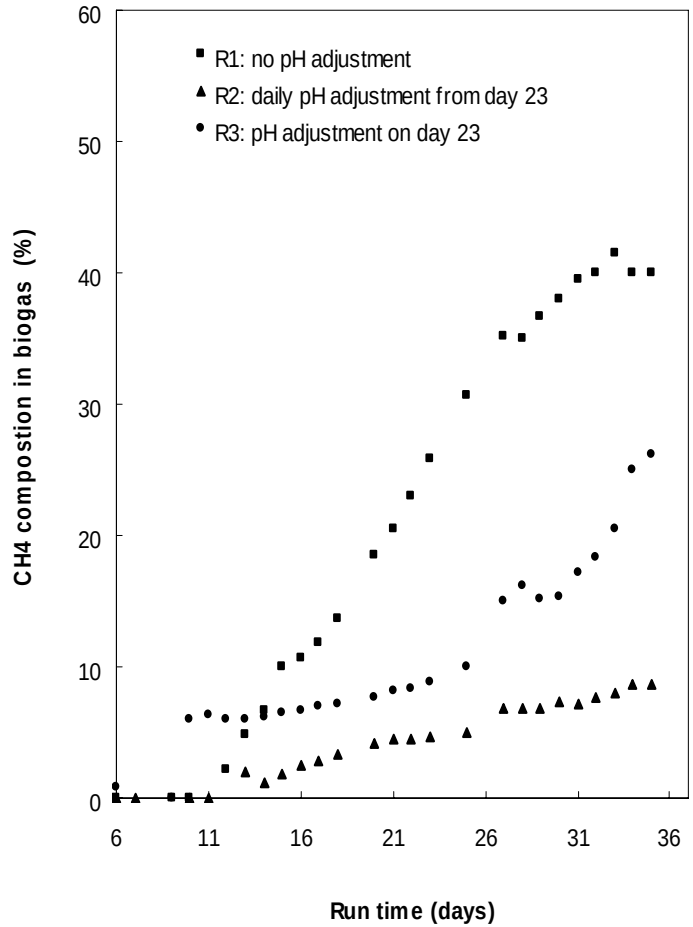
- methanogenic activity was dependent on the level of ammonium, NH4+ not NH_3
- high concentration of NH4+-N reduces the biogas production
- Higher pH → lower NH_4^+

Affect of short time aeration (Run 2)



Start up methanogenesis (Run 2) → importance of pH adjustment



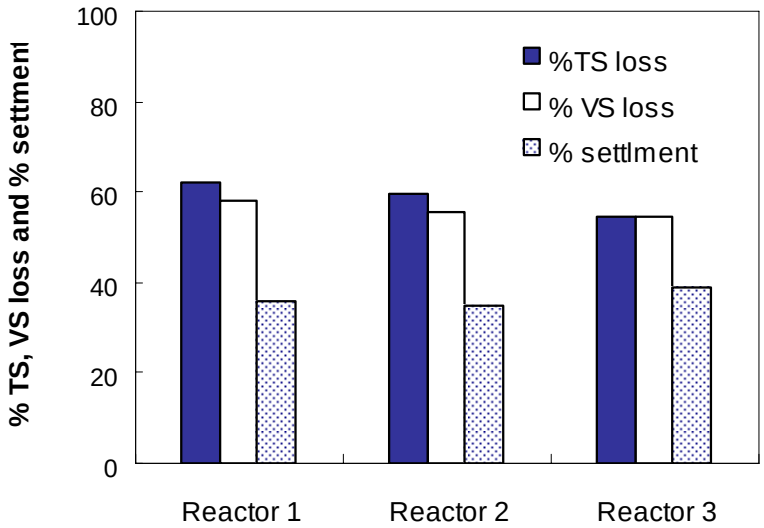


Micro-aeration

- Improve hydrolysis in main-stage → provide more substrate for methanogens
- Create more void space →create more contact surface between inoculums and substrate

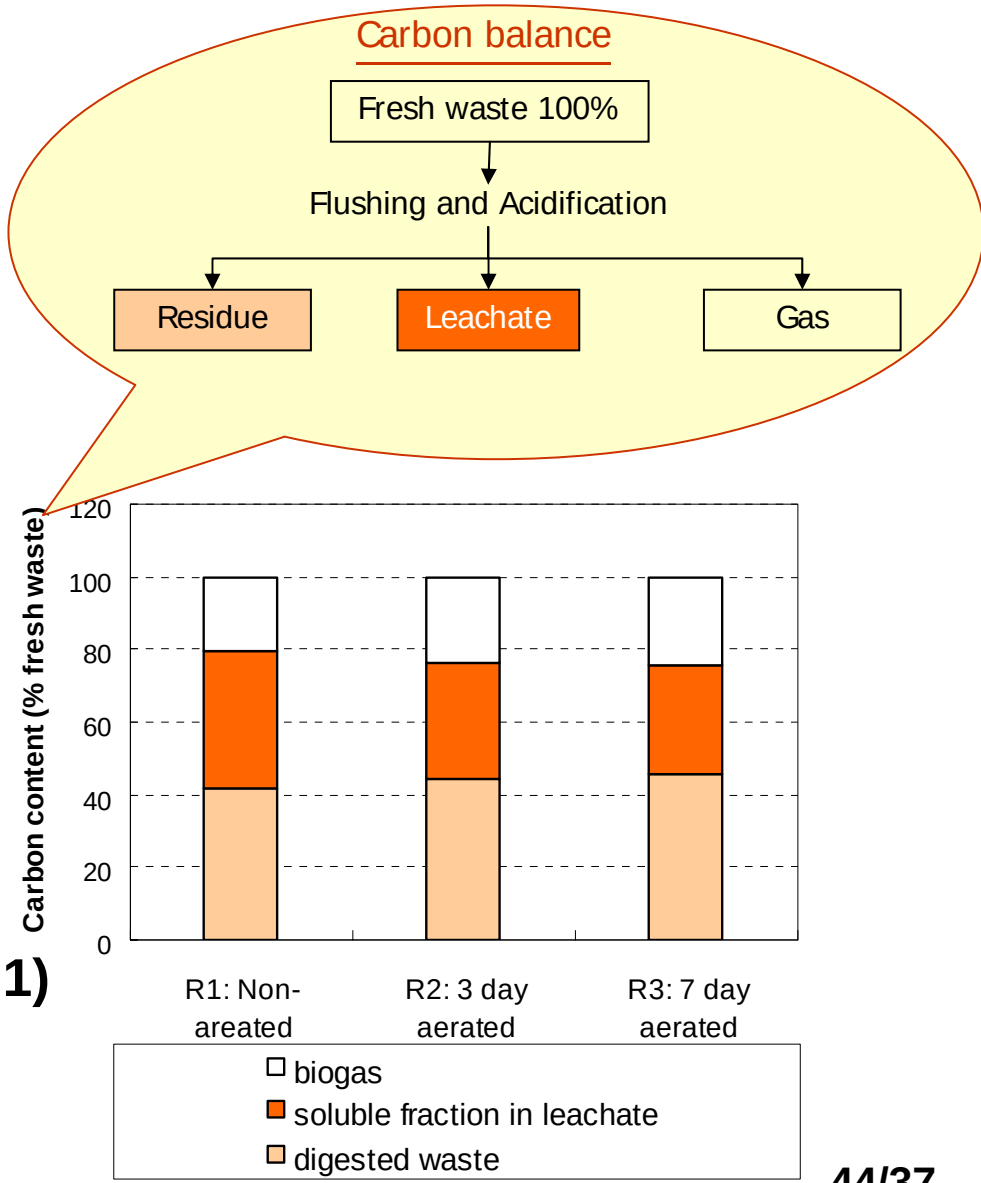
Pre-stage optimization

3. Waste stabilization and …



→ High VS, TS destruction > 50%

→ ~ 40% settlement



…C balance in Pre-stage (Run 1)