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ORGANIC ACID PRODUCTION FROM THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE IN LEACHING BED REACTORS

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Approval of the Graduate School of Natural and Applied Sciences

_____

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_____

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

ORGANIC ACID PRODUCTION FROM THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE IN LEACHING BED REACTORS

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This study was carried out to evaluate the potential of high-rate anaerobic digestion of high-solids organic fraction of municipal solid waste (OFMSW) for the production of organic acids and alcohols in leaching bed reactors (LBRs). For this purpose, two different experimental set-ups, namely Set-1 and Set-2, were operated. In the Set-1, only OFMSW without paper was studied in two identical LBRs, whereas, four identical LBRs, fed with OFMSW with paper and cow manure in different proportions, were operated in the Set-2.

In this study, 50-60% of hydrolysis efficiency was achieved in the LBRs of Set-1, whereas this value was decreased to 20-25% in the LBRs of Set-2; which was resulted from OFMSW containing cellulose and less volume of water addition in the Set-2.

The mass of total volatile fatty acids (tVFA) production was found as 7000-9000 mg at the end of 80 days in the LBRs of Set-1, fed with OFMSW without paper, whereas it was 3000 mg at the end of 40 days in the LBR of Set-2, containing only OFMSW with paper. It was also observed that cow manure addition increased the amount of tVFA production in the LBR of Set-2.

In conclusion, LBRs were found as alternative reactors for the degradation of OFMSW compared to completely stirred tank reactors (CSTRs) in terms of rapid hydrolysis and acidification, which can result in high hydrolysis yield and tVFA production.

Key Words: Anaerobic digestion, Organic fraction of municipal solid waste, Cow manure, Leaching bed reactor, Total volatile fatty acids

ÖZ

SIZDIRMA YATAKLI REAKTÖRLERDE ORGANİK BAZLI EVSEL KATI ATIKLARDAN ORGANİK ASİT ELDE EDİLMESİ

Doğan, Evrim
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Bu çalışma, organik asit ve alkol elde etmek için yüksek katı madde içeren organik bazlı evsel katı atıkların (OBEKA) sızdırma yataklı reaktörlerde yüksek hızlarda anaerobik olarak verimli bir şekilde bozundurulma potansiyelini değerlendirmek için yürütülmüştür. Bu amaçla, Set-1 ve Set-2 olmak üzere iki farklı deney düzeneği çalışılmıştır. Set-1'de sadece kâğıt içermeyen OBEKA, iki adet aynı sızdırma yataklı reaktörde çalışılırken, Set-2'de ise kâğıt içeren OBEKA ve hayvansal gübre, farklı oranlarda karıştırılarak, dört adet aynı sızdırma yataklı reaktörde çalışılmıştır.

Bu çalışmada, Set-1'deki sızdırma yataklı reaktörlerde %50-60 hidroliz verimi sağlanırken, Set-2'deki sızdırma yataklı reaktörlerde bu değer %20-25'lere düşmüştür. Bu durum, Set-2'de kullanılan OBEKA'da bulunan selülozdan ve az miktarda su eklenmesinden kaynaklanmıştır.

Toplam uçucu yağ asit (tUYA) üretimi ise Set-1'de kağıt içermeyen OBEKA ile beslenen sızdırma yataklı reaktörlerde 80 günün sonunda 7000-9000 mg iken, Set-2'de sadece kağıt ve OBEKA içeren sızdırma yataklı reaktörde 40 günün sonunda 3000 mg olarak bulunmuştur. Ayrıca, Set-2'de sızdırma yataklı reaktörde hayvansal gübre eklemesinin tUYA üretim miktarını arttırdığı gözlenmiştir.

Sonuç olarak, yüksek katı madde içeren OBEKA'nın bozundurulmasında, sızdırma yataklı reaktörlerin, yüksek hidroliz verimi ve tUYA üretimi gerçekleştirebilen, hidroliz ve asidifikasyon hızı bazında, tam karıştırmalı reaktörlere alternatif reaktörler olduğu saptanmıştır.

Anahtar Kelimeler: Anaerobik bozundurma, Organik bazlı evsek katı atık, Hayvansal gübre, Sızdırma yataklı reaktör, Toplam uçucu yağ asiti

To My Parents

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LIST OF ABBREVIATIONS

AD: Anaerobic Digestion

ASBR: Anaerobic Sequencing Batch Reactor

Buty: Butyric acid

COD: Chemical Oxygen Demand

CSTR: Completely Stirred Tank Reactor

DIE: Devlet İstatistik Enstitüsü

DRANCO: Dry Anaerobic Composting

EtOH: Ethanol

GC: Gas Chromatograph

HAc: Acetic acid

HPr: Propionic acid

HRT: Hydraulic Retention Time

LBR: Leaching Bed Reactor

MLSS: Mixed Liquor Suspended Solids

MLVSS: Mixed Liquor Volatile Suspended Solids

MSW: Municipal Solid Waste

OFMSW: Organic Fraction of Municipal Solid Waste

OLR: Organic Loading Rate

PVC: Polyvinyl Chloride

sCOD: Soluble Chemical Oxygen Demand

SEBAC: Sequenced Batch Anaerobic Composting

SRT: Solids Retention Time

SS: Suspended Solids

tCOD: Total Chemical Oxygen Demand

TS: Total Solids

TSS: Total Suspended Solids

TURKSTAT: Turkish Statistical Institute

tVFA: Total Volatile Fatty Acid

UASB: Upflow Anaerobic Sludge Blanket

VFA: Volatile Fatty Acid

VS: Volatile Solids

VSS: Volatile Suspended Solids

CHAPTER 1

INTRODUCTION

Municipal solid waste (MSW) management has been a major concern around the world for the last thirty years due to high population increase rate, high living standards of people, changes in the packaging of goods as a result of increasing industrial developments and decreasing space for landfills. The promotion of waste minimization, re-use and recycling are important components of modern waste management strategies. Nevertheless, even when the waste reduction, recycling and transformation technologies are fully exploited, the disposal of residual solid waste in landfills still remains an unavoidable component of an integrated solid waste management strategy. Although sanitary landfills represent a common, economical and environmentally acceptable method for the disposal of solid wastes, the enormous production of MSW, especially in big cities, and the diversity of solid wastes generated have concerned both authorities and researchers for many years, since the disposal of MSW creates serious environmental and human health problems in the long term. Some of these problems are surface water, groundwater and soil contamination due to potential loss of leachate, global warming due to greenhouse gas emissions such as methane and carbondioxide into the atmosphere, fire and explosion hazards and health problems related to human. Especially in the poorer countries of the world, scattered trash and unauthorized garbage dumps are promoting the frighteningly rapid spread of infectious diseases and odor nuisances and causing diverse damage to the environment. All of these problems have spawned research involving the treatment of MSW.

MSW handling and management is also a serious problem in Turkey that should be considered consciously. According to the statistical data taken from Turkish Statistical Institute (TURKSTAT, alias DIE), the average MSW production per capita in Turkey was 1.31 kg/day and the total average MSW collected annually was

25 million tons in Turkey in 2004. Only 7.6 million tons of the annual total collected waste was handled, which corresponds to about 30% of the total collected MSW. In other words; in 2004, 17.4 million tons of MSW was dumped to the environment without public health safety and environmental protection consideration. In addition, according to the statistical data taken from TURKSTAT (alias DIE), about 1.4% of the annual collected solid waste was sent to the composting, about 0.3% was sent to the incineration and approximately 28.9%, which corresponds to 7.2 million tons of solid waste, was sent to the landfills. However, the remaining portion was just given to the environment unconsciously. There are only 16 landfills, 5 composting facilities and 3 incineration facilities in Turkey today (TURKSTAT).

MSW is the solid waste generated in a community with the exception of industrial and agricultural wastes (Tchobanoglous, 1993). An important fraction of the MSW stream can be defined as municipal solid biowaste or organic fraction of MSW (OFMSW). This is paper, garden waste and food waste from the kitchen, which corresponds to fruit and vegetable residues resulting from the handling, preparation, cooking and eating of food. The OFMSW may consist of paper, which can be recycled, but the remaining waste is food waste (kitchen waste) and other highly biodegradable materials that pose health and sanitation concerns. The biodegradable fraction (paper, garden and food waste) accounts for 53% of waste composition (Kayhanian, 1995). However, the OFMSW makes up about 65% of the waste composition in Turkey (DIE, 1993).

TURKSTAT (alias DIE) made an inquiry on the typical composition of MSW in the eleven big cities of Turkey in July and December, 1993. It was found that 65.5% of the total production of MSW is food waste (kitchen waste). Based on this information, the total production of food waste that was dumped to the environment unconsciously in 2004 constitutes about 11.4 million tons, with a daily production of about 31.200 tons in Turkey. According to this inquiry, it was also determined that the paper content of the total production of MSW is 5.8% (DIE, 1993). It corresponds to over one million tons of paper collected annually, which can be partially recycled. Most of the OFMSW, consisting of food waste and non-recycled paper, is generally trucked to landfill and disposed by dumping on the outskirts of

cities, imposing economic and environmental burdens on the cities in Turkey.

The most conventional MSW handling and disposal methods used in Turkey can be listed as incineration, composting and landfilling. Since a large fraction of MSW comprises of high percentage (>40%) of natural organic compounds (food wastes and garden waste) with high moisture content (>50%) and low heating value, these properties are undesirable during the combustion of MSW in waste-to-energy plants. High moisture content makes the waste rather unsuitable for thermo-chemical conversion processes such as incineration and pyrolysis/gasification for energy recovery, as heat must first be supplied to remove moisture. Although incineration and pyrolysis/gasification can recover energy as heat, fuel oil and gas from the OFMSW as a result of thermal decomposition of organic matter, they are very costly and they cause air pollution problems due to air emissions.

Another handling method, composting, as one of the biological treatment methods, produces only soil conditioner as by-product; it requires long time and large portion of land for aeration. Furthermore, it causes odor and aesthetic problems.

At present, landfilling, which is also based on biological degradation as composting, is the most widespread method for disposal of MSW in Turkey and worldwide. Solid waste landfill is also a final destination for the disposal of the wastes produced through recycling, composting and incineration in a waste-to-energy facility. A variety of physical, chemical and biological processes taking place in the landfill lead to the anaerobic degradation of wastes in the presence of moisture and microorganisms. However, due to the unpredictable nature of the processes involved during the stabilisation of the waste in a landfill and differences in the waste composition, identification of the key parameters controlling waste degradation in a landfill is difficult. In addition, it is well recognised that unassisted, natural degradation in landfills occurs very slowly, and may continue over scores of years. As a result, waste deposited in engineered landfills can take long time (minimum 3-4 years) for biogas production. Methane (CH_4) and carbondioxide (CO_2), both greenhouse gases, are the major products of the biological processes occurring in a landfill. Landfill sites also pose another major threat to the environment, namely the

potential loss of leachate, which may carry toxic contaminants to the underground water supplies, surface waters and soil. The land for the disposal of MSW is far from the cities, where the majority of waste is produced and the availability of land is also becoming scarce. In current landfills, the landfill leaves a legacy of care, management, monitoring and potential catastrophic failure over several generations since the breakdown of MSW occurs very slowly. Social concern over these long term issues, with their legislative and economic implementation, increasingly favour practices, which promote short stabilization times and minimize environmental impact (Chugh et al., 1999).

All the conventional waste disposal methods meet the limits throughout most of the world with increasing waste generation and decreasing land available. It appears that not one of the processes considered up to now is ideal, or in other words, none can be considered an absolute solution for the OFMSW problem. In addition, these circumstances are to be found all over the world and they make new strategies for waste management necessary. Since MSW contains organic as well as inorganic matter, the latent energy present in its organic fraction can be recovered for gainful utilisation through adoption of suitable waste processing and treatment technologies.

Biological treatments (biochemical conversion processes) are the clearest alternative for the putrescent fraction of MSW, in other words, for the OFMSW. These processes are based on enzymatic decomposition of organic matter by microbial action to produce valuable by-products. The biochemical conversion processes are preferred for wastes with high percentage of biodegradable (putrescible) matter and high level of moisture/water content, which aids microbial activity. These technologies can also maximise recycling and recovery of waste components. Therefore, treatment of these wastes should be an important component of an integrated solid waste management strategy, since it reduces both toxicity and volume of MSW requiring final disposal in a landfill.

Among biological treatments, anaerobic digestion (AD), also referred as biomethanation, is frequently the most effective method due to the high energy recovery linked to the process and its limited environmental impact (Mata-Alvarez et

al., 2000). The most promising alternative to incineration and composting of the MSW is to digest its organic matter using the AD in a short time (Mata-Alvarez et al., 1992a; Bouallagui et al., 2003). The easily biodegradable organic matter content of MSW (75%) with high moisture facilitates the biological treatment and shows the trend of these wastes for AD (Viturtia et al., 1989; Raynal et al., 1998). The OFMSW is considered more as a resource rather than waste material, since one of advantages of the anaerobic process is the recovery of useful matters. Through AD, organics are decomposed by specialized bacteria in an oxygen-depleted environment to produce biogas and a stable solid (solid compost material). The biogas, which consists of up to 65% methane, can be combusted in a cogeneration unit and produce electricity. In general, the recovery of useful matters in the anaerobic process has been focused on methane only, which is the final product in the anaerobic process (Hwang et al., 2004). In addition to biogas, AD may generate other intermediary and valuable products, which can compete with methane in the market, such as solvents and volatile fatty acids (VFAs), which can be valued or sold. Furthermore, earlier reports show that the conversion of the organic fraction of solid wastes can be achieved as VFA production at useful conversion rates (Ten Brummeler et al., 1991; D'Addario et al., 1993). A valuable stable solid is also obtained, which can eventually be used as an excellent soil conditioner. The quality of digested sludge (compost) is better in AD than that in composting, as nitrogen is not lost by oxidation.

Apart from the recovery, disposal costs are significantly lowered and a high degree of stabilization is possible with AD. The total quantity of waste being sent to landfill gets reduced by nearly 60% to over 90%, depending upon the waste composition and therefore, this decreases greenhouse gas emissions produced from its decay in the landfill. Additional environmental gains include improvements in water and soil quality. AD is an efficient way of waste treatment in terms of chemical oxygen demand (COD) removal. High organic loading rates (OLRs) and low sludge production are among many advantages of anaerobic process exhibited over other biological unit operations. Therefore, AD technology was explored as one of the main options for processing the biodegradable organic materials of MSW and the AD of OFMSW was examined as one of the feasible biological treatment strategies in the scope of this thesis.

One method to hasten the adoption of AD is to make the process more efficient, thereby reducing retention time and space requirements. The rapid in-vessel AD of the OFMSW is one example of several alternative engineered systems available for MSW disposal. The advantages of this bioreactor approach include complete containment and control over gas and leachate, the ability to harness biogas as a fuel source, rapid stabilisation of waste and the reduction in waste being sent to landfill. Other environmental benefits include improved water and soil quality, rapid renewable energy generation, enhanced air quality due to less truck traffic and prevention of escaping greenhouse gas emissions to the atmosphere because of its totally enclosed system. The cost of transportation of waste to far-away landfill sites also gets reduced proportionately. The demand for land, which is already scarce in cities for landfilling, is also reduced. The biological process of waste stabilisation in a reactor is essentially the same as that in a landfill. However, the in-vessel process provides improved control over operating conditions, allowing the process to be manipulated to achieve more efficient digestion of waste.

The objective of this thesis is to investigate the in-vessel solid-state AD of OFMSW and to examine the performance of leaching bed reactors (LBRs) used for the hydrolysis/liquefaction and acidification of OFMSW. The aim is also to attain high-rate anaerobic biodegradation of high-solids (25-30%) OFMSW and to produce organic acids and alcohols as by-products as a result of hydrolysis and acidification using LBRs. Besides, the individual VFAs production was specifically investigated for the potential recovery of these bio-products. The feasibility of using LBRs in order to recover maximum total VFA (tVFA) as a result of acidification (fermentation) of high-solids OFMSW is the main issue of this research.

While the effects of combining various liquid wastes on the overall AD process have been explored, very little is known about the influence of combining OFMSW with agricultural wastes such as manure on the acid-phase step of AD (Banerjee et al., 1999). The production of organic acids from the co-treatment of OFMSW and cow manure was also investigated in the LBRs in the scope of this study.

CHAPTER 2

THEORETICAL BACKGROUND

2.1. Biochemistry of Anaerobic Digestion of Municipal Solid Waste

Anaerobic digestion (AD) is a series of chemical reactions during which complex organic material is decomposed to a stable solid and biogas, a mixture of methane and carbondioxide, through the metabolic pathways of naturally occurring microorganisms, including protozoa, fungi, and bacteria in an oxygen depleted environment (Speece, 1996). AD can be used to process any carbon-containing material, including food, paper, sewage, manure, yard trimmings and MSW, with varying degrees of degradation. OFMSW, for example, is a complex substrate that requires a complex series of metabolic reactions to be degraded. This section describes these reactions detailing the intermediary products produced and the bacteria involved.

The biomethanization of OFMSW is accomplished by a series of biochemical transformations, which can be roughly separated into four metabolic stages, as illustrated in the Figure 2.1. These stages are hydrolysis, in which complex molecules are broken down into constituent monomers; acidogenesis, in which acids are formed; acetogenesis, or the production of acetate; and methanogenesis, the stage in which methane is produced from either acetate or hydrogen, respectively. Digestion is not complete until the substrate has undergone all of these stages, each of which has a physiologically unique bacteria population responsible that requires disparate environmental conditions and moreover, coexists in synergetic interactions (Bouallagui et al., 2005).

The biochemistry of anaerobic process of organic materials is complex. All AD processes involve a consortium of bacteria and is based on series reactions, the slowest of which will determine the overall safety factor for that system. The

bioconversion of organic materials to methane is accomplished by different bacteria, namely by chemoheterotrophic, non-methanogenic and methanogenic bacteria, with larger, polymeric compounds first hydrolysed to free sugars, after which they are fermented to alcohols, VFAs, hydrogen and carbondioxide by acidogens. This mixture is oxidized to acetic acid (acetate), carbondioxide and hydrogen, which are then converted to methane by methanogens. The Figure 2.1 shows series of metabolisms taking place in AD process.

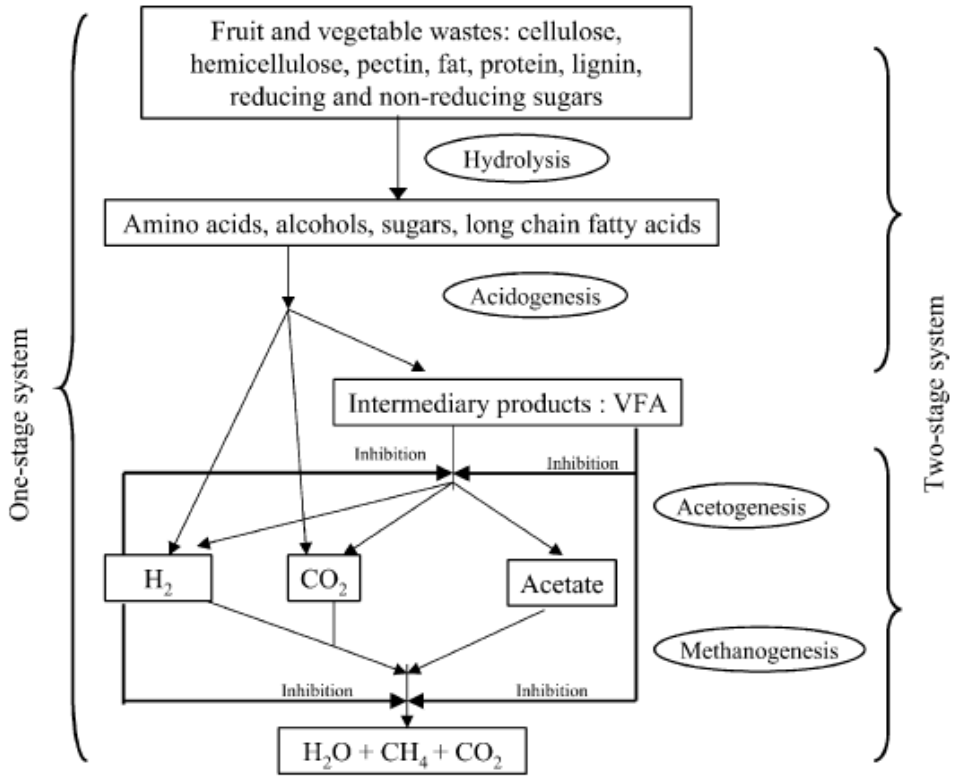

Figure 2.1. Reactions scheme for the AD of particulate organic material of MSW (Bouallagui et al., 2005)

As it can be seen from the Figure 2.1, when the acidogenic phase as well as methanogenic phase can proceed in the same reactor; this is called one-stage system. If these reactions take place in two separate reactors, then these are called two-stage systems.

The first stage involves the fermentative bacteria, which include anaerobic and facultative microorganisms. In the first stage, complex particulate organic materials

of OFMSW like cellulose, hemicellulose, pectin and lignin must undergo liquefaction by extracelular hydrolytic enzymes such as cellulase, amylase, protease, and lipase, excreted from the fermentative bacteria, before being taken up by acidogenic bacteria. The particulate materials are hydrolysed and broken down into their constituent parts in a process known as hydrolysis. The result is soluble monomers: Proteins are converted to amino acids; lipids to fatty acids, glycerol and triglycerides; complex carbonhydrates such as polysaccharides, cellulose, lignin, starch and fiber converted to simple sugars, such as glucose. Hydrolic or fermentative bacteria are responsible for the creation of monomers, which are then available to the next group of bacteria. If the feedstock is complex, the hydrolytic phase is relatively slow. This is especially true for raw cellulolytic waste, which contains lignin. Lignin is not degraded by most AD systems. For this reason, woody waste is not an ideal feedstock for the AD process. Carbonhydrates, on the other hand, are known to be more rapidly converted via hydrolysis to simple sugars and subsequently fermented to VFAs. The rate of cellulose breakdown is slow (weeks), hemicellulose and protein somewhat faster (days) and small molecules such as sugars, fatty acids and alcohols fast (hours) (Wheatley, 1990). The rate of hydrolysis is a function of factors, such as pH, temperature, composition, and particle size of the substrate and high concentrations of intermediate products (Veeken et al., 2000).

Despite the heterogeneity of materials in the MSW, an approximate chemical formula for the mixture of organic waste is $C_6H_{10}O_4$ (Themelis and Verma, 2004), excluding nitrogen and other minor components. A hydrolysis reaction, where organic waste is broken down into a simple sugar, in this case glucose, can be represented by the following equation (carbonhydrate fermentation):

$$C_6H_{10}O_4 + 2\ H_2O \rightarrow C_6H_{12}O_6 + 2\ H_2 \qquad \text{(Eqn. 1)}$$

The products of hydrolysis are soluble smaller molecules and hence, this step is also known as solubilization. Hydrolysis of the degradable polymeric substrates converts them into a form, which can be assimilated into the microbial cell and metabolized. A distinct physiological population, the hydrolytic bacteria, is responsible for hydrolysis of these organic polymers and fermentation to products, including organic acids, alcohols, and the methanogenic substrates. Hydrolysis is an important

step during AD, since the rate of conversion of the solids into methane and carbondioxide depends on the rate of hydrolysis. In general, if the substrate is in particulate form, hydrolysis is the slowest step and hence the rate limiting step in the overall AD process (Eastman and Ferguson, 1981). The authors argue that the increase in hydrolysis rate at increasing biodegradability suggests that the rate of hydrolysis of particulate organic matter is determined by the adsorption of hydrolytic enzymes to the biodegradable surface sites (Veeken and Hamelers, 1999). The efficiency of the hydrolysis step dictates the ultimate methane yield. Normally in solid waste anaerobic digesters, only 50% of the organic matter (measured as volatile solids) is converted. The rest of the organic matter remains undegraded because of the inaccessibility of hydrolysis enzymes to sites within the solid matrix and due to a lack of appropriate organisms that secrete the essential extracellular enzymes (Chynoweth and Pullammanappallil, 1996).

Hydrolysis is immediately followed by the acid-forming phase of acidogenesis. In this stage, acidogenic bacteria convert the soluble organic components including the products of hydrolysis into simple organic compounds, mostly short chain (volatile) acids (e.g., propionic, formic, acetic, lactic, butyric, or succinic acids), ketones (e.g. acetone, glycerol), alcohols (e.g., ethanol, methanol), H_2 and CO_2. The specific concentrations of products formed in this stage vary with the type of bacteria as well as with culture conditions, such as temperature and pH (Bouallagui et al., 2005).

The typical reactions in the acid-forming stages are shown in the following equations. In the equation 2, glucose is converted to ethanol and the equation 3 shows glucose is transformed to propionate.

$$C_6H_{12}O_6 \leftrightarrow 2\ CH_3CH_2OH\ (\text{ethanol}) + 2\ CO_2 \qquad \text{(Eqn. 2)}$$

$$C_6H_{12}O_6 + 2\ H_2 \leftrightarrow 2\ CH_3CH_2COOH\ (\text{propionate}) + 2\ H_2O \qquad \text{(Eqn. 3)}$$

The next stage of acetogenesis is often considered with acidogenesis to be part of a single acid forming stage. In this stage, the acetogenic bacteria consume these primary products and produce CO_2, H_2 and acetic acid (acetate). Biological oxygen

demand (BOD) and chemical oxygen demand (COD) are reduced through these pathways. Acetogenesis occurs through carbonhydrate fermentation, through which acetate is the main product, and other metabolic processes. The role of hydrogen as an intermediary is of critical importance to AD reactions. Long chain fatty acids (having greater than three carbon atoms), formed from the hydrolysis of lipids, are oxidized to acetate or propionate and H_2 gas is formed. Under standard conditions, the presence of hydrogen in the solution inhibits the oxidation. The reaction only proceeds, if the hydrogen partial pressure is low enough to thermodynamically allow the conversion. The presence of hydrogen scavenging bacteria that consume hydrogen, thus lowering the partial pressure, is necessary to ensure thermodynamic feasibility and thus the conversion of all the acids (Bouallagui et al., 2005).

As an example, the reaction that converts propionate to acetate is shown in the equation 4 below.

$CH_3CH_2COO^-$ (propionate) + 3 $H_2O \leftrightarrow CH_3COOH$ (acetate) + HCO_3^- + 3 H_2 (Eqn. 4)

Other important reactions in the acetogenic stage involve the conversion of glucose (Eqn. 5), ethanol (Eqn. 6) and bicarbonate (Eqn. 7) to acetate.

$$C_6H_{12}O_6 + 2\ H_2O \leftrightarrow 2\ CH_3COOH\ (\text{acetate}) + 2\ CO_2 + 4\ H_2 \qquad \text{(Eqn. 5)}$$

$$CH_3CH_2OH\ (\text{ethanol}) + 2\ H_2O \leftrightarrow CH_3COOH\ (\text{acetate}) + 2\ H_2 \qquad \text{(Eqn. 6)}$$

$$2\ HCO_3^-\ (\text{bicarbonate}) + 4\ H_2 + H^+ \leftrightarrow CH_3COO^- + 4\ H_2O \qquad \text{(Eqn. 7)}$$

The transition of the substrate from organic material to organic acids in the acid forming stages causes the pH of the system to drop. This is beneficial for the acidogenic and acetagenic bacteria that prefer a slightly acidic environment, with a pH of 4.5-5.5, and are less sensitive to changes in the rate of incoming feed stream, but is problematic for the bacteria involved in the next stage of methanogenesis (Bouallagui et al, 2005). A pH range of 4-6.5 was accepted as optimal for the first stage, namely acidification, while a pH range of 6.5-8.2 was reported optimal for the second stage, namely methane production.

The methanogenic anaerobic bacteria involved in the fourth stage, known as methanogenesis or methane fermentation, are the same fastidious bacteria that occur naturally in deep sediments or in the rumen of herbivores. The methanogenic anaerobic bacteria converts the soluble matter into methane, about two thirds of which is derived from acetic acid conversion (Eqn. 8 followed by 9), or directly from other substrates, such as formic acid and methanol (Eqn. 10), and one third is the result of carbondioxide reduction by hydrogen (Eqn. 11) (Bouallagui et al, 2005).

$$2\ CH_3CH_3OH + CO_2 \leftrightarrow 2\ CH_3\ COOH\ (acetate) + CH_4 \qquad \text{(Eqn. 8)}$$

$$CH_3COOH\ (acetate) \leftrightarrow CH_4 + CO_2 \qquad \text{(Eqn. 9)}$$

$$CH_3OH\ (methanol) + H_2 \leftrightarrow CH_4 + H_2O \qquad \text{(Eqn. 10)}$$

$$CO_2 + 4\ H_2 \leftrightarrow CH_4 + 2H_2O \qquad \text{(Eqn. 11)}$$

Methane production is higher from the reduction of carbondioxide, but limited to hydrogen concentration in the digesters. Therefore, the acetate reaction is the primary producer of methane. Methanogenic substrates include acetate, methanol, carbondioxide, formate, carbonmonoxide, methylamines, methyl mercaptans, and reduced metals. Methane is formed from two primary substrates, acetate and hydrogen/carbondioxide (or formate). In the absence of methanogens to utilize these substrates, hydrogen (and electrons) backs up the overall degradative process and organic acids accumulate causing a decrease in pH, which ultimately inhibits and stops the fermentation (Chynoweth and Pullammanappallil, 1996). In general, it is known that methanogenic activity can be inhibited by a weakly acidic pH. Methanogens are very sensitive to changes and prefer a neutral to slightly alkaline environment. If the pH is allowed to fall below 5, methanogenic bacteria cannot survive. However, some methanogens have been reported to be able to produce methane even at pH 5 (Speece, 1996).

Methanogenesis is the rate-controlling portion of the process, because methanogens have a much slower growth rate than acidogens. Therefore, the kinetics of the entire process can be described by the kinetics of methanogenesis (Davis and Cornwell, 1998). The anaerobic degradation of cellulose-poor wastes like fruit and vegetable

wastes is limited by methanogenesis rather than by the hydrolysis (Cecchi et al., 1986; Mata-Alvarez et al., 1990). These wastes are very rapidly acidified to VFAs and tend to inhibit methanogenesis, when the feedstock is not adequately buffered.

Higher acids (propionate and above) are formed primarily under the conditions of overloading. For example, in a balanced fermentation, acids other than acetate and formate are only formed from odd numbered carbon skeletons (e.g., from decomposition of aminoacids and unsaturated fatty acids). A defined consortium, including a cellulolytic, acetolytic, and hydrogenolytic bacteria, did not produce acids other than acetate and balanced anaerobic digesters have a limited capacity to utilize propionic acids. Because organic acids, including propionate and larger, are not major intermediates in a balanced methane fermentation, they are not metabolized after formation during imbalance until a population of bacteria capable of their metabolism can develop by enrichment. Since their growth rates are slow in comparison to other organisms, this can often require weeks (Chynoweth and Pullammanappallil, 1996).

In a well-balanced AD process, all products of a previous metabolic stage are converted into the next one without significant build up of intermediate products. The overall result is a nearly complete conversion of the anaerobically biodegradable organic material into end products like methane, carbondioxide, hydrogen sulphide, and ammonia. The overall role of biomethenogenesis is to complete the degradation process by the removal of inhibitory fermentation products (Bouallagui et al., 2005).

The complete degradation of the OFMSW under anaerobic conditions requires the concerted action of several groups of microorganisms. The fact that the methane-forming microorganisms grow at a rate that is much slower than the acid formers and that methane-forming microorganisms cannot directly consume landfill waste means that the acid formers will normally outgrow the methane formers. As a consequence, the degradable fraction of landfill waste will normally become acidic, which slows down microbial activity and inhibits further degradation (Chugh et al., 1999).

Although AD can be considered to take place in these four stages, all processes occur simultaneously and synergistically, in as much as the first group has to perform its metabolic action before the next can take over, and so forth.

2.2. Characteristics of Municipal Solid Waste

Municipal solid waste (MSW) has been identified as a heterogeneous material, in which the composition varies widely. The production and composition of MSW vary from site to site and are influenced by various factors, including region, climate, extent of recycling, collection frequency, season, and cultural practices as well as changes in technology. The composition of wastes affects both yield and biogas quality as well as the compost quality. In considering MSW as a feedstock for AD, it is important to know the feed characteristics, illustrated in the Table 2.1 and 2.2.

MSW is contaminated with non-organics, such as glass and metal, and therefore requires pre-treatment before being loaded to the reactors to obtain homogeneous feedstock (Converti et al., 1999). The pre-processing involves separation of non-digestible materials and shredding. The waste received by AD digester is usually source separated or mechanically sorted. The separation ensures removal of undesirable or recyclable materials such as glass, metals, stones etc. as well as decreasing heterogeneity. In source separation, recyclables are removed from the organic wastes at the source. Mechanical separation can be employed if source separation is not available. The most common mechanical pretreatment, known as shredding, reduces the size and solid content of entering waste and gives bacteria access to a greater surface area, reducing retention time and increasing the amount of soluble organics. The size reduction can lead to more rapid digestion (Rivard et al., 1990; Mata-Alvarez et al., 2000).

In general, the major components of OFMSW are paper and putrescible fractions (yard and food wastes), which typically comprise over 50% of the wet weight. In developing countries, the organic fraction is higher because of the effective removal of recyclables by scavengers. In countries like Denmark and Switzerland, the organic fraction is concentrated by source separation. The organic matter can be effectively

digested as unsorted or sorted MSW; however, the degree of separation of organics influences the materials handling and the quality of the process residues as compost. The trend in sorting is toward source separation of the organic and non-organic fractions. This sorting not only facilitates sorting of recyclables from the non-organic fraction, but also results in digester feedstocks (and thus residues) that are relatively free of undesired components such as plastics, metals, glass and heavy metals (Chynoweth and Pullammanappallil, 1996).

Table 2.1. Organic Composition of Municipal Refuse

Constituent	Barlaz et al. (1990)	Ten Brummeler et al. (1991)	Peres et al. (1992)	Conversion (%) (Peres et al., 1992; at 35°C; 20 day HRT)
	% Dry Wt.	% Vol. Sol.	% Dry Wt.	
Volatile Solids	78.6	--	73	58
Cellulose	51.2	40	32.9	75
Hemicellulose	11.9	--	5.2	94
Protein	4.2	5.6	9.6	10
Lignin	15.2	27.3	12.5	17
Lipids	--	6	5.9	66
Starch/Sol. Sugars	0.5	3.3	--	--
Pectin	<3	--	--	--
Soluble Sugars	0.35	--	--	--

Considering the percentages of volatile solids (VS) of OFMSW in the literature, two groups can be denoted. The first, with a VS content of above 82% corresponds to the hand-sorted, source-sorted, separated collection or simulated OFMSW (Chynoweth et al., 1990; O'Keefe et al, 1993; Mata-Alvarez et al., 1990; Cecchi et al., 1986, 1988). The second refers to most of the data for mechanically-sorted OFMSW with VS content less than 60% (O'Keefe et al., 1993; Mata-Alvarez et al., 1990, 1993). A comparative analysis of the performance of digesters in the treatment of the OFMSW sorted at source or mechanically, was carried out by Mata-Alvarez et al. (1990). The comparison is performed in terms of the percentage of biodegradation achieved, the kinetics of the process and the biodegradability of the substrate. The higher biodegradability and consequently, higher yields were achieved from the AD of

hand-sorted or source-sorted OFMSW. Kayhanian (1995) showed that knowledge of the biodegradable VS fraction of MSW helps in better estimation of the biodegradability of waste, biogas generation, OLR and C/N ratio. Lignin is a complex organic material that is not easily degraded by anaerobic bacteria and constitutes the refractory VS in the organic MSW. Waste characterized by high VS and low non-biodegradable matter, or refractory VS, is best suited to AD treatment.

Table 2.2. Characteristics of the OFMSW (Kayhanian and Hardy, 1994)

Physical Characteristics	**Value**
Moisture, %	21
Bulk Density, kg/m^3	560
Chemical Characteristics	**Value**
Carbon, %	46
Nitrogen, %	1.5
Phosphorous, %	0.08
Sulfur, %	0.2
Carbon/Nitrogen (C/N)	37
Carbon/Phosphorus (C/P)	575
Hydrogen, %	6
Oxygen, %	41

A number of factors contribute to the slow rate of waste degradation, including moisture limitation, poor shredding of waste, high bulk density and lack of inoculum (Barlaz et al., 1990).

The average moisture content of fresh refuse is typically between 20 and 40%, compared with waste field capacity values of about 60% (Chynoweth and Pullammanappallil, 1996). The OFMSW is solid organic waste, which is organic-biodegradable waste with moisture content below 85-90% (Mata-Alvarez et al., 2000). The biodegradable fraction of MSW contains anywhere from 15%-70% water. Past investigations have shown that the addition of water to raise moisture content to field capacity accelerates rapid reduction in the leachate organic strength, waste stabilisation processes and stimulates early production of methane (Wujcik and Jewell, 1980; Farquhar and Rovers, 1973; Chugh et al., 1999). The feed is also diluted to achieve desired solids content and then to operate the reactors with optimal OLR (Mata-Alvarez et al., 1992a; Bouallagui et al., 2003). For dilution, a varying range of water sources can be used such as clean water, sewage sludge, or re-

circulated liquid from the digester effluent. Diluting the waste with water also allows the bacteria to move more freely inside the digester.

From a microbiological viewpoint, the OFMSW has a high solids content (~50%), limiting N content (C/N>30), and limited surface area for degradation. The principal organic components are cellulose and hemicellulose, with cellulose constituting approximately 50% by weight (Rivard et al., 1990). The biochemical methane potential of several MSW components was determined in order to compare the potential extent and rate of their conversion to methane (Owens and Chynoweth, 1993; Eleazer et al., 1997). Owens and Chynoweth (1993) studied with MSW to determine sample biodegradability and the extent of the decomposition process during the operation of the reactors. These data indicate that a typical conversion efficiency of MSW is 50%, corresponding to a methane yield of 0.2 m^3/kg VS. The highest methane yields were observed for various types of paper, including office paper and food packaging. The lowest methane yield was observed for newspaper, and ink did not influence its biodegradability. The biodegradability of different types of yard wastes was quite variable. These data provide a basis for predicting potential methane production from wastes with known composition. The undegraded fraction undoubtedly consists of lignin and cellulose that is tightly complexed with lignin, which is refractory to anaerobic metabolism (Chynoweth and Pullammanappallil, 1996).

Due to the lower pH of OFMSW, some authors also buffered these waste by the addition of NaOH solutions (Mata-Alvarez et al., 1992a; Rodriguez-Iglesias et al., 1997). Without any regulation, the pH quickly decreased and tended to inhibit the methanogenic bacteria (Verrier et al., 1987).

2.3. Development of Anaerobic Digestion of Municipal Solid Waste

In the late 70's, most of the AD plants were designed to treat sewage and were predominantly low-solids operations. However, during the last decade, AD systems are becoming more complex and not limited to agriculture waste or animal waste treatment. As greater cost and impending depletion of fossil fuels became apparent in

the 1970's and early 1980's, the search for renewable alternative fuels resulted in an expanded interest in AD to include MSW (Cecchi et al., 1993a) as feedstocks. Research on AD of MSW also blossomed, resulting in new digester designs for high solids feedstocks (Cecchi et al., 1988). AD has become an established and proven technology for MSW treatment as well as industrial waste today.

Anaerobic biological treatment of the OFMSW is a process which has received increased attention during the last few years (Raynal et al., 1998; Converti et al., 1999). Animal manure has been successfully used as a high solids feedstock for many years, however OFMSW has a different composition and experience of AD of MSW alone is more recent and less extensive. The majority of plants digesting MSW is large scale, processing over 2500 tons of waste per day and involves complex plant design. Much of the technology (91%) is based in Europe, with Germany (35%), Denmark (16%), Sweden (14%), Switzerland (11%) and Austria (8%), leading the field in technology and in the number of successful plants in operation. Development has been encouraged by high energy prices, higher tipping fees at landfills, stricter environmental legislation prohibiting landfilling of organics, including renewable energy laws and landfill restrictions, and other tax incentives in recent years (De Baere, 1999; Mata-Alvarez et al., 2000).

The state of the art of research& development in the field of AD of MSW in Europe is reviewed by Cecchi et al. (1988). The conclusion to be drawn from this analysis is that in programmes involving demonstration and full scale plants, it is necessary to carry out more detailed studies of the process and its control, as well as carrying out further work on the microbiological aspects of AD of MSW.

AD of organic solid waste, especially the OFMSW, is of growing importance in the field of solid-waste management. The use of leachate containment, collection and recirculation on a landfill has provided opportunity to transfer it into a controlled bioreactor system. Several types of bioreactors have been developed for the treatment of OFMSW, such as high-solids (dry) digestion (Wujcik and Jewell, 1980; Chynoweth et al, 1990), two-phase AD (Ghosh, 1983), semi-dry digestion (Mata-Alvarez et al., 1993).

The digestion efficiency and stability can vary significantly depending upon the type of digester used and the parameters of its operation. Design considerations for digestion facilities are capacity, vertical/horizontal orientation, batch/continuous flow, total solids (TS) content, number of stages, mixing and pretreatment. AD processes can be categorized on the basis of TS content, into dry and wet digestion, and on the basis of the number of reactors used, into single-stage and two-stage digestion. However; for MSW, the most important reactor classification is whether or not the reactor can be used to convert solid waste solids to gas, while meeting the goals of AD. MSW consists, mostly, of solid matter and all of the energy value is in the solids. Consequently, the process must be able to convert solids to gas without clogging the anaerobic reactor (Vandevivere et al., 1999).

Independent of influencing digester size, solids concentration has a significant effect on digester design, performance and materials handling in AD. The conventional completely stirred tank reactor (CSTR) design is being replaced by more innovative designs, which are selected primarily on the basis of feed TS content. Low-solids systems contain less than 2% TS, medium-solids contain about 2%-15%, and high-solids processes range from 20% to 40% (Tchobanoglous, 1993). Table 2.3 outlines preferred designs based upon TS concentrations. The objectives of most of the advanced designs are to increase solids and microorganism retention, decrease reactor size, and reduce process energy requirements.

Table 2.3: Anaerobic Digester Designs for Different Feedstocks (Chynoweth and Pullammanappallil, 1996)

Feedstocks	Design Options
Low Solids (<2% TS) *solid industrial wastes, biomass pressate, acid-phase effluent*	anaerobic filter, fluidized bed, anaerobic contact, UASB
Medium Solids (2-15% TS) *sewage sludge, partially industrial wastes, aquatic/marine plants*	CSTR, solids-concentrating, two-stage
High Solids (>20% TS) *MSW, industrial wastes, grasses, wood*	CSTR, leachbed, two-stage

As it is seen in the Table 2.3, since MSW is a high-solids feedstock, containing greater than 20% TS, the effective anaerobic digester design types are CSTR, leachbed and two-phase systems.

Feeds with low concentrations of TS (<2%) such as food processing wastes can be digested in high rate attached-film reactors such as UASB, anaerobic filter, fixed film packed bed reactors, anaerobic baffled reactors, attached-film expanded bed reactors, anaerobic contact digesters, anaerobic sequencing batch reactor (ASBR) and fluidized bed (Sharma et al., 1999). These processes differ especially in the way the microorganisms are retained in the bioreactor, and the separation between the acidogenic and the methanogenic bacteria, which reduce the AD limitations. Methanogenic bacteria may have long mass doubling times in anaerobic reactors and this makes it very difficult to obtain fast acting reactors without retaining most of the biomass normally washed out with the effluent (Bouallagui et al., 2005). However, these reactors retain high concentrations of attached microorganisms and permit low hydraulic retention times (HRTs) without organism washout. These high-rate digesters have reduced HRTs from 20 days to a few hours.

The drawback of low-solids reactors is the large amount of water used, resulting in high reactor volume and expensive post-treatment technology due to dewatering required at the end of the digestion process. However, these high-rate reactors are extremely effective processes for converting soluble organic materials, such as sugar to methane gas. The bacteria convert the soluble constituents to gas, but have little opportunity to hydrolyze and degrade the particulate solids, unless the solids become attached to the biomass. Although these are very successful anaerobic reactors and they are known as high-rate reactors, they are not effective in digesting particulate waste. In other words, these reactors are not suitable for digesting MSW, since they are not effective in converting particulate solids to gas and unless the solid waste is thoroughly screened and all particulate matter removed, these reactors tend to become clogged. The removal of solids by screening and gravity sedimentation eliminates up to 80% of the energy generating potential from solid waste. As a result, it can be said that these reactors are primarily used to convert non-particulate or soluble waste to gas.

Designs for medium-solids (2-10%) (e.g., sewage sludges or aquatic plants), either require high retention times (>15 days) or some mechanism of retaining TS such as solids recycle or concentration of solids within the reactor. This results in a ratio of SRT/HRT greater than 1 for increased retention of solids and microorganisms.

For high-solids (>10%) feedstocks, high-solids stirred digesters or leach-bed batch systems are being used. A number of advantages of high solids designs (often referred to as dry digestion) include higher potential loading rates, lower heat energy requirements, and usage of less water. The dry anaerobic composting (DRANCO), BIOCEL and sequenced batch anaerobic composting (SEBAC) are some examples to the dry fermentation processes using MSW as the substrate (Cecchi et al., 1988).

Anaerobic fermentation has been thought to be limited to wet organic waste, such as sewage sludge that contains greater than 90% water. The processing of drier biomass at these high water contents requires the addition of many tons of water for every dry ton of biomass. Solid biowaste is particularly troublesome, since it not only requires large amounts of water, but is also extremely difficult to handle. One approach to fermentation of solid biowaste is to develop a method that could ferment the high-solids material without the addition of large quantities of water, which is called "dry fermentation" (Ghanem et al., 2001). In this process, AD takes place at TS concentrations greater than 20%. In dry digestion, the wastes are digested as received and in "wet digestion," with dry solids content of less than 15%, the wastes are slurried with water. When the feedstock is MSW, both systems require adding water to the feedstock in order to lower the TS content (Sharma et al., 1999).

The anaerobic degradation of MSW in a high solids-content reactor is more difficult to start up and control than that in a low solids-content digester (Nopharatana et al., 1998). In dry systems, the fermenting mass within the reactor is kept at a solids content in the range 20-40% TS, so that only very dry substrates (> 50% TS) need be diluted with process water (Oleszkiewicz and Poggi-Varaldo, 1997). While wet systems typically consume 1 m^3 fresh water per ton OFMSW treated, the water consumption of their dry counterparts is ten-fold less. As a consequence, the volume of wastewater to be discharged is several-fold less for dry systems.

The dry designs require much smaller reactor volumes and thus less costly, but more expensive equipment (conveyor belts, screws, powerful pumps, etc.). They have been proven to be reliable due to their higher biomass concentration and controlled feeding. Wet design may achieve similar reliability via dilution of potential inhibitors with fresh water. The dry systems appear more robust as frequent technical failures are reported with wet systems due to sand, stones, plastics and wood. The high solids systems can handle impurities such as stones, glass or wood that need not be removed as in single stage low solids. The retention time for most dry processes ranges between 10 and 40 days and for wet processes can be as low as 3 days. The timing depends on the volume of the digester, loading rate of the feedstock, removal rate of digestate, temperature of the digester, VS content of the feedstock and the desired degree of digestion (Vandevivere et al., 1999).

The greater inhibition problems may be expected in the dry designs, since no fresh dilution water is added. OLR is a measure of the biological conversion capacity of the AD system. Feeding the system above its sustainable OLR results in low biogas yield due to accumulation of inhibiting substances such as fatty acids in the digester slurry (Vandevivere et al., 1999). In such a case, the feeding rate to the system must be reduced. OLR is a particularly important control parameter in continuous systems. Many plants have reported system failures due to overloading. Vandevivere et al. (1999) reports OLR is twice in high-solids in comparison to low-solids. The high OLR that are being achieved in both bench-scale and full-scale applications of one stage dry systems indicate however that the dry systems are not more sensitive to inhibition than the wet systems. In fact, dry systems can sustain at least as high OLR as wet systems, without suffering inhibition. The sturdiness of the dry systems toward inhibition was documented by Oleszkiewicz and Poggi-Varaldo (1997). The possible explanation to less inhibition in dry systems is that microorganisms within a dry fermenting medium are better shielded against toxicants.

Most of the treatment capacity for solid waste was provided by wet digestion systems at the beginning of the 1990's. From 1993 onwards, more dry digestion plants were constructed and in 1998, more than 60% of digestion capacity was provided by dry fermentation systems (De Baere, 1999).

Along with the advent of high-solids AD, there has been progressing in using the thermophilic range. Earlier, long periods of time were required for complete degradation. Mesophilic temperatures (about 35°C) would require up to 30 days for digestion. The development of thermophilic (60-65°C) AD has reduced the retention time for solids in the digester to less than 15 days. Converti et al. (1999) pre-treated organic matter of fruit and vegetable wastes at high temperature to improve the efficiency of their AD. The benefits offered are hygenizaion of waste, lower retention time and higher biogas yield. The thermophilic conditions guarantee the complete hygienization of the wastes and pathogen-free compost as an end-product (Baeten and Verstraete, 1993). Thermophilic temperature was found optimal for digesting mechanically selected OFMSW by Cecchi et al. (1991) in a pilot-plant study. Its advantages were not the same when digesting source-sorted OFMSW. The start-up phase was to change the reactor temperature from the mesophilic (37^oC) to the thermophilic range (55^oC). According to Cecchi et al. (1993b), the digester loading was stopped for a week to prevent the process from becoming unstable during the transient conditions. The change of temperature was performed abruptly and the thermophilic temperature was soon reached.

A recent development in the development of AD of MSW is the co-digestion of MSW with animal manure. Co-digestion is an interesting option for improving yields of AD of solid wastes. That is, the use of a co-substrate, that in most cases improves the biogas yields due to positive synergisms established in the digestion medium and the supply of missing nutrients by the co-substrates. Sometimes, the use of a co-substrate can also help to establish the required moisture contents of the digester feed. Other advantages are the easier handling of mixed wastes, the use of common access facilities and the known effect of economy of scale. In fact, the capacity provided by co-digestion systems is limited. Less than 7% of the overall AD of OFMSW capacity is at present co-digested. Nevertheless, there is ongoing research (Mata-Alvarez et al., 2000; De Baere, 1999). Most of the larger scale, industrial systems process MSW alone; however the simpler, smaller scale systems are more successful when co-digested with animal manure. MSW is more suitable to co-digestion with more dilute feedstocks, such as manure. The concept of co-digestion is especially well established in Denmark.

The OFMSW is mixed with animal manure and the two fractions are co-digested. This improves the C/N ratio and improves gas production (Nopharatana et al., 1998). Optimum C/N ratios in anaerobic digesters are between 20 and 30. A high C/N ratio is an indication of rapid consumption of N by methanogens and results in lower gas production. On the other hand, a lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria. Optimum C/N ratios of the digester materials can be achieved by mixing materials of high and low C/N ratios, such as organic solid waste mixed with sewage or animal manure.

Adding OFMSW will, however, change the process characteristics due to the different characteristics of OFMSW compared to manure: it has low water content, a low pH and it can have low concentrations of nutrients, when it consists of high ratio of, e.g. garden waste (Rivard et al., 1990). The pH of the manure ranges between 7.3 and 8.1, whereas the pH of OFMSW is below 5. Due to the acidity of OFMSW, the pH dropped from 7.3 of pure manure to 6.3 in the 50% co-digestion mixture. The pH in the reactors dropped from 8.5 to 8.0, showing that the co-digestion system was well buffered (Hartmann and Ahring, 2005b).

Some examples of operating and performance data of AD designs co-digesting MSW with manure are presented in the Table 2.4.

Table 2.4. Examples of Operation and Performance Data of Digesters for AD of MSW and manure

Design	MSW: Manure Ratio	Loading Rate, kgVS/m^3/d	HRT (days)	Temp. (^{o}C)	Organic Reduction (%)	Reference
Single-phase	50:100	3.3-4	14-18	55	59	Hartmann and Ahring (2005b)
Single-phase	20:70	8	-	35	52.1	Callaghan et al., (1999)
Single-phase	50:50	3.19-5.01	21	35	60	Callaghan et al., (2002)
Two-phase	100:10	-	-	-	72	Hanson et al. (2001)

According to the Table 2.4, it can be concluded that when the MSW is co-digested with manure, the efficiency of degradation and the biogas production increase. In addition, as the amount of manure in the feed and the OLR increase, the organic reduction and methane yield decrease (Callaghan et al., 2002).

In conclusion, the future of AD as a MSW management strategy depends on several factors ranging from environmental concerns to economic considerations. Some of these include increased process efficiency, reduced construction and operation costs, expanding markets for products and decrease in the availability of landfills. It seems that AD will continue to play an important role in the MSW treatment.

2.4. Anaerobic Digestion Technologies for Municipal Solid Waste

In attempts to steer away for landfilling, processes such as the in-vessel AD of MSW have been investigated intensively. There are currently a number of technologies, both proven and experimental, that have been described in the literature. However, it is hard to find papers with similar experimental set-ups in the literature.

Many papers have been published dealing with the performance of different reactor designs and configurations, digesting MSW (Cecchi et al. 1988; Cecchi and Mata-Alvarez, 1991). Each has its own benefits and constraints and selection is dependent upon waste characteristics and personal preference. The comparison of research data and drawing of conclusions is difficult, because the great diversity of reactor designs is matched by large variability of waste composition and choice of operational parameters (retention time, solids content, mixing, recirculation, inoculation, number of stages, temperature). Therefore, there certainly does not exist a consensus over the optimal reactor design to treat MSW. The reason most likely lies in the complexity of the biochemical pathways involved and the novelty of the technology (Vandevivere et al., 1999). The designs are dependent upon factors such as reactor solids concentration, mixing strategy, temperature (mesophilic and thermophilic), and number of stages (two-phase and one-phase reactors) (Chynoweth and Pullammanappallil, 1996). The more popular ones are broadly categorised as low and high solids (wet and dry digestion), two-phase and leach bed systems. Most of

them focus on aspects of the anaerobic biodegradation of the putrescent fraction of MSW. Despite the increasing number of full-scale plants, research activity continues on lab-scale (Mata-Alvarez et al., 2000).

2.4.1. One-phase Systems

The first digestion facilities were simple, single chamber designs where every stage, i.e. hydrolysis through methanogenesis, occurred simultaneously in the same volume. This approach is still the most often used in modern designs (Themelis and Verma, 2004). In a one-phase digester, the growth of both groups of bacteria (acidogenic as well as methanogenic bacteria) exist in a single reactor and the environmental conditions are kept at equilibrium. These parameters are not necessarily optimal for any bacteria, but are acceptable to all. The growth of both groups of bacteria, and, therefore, the efficiency as well as the stability can be substantially low. The most crucial parameter is the pH, which must always be kept close to neutral in order to ensure the survival of the methanogens. A pH lower than 5.5, in which acidogens thrive, is fatal to methanogens. In a one-stage system, combining acidogens and methanogens in one vessel, hydrogen formed by acidogenic metabolism is assimilated by the methanogens to reduce carbondioxide to methane and water (Poggi-Varalgo et al., 1997). Once in operation, these digesters are simpler to operate than two-phase digesters, because the equilibrium is fairly stable. The HRT is generally maintained between 20 to 40 days depending on the operational conditions, thus requiring large tanks (Vandevivere et al., 1999).

On an industrial scale, one-phase systems for OFMSW digestion are absolutely predominant, probably because they are cheaper (investment and maintenance). About 90% of the full scale plants, currently in use in Europe for AD of OFMSW and biowastes, rely on continuous one-phase systems (De Baere, 1999; Bouallagui et al., 2005). However, a considerable amount of literature has appeared concerning wastes treatment in two phases; first an acid forming phase followed by a methanogenic phase (Pavan et al., 1999a). Industrial applications of one-phase wet digestion systems and one-phase dry digestion systems are about the same (Vandevivere et al., 1999).

2.4.1.1. One-Phase Wet Digestion Systems

One-phase low-solids processes are attractive because of their simplicity. Also they have been in operation for several decades for the treatment of sludge and wastewater. The predominant reactor for one-phase low-solids processes used is the CSTR. The CSTR reactor ensures that the digestate is continuously stirred and completely mixed. Feed is introduced in the reactor at a rate proportional to the rate of effluent removed. Generally, the retention time is 14-28 days depending on the kind of feed and operating temperature. Some of the one-phase low-solids commercial AD plants are WASSA process in Finland, ECOTEC in Germany, and REFCOM and SOLCON processes in Florida (Vandevivere, 1999).

One of the first-full scale plants to be built in Finland in 1989 is WASSA process. Digestion occurs in a CSTR with vertical impeller at either mesophilic or thermophilic temperatures with 10-15% TS content. The feed used in this process is mechanically pre-sorted MSW mixed with sewage sludge. The retention time in the mesophilic process is 20 days as compared to 10 days in the thermophilic. The OLR differs with the type of waste. The OLR was 9.7 kg/m^3.day with mechanically sorted organic MSW and 6 kg/m^3.day with source separated waste. The gas production was in the range of 170-320 m^3 CH_4/ton of VS fed and 40-75% reduction of the feed VS was achieved. Mixing is attained through injection of biogas at the base of the reactor and through top mixing when digesting household waste. The WASSA process achieves 60% volume reduction and 50-60% weight reduction (Vandevivere et al., 1999).

ECOTEC has had a bio-waste facility operating in Germany since 1995. The organic material is conveyed to the tank, where it is mixed with process water to 15% TS content. Digestion occurs at 35ºC or 55ºC and the retention time of the material is 15 to 20 days. The reactor mass is mixed by a circulating biogas system.

Wet continuous digester design is the basis for the REFCOM demonstration plant operated in Florida, U.S. in the early 1980s on mechanically sorted MSW (Isaacson et al., 1987). Problems faced are related in part to separation and preparation of the

feed. The mechanical stirrers caused problems leading to cracking of the concrete roofs of the digesters. The constant methane content (53%) during various retention times of between 6 and 26 days was achieved. There was up to 75% destruction of VS (Wheatley, 1990). The major disadvantages include washout of unreacted solids and microorganisms, mixing problems, and liquid heating and disposal requirements. Since MSW is initially >80% solids, this design is often ruled out.

Table 2.5 exhibits some experimental studies of CSTR type of reactors as one-phase wet digestion systems for AD of MSW.

Table 2.5. Examples of Operation and Performance Data of CSTRs for AD of MSW

Loading Rate, kg VS/m^3.d	HRT (days)	Temperature (^oC)	VS Reduction (%)	Reference
2.1-6.9	9-25	33-37	63-69	Cecchi et al. (1986)
3.9	14	33-37	70-75	Cecchi et al. (1988)
--	20	37	--	Rivard et al. (1990)
2.1-4.2	13.6-25	35	67-69	Mata-Alvarez et al. (1990)

As it can be concluded from the CSTR studies for AD of MSW in Table 2.5, the VS reduction increases with increase in HRT and decrease in the OLR.

Different AD experiments on fruit and vegetable wastes were carried out using different one-phase systems. Mata-Alvarez et al. (1992b) examined the performance of the mesophilic one-phase CSTR for the treatment of the organic fraction of the wastes coming from a large food market. The maximum OLR tested was below 3 kg VS/m^3.day and the HRT was 20 days with the OLR of 1.6 g VS/L.d. The VS removal was 88% and the methane yield was 0.47 L/g VS. Verrier et al. (1987) studied continuous one-phase CSTR at OLR of 3.6 g VS/L.d. The VS removal was 83% and the methane yield was 0.37 L/g VS in 23 days. The OLR of 6 kg VS/m^3.d

was found to be a limit condition for a similar waste digestion by Cecchi et al. (1986). Moreover, as mentioned by Mata-Alvarez et al. (1990), vegetable waste was presumably more biodegradable, which meant a larger and faster VFA production, which stressed the validity of this OLR limit. Overloading of digesters with this waste above 4 kg VS/m^3.d was also reported to result in a fall in pH and gas yield and an increase in the CO_2 content of gas produced using a CSTR. A semi-continuously mixed tubular digester was tested and the best results were obtained by applying an HRT of 20 days with an OLR of 2.8 kg VS/m^3.day. The pH may fall in the hydrolysis shortly to 6.1, but it remains most of the time at 7.2. When reducing the HRT to 10 days, the pH fell to 5 and inhibition was observed. The most significant factor of the tubular reactor is its ability to separate acidogenesis and methanogenesis longitudinally down the reactor, allowing the reactor to behave as a system of two phases. The VS destruction was 76% and the methane yield was 0.45 L/g VS (Bouallagui et al., 2003).

AD of the shredded OFMSW has been investigated in a pilot-scale CSTR, under mesophilic conditions. Detailed comparisons of the size distributions of the particles in the feed and in the digester effluent are reported under varying OLRs and HRTs. About 20% of the particulate matter in the organic feed is refractory and resists hydrolysis. Hence, the maximum removal of VS attainable under HRTs of practical interest is about 70%. The optimum HRT is around 14 to 15 days (Traverso and Cecchi, 1988).

The advantages offered by one-phase low-solids are operational simplicity and technology that has been developed for a much longer time than high-solids systems. One-phase low-solids processes make use of less expensive equipment for handling slurries. The pre-treatment involves removing of coarse particles and heavy contaminants. These pre-treatment steps cause a loss of 15-25 % VS, with corresponding decrease in biogas yield. The other technical problem is formation of a layer of heavier fractions at the bottom of the reactor and floating scum at the top, which indicate non-homogeneity in the reacting mass. The bottom layer can damage the propellers, while the top layer hinders effective mixing. This requires periodic removal of the floating scum and of the heavy fractions, thus incurring lower biogas

yield. Another flaw is the shortcircuiting. This lowers the biogas yield and impairs hygienization of the wastes. For the solids content to be maintained below 15%, large volumes of water are added to reduce the solids content, resulting in large reactor volumes, higher investment costs, and amount of energy needed to heat the reactor. Also, more energy and equipment are required for dewatering the effluent stream to reuse process water. The high investment costs associated with dilution and reactor volume plus the complex pre-treatment step offset the gains from the low cost equipment to handle slurry. One-phase wet digestion systems tend to have much better mixing, thus increasing the degree of digestion. Additionally, lower TS values tend to have heavy particles, such as sand and glass, settle to the bottom (Nopharatana et al., 1998).

2.4.1.2. One-Phase Dry Digestion Systems

While the one-phase wet systems had initially been inspired from technology in use for the digestion of organic slurries, research during the 80's demonstrated that biogas yield and production rate were at least as high in dry digestion systems where the wastes were kept in their original solid state, i.e. not diluted with water (Spendlin and Stegmann, 1988; Baeten and Verstraete, 1993; Oleszkiewicz and Poggi-Varaldo, 1997). The advances of the dry digestion technology were the result of research undertaken in the 80's that established higher biogas yield in undiluted waste.

As it was stated, due to the high concentration of solids in the MSW itself or in the suspension, high performance digesters such as anaerobic filters and UASB digesters can not be used effectively for one-phase dry digestion processes. For one-phase continuous biowaste treatment processes, the choice is reduced to CSTR or plug-flow digesters, with the biowaste retention time corresponding to that of the active biomass. The contents of the CSTRs are kept in a state of agitation by external pumps, screw pumps, or injected methane. The plug-flow digesters are particularly advantageous, because it subjects the microorganisms to minimal shear forces despite intensive agitation. However, it also increases the danger of scum formation. To improve upon the standard rate digester, engineers also incorporate external mixing to the process. This additional mixing improved the process tremendously by

reducing the required SRT to 6-30 days, while increasing the OLR approximately 5 times. Although different system configurations (horizontal and vertical digesters) and mixing methods such as agitators and biogas injection are used, some operational problems and performance problems are faced with one-phase dry digestion systems (Vandevivere et al., 1999).

Some of the examples of one-phase dry digestion systems are the DRANCO, KOMPOGAS, and VALORGA processes. All three processes consist of a one-phase thermophilic reactor (mesophilic in some Valorga plants) with retention time of 14-20 days. The differences in design of one-phase dry digestion systems are based on mechanisms of feeding and mixing. All designs recycle effluent, which is mixed with the feed for inoculation. The DRANCO design (Six and De Baere, 1992) in Belgium does not mix after feeding. The VALORGA design (Saint-Joly, 1992) in France blast mixes with pressurized biogas. The KOMPOGAS design (Wellinger et al., 1993) in Switzerland is horizontal and mixed continuously at a low rate. The designs of these three dry digesters are exhibited in the Figure 2.2.

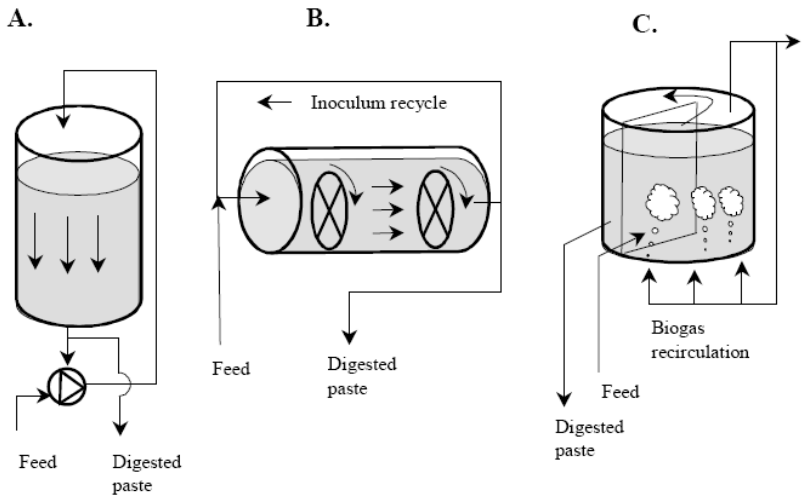

Figure 2.2. Different Digester Designs used in Dry Systems, **A.** DRANCO Design, **B.**KOMPOGAS Design, **C.** VALORGA Design (Vandevivere et al., 1999)

Due to the high viscosity of MSW, the fermenting wastes move via plug-flow inside these dry systems, as it is seen in the Figure 2.2, contrary to wet systems, where complete mix reactors are usually used. The use of plug flow within the reactor offers the advantage of technical simplicity as no mechanical devices need to be

installed within the reactor. These designs achieve high loading rates and minimize water requirements. Mixing, feeding and start-up are challenges for these designs.

The DRANCO digestion (Dry Continuous System) consists of a one-phase, vertical gravity driven plug flow system, where the waste is introduced continuously through the top of the reactor and digested material is removed from the bottom continuously with no other means of mixing apart from the downward plug-flow of the waste due to gravity. In other words, the mixing occurs via recirculation of the wastes extracted from the bottom end, mixing with fresh wastes, and pumping to the top of the reactor. This simple design has been shown effective for the treatment of high solids wastes ranging from 20 to 50% TS, requiring retention time of 15-30 days. The feedstock is mixed with water, recycled from the process. The DRANCO process, which treats highly biodegradable kitchen wastes, achieves a mean OLR of 5 kg VS/m^3.d with 80% VS destruction. On the basis of the Dranco technology, one-phase thermophilic dry digestion process performances were reached similar to high-rate wastewater digestion. Part of the extracted matter is reintroduced with the new feed, while the rest is dewatered to produce compost product (Wheatley, 1990; Six and De Baere, 1992; De Baere, 1999). The process operates at 50-58°C with retention time of 15-20 days. The biogas yield is between 100-200 m^3/ton of waste.

KOMPOGAS, a new digester system, designed specifically to treat fruit, yard and vegetable wastes with 15-40% TS. The feedstock is sent to the digestion chamber, a thermophilic single-stage and horizontal plug-flow reactor, requiring retention time of 15-20 days. The horizontal plug flow is aided by slowly-rotating impellers inside the reactors. Slowly rotating intermittent propellers help to push the waste through the digester, to homogenize and degas the pulp and to keep heavier particles in suspension. From the test run, it was observed that the system under investigation is best suited to treat substrates with low dry matter content. Based upon the preliminary experimental results, it has been concluded that the digester performed best at TS concentrations of around 27%. The solid content must be maintained between 23 and 28%, so that flow can continue unimpeded and heavy particles remain in suspension. Due to the mechanical requirements of the system, the size of the reactors is limited. The KOMPOGAS process works similar to DRANCO

process, except that the plug flow digester takes place horizontally and the system is mixed by agitator (Vandevivere et al., 1999; Wellinger et al., 1993).

The VALORGA process was developed initially in France, The feedstock, diluted to 35-40% TS, is introduced at the bottom of the reactor, which can be thermophilic or mesophilic. Therefore, the water requirement is minimal. The one-phase reactor is a vertical, plug-flow cylinder with an inner wall that forces material to go up and around it before being extracted from the bottom. They are designed so as to maintain plug flow through the reactor. The feed enters through an inlet near the bottom of the reactor and slowly moves around the vertical plate until it is discharged through an outlet that is located diametrically opposite to the inlet. Mixing in the digester is done without mechanical mixing equipment through a pneumatic pump that injects biogas into the base of the reactor. The biogas production is pressurized and pumped back into the reactor to improve mixing. Recirculated biogas is injected through a network of injectors at the bottom of the reactor and the rising bubble results in pneumatic mixing of the slurry. The injectors require regular maintenance, as they are subject to clogging. The Valorga process is ill-suited for low solid concentration wet digestion, as sedimentation of heavy particles inside the reactor will occur at TS content less than 20% (Saint-Joly, 1992; Fruteau de Laclos et al., 1997). The retention time is 20-28 days at a mesophilic temperature of 38°C. The retention time of 20-28 days was reduced to 12-14 days by thermophilic operation.

In terms of extent of VS destruction, the three dry digestion reactor designs discussed, which are named as DRANCO, KOMPOGAS and VALORGA seem to perform very similarly, with biogas yields ranging from 90 m^3/ton fresh garden waste to 150 m^3/ton fresh food waste (Fruteau de Laclos et al., 1997; De Baere, 1999). These yields correspond to 50-70 % VS destruction. These values are comparable to those achieved with wet systems, which fall in the range 40-70 % VS destruction (Pavan et al., 1999b). Some examples of operating and performance data of single-phase AD designs are presented in the Table 2.6.

Table 2.6. Examples of Operation and Performance Data of One-Phase Continuous Dry Digestion Systems for AD of OFMSW

Process	Design	Loading Rate, kgVS/m^3.d	HRT (days)	Temperature (^{o}C)	Organic Reduction (%)	Reference
REFCOM	low sol. CSTR	3-9	6-27	60	-	Isaacson et al. (1987)
SOLCON	solids-conc.	3.2	18	35	48	Chen et al. (1990)
DRANCO	high-sol. mixed	10-13	18-21	35 and 55	60	Six and De Baere (1992)
VALORGA	high sol. mixed	15	10-15	37	40-50	Saint-Joly (1992)
KOMPO-GAS	high sol. mixed	8.1	21	55	68	Wellinger et al. (1993)

*Variations in performance may be a reflection of differences in waste characteristics

As it can be seen from the Table 2.6, differences among the dry systems are more significant in terms of sustainable OLR. Optimized dry systems may however sustain much higher OLR such as the Dranco plant in Belgium, where OLR values are 15 kg VS/m^3.d (De Baere, 1999). This very high value is achieved without any dilution of the wastes, i.e. 35% TS inside the reactor, and corresponds to a retention time of 14 days during the summer months with 65% VS destruction. Typical design OLR values of the Dranco process remain about twice as high as those for wet systems. As a consequence, at equal capacity, the reactor volume of a Dranco plant is two-fold smaller than that of a wet system. However, the physical characteristics of the wastes at such high solids content impose technical approaches in terms of handling, mixing and pre-treatment, which are fundamentally different from those of wet systems (Fruteau de Laclos et al., 1997).

The comparison between one-phase low-solids and one-phase high-solids operation indicates higher gas yields from high-solids facilities. For example, the WASSA process for low-solids reports 100-150 m^3/ton of waste input and the VALORGA process for high-solids achieves 220-250 m^3/ton of feed to digester. The biogas yield is usually high in one-phase high solids as heavy fractions or the scum layer is not removed during the digestion. In addition, the OLR for one-phase high-solids (e.g., DRANCO, 15 kg VS/m^3.d) is about twice that of the one-phase low-solids (WASSA, 6 kg VS/m^3.d). Contrary to the complete mixing prevailing in single stage low solids, the single stage high solids are plug-flow reactors hence require no mechanical device within the reactor (De Baere, 1999). The economic differences between the single stage low solids and single stage high solids are small. However, there are pronounced differences between one-phase high solids and one-phase low solids reactors, in terms of water usage.

Dry batch digestion is closest to the accelerated landfill concept. Batch reactors are used where the reactor is loaded with feedstock at the beginning of the reaction and products are discharged at the end of a cycle and loaded with a new batch. The batch systems may appear as in-vessel landfills, but in fact achieve much higher reaction rates and 50-100% higher biogas yields than landfills due to continuous recirculation of leachate and higher operation temperatures. The one-phase dry anaerobic batch digestion system involves recirculating the leachate to the top of the same reactor. The waste in a batch reactor is normally not mixed, allowing the content of the digester to stratify into layers of gas, scum, supernatant, an active layer, and stabilized solids at the bottom. Retention times range from 30-60 days with an OLR between 0.48 and 1.6 kg VS/m^3.day (Davis and Cornwell, 1998). An example of such a system is the BIOCEL process in the Netherlands that was started in 1997 and treats 35000 tons/year of source-sorted biowaste. The BIOCEL plant produces on the average 70 kg biogas/ton of source-sorted biowaste (Vandevivere, 1999). The BIOCEL process (Ten Brummeler et al., 1991) digesting OFMSW occurs in percolating digester at mesophilic conditions. Dilution with compost and leachate recycle increased the stabilization rate significantly. The digestion time was 36 days.

A batch reactor for dry digestion of biowaste was proposed by Ten Brummeler and Koster (1990). In this type of reactor system, biowaste is mixed with seeding material and digested at a TS content of approximately 40%. The digestion process is promoted by recycling the leachate over the biowaste bed. The main disadvantage of the batch system could be irreversible acidification at the start-up of the batch process, because the rate of hydrolysis is much higher than the methanogenic rate at the beginning. The results of Ten Brummeler and Koster (1990) showed that a lagphase was observed during start-up of the batch reactor but irreversible acidification did not occur. A batch digester, such as a landfill bioreactor, treating the OFMSW is in essence simpler than a continuous anaerobic digester and the lower cost per ton of waste treated in a landfill reactor is a consequence of the simple technology applied (Ten Brummeler and Koster, 1990). Compared with conventional sanitary landfills, landfill bioreactors provide the potential for more rapid, complete and predictable attenuation of solid waste constituents, enhance gas recovery and utilization and reduce adverse environmental impact of landfills.

The main advantages of one-phase dry batch digestion are the simplicity of the containment vessel and the need for only minimal feed preparation and mechanical handling. The disadvantages include process stability and materials handling related to batch operation. Batch processes offer the advantages of being technically simple, inexpensive and and robust. However, they require a large land footprint as compared to continuous reactors since they have much longer HRT and their OLR are two-fold less (Vandevivere, 1999).

In semi-dry digestion, substrate concentration in the range of 16-22% TS is used. The mesophilic application of a semi-dry process was studied (Cecchi et al., 1990), where a start-up of the process was performed using mechanically-sorted OFMSW as substrate. In that case, an OLR of 4.1 kg VS/m^3.d was applied for the first 30 days. After that period, the OLR was increased up to 6.8 kg VS/m^3.d, without any problem of reactor stability, but in that experimentation the digester TS content was about 15%. Cecchi et al. (1990) reported that the final biogas yield in those conditions was 0.23 m^3/kg VS.

Bolzonella et al. (2003) studied a pilot-scale study of the simulation of the start-up phase of the thermophilic semi-dry AD of the OFMSW. The aim of the study was to aid and shorten the start-up phase. The design OLR of 9 kg VS/m^3.d was reached in about 30 days, during which the TS content in the feed was increased. The TS value in the feed ranges from 10% to 20%. According to the study, it was found that the mesophilic start-up of the pilot-scale digester was successfully carried out directly feeding the OFMSW and increasing the OLR to the final design values; the change from a mesophilic (37ºC) to a thermophilic (55ºC) environment in the reactor can easily be performed in a short time with interruption of feeding for a few days. So, the possibility to have a short start-up phase to reach the thermophilic conditions with a mesophilic inoculum has been confirmed also at full scale. Besides, the lower yields obtained in terms of biogas production in thermophilic steady state conditions (0.23 m^3/kg VS) can be considered appropriate due to the low OLR applied (1.2 kg VS/m^3.d) instead of 9.5 kg VS/m^3.d.

Pavan et al. (1999b) examined the performance of the application of the semi-dry single-phase thermophilic AD process of two different kinds of substrates at pilot-scale: the mechanically sorted and source-sorted OFMSW, the two with very different biodegradabilities. The digester was a CSTR type and was fed with different mixtures of both substrates. To ensure the complete stability of the operation, it was necessary to reduce the organic load, when the contents of source-sorted OFMSW increased. The sustainable OLR_{max} for mechanically-sorted OFMSW under thermophilic conditions was 9.7 kg VS/m^3.d. The same OLR was however unsustainable when the feed was switched to source-separated biowaste, for which the OLR_{max} was 6 kg VS/m^3.d. The results obtained with source-sorted OFMSW alone suggest the use of the two-phase process to give more stable conditions. Pavan et al. (1999b) observed a two-fold larger VS reduction with source-separated biowaste relative to mechanically-sorted OFMSW. Such difference is not due to process performance but rather to the smaller biogas production potential of the mechanically-sorted OFMSW, which contains a greater proportion of poorly degradable organic material such as plastic impurities.

Consequently, it can be concluded that one-phase AD systems are not much effective in terms of organic matter reduction for the treatment of OFMSW. The

conventional AD of organic waste is conducted in a one-phase digester that recovers only 50-70% of the feed organic carbon as methane. One-phase systems are preferred, because simpler designs suffer less frequent technical failures and have smaller investment costs. However, the disadvantages are large volume of reactors required due to long retention time, particularly sensitive to shock loads as inhibitors spread immediately in the reactor, formation of a scum layer, VS lost with inerts and plastics, high consumption of water and higher energy consumption for heating large volume. Only about 1/3 of the tank volume is used for active digestion, making this a poor option in crowded urban settings. In the literature, it was also observed that the OLRs of one-phase systems are lower than those of two-phase systems. In one-phase AD of solid wastes, the slower growing methanogens are overfed at higher loading rates, causing imbalances and cessation of methane production. In one-stage AD of solid wastes, problems may occur if the substrate is easily degradable because in solid waste digestion, there is no possibility for the accumulation/retention of biomass within the reactor. The conventional one-phase anaerobic systems, which are used to produce methane from organic waste are often inefficient and take a long time (Ghosh, 1983; Davis and Cornwell, 1998).

2.4.2. Two-Phase Systems

The limitations of most one-phase designs for AD are heavy inoculation, mixing and possibility of instability. In order to overcome these difficulties and to improve the process stability and efficiency in high-solids AD systems, the concept of two-phase reactor was thus proposed. In fact, many of the experimental studies of reactor performance consider the possibility of a two-phase configuration. A likely reason for this discrepancy is that two-stage systems afford more possibilities to the researcher to control and investigate the intermediate steps of the digestion process. Industrialists, on the other hand, prefer one-stage systems because of their simpler designs and lower investment and operational costs (Bouallagui et al., 2005). The survey of De Baere (1999) indicates that only 10.6% of the current available capacity is provided by two-phase digestion systems.

Acid forming and methane forming microorganisms differ in terms of their environmental conditions (Pohland and Ghosh, 1971). Pohland and Ghosh (1971)

were the first to propose to separate two phases in two different reactors, where optimum conditions for microorganisms responsible for acidification and methanogenesis would be provided. The introduction of two-stage AD processes was intended to improve digestion by having separate reactors for the different stages of AD, thus providing flexibility to optimize each of these reactions. Two reactors are used, the first for hydrolysis/liquefaction and acidogenesis and the second for acetogenesis and methanogenesis. The first tank in two-phase systems allows hydrolysis and acidogenesis to occur, with a rate limited by the hydrolysis of cellulose, while the second reactor optimizes methanogenesis, with a rate limited by the slow microbial growth rate (Liu and Ghosh, 1997). For methanogenesis, the optimum growth rate of microbes is achieved by designing the reactor to provide a longer biomass retention time with high cell densities or attached growth (also known as fixed-film reaction, where the microbes responsible for conversion of the organic matter are attached to an inert medium such as rock or plastic materials). An important requirement to be met in such reactors is the removal of the SS after the hydrolysis stage.

These recent two-phase designs take the advantage of the fact that the biochemical pathways of digestion occur in phases, each one optimized under distinct environmental conditions. The design physically separates the bacteria populations and the reactions take place sequentially in two reactors. Optimizing the reactions separately in different stages or reactors may lead to a larger overall reaction rate and biogas yield (Ghosh et al., 1999). The most commonly used and the simplest two-stage digestion system involves two CSTRs in series, controlled to provide variation in temperature and pH. In a two-stage digester, fermentation and methanogenesis are separated by using different retention times. The second stage could also be a plug-flow digester or an anaerobic filter (Gunaseelan, 1997). Pavan et al. (1999a) compared the performances of the one-phase and two-phase systems, using pilot completely mix reactors fed with very rapidly hydrolyzable biowastes from fruit and vegetable markets. While the one-stage system failed at 3.3 kg VS/m^3.d, the performance of the two-stage plant remained stable at an overall system OLR of 7 kg VS/m^3.d. For quickly fermentable wastes, a two-stage reactor can have a lower overall retention time than a single stage. Pavan et al. (1999a) stated that the main

advantage of the two-stage system is the greater biological stability it affords for very rapidly degradable wastes like fruits and vegetables by keeping the acidogenesis and methanogenesis separately. The reason commonly invoked is that the slower metabolism of methanogens relative to acidogens would lead to inhibiting accumulation of acids. Two-phase digestion was considered the right option for treating high-solid wastes (Ghosh et al., 1999; Vieitez et al., 2000), and source-sorted OFMSW or fruit and vegetable market wastes (with very high biodegradability), which permits much higher loads in the digester. (Pavan et al., 1999a). These latter authors, in a detailed study including kinetics, found optimal operating conditions for both hydrolytic (meso and thermophilic temperatures) and methanizer (thermophilic temperature) reactors. The overall HRT was around 12 days, with an optimal specific biogas production of around 0.6 m^3/kg VS.

Two-phase fermentation of MSW enhances the biologically mediated hydrolysis. Two-phase operation also allows for a lower pH that is preferred in the acid phase and correspondingly faster hydrolysis could be achieved in the digester itself, which requires a pH of 6.5-7.5. The first acid-phase is operated at short retention times of 1 to 3 days, leading to formation of acids. The effluent is transferred to a methane-phase digester (usually an attached-film design), where acids are converted to methane. With these two steps occurring in distinct reactors, it becomes possible to increase the rate of methanogenesis by designing the second reactor with a biomass retention scheme or other means (Vandevivere et al, 1999). When feed is transferred from the first to the second digester, the acidogenic bacteria can not thrive as they have already consumed most of the feed material. Alternately, the methanogenic bacteria will die in the acidic first digester. The second tank must maintain a higher pH and residence times range from 7-10 days, depending upon the waste characteristics, providing capacity for gas collection or storage (Sharma et al., 1999).

Two-phase digestion was first promoted by Ghosh (1983) for the digestion of MSW. The total digestion time was considerably lower than the conventional one-phase digestion. The hydrolyzer can have a relatively small volume, and the resultant feedstock for the digester is extensively solute and, hence, rapidly decomposable, meaning that the methane digester can also be made smaller than normal. Since the

pre-acidified biowaste from the hydrolysis stage naturally contains a very large share of dissolved substrate, the methanization process requires enough biomass to prevent acidification of the digester content. Indeed, the main advantage for two-phase digestion, which is the reduction in overall tank sizes, has been demonstrated in the literature.

The two-phase processes, providing an optimal environment for each of these distinct microbial populations, allow an overall faster reaction and improved process stability (e.g., reducing the reactor size and retention time of the combined first and second stage compared to conventional systems). Two-phase digestion is also claimed to result in a greater overall yield of methane, as a larger fraction of the substrates will be metabolized and converted to biogas, presumably by action of the more vigorous acidogenic bacteria. Problems of variation in the rates of acid production and methane generation have been tackled using two-phase systems. Two-phase systems also reduce the waste stabilization time and they are effective in enhancing by-products such as VFAs, solvents and gas production (Rodriguez et al., 1998; Bakke et al., 2003). All types of two-stage systems, regardless of whether biomass is accumulated or not, provides some protection against the fluctuations of OLR. In addition, the main advantage of two-stage systems is not a putative higher reaction rate, but rather a greater biological reliability for wastes which cause unstable performance in one-phase systems (Vandevivere et al., 1999).

In a single combined phase digester, overloading and inhibitors result in accumulation of volatile organic acids, for which populations of organisms are not available to metabolize. However, in a two-phase system, formation of acids is encouraged in the acid phase. Therefore, the methane phase is constantly receiving acids to encourage maintenance of high populations of these organisms. In other words, the acid-phase is an intentionally maintained imbalanced digester, which is resistant to further imbalances resulting from overloading or inhibitors. The other advantage is that most of the methane is produced in the methane-phase digester and the methane content of this gas is higher because of the release of much of CO_2 in the acid phase (Cyhnoweth and Pullammanappallil, 1996).

Continuous two-phase systems appear as more highly efficient technologies for AD of fruit and vegetable wastes. The greatest advantage of two-phase systems lies in the buffering of the OLR taking place in the first stage, allowing a more constant feeding rate of the methanogenic second stage. This is a substantial advantage in the case of substrates, whose degradation is limited by the methanogenesis rather than by the hydrolysis, e.g. cellulose-poor kitchen wastes such as fruit and vegetable wastes. These wastes, being very rapidly acidified, tend to inhibit the methanogenesis in one-stage reactors when the feedstock is not adequately mixed, buffered and dosed. In the case of feeding exclusively source-sorted OFMSW, or fruit and vegetable wastes, or, in general, highly biodegradable wastes, it is advisable to use a two-phase AD process, which permits much higher loads in the digester. A special type of two-stage system, designed with biomass accumulation devices in the second stage, displays a larger resistance toward toxicants and inhibiting substances such as ammonia. The drawback of this type of two-stage system is that solid particles are removed from the feedstock to the second stage, which decreases the biogas yield. Another consequence of two-stage systems with biomass retention is the possibility of applying higher OLR without shock to methanogenic bacteria in the methanogenic reactor. These relatively high OLRs were however only achieved at the cost of 20-30% lower biogas yields, due to the removal of solids that contain some biodegradable matter, after the short hydrolysis period, before feeding the methanogenic reactor (Vandevivere et al., 1999).

The two-stage systems provide higher efficiencies, a more stable design, a higher throughput, smaller tank sizes by 40-60%, higher methane content in the biogas (65-75% methane vs. 50-55% for conventional technologies), higher pathogen destruction, and lower VS in the digested solids, thus producing much lower odor and more stable soil conditioners. The two-phase systems are highly efficient because of the main fact that both groups of acidogenic and methanogenic organisms are different with respect to their nutritional requirements, physiology, pH optima, growth, and nutrient uptake kinetics, and their ability to withstand environmental stress factors (Weiland, 1993).

2.4.2.1. Two-Phase Wet Digestion Systems

In two-stage wet digestion systems, the MSW is slurried with water or recycled liquor and fermented by hydrolytic and fermentative bacteria to release VFAs, which are then converted to biogas in a special high-rate attached film reactors, usually an anaerobic filter or an UASB reactor. Some of the two-phase low-solids facilities are Pacques process (Netherlands), BTA process (Germany, Canada) and Linde-KCA-Dresden GmbH design (Germany). They claim lower retention times and more complete conversion of solids. The major disadvantage is the complexity of design and operation (Chynoweth and Pullammanappallil, 1996).

The Pacques process uses two reactors at mesophilic temperature. Initially, the feed consists of fruit and vegetable waste, but recently, source-separated MSW is also being processed. The first reactor, where hydrolysis occurs, has solids content of 10%. Mixing is achieved by means of gas injection. The digestate from the first reactor is dewatered, and the liquid is fed to an UASB reactor, where methanogenesis occurs. The fraction of the digestate from the hydrolysis reactor is recirculated with the incoming feed to the first reactor for inoculation.

The BTA process was initially developed in 1986 to treat OFMSW from households, agriculture and commercial plants. Co-digestion of OFMSW and agrowastes occurs in BTA process. Feedstock is shredded and diluted to 8-12% TS. Anaerobic hydrolysation reactor is used as the first reactor and high-rate anaerobic filter is used as second reactor, and the both reactors are operated at mesophilic temperatures. Solids are mixed with process water and hydrolysed for 2-4 days. The retention time in the methane reactor is 2 days. The biogas produced at BTA plants is 60-65% methane and the water needs are met entirely by recirculating process water. In the BTA process, solids and liquids are separated. Incoming waste is pulped and dewatered, and the liquid, which contains soluble organics, is sent immediately to a methane-producing tank. The advantage to this system is that it can take advantage of the significantly lower retention time of liquids compared to solids. The OLR was 10 kg VS/m^3.d for the BTA process (Vandevivere et al, 1999). It is very similar to the Pacques process except that the methanogenic reactor is designed with attached growth (fixed film reaction) to ensure biomass retention. The effluent from

the hydrolysis reactor is dewatered and the liquor is fed to the methanogenic reactor. This reactor receives only the liquid fraction from hydrolysis reactor to avoid clogging of the attached growth. In order to maintain the pH within the hydrolysis reactor in the range of 6-7, the process water from the methanogenic reactor is pumped to the hydrolysis reactor at times.

Linde-KCA-Dresden GmbH was developed in 1980, processing MSW using AD. The Linde wet digestion systems can be mesophilic or thermophilic. The defining characteristic of the Linde system is the gas recirculation in the digester using a centrally located tube that also supplies heat. Many wet digestion plants employ co-digestion with sewage sludge or manure.

One- and two-phase AD of vegetable solid wastes were compared at laboratory scale. Verrier et al. (1987) studied two-stage wet digestion system, consisting of thermophilic liquefaction CSTR hydrolyser and mesophilic anaerobic filter methanizer. The volumetric loading rate was 5.65 g VS/L.d and the HRT was 2 days in the CSTR, whereas the HRT was 2.3 days in the anaerobic filter. The total VS removal was 96% and the methane yield was 0.42 L/g VS. The methane production yield was about 420 L/kg VS. These authors generally found that phase-separated digesters may offer the best choice for high efficiency, concerning both rates and energy recovery. Both mesophilic and thermophilic liquefaction and acidogenesis were shown to be maximal when the pH was maintained at approximately 6.5 in the reactor. The distribution and concentrations of the VFAs and alcohols produced varied with the temperature, the nature of the wastes and the retention time. Methanogenic fermentation of the liquefaction products was efficiently performed in an anaerobic filter and high methane productivities were obtained. Phase separation under mesophilic conditions resulted in significantly higher methane productivity than was obtained by operation in a one-phase CSTR reactor. Under thermophilic conditions, the advantage of two-phase operation was far less marked (Verrier et al., 1987).

The two-step wet digestion technology applied by Rajeshwari et al. (2001), allowed the conversion of over 94% of vegetable market waste into biogas, with methane

yield of 0.35 L/g VS at an HRT of 2.5 days and OLR of 6.8 g VS/L.d. The leachate obtained after completion of acidification phase was further treated in an UASB reactor for biogas production.

The two-stage low solids processes are plagued with similar problems to those of the one-phase low solids reactors, such as short-circuiting, foaming, formation of layers of different densities and expensive pre-treatment. In addition, the two-stage low solids processes are technically more complex and thus require a higher capital investment.

2.4.2.2. Two-Phase Dry Digestion Systems

The Biopercolat process is a two-stage high-solids process, consisting of a liquefaction/hydrolysis reactor followed by a methanogenic UASB with attached growth. It follows the same principles as the BTA process; with the difference that hydrolysis is carried out under high-solids and is continuously percolated with process water to accelerate the liquefaction reaction. The separate optimization of the first stage and of the second stage, via biofilm growth, allows the system to run at the exceedingly low overall retention time of only 7 days. The OLR was 15 kg VS/m^3.d for the Biopercolat processes. This is due to higher biomass retention with attached biofilm, which increases the resistance of methanogens to high ammonium concentrations (Edelmann et al., 1999; Wellinger et al., 1999).

There is variety of studies related with the anaerobic treatment of OFMSW in two-phase AD systems. These studies are summarized in Table 2.7 as two-phase AD systems.

Table 2.7. Examples of Operation and Performance Data of Two-phase Systems for AD of OFMSW

Operational Conditions	Removal Efficiency	Reference
HRT= 10 d pH= 4-7 OLR=0.4-10 lb VS/ft^3.d mesophilic	87% (COD)	Ghosh (1983)
pH= 5.5-5.9 ambient 25ºC (Acid phase digester) mesophilic (upflow anaerobic filter)	81% (VS)	Ghosh (1985)
HRT= 14 d mesophilic	75 % (COD)	Viturtia et al. (1989)
OLR= 61000 mg/L COD ambient (25ºC)	54% (VS)	Vieitez et al. (2000)
pH= 4.5-6.5 Temperature= 38ºC	75% (COD)	Silvey et al. (1999)
pH= 7.6-7.9 HRT=12 d mesophilic/thermophilic	83.5% (VS)	Pavan et al. (1999a)
OLR= 10 g COD/L mesophilic	74-93% (COD) 65% (VS)	Zhang and Noike (1991)
HRT= 6 d OLR= 3.1 g VS/L.d thermophilic and hyperthermophilic	89% (VS)	Hartmann and Ahring (2005a)

As it can be seen from the Table 2.7, higher VS destruction and higher COD removal efficiencies were achieved in two-phase AD systems compared to one-phase AD systems. Therefore, it can be concluded that more stable digestion and higher digestion efficiencies can be achieved in smaller-size tanks at hig OLRs in two-phase AD systems. According to the Table 2.7, it has been determined that the range of pH value studied for AD, lies between 4 and 7.9. As it can be seen from the Table 2.7, there are mainly two temperature ranges that provide optimum digestion conditions for the production of methane-the mesophilic and thermophilic ranges. Although

thermophilic temperature range reduces the required retention time, the mesophilic range was mostly used.

Although the HRT for the whole system in two-phase AD systems are higher in the overall system, it is about two times more efficient than one-phase AD systems in terms of treatment efficiency. In addition, the volumes of reactors are lowered, especially in the high-rate anaerobic systems. The main advantage of two-phase anaerobic systems is the stability of the system and the treatment efficiency of the system does not vary seriously due to changes in OLRs and organic matter content (Vandevivere et al., 1999). The potential advantages expected of a two-step anaerobic treatment are better control of both acidogenic and methanogenic steps, smaller size of reactors, higher SS removal efficiency, enhancement of acidogenic microorganism's growth without disturbing methanogens, and a higher methanogenic specific activity in the second reactor (Speece, 1996).

In conclusion, although the initial investment cost of one-phase systems may be lower and may have simpler operation than two-phase systems, the operational time of one-phase systems are longer and it is difficult to control their stability. In addition, two-phase systems are more advantageous in terms of shorter operation time, higher system stability, high efficiency in terms of degradation yield and biogas productivity and smaller reactor volume requirement. In two-phase AD systems, good quality effluent with low SS, high COD removal and high methane recovery are attained. In addition, the OLR in two-phase systems with respect to those of one-phase systems is higher.

2.4.3. Leaching Bed Reactor (LBR) Systems

The acid phase digestion (hydrolysis and acidification), which proceeds in the acid phase digester, is an initial step involved in the AD. The final products of these two related processes are VFAs and alcohols, which are being produced as a dissolved material at the end of acid phase digestion process. The VFA is used as an intermediate product by methanogenic bacteria to produce CH_4 and CO_2 as a final product. Acid phase digestion is a short AD process typically with HRT of 1-3 days.

The acid phase digestion can occur in CSTR or in leaching bed reactor (LBR).

The LBRs were designed mainly to treat the high-solids organic wastes and to recover biogas at high rates. The results of the OFMSW studies cause the development of two-phase processes including LBRs (Ghosh, 1985; Chugh et al., 1999; Sharma et al., 1999; Vieitez et al., 2000). In the LBRs, as the water/leachate passes through over the waste, it extracts/separates the organic acids produced as a result of hydrolysis and fermentation of particulate solids. The solubilisation of complex solid-state organic wastes to simple organic compounds (known as liquefaction/hydrolysis) by hydrolytic microorganisms and their acidification to VFAs and alcohols efficiently by acidogens take place in LBRs. The separated organic acids can be sent to an optimized methanogenic reactor for the biogas production. The LBRs provide the fermentation of the mixture of solid waste by the aid of acidic leachate and the separation of acid production from the methanogenesis phase.

There are several processes which have been developed to overcome long start-up periods in high-solids reactors. One such process is a two-stage leachate recycle configuration employed by Chynoweth et al. (1992). The process uses a leachate management strategy that provides microorganisms, moisture, and nutrients required for rapid conversion of MSW in the LBRs and removal of inhibitory fermentative products during start-up (Chynoweth et al., 1992).

Leach-beds are operated at different stages ranging from start-up to mature (Chynoweth et al., 1991, 1992; O'Keefe et al., 1993). Leachate is recycled between new and mature digesters to wet and inoculate the new bed and to remove organic acids, which accumulate during start-up. The acids are conveyed to the mature bed, where they are converted to methane. After the shredded waste is placed into the new reactor, leachate will be recirculated between the mature reactor and the new reactor, providing nutrients, uniform moisture and bacteria from the mature reactor to the new reactor and removing soluble substrates (VFAs) from the new reactor. Fermentation products, such as volatile acids formed during start-up, are removed to the old reactor where they are converted to methane. Then, the reactor is activated

and leachate is recycled to itself. After that, the reactor is recycled with a new reactor for start-up. Several experiments at the laboratory-scale have shown that the sequencing process enables rapid start-up of degradation and guarantees stability with a built-in mechanism that prevents unbalanced growth of microbial populations (Chynoweth et al., 1992). In the sequential batch design, the conversion of acids in a separate mature reactor ensures the rapid depletion of the produced acids, thus a more reliable process performance and less variable biogas composition. At OLR of 3.2 kg VS/m^3.d, biogas yields equivalent to 80-90 % of the maximal yield could be obtained in reactors at 55 °C (O'Keefe et al., 1993; Silvey et al., 1999), which is considerably more than the yield in the Biocel plant.

High-solids leach-bed AD is a solid state biological waste treatment process that has been successfully demonstrated for solid waste treatment. This process yields a stabilized organic residue and recycles nutrients. The process involves solid phase leach-bed fermentation, employing leachate recycle between new and mature reactors for inoculation, wetting, and removal of volatile organic acids during start-up. Compared with other biological technologies, leach-bed has advantages, including simple operation, low water requirements, low energy requirements, low temperature and pressure working conditions, and is a potential energy producer (Chynoweth et al., 1991; Xu et al., 2002). Chynoweth et al. (1991) studied to enhance degradation of sorted MSW under thermophilic conditions in the LBRs. The process arrangement serves three purposes. Firstly, the VFAs produced by the fresh-waste (which reduce the system pH) are flushed out into the leachate; the acids are then removed. Secondly, a stabilised-waste reactor provides a convenient site for the consumption of high strength leachate generated by the fresh-waste reactor. Thirdly, the leachate, when passed through the stabilised-waste reactor, carries the inoculum to seed the fresh-waste to speed up the degradation.

In practice, leach-bed AD is a very stable waste management system, which has been proven by successful demonstration on a variety of high-solids feedstocks, including woody biomass, OFMSW and yard waste (Chynoweth et al., 1991). The conversion efficiency is a function of the biodegradability of the feed components, ranging from 50-90% and the organic matter is converted to methane, carbondioxide, and compost

with a residence time of less than 15 days. The process is resilient and can start up rapidly after being dormant. Compared with other biological waste processes, leach-bed AD system has a relative low equivalent system mass value, which indicates to some extent that it is a cost effective technology (Xu et al., 2002).

Leach-bed AD uses a combination of solid phase fermentation and leachate recycle to provide a simple, reliable process that inoculates the new batch, removes volatile organic acids and concentrates nutrients. It not only operates at low temperature and pressure, but can also transform the biodegradable waste into resources without production of any odors or pollution, and has the potential for being a net energy producer. Leach-bed process concept is similar to dry batch digestion; except that leachate from the base of the vessel is exchanged between established and new batches to improve start-up, inoculation of fresh waste with microorganisms from digested waste and removal of volatile organic acids with leachate in the active reactor. This is also called sequential batch anaerobic composting (SEBAC) (Chynoweth et al., 1991), which is one of the leach-bed processes. The reactor containing the organic material is inoculated with previously digested waste from another reactor, sealed and allowed to digest naturally.

The leachate from the bottom of the reactor, containing a high level of organic acids, is recirculated and heated, if required, to promote the degradation process. After a while, when methanogenesis is established in the solid waste, the leachate flow is uncoupled and connected to a new batch of fresh solid waste. This guarantees inoculation between the two reactors. The leachate of the methanogenic reactor, containing little or no acid, is combined with pH buffering agents and recirculated to the first reactor. Leach-bed designs do not mix the solids but use leachate to wet, inoculate, and remove inhibitory organic acids during start-up (Ghosh, 1985; Chynoweth et al., 1991). In some leachbed designs (Chynoweth et al. 1991), acids formed during startup may be removed via leachate to a started-up combined-phase or methane-phase digester for conversion. Inocula may also become imbalanced when exposed to toxic substances or environmental stress factors (e.g., abnormal temperature) for which they are not acclimated.

In leach-bed systems also referred to as SEBAC systems, the leachate is treated in a digester prior to recirculation, and thus the solid phase digester essentially acts like a hydrolysis/acid forming stage of a two phase system. SEBAC involves the inoculation of sorted waste with leachate from anaerobically degraded waste, which is a viable option in a landfill. However, this process is also carried out thermophilic temperatures, which is not practical in a real landfill. The SEBAC process is a leach-bed design with a loading rate of 6.4 kg VS/m^3.d achieves 49% organic reduction at HRT of 21 days and at thermophilic conditions (50ºC).

The leach-bed design uses recycle of leachate between new and mature reactors to inoculate, wet, and provide nutrients for rapid startup of new cells. Organic acids produced during startup are conveyed via leachate to the mature reactor for conversion (Ghosh, 1985; Chynoweth et al., 1991, 1992; O'Keefe et al., 1993). This design operates at high solids (>35%) and can be conducted in reactors or simple controlled landfill cells. It does not require mixing. A disadvantage is the lack of a mechanism for continuous feed. This design was developed as the SEBAC process.

The concept of SEBAC has been used to overcome the limitations of most designs for AD, such as the requirement for heavy inoculation, mixing, possibility of instability etc. A pilot plant was constructed and operated at the University of Florida. The plant was used to treat two fractions of MSW, the organic fraction of the processed MSW and yard waste. The sequential batch anaerobic composting of the two primary organic fractions has been reported to be stable, reliable and effective.

The laboratory study carried out by Chugh et al. (1999) showed that rapid stabilisation of MSW can be achieved by providing improved environmental conditions for the microorganisms. The process investigated involved exchange of leachate (sequencing) between an existing batch of anaerobically degraded waste and a batch of fresh waste. Leachate generated from the fresh waste reactor is fed into a reactor containing stabilised waste. The leachate from the fresh waste reactor is high in COD and has a limited supply of microorganisms. The stabilised waste has well established populations of bacteria, which convert COD to methane and carbondioxide. As leachate percolates through the stabilised waste reactor, it

becomes inoculated with microorganisms. This leachate is then exchanged back into the fresh waste reactor to expedite the establishment of a balanced microbial community. Once a balanced population has been achieved, indicated by a leachate pH of 6.5, the fresh waste reactor is uncoupled from the digested waste reactor. The decision to cease leachate sequencing at a pH value of 6.5 was based on the work by Farquhar and Rovers (1973), who stated that methanogenesis is favoured in the pH range of 6.4-7.2. Leachate recirculation continues without passing the leachate through the stabilised waste until the fresh waste has been completely exhausted of its methane-producing potential. At this time, the newly stabilised waste will be recoupled with another reactor containing fresh waste to continue the digestion process.

Based on the experimental data collected from the LBRs, the acidogenic stage was characterized in the study of Borzacconi et al. (1997). There was an inhibition due to the accumulation of VFA in the LBR fed with a higher than usual content of easily biodegradable matter. According to the literature, MSW initially undergoes a stage of rapid VS destruction under methanogen-deficient conditions in the LBRs.

Raynal et al. (1998) studied the hydrolysis–acidification of fruit and vegetable waste in anaerobic sequencing batch reactor and methane fermentation was performed in a fixed film reactor operated in the upflow mode. On an average, except for apple pomace, hydrolysis yields were high (up to 80%) during the liquefaction step. Likewise, the acidogenic effluent was degraded in a methanation reactor by up to 80%. The overall organic matter removal reached a value as high as 87% and the biogas production yield was about 0.29 L/g COD. The loading rate was 4.4 g VS/L.d and 17 days of HRT. According to this study, it was found that the high concentrations of hydrolytic microorganisms and VFA could inhibit the acidogenic activity. During the liquefaction phase, the production of carbondioxide and small quantities of methane and hydrogen resulted from COD degradation.

A good example of how fundamental analysis leads to quite practical conclusions is reported in a detailed microbiological study of the well-known leach-bed process (Silvey et al., 1999). Results showed that a new batch could be started in 18-38 days,

rather than 60-90 days. Thus, the analytical methods enabled the ecological system to be followed, with control of when the the microbial community in the leachate was at its best point for metabolizing soluble substrates. Starting another round of the sequencing system at an earlier stage would not only result in a faster turnaround in the reactor, but would lead to a higher quality and quantity of biogas.

LBR systems can be considered as in-vessel AD systems of landfills. The most significant parameters that simulate the hydraulic and biological behavior of a sanitary landfill were particulate matter, hydrolysis and waste porosity. Table 2.8 shows the studies of LBR systems for the anaerobic treatment of OFMSW.

Table 2.8. Examples of Operation and Performance Data of LBRs for AD of OFMSW

Operational Conditions	Removal Efficiency	Reference
OLR= 6.4 kg VS/m^3.d Temperature= 50-55ºC	36-49 % (VS)	Chynoweth et al. (1991)
pH= 5-6 OLR= 4-10 g COD/L.d Temperature = 35ºC	20-38% (COD)	Raynal et al. (1998)
pH=4.2-6.4 Temperature= 38ºC	55-69% (VS)	Chugh et al. (1999)
pH= 5-7 HRT= 14-30 d Temperature= 35ºC	26-44% (VS)	O'Keefe and Chynoweth (2000)
pH=3.6-4.8 OLR=11 g COD/L.d Temperature= 35ºC	46% (COD)	Ghanem et al. (2001)
pH=4-6.5 Temperature= 38ºC	30-36% (sCOD/COD)	Lai et al. (2001)
pH= 6.4-6.8 HRT=3.9 d OLR=1.8-18.7 g COD/L.d Temperature= 37ºC	-	Shin et al. (2001)
OLR= 10.9 kg VS/m^3.d pH= 6.9 SRT= 8 d Temperature= 37ºC	80.5% (VS)	Han and Shin (2002)
OLR= 11.9 kg VS/m^3.d SRT= 8 d Temperature= 37ºC	72.5% (VS)	Han and Shin (2004)
pH= 5.23 Temperature= 30ºC	-	He et al. (2005)
pH= 5-7 HRT=5-7 d OLR= 3-5 kg COD/m^3.d	66-90 % (COD)	Sanphoti et al. (2006)

As it can be seen in the Table 2.8, many of the typical MSW feedstocks can be hydrolysed in a solid-state LBR to effect a VS conversion greater than 25%. Higher VS destruction and higher COD removal efficiencies were achieved in short times in the LBRs. For example, an overall of 45% VS destruction was achieved in two-phase batch digesters systems, whereas this amount of VS destruction was achieved in the LBRs. Besides, an overall of 81% COD removal was achieved in two-phase batch digesters, whereas an overall of 85-87% COD removal could be realized when the LBRs were used as the first reactors of two-phase digestion.

CHAPTER 3

MATERIALS AND METHODS

Organic acids and alcohols production as a result of hydrolysis and acidogenesis of organic solid wastes was studied at laboratory scale. LBR systems, in which the liquefaction/hydrolysis and acidogenesis processes took place, were operated to treat OFMSW and produce organic acids and alcohols. In this study, experiments conducted can be grouped into two parts; namely Set-1 and Set-2. In the Set-1, only the OFMSW without paper was studied in two identical LBRs, whereas, four identical LBRs, fed with the OFMSW with paper and cow manure in different proportions, were operated in the Set-2.

In this chapter, chemicals and laboratory apparatus, inocula, analytical methods, experimental setups and procedures used in this study are described.

3.1. Chemicals and Laboratory Apparatus

Chemicals: Formic acid was used in order to decrease the pH values of the leachate samples to deionize all the VFAs for the Gas Chromatograph analysis. The VFAs such as formic acid, acetic acid, propionic, iso-butyric, butyric, iso-valeric, valeric, iso-caproic, caproic and heptanoic acids and also ethanol were used for the calibration of Gas Chromatograph (GC). EUTEC Instrument pH buffer solutions (4, 7 and 10) were used for the calibration of pH-meter and pH-controller.

Laboratory Apparatus: The laboratory apparatus used in the experimental analysis were as follows; Trace GC Ultra (Thermo Co.) equipped with a flame ionization detector (FID) and with a length of 30 m Zebron ZB-FFAP column, pH meter (Model 2906, Jenway Ltd, UK), Photometer (Aqualytic PC Multidirect), LaborBrand magnetic stirrers (Model L-71), 2 mL vials with PTFE/silicone septa, 0.45 and 0.22

μm filter paper (Milipore) and Laboratory glass apparatus.

The laboratory apparatus used in the feed preparation, LBR design and operation of LBRs were as follows; meat mincer for shredding of the OFMSW, variable speed peristaltic pumps (Model No: 77120-52, 7521-10 Cole Parmer Instrument Co., USA) for pumping water into the LBRs through a sprinkler, Masterflex Norprene pump tubing (Model No: 6404-14), PVC tubes, stainless steel mesh (pore size of 155 μm), cable ties (Cole Parmer Instrument Co., USA), silicone, Teflon connectors/fittings (World Precision Instrument Inc., USA), Teflon sealer tape and Latex rubber tubing for the design of LBRs and aluminum foil for covering the top of LBRs.

3.2. Inocula

Different seed cultures were used in both sets of experiments. Their characteristics are given below.

3.2.1. Acidogenic Cultures

In the Set-1, the solid-state hydrolytic-acidogenic fermentation was induced by an acidogenic inoculum. The LBRs of Set-1 were seeded with acidifying culture.

The acidogenic culture, which was used in the LBRs of Set-1, was taken from a 2 L fed-batch reactor with alkaloid wastewater and maintaining pH at 5-5.5 by a pH-controller. The digesters have a HRT and SRT of 2 days. These two digesters were operated for 30 days. The obtained culture was preserved and acidogenic activity assay was carried out with these inocula.

In order to determine and calculate non-methanogenic sludge activities, acidogenic activity test was applied to the culture according to the literature (Soto et al., 1993; Punal et al., 1999). According to the acidogenic activity assay, some operational parameters of batch experiments like initial substrate concentration and inoculum size can be estimated from the expected kinetic constants. Although the acidogenic step is not the limiting one, the evaluation of acidogenic activity may offer important information about biomass development and dynamic behaviour of anaerobic

digesters. The pH and glucose were determined according to the literature. The results of acidogenic activity assay are exhibited in the Section 4.1 (See for details).

Before being used as inocula in the experiments, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) concentrations of the acidogenic anaerobic culture were analyzed. The MLSS and MLVSS measurement values of the acidogenic culture were calculated as 4230±141 mg/L and 3680±165 mg/L, respectively. Alternate layers of sludge and waste were mixed and placed in the LBRs in the Set-1, giving sludge to waste ratio of 1:10 by volume. In other words, the volume of acidogenic sludge added to the LBRs of Set-1 was 250 mL, whereas the volume of the waste added was 2500 mL.

3.2.2. Mixed Anaerobic Cultures

Mixed anaerobic cultures, which were used in the LBRs of Set-2, were obtained from the anaerobic sludge digesters of the Greater Municipality of Ankara Tatlar Domestic Wastewater Treatment Plant. The digesters have a retention time of 14-20 days. The pH in the digesters ranges from 7 to 7.5. The inocula were mixed before being used.

Before being used as inocula in the experiments, MLSS and MLVSS concentrations of the mixed anaerobic culture were analyzed. The MLSS and MLVSS measurement values of the mixed anaerobic cultures used in the Set-2 were 6833±122 mg/L and 6750±124 mg/L, respectively. Alternate layers of cultures and feedstock were mixed and placed in the LBRs of Set-2, giving culture to waste ratio of 1:10 by volume. In other words, the volume of mixed anaerobic sludge added to the LBRs of Set-2 was 100 mL, whereas the volume of the waste added was 1000 mL.

3.3. Analytical Methods

pH and Temperature: The pH values were determined with pH-meter (Model 2906, Jenway LTD., UK) and a pH probe (G-05992-55, Cole Parmer Instrument Co., USA). The temperature values were determined with pH-meter and a temperature-probe.

Suspended Solids (SS) and Volatile Suspended Solids (VSS): The SS and VSS of culture used were determined by Standard Methods (2540 D-E, 1998)

Total Solids (TS) and Volatile Solids (VS): The TS and VS analysis of solid waste were measured using Standard Methods (2540) (APHA, 1995).

Total Phosphorous (TP) and Total Kjeldahl Nitrogen (TN): The TP and TN analysis of solid waste were measured using Standard Methods (4500-P B-E, 1998; 4500-N_{org} B, 1998; respectively).

Total Chemical Oxygen Demand (tCOD) and Soluble Chemical Oxygen Demand (sCOD): All tCOD and sCOD analyses of leachate were carried out using the spectroquant analysis system, on a PC Multidirect Autotest photometer (Aqualytic) and Aqualytic PC COD vials for COD 0-15000 ppm (for High Medium Range-COD values) and COD 0-1500 ppm (for Low Medium Range-COD values) as given in Aqualytic PC Multi Direct Instruction Manual. For digestion and heating of samples for 2 hr, a thermoreactor at a temperature of 150°C was used. The basic principal is that oxidizable substances react with sulphuric acids-potassium dichromate solution in the presence of silver sulfate as catalyst. Chloride is masked with mercury sulfate and the reduction in the yellow coloration is evaluated after digestion. The leachate samples were filtered from 0.45 Millipore filter papers before the sCOD analysis.

Volatile Fatty Acids (VFA): VFA analyses were done by using a Trace GC Ultra (Thermo Co.) device, fitted with a Zebron ZB-FFAP column, with a length of 30 m, internal diameter of 0.32 mm and film thickness of 0.25 micron, injector temperature, 250°C; flame ionisation detector (FID) temperature, 350°C; oven temperature program: 100 to 250°C (8 °C/min); duration, 2 min. Helium was used as a carrier gas. The leachate samples were initially centrifuged for 10 minutes at 4000 rpm and then they were stored frozen at a temperature of about -20°C until the analysis of leachate samples by GC. The 0.22 µm filter papers and glass fiber filter (Whatman Co.) were used to filter the leachate sample, which contain solids, otherwise the column of GC can be clogged easily in short time. The filtered samples were acidified with 99% formic acid to decrease the pH values of the samples below

3, since low pH values cause deionization of all organic acids, converting the volatile fatty acids to their undissociated forms (i.e., acetic acid, propionic acid, butyric acid, etc.) before injecting 1 μL of the acidified samples into the GC. The acids release hydrogen ions into water, when they are in solution in water. This equilibrium is sometimes simplified by leaving out the water to emphasise the ionisation of the acid. The organic acids are weak in the sense that this ionisation is very incomplete. At any time, most of the acid will be present in the solution as un-ionised molecules. The pKa is the negative logarithm value of the indication of acid strength (Ka). If pKa is large, the acid will be weak and it does not complete its ionisation in water. In order to deionise all the organic acids in the leachate, pH should be lowered by the addition of formic acid. After the addition of formic acid, the samples were analysed for ethanol, acetic acid, propionic, iso-butyric, butyric, iso-valeric, valeric, iso-caproic, caproic and heptanoic acids.

Glucose: Glucose concentration in the acidogenic activity assay was determined using the dinitro salicyclic acid (DNS) reactive method (Miller, 1959).

3.4. Experimental Set-ups and Procedures

In this study, the experiments were conducted in two different sets of LBRs. In the Set-1, there were two identical LBRs, fed only with OFMSW without paper and there were four identical LBRs, fed with OFMSW with paper and cow manure in different proportions, in the Set-2, operating both sets in the mesophilic conditions (35±2ºC).

3.4.1. Characterization of OFMSW and Cow Manure

The organic fraction of solid wastes, which were separated from glass, plastic materials and other inorganic materials, were collected from houses of students and supermarkets. To ensure minimal variations in the waste, all the waste used in the LBRs of Set-1 was apportioned from a total of 6 kg of waste that was mainly composed of fruit waste, vegetable waste and kitchen waste. However, all the waste used in the LBRs of Set-2 was apportioned from a total of 20 kg of waste that was mainly composed of fruit waste, vegetable waste, kitchen waste and also paper. The paper was added into the composition of the OFMSW in order to represent the

MSW composition in Turkey more realistically. Therefore, 1.2 kg paper was added into the OFMSW, since the percentage of paper content in the MSW in Turkey is 5.8% (TURKSTAT). The rate and extent of hydrolysis appears to be dependent upon the initial composition of biomass substrate. Therefore, another reason for the change in the OFMSW composition added to the LBRs was to investigate the effect of feedstock composition on the hydrolysis and acidification processes.

The collected OFMSW was coarsely shredded by meat mincer to an average particle size of about 4 mm and it was well mixed manually for both sets. In order to avoid degradation of the collected waste at ambient temperature, it was loosely packed in bags and stored frozen at a temperature of about -20°C until the operation of LBRs. The bags were removed approximately 18 h prior to the loading of LBRs, to allow sufficient time for thawing of the waste. The weight proportions of the fruit waste, vegetable waste and kitchen waste in the mixed waste of Set-1 were 3:2:1, whereas the weight proportions of the fruit waste, vegetable waste and kitchen waste in the mixed waste of Set-2 were 1:1:1, respectively. The Table 3.1 exhibits the general characteristics of OFMSW that was used as feedstock in the Set-1 and Set-2.

Table 3.1. Characteristics of OFMSW used in the Set-1 and Set-2

PARAMETER	SET-1	SET-2
Real Density (kg/m^3)	1084±9.7	1022±8.5
Bulk Density (kg/m^3)	938±5.3	963±9.2
Porosity (%)	13.5±0.5	25±1
Total Solids (g/kg)	248.6±4.9	298.6±6.4
Volatile Solids (g/kg)	212±4.7	262±3.7
Total COD (g/kg)	97±2.1	220±3.8
Total N (g/kg)	2±0.1	4±0.5
Total P (g/kg)	3±0.2	2±0.1
pH	3.95±0.2	5.18±0.2

As it can be seen from the Table 3.1; the TS concentration of OFMSW is 25% in the Set-1, with a VS content of about 85% and the TS concentration of mixed waste is 30% in the Set-2, with a VS content of about 88%. Besides, the COD value and the bulk density of OFMSW used in the Set-2 were higher as a result of the addition of

paper. It can also be seen from the Table 3.1 that the pH value of the OFMSW used in the Set-2 was higher.

For the Set-1, a total of 2.25 kg, high-solids (25 wt % solids) OFMSW, were mixed well homogeneously with the acidogenic culture of 250 mL and packed into each LBR. In the Set-2, cow manure, which was obtained from a farm in Ankara, was added into the OFMSW in different proportions as it is exhibited in the Table 3.3 in order to use the buffering capacity of cow manure. The general characteristic of the manure that was used in the Set-2 is shown in the Table 3.2. For the Set-2, the composition of the total feedstock in four LBRs is exhibited in the Table 3.3. In the first LBR, a total of 1 kg, high-solids (30 wt % solids) substrate, namely OFMSW, was packed. In the second LBR, a total of 0.75 kg OFMSW and 0.25 kg manure were packed. In the third one, a total of 0.25 kg OFMSW and 0.75 kg manure were packed and a total of 1 kg manure was packed into the last LBR.

Table 3.2. Characteristics of Cow Manure used in the Set-2

PARAMETER	VALUE
pH	7.5±0.2
Total Solids (mg/L)	3032.64±1.46
Volatile Solids (mg/L)	2548.96±3.98
Total COD (g/kg)	612.36±3.94

Table 3.3. Composition (% wt) of Feedstock in the LBRs of Set-2

	OFMSW	Manure
1. LBR	100%	-
2. LBR	75%	25%
3. LBR	25%	75%
4. LBR	-	100%

As it can be observed from the Table 3.1 and 3.2, cow manure used in the Set-2 had a much higher COD value and pH value than OFMSW. Therefore, it was expected that the pH value in the LBR, fed with OFMSW and manure, would be increased due to the addition of cow manure with high buffering capacity.

3.4.2. Reactor Design

The research was carried out in two identical laboratory-scale LBRs with a volume of 5 L in the Set-1 and four identical laboratory-scale LBRs with a volume of 3 L in the Set-2, fabricated using polyvinyl chloride (PVC) based materials. The LBRs used in the Set-1 were identical, except for the opening area of the screen used in the LBRs. The opening area of the screen used in the Reactor 1 was smaller that that in the Reactor 2 by 20%. The volume of the LBRs was smaller, whereas the height of the LBRs was higher in the Set-2 than those of the LBRs in the Set-1. The leaching-bed types of reactors used were subjected to operating conditions approximating to those of large-scale landfills in terms of solubilization of wastes by water through leaching. In addition, well representative raw waste feedstock was used in both sets and sprinkler was placed at the top of the LBRs in the Set-1 in order to distribute the water homogenously over the bed. However, instead of ambient temperature conditions of landfills, the mesophilic temperature of 35± 2°C was chosen in order to increase the efficiency of the processes in both sets. The Figure 3.1 shows a schematic diagram of the LBR design for both experimental set-ups. The LBR designs used in this Set-1 and in the Set-2 are exhibited in the Appendix-A and Appendix-B, respectively.

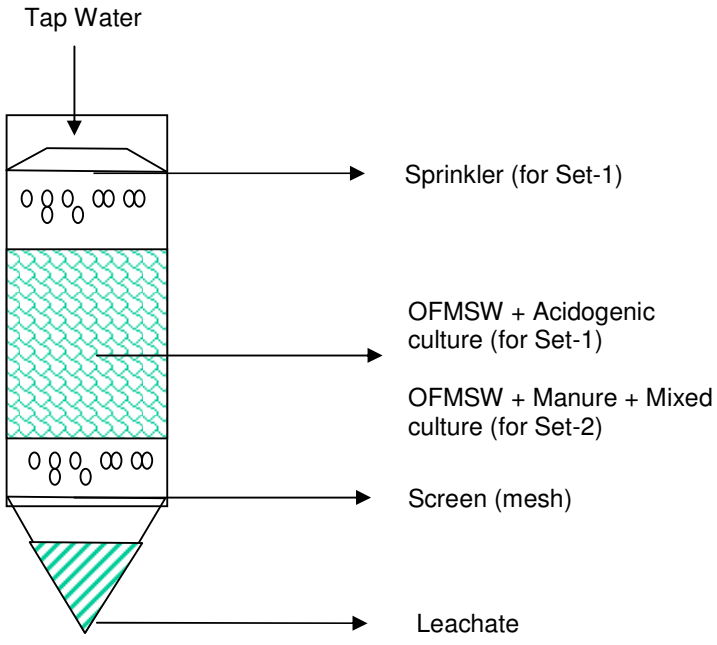

Figure 3.1. Schematic diagram of LBRs

Two cylindrical, cone-bottomed LBRs shaped as shown in the Figure 3.1 were operated out at the same time in the Set-1, whereas four cylindrical LBRs were operated in the Set-2. The conical shape at the bottom of LBRs provides the leachate collection from the LBRs. A 155 µm pore size of stainless steel mesh (screen) was placed at the bottom of the LBRs over the cone-bottomed surface to prevent the mixing of organic solid waste particulates into the leachate. The total volume was 5 L and deducting the volume of the sprinkler at the top of the LBR and leachate collection system at the bottom of the LBR provided an effective volume of 4 L. In the Set-2; 3 L of bench-scale, anaerobic LBRs with effective volume of 2.5 L were used. Besides, no sprinkler was used in the Set-2.

3.4.3. Operation of Reactors

The LBRs were incubated at 35°C (± 2°C), known as mesophilic condition for both sets. During the initial 2 days, no tap water was added to the LBRs of both sets, except for the initial added water of 1.2 L in the Set-1 and 0.5 L in the Set-2 and no leachate was collected from the LBRs of both sets in order that the water fills the pore volumes in the waste and the waste is saturated with water. After 2 days, the daily addition of water to LBRs and the daily collection of leachate from LBRs were carried out during 80 days of operation time for the Set-1 and 40 days of operation time for the Set-2. During the operation time for the Set-1, the volume of water in the LBRs was kept at costant level of 1.2 L by the addition of water through a sprinkler, whereas the LBRs in the Set-2 were operated at HRT of 23 hours. The water level control in the LBRs of Set-1 has been performed manually throughout the experiments. The leachate sampling valves kept opened about 1 hour daily in the Set-2. The amount of water addition to the LBRs of Set-2 was set equal to the volume of leachate collected at the end of 1 hour. No digested feedstock was removed from the LBRs during the operation period in both sets.

The leachate flow from the LBRs in both sets was monitored daily. The pH, VFA production, tCOD and sCOD, TS and VS values of leachate were analysed.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results of acidogenic activity assay experiment and the results of LBR experiments of Set-1 and Set-2 are presented and discussed.

4.1. Results of Acidogenic Activity Assay Experiment

The acidogenic culture, used in the LBRs of Set-1, was obtained from a 2 L fed-batch reactor with alkaloid wastewater as mentioned in Chapter 3. The substrate utilization rate and pH variations of batch reactors fed by glucose were monitored throughout the acidogenic activity assay experiment. Acidogenic activity assay (used to determine the acidogenic activity of cultivated inocula) results are presented in the Figure 4.1.

Glucose was used as substrate since it is considered as the main and the simplest intermediate in the pathway of AD of carbonhydrate complex organics. After the first feeding, once the substrate (glucose) was completely consumed, a second addition of glucose was carried out in both batch reactors. During the first addition of glucose in the acidogenic activity assay experiment, 8 hours of lag period was observed in both reactors. This lag phase was also observed in the study of Soto et al. (1993), in which the acidogenic assay methodology was developed. The lag phase disappeared in the second feeding in both reactors.

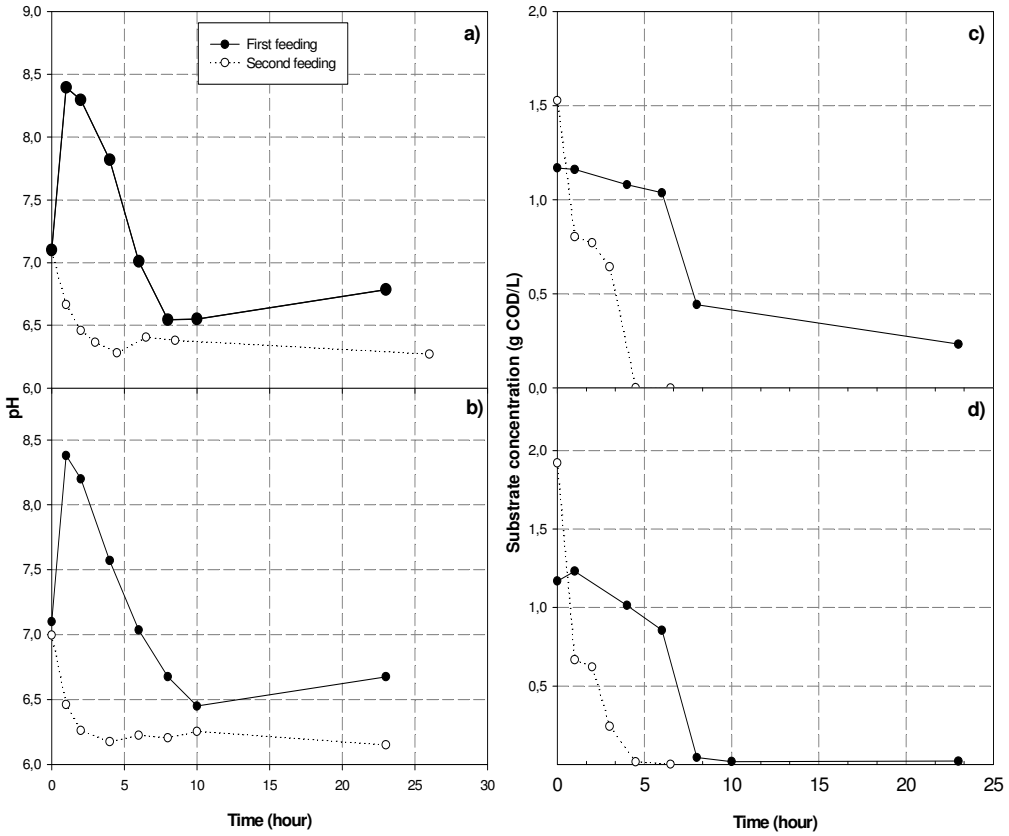

Figure 4.1. Substrate utilization rate and pH values recorded during acidogenic activity assay in **a)** Batch 1, **b)** Batch 2, **c)** Batch 1 and **d)** Batch 2 reactors

As depicted from the second feeding data in the Figure 4.1.a and 4.1.b, a sharp increase in pH from 7.1 to 6.3 was observed in the 2nd day, while the substrate was consumed from 1.5-2 g/L. The substrate consumption was indeed rapid that in the first hour, around 50% of glucose was vanished in the Batch 1, whereas 70% of glucose was vanished in the Batch 2. By pre-feeding (day 1), sludge adaptation was achieved and it was possible to obtain a correct activity value in the second feeding (Soto et al., 1993). The acidogenic activity of sludge, which is the ratio of substrate utilization rate to microorganism concentration, was found from the second feeding data of Figure 4.1.c and 4.1.d. The first consumption rate in the second feeding was used to estimate the activity as 12 g COD/g VSS.d in the Batch 1 and 22.6 g COD/g VSS.d in the Batch 2. The acidogenic activity assay was determined from the substrate (glucose) removal rate. To calculate specific activity, the value obtained was divided by the VSS concentration in each case.

Soto et al. (1993) found the specific acidogenic activity of sludge from an anaerobic filter at different filter heights. The highest activity occurred at 5 cm with a value of around 24 g COD/g VSS.d and activity dropped to 17 g COD/g VSS.d at filter height of 40 cm. In another study, the maximum specific acidogenic activity was found as 38.1 g COD/g VSS.d for lab-scale anaerobic baffled reactor sludge (first compartment). The activity decreased a value of below 5 g COD/g VSS.d in the second compartment of anaerobic baffled reactor (Punal et al., 1999).

Comparing the values in the literature with the found values in this experiment, the acidogenic activity of culture cultivated was considerably high and suitable for usage in the pre-acidification, especially in the Batch 2. Therefore, the acidogenic culture obtained from the Batch 2 was used as inocula for the LBRs of Set-1 in this experiment.

4.2. Results of Experiments of Set-1

The LBRs of Set-1 were operated in order to produce organic acids from the high-solids OFMSW without paper. The water volume in the LBRs of Set-1 was kept constant at 1.2 L manually, which is the half of the volume of OFMSW in the LBRs, by the addition of water through sprinkler by peristaltic pump throughout operation.

4.2.1. Water Addition and Leachate Collection

The only sources of moisture in a conventional landfill are precipitation and the water that may be produced chemically during the waste decomposition process. Past investigations have shown that the addition of water to raise moisture content to field capacity accelerates waste stabilization processes and stimulates early production of methane (Chugh et al., 1999).

The leachate contains microbial inoculum and buffering capacity, while the source of leachate in a landfill is rain, which lacks both a high inoculum potential and buffering capacity. The system used in this research was most analogous to the chemical environment of a recently filled landfill in this respect, since there was water addition to the LBRs, but no leachate recycle in the LBRs.

Two identical LBRs, except for the opening area of the screen, were set to search the potential of organic acid production as a result of hydrolysis and acidification of high-solids (25%) OFMSW. The opening area of the screen used in the Reactor 1 was smaller that that in the Reactor 2 by 20%. The LBRs were operated for 80 days. The volume of tap water in the LBRs was observed periodically to keep it at 1.2 L manually by the addition of water to the LBRs through a sprinkler by using peristaltic pump over the bed of OFMSW and acidogenic culture mixture and the leachate were collected from the LBRs daily. The graph of daily volume of tap water addition and the daily volume of leachate collection is shown in the Figure 4.2.

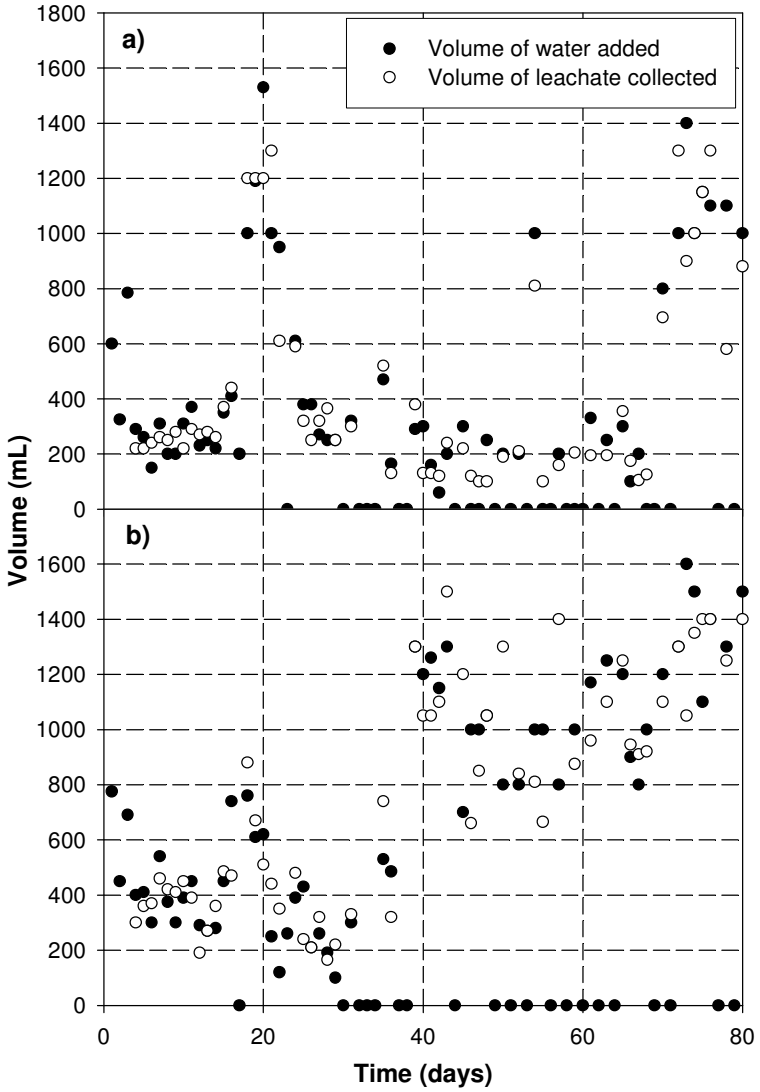

Figure 4.2. Daily volume of water addition to and volume of leachate collection from **a)** Reactor 1 and **b)** Reactor 2 throughout operation

As it can be seen in the Figure 4.2.a and 4.2.b, the daily volume of water addition was almost the same as the daily volume of leachate collection for both reactors during 80 days. This shows that the added water to the LBRs was collected as leachate from the LBRs, in which the particulate solids were solubilized through water addition and they were passed into the leachate as soluble organics. These results exhibit the unclogging of the LBRs, since there was leaching and leachate collection from both LBRs throughout the experiment. The daily volume of water addition and leachate collection in the Reactor 1 was almost equal to the daily volume of water addition and leachate collection in the Reactor 2 during 40 days. However, after 40 days, the daily volume of water addition and the daily volume of leachate collection between the reactors changed. After 40 days, as it can be seen from the Figure 4.2.a and 4.2.b, there are serious differences between the volumes of water added to the LBRs and also between the volumes of leachate collection from the LBRs. The volume of water addition and the leachate collection in the Reactor 1 was less than those in the Reactor 2, which might have resulted from the smaller opening area of the screen in the Reactor 1 compared to that in the Reactor 2 by 20%. As a result, it was expected that the hydrolysis rate and the hydrolysis efficiency in the Reactor 2 were higher than those in the Reactor 1 after 40 days with the addition of much water to the Reactor 2.

The cumulative water added to the LBRs and the cumulative leachate collected from the LBRs during 80 days of operation time were also calculated and the graph of the cumulative volume of leachate collection vs. the cumulative volume of water addition in both LBRs is shown in the Figure 4.3.

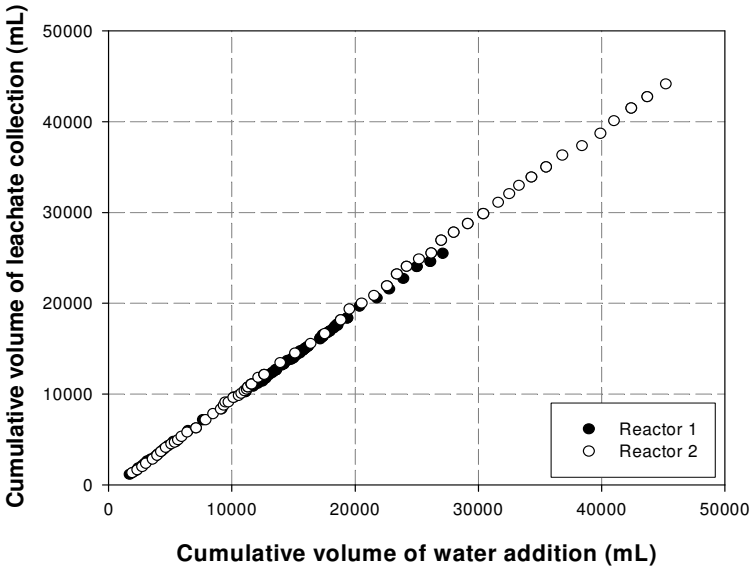

Figure 4.3. Cumulative volume of leachate collection from the LBRs vs. cumulative volume of water addition to the LBRs

According to the Figure 4.3, it can be observed that the total volume of water addition and the total volume of leachate collection in the Reactor 2 were about twice of those in the Reactor 1, which might have resulted from the smaller opening area of the screen in the Reactor 1 compared to that of Reactor 2. The volume of water added and leachate collected in the Reactor 2 was approximately 40 times of the initial volume of water in the Reactor 2 and it was 10 times of the volume of reactor. The volume of water added and leachate collected in the Reactor 1 was approximately 20 times of the initial volume of water in the Reactor 1 and it was 5 times of the volume of reactor. This might have resulted from the different leaching rates through the beds in the LBRs. The leaching rate in the Reactor 1 was smaller than that in the Reactor 2 due to the smaller opening area of the screen and the partial clogging of the screen in the Reactor 1. In other words, the HRT in the Reactor 1 was higher that that of Reactor 2. As a result of less volume of water passing through the bed and less amount of leaching taking place in the Reactor 1, less volume of leachate was collected from the Reactor 1. The cumulative volume of water passed through the Reactor 1 was approximately 25 L, whereas it was about 45 L for the Reactor 2 during the entire study. During the 80 days of operation period, as it can be observed from the Figure 4.3 that the total amount of leachate collected from each

LBR was approximately the same with the total amount of water added to each LBR.

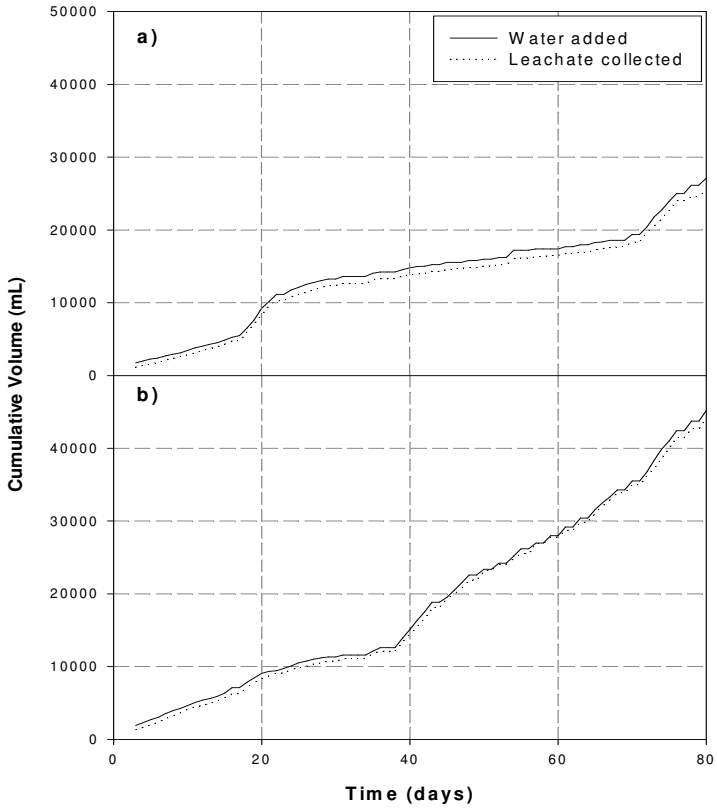

Figure 4.4. Cumulative volume of water added and cumulative volume of leachate collected in **a)** Reactor 1 and **b)** Reactor 2 throughout operation

In the Figure 4.4.a and 4.4.b, the cumulative volume of water addition and the cumulative leachate collection for each LBR is exhibited. It can be observed from the Figure 4.4.a and 4.4.b that the cumulative volume of water added and cumulative leachate collected from the Reactor 1 were approximately equal to those in the Reactor 2 in the initial 40 days. As it can also be seen from the Figıre 4.4, the cumulative volume of leachate collected from both LBRs was about 15 L in the initial 40 days. However, after 40 days, the water added and leachate collected in the Reactor 1 was lower than those of Reactor 2. This may cause higher amount of solid organic wastes hydrolysed and high hydrolysis yields due to the much water addition to the Reactor 2. At the end of 80 days, the total volume of leachate collection from the Reactor 1 and the Reactor 2 were approximately 25 L and 45 L, respectively, according to the Fgure 4.4.a and 4.4.b. It can also be figured out from the Figure 4.4.a and 4.4.b that the total volume of water added to the LBRs was

approximately the same as the total volume of leachate collected from the LBRs throughout the operation.

When the daily volume of tap water added and the daily leachate collected in the LBRs are examined in the Figure 4.2, it can be seen that the leaching in the Reactor 2 was regular and the slope of the graph of cumulative volume of water added and leachate collected in the Reactor 1 after 40 days was smaller than that in the Reactor 2 according to the Figure 4.4 due to the smaller opening area of the screen in the Reactor 1. The irregular trend of the collected leachate volumes in the Reactor 1, as it is seen in the Figure 4.2.a, proves the irregular leaching due to partial clogging in this reactor. This observation may also support the differences in the hydrolysis efficiencies of the LBRs, which appeared most probably after 40 days.

As a result of these differences in the volumes of water added and leachate collected, especially after 40 days, it can be expected that the amount of solid organic wastes hydrolysed was higher in the Reactor 2 due to much water addition and consequently, the passing area of the leachate through the pore volumes and the hydrolysis and acidification processes were improved in the Reactor 2 as a result of the degradation of solid waste in a shorter time with higher volume of water addition, compared to the Reactor 1.

The amount of leachate collected daily from the LBRs can be set equal to the amount of water added to the LBRs when there is no clogging in the LBRs; since, it was observed that the amount of water added to the LBRs was equal to the amount of leachate collected from the LBRs in the Set-1.

According to the cumulative volume of water addition to the LBRs, it can be concluded that the HRT in the Reactor 2 was lower than that in the Reactor 1, since the total volume of water addition in the Reactor 2 was higher than that in the Reactor 1, especially after the initial 40 days.

4.2.2. The Total Solids (TS) and Volatile Solids (VS) Variations

The variations of TS and VS concentrations in the the leachate samples of LBRs were exhibited in the Figure 4.5.

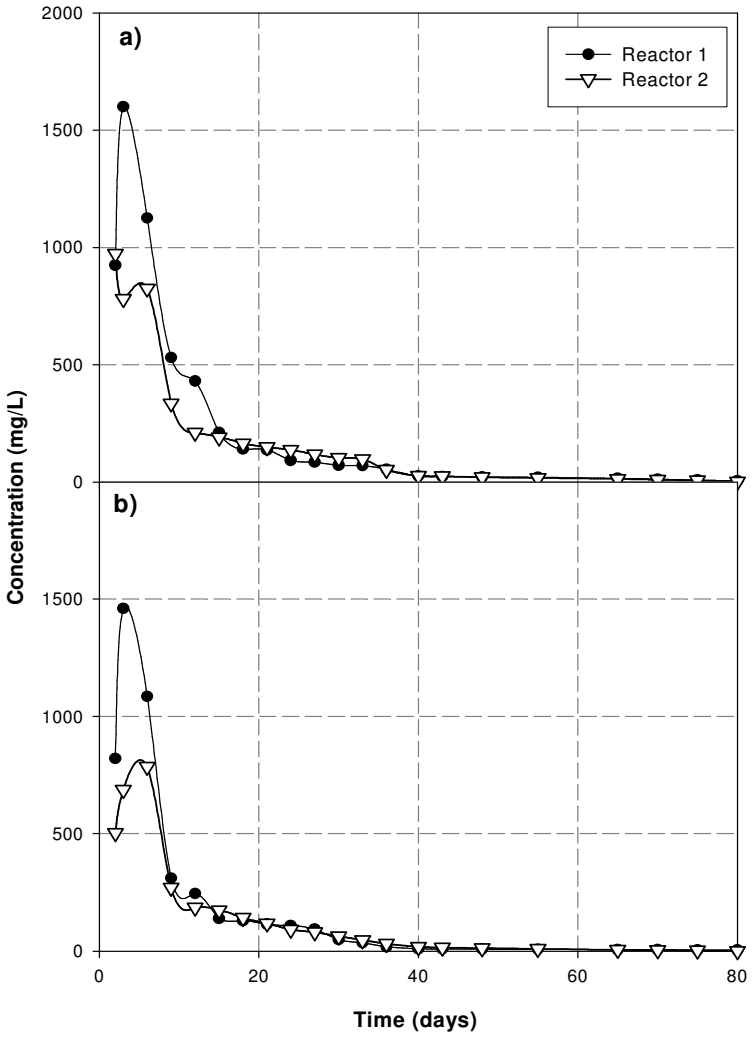

Figure 4.5. Daily concentration variations of **a)** TS and **b)** VS in the LBRs

According to the Figure 4.5.a and 4.5.b, the effluent TS and VS concentrations in the LBRs increased rapidly and reached to 1500 mg/L in the initial 5 days. In the LBRs, the leaching conditions caused strong liquefaction of the organics, which resulted in highly turbid leachates in terms of solids with elevated content of microbial biomass and suspended material in the initial 5 days. After the initial 5 days; the TS and VS concentrations in the leachate decreased rapidly and the concentrations reached to below 150 mg/L at the end of 20th day. At the end of 40th day, the concentrations

of TS and VS reached to about zero in both LBRs. The increases in the TS and VS concentrations in the initial 5 days show that there was possible wash-out of solid particles from the LBRs. As it can be seen from the Figure 4.5, the wash-out of solid particles in the Reactor 1 was higher than that in the Reactor 2. The decreases in the solids concentrations after 5th day suggest that solid organic materials were solubilised and they were degraded by microorganisms in the LBRs after 5 days. The organic solids changed state, in other words, they were dissolved by the addition of water in time. The solid organic materials were almost completely converted to soluble organic materials in the LBRs during 40 days, which suggests that the hydrolysis was efficient in the LBRs and leaching of water significantly solubilized most of the solid particulates contained in the feedstock during 40 days. As a result, solubilized organics in the leachate started to increase after 5 days, as the particulate organics solubilized. After 40th day, there was almost no solids escaping from the LBRs and most of the particulate organics were converted to soluble organics in the LBRs.

The cumulative TS and VS values of the leachate throughout operation are calculated in terms of mass in order to eliminate the dilution effect and they are exhibited in the Figure 4.6 and Figure 4.7.

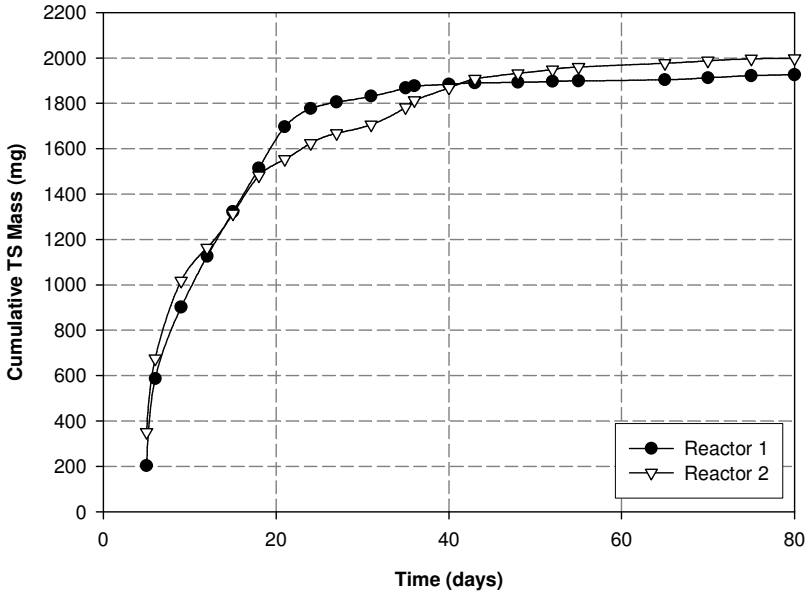

Figure 4.6. Cumulative mass variations of TS in the leachate

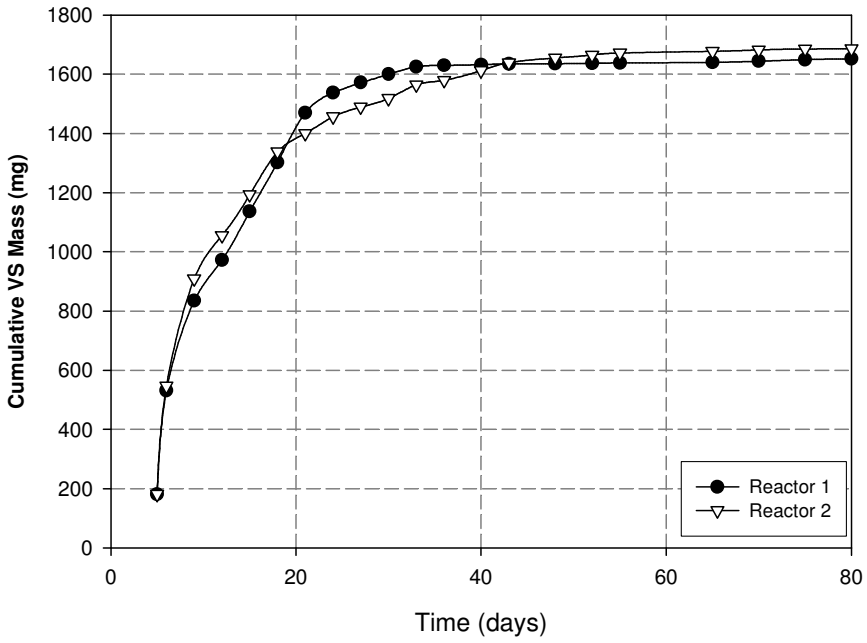

Figure 4.7. Cumulative mass variations of VS in the leachate

The similar conclusion from the Figure 4.6 and 4.7 can be figured out as in the Figure 4.5. The solid particles continued to be removed from the LBRs, especially in the initial 40 days, and after 40th day, there was almost no particulate solids escaping from both LBRs. Particularly, the increase of TS and VS masses in the leachate in the initial 5 days, can be interpreted as washing out of the small particulates in the OFMSW and their removal from the LBRs or this situation can be explained as the particulates formation due to the hydrolysis in the initial 5 days, when the hydrolysis mainly took place and the particulates from the LBRs were removed. After the initial 5 days, the slope of the graphs of the cumulative TS and VS masses of leachate started to decrease, which shows the solubilization processes in the LBRs.

According to the Figure 4.6 and 4.7, the cumulative TS and VS removal in the Reactor 2 was higher that that in the Reactor 1 after 40 days, which might have resulted from the higher amount of water addition to the Reactor 2 after 40th day.

4.2.3. The pH, Total COD (tCOD) and Soluble COD (sCOD) Variations

Since hydrolysis is carried out by the enzymes synthesized by the biomass, it is important to maintain the proper conditions such as pH for bacterial growth. The pH is also one of the major conditions affecting the product formation in anaerobic acidogenesis (Zootemeyer et al., 1982). However, there are only few studies and little information available on the effect of pH on the anaerobic acidogenesis. It is known that the pH conditions of the system do not only influence the product formation, but also the product spectrum in the acidogenic phase.

The pH values in the LBRs were observed and VFA analyses were performed during the experiment in order to have a comment on the acidogenesis process taking place in the LBRs during this study in addition to the hydrolysis process.

The pH, tCOD and sCOD profiles of leachate in the LBRs were analysed over time to examine the operation of LBRs and to investigate the efficiency of hydrolysis processes in the LBRs. The variations in these parameters through the operation of LBRs are shown in the Figure 4.8.

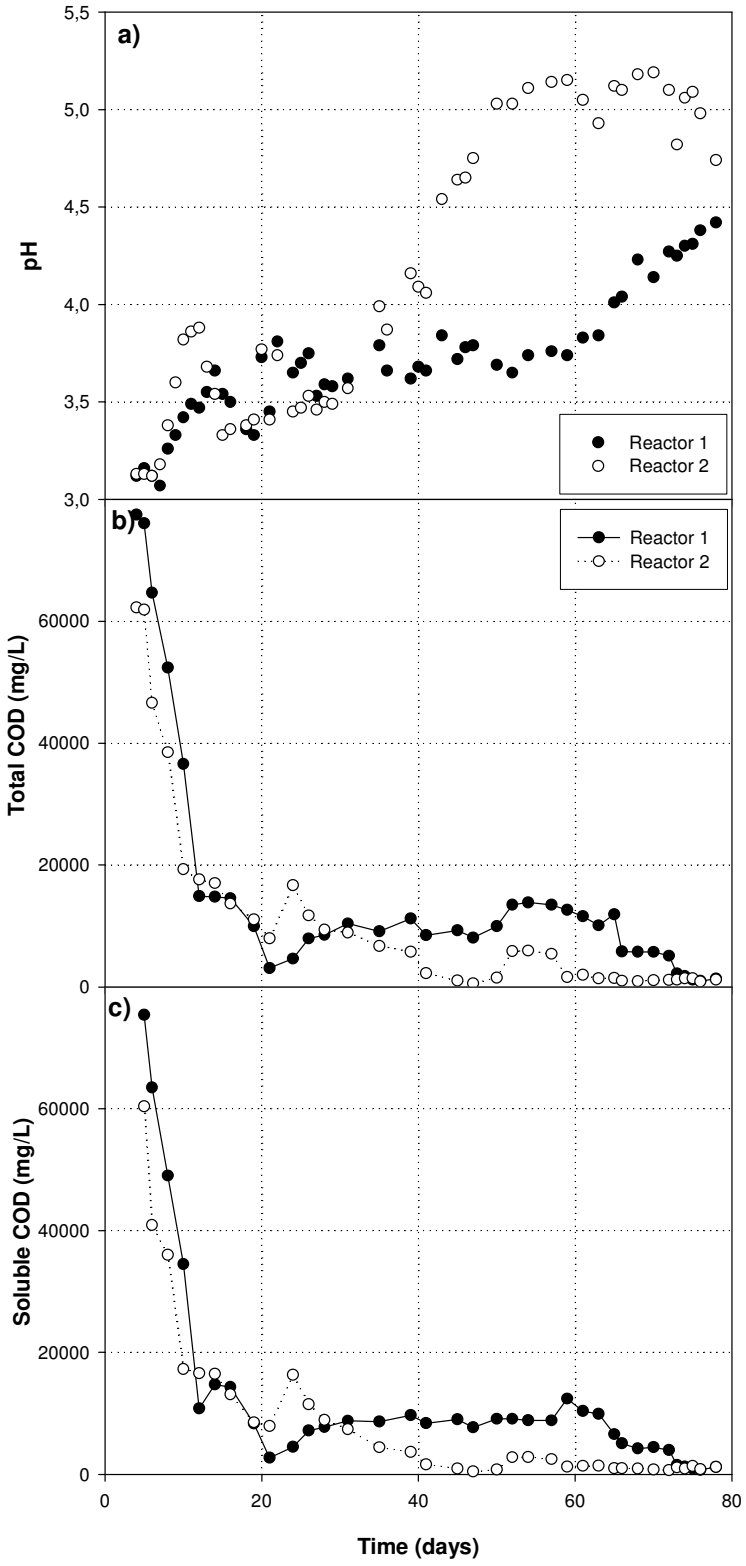

Figure 4.8. Daily variations of **a)** pH, **b)** tCOD and **c)** sCOD concentrations in the leachate samples throughout operation

As it can be figured out from Figure 4.8.a, the pH values of leachate from the LBRs increased slightly with the addition of tap water through the experiment. The initial pH value of the OFMSW was 3.95±0.2 and the pH values decreased to 3 in the leachate from the LBRs at the end of 5th day. The pH values in both LBRs increased slightly in both LBRs after 5th day. The pH values of effluent in the Reactor 2 increased and reached to above 4 rapidly after 40th day, and then it continued to increase and reached to 5 at the end of the experiment. The pH values of effluent in the Reactor 1 reached above 4 at the end of the 65th day and it reached to 4.5 at the end of the experiment. The pH values in the Reactor 1 and in the Reactor 2 reached to above 4 in the 65th and 40th days, respectively.

The pH may vary during acidogenesis, which causes that the system tends to buffer itself towards a pH value in the range of 5-6.5, if no control is carried out (Guerrero et al., 1999). According to that, it can be thought that the LBRs tend to buffer themselves towards a higher pH value during acidogenesis stage in this study. However, the increase in the pH may also result from the addition of tap water into the LBRs, which hold the pH of leachate at between 3.0 and 4.5 (generally below 4) in the Reactor 1 and 3.0 and 5.5 (generally below 5) in the Reactor 2. These pH values are below the optimum pH values stated, which is between 4 and 6.5 for acidification (Speece, 1996). However, the bacteria of the hydrolysis and acidification stages are able to withstand fluctuations in the environmental conditions without any loss of activity, and they remain active through a pH range from about 3 to 7 (Wu et al., 2005). In addition, the pH values of both reactors are below the optimum pH values, stated as in the range of 6.6-8.5 for the acetogenesis and methanogenesis (Demirer and Chen, 2004). Therefore, it might be considered that these reactions were not dominant in the LBRs and the sCOD removal in the LBRs did not occur due to these reactions.

The low pH values observed in this study may also occur due to the feedstock composition, which includes mainly fruit waste that was very acidic. Although the feedstock composition in both LBRs was similar, the pH values of the Reactor 2 were higher than that of the Reactor 1, especially after 40 days, according to the Figure 4.8.a. This may result from the fact of higher volume of water addition to the

Reactor 2 after 40th day, as it can be seen from the Figure 4.4, since tap water has a greater pH value (varying between 6.5 and 7.5) than that of OFMSW, which was 3.95±0.2 in this experiment.

Such low pH values observed during this study may indicate successful acidification in the reactors. Methanogens prefer nearly neutral pH conditions with a generally accepted optimum range of 6.5 to 8.2 (Speece, 1996). Although most methanogens have pH optima near neutral, there are some methanogens that live in the extreme pH environments. Methanogenesis has been shown to occur at low pHs (pH=3) with reduced rates. Therefore, since the optimum pH conditions for methanogens are mainly at higher values, it can be said that most of the methanogens were successfully inhibited in the LBRs. On the other hand, acidogens grow faster and are relatively less sensitive to low pH conditions than acetogens/methanogens (Cohen et al., 1980). Acidogens are more versatile and have much wider working pH range, 5 to 8, with the optimum level being 5 to 6. On the other hand, Speece (1996) had reported a case in which acidogens were active at pH 3.6 in a starch mill wastewater treatment plant.

The pH effect on the hydrolysis process was studied by Veeken et al. (2000). The anaerobic hydrolysis rate of organic solid waste was studied at fixed pH values between 5 and 7. Using a statistical analysis, it was found that the hydrolysis rate constant was pH dependent, but it was not related to tVFA and undissociated VFA concentrations (Veeken et al., 2000). Therefore, in this experiment, it was expected that the efficiency of the hydrolysis processes and the hydrolysis rates in the LBRs changed with the pH variations. In addition, the different hydrolysis rates in the LBRs might have occurred due to the different pH values observed in the LBRs, especially after 40th day.

Most of studies of the pH effect on the acidogenesis were conducted for the degradation of simple substrates, such as glucose, sucrose, and lactose. The acidifying glucose at pH 5.7–6.0 produced stable intermediates favored by the bacteria in the methanogenic reactor downstream. The variations in the pH between 4.3 and 5.2 did not affect VFA production and COD solubilization. The variations in

higher pH levels from 6.0 to 8.0 were reported to be affecting the dominant microbial populations in the acid reactor, and at a lower pH value of 4.5 (Demirel and Yenigün, 2002). Therefore, in this experiment, the low pH values below 4.5 in the Reactor 1 (through the experiment) and in the Reactor 2 (in the initial 40 days) observed were expected to affect the dominant microbial populations in the LBRs.

Similarly, the optimum pH for the acidification of sucrose and lactose were reported as pH of 6.5 and pH of 6.0–6.5, respectively. However, wastewater from many food and agricultural industries contain high levels of not just carbonhydrates, but also proteins and lipids. Hydrolysis and fermentation of complex colloidal particulates, such as proteins and lipids, may prefer pH levels different from those for the acidogenesis of simple carbonhydrates and yet little information is available on this matter (Yu and Fang, 2002). The different pH levels observed during the experiment were expected to improve the hydrolysis and fermentation of the different particulates such as carbonhydrates, proteins and lipids in the composition of OFMSW.

As it was stated, the aim of this study is to provide the hydrolysis and acidification of high-solids OFMSW with the aid of leaching and acidogenic culture in the LBRs and to search the potential of organic acids and alcohols production. In the hydrolysis stage, complex particulate organic materials of OFMSW such as protein, polisaccharides, cellulose, lignin and lipids decompose into their soluble monomers such as aminoacids, glucose, alcohol, long chain fatty acids by extracelular enzymes excreted from the hydrolytic and fermentative bacteria. In the acidogenesis, the products of hydrolysis are converted into VFAs, alcohols, CO_2 and H_2 by the acidogenic bacteria. Accordingly, in this experimental study, solid particulates were expected to be converted into the soluble organics (monomers, VFAs and alcohols) and passed into the leachate as a result of hydrolysis/acidification processes after the start-up of the LBRs and as a result, the sCOD values were expected to increase. However, since no leachate was collected from the LBRs in the initial two days and the first analysis was done in the 5^{th} day of the experiment, the time required for the hydrolysis of carbonhydrates/lipids/alcohols and proteins, defined as hours and days for, respectively, (Wheatley, 1990), could not be observed clearly. The increase in

tCOD and sCOD in the leachate could not be observed throughout the experiments and it was expected that the hydrolysis process in the LBRs took place essentially in the initial 5 days (Figure 4.8.b and 4.8.c).

Particulate organic matter first undergoes liquefaction by extracellular enzymes before being taken up by the microorganisms. Since most of the organic matter in the feed is in the particulate form, solubilization is a crucial step in the digestion process in this study. The substrate solubilization can be estimated from a variety of parameters like sCOD, VS and TS (Banerjee et al., 1999).

Hydrolysis and acidification, as quantified by sCOD and VFA concentrations, respectively, are the predominant reactions during solid-bed fermentation. The COD concentrations in the leachate were monitored as an indicator parameter of the leachate organic strength and the hydrolysis process development. The Figure 4.8.b shows the variation of tCOD concentrations in the leachate samples for both LBRs. The initial tCOD values of the leachate samples were higher as expected because of high organic matter content of the feedstock in the LBRs at the beginning of the experiment. The tCOD values of the leachate decreased rapidly in the initial 20 days for both LBRs due to the hydrolysis process and conversion of most of COD to sCOD for the utilization of hydrolytic microorganisms. As the complex organics, which were converted to soluble organics by the addition of water in time and utilized by the microorganisms in the LBRs, the sCOD and tCOD values in the leachate decreased rapidly in the initial 20 days. After 20^{th} day, there was no significant decrease in the tCOD and sCOD values in both LBRs.

The decrease in tCOD and sCOD concentrations in the leachate of LBRs in time shows that there was a liquefaction/hydrolysis in the LBRs and the initial COD at the beginning of the experiment was converted to sCOD by the addition of water in time. This value decreased with time due to the hydrolysis and acidification of the waste in the LBRs by the addition of much water. As the water passes through the LBR, it helps to hydrolyse the OFMSW and its acidification by the microorganisms. As water solubilizes the particulate matter, the sCOD values in the leachate increased in time. Hydrolysis started rapidly with the addition of water to the LBRs.

The variations in sCOD concentrations observed were similar with the variations of tCOD concentrations. As it can be seen from the Figure 4.8.c, the sCOD concentrations in the leachate of Reactor 1 and Reactor 2 were 80000 mg/L and 60000 mg/L, respectively, at the end of 5th day and the sCOD concentrations in leachate of both LBRs decreased rapidly after 5th day, which shows a similar trend with tCOD variations as in the Figure 4.8.b. The sCOD concentration values decreased rapidly from 80000 mg/L to 15000 mg/L in the Reactor 1, whereas the sCOD concentration values decreased rapidly from 60000 mg/L to 15000 mg/L in the Reactor 2 in the initial 10 days. At the end of 20 days, the sCOD values in both LBRs decreased to below 10000 mg/L. The sCOD concentration values in the effluent of both LBRs showed a similar decrease trend in the initial 20 days. The daily variations in tCOD and sCOD concentrations were the same in the initial 20 days in both LBRs, however, they showed a different trend after 20th day. The effluent sCOD and tCOD concentration values of the Reactor 1 remained constant at about 10000 mg/L between 20 and 65 days, then it decreased to 5000 mg/L, and it decreased eventually to 1000 mg/L after 70 days. However, the effluent sCOD and tCOD concentration values were constant at 1000 mg/L after 40 days in the Reactor 2. After 40th day, it was observed that the decrease in tCOD and sCOD concentrations in the Reactor 2 was higher with respect to those in the Reactor 1. This might have also resulted from the fact of much water addition to the Reactor 2 after 40th day, as it can be seen from the Figure 4.4. Water addition helps the solubilization of organic solids and their degradation by the microorganisms in the LBRs through acidification process.

COD is reduced through the acidogenesis and acetogenesis stages in the AD process (Mata-Alvarez, 2000). This information also suggests that acidogenesis and acetogenesis stages started in the LBRs with COD reductions starting from the 5th day and continued throughout the experiment. This is also an evidence of the fact that the biochemical reactions in AD processes occur simultaneously and synergistically. However, since there was no serious decrease in the COD values in the Reactor 2 after 40th day, it can be said that the acidogenic and acetogenesis stages were dominant before 40th day in the Reactor 2.

The acid phase digestion process is influenced by various factors including: feedstock characteristics; operational parameters like HRT and SRT; and environmental factors like temperature, pH and reactor configuration (Banerjee et al., 1999). The degree of VFA production, COD solubilization and organic substrate degradation primarily depended on the HRT for complex substrates (Demirel and Yenigün, 2002).

The increases and decreases observed in the sCOD concentration values can be related to the hydrolysis/acidogenesis processes and the dilution rates in the LBRs due to the water addition. High sCOD concentration values show that the hydrolysis process continues in the LBRs. The decrease in the sCOD concentration values in both LBRs in time can be explained as the decrease of sCOD concentrations with the effect of decreasing of particulate substrates (organics) that is hydrolysed in the LBRs and with the effect of water addition to the LBRs. It is known that the amount and the composition of OFMSW packed into both LBRs and consequently, the initial COD value of the feedstock in the LBRs at the beginning of the experiment, and the cumulative water added to and cumulative leachate collected from both LBRs during the initial 40 days were the same (Table 3.1 and Figure 4.4). Therefore, the sCOD concentration variations in the LBRs showed a similar trend until 40^{th} day. Therefore, the hyrolysis efficiencies in the LBRs were expected to be the same in the initial 40 days. However, the sCOD concentration trend in the LBRs changed due to the different amount of water addition to the LBRs after 40^{th} day. Consequently, the hydrolysis efficiencies in the LBRs were expected to be different and the hydrolysis efficiency in the Reactor 2 was expected to be higher than that in the Reactor 1 after 40^{th} day, as a result of higher amount of water addition to the Reactor 2 after 40^{th} day. However, when it is considered that the initial tCOD and sCOD values in the effluent of Reactor 1 were about 20000 mg/L greater than those of Reactor 2, it can be understood that the hydrolysis was effective in the Reactor 1 in the initial 5 days (Figure 4.8.b and 4.8.c). However, this conclusion may not be true when the sCOD decrease due to the acidogenesis and the dilution effect on the sCOD values are considered.

In order to eliminate the dilution effect and to compare the hydrolysis efficiency of the LBRs, the daily and cumulative tCOD and sCOD values in the effluents of both LBRs were calculated in terms of mass and exhibited in the Figure 4.9 and 4.10, respectively.

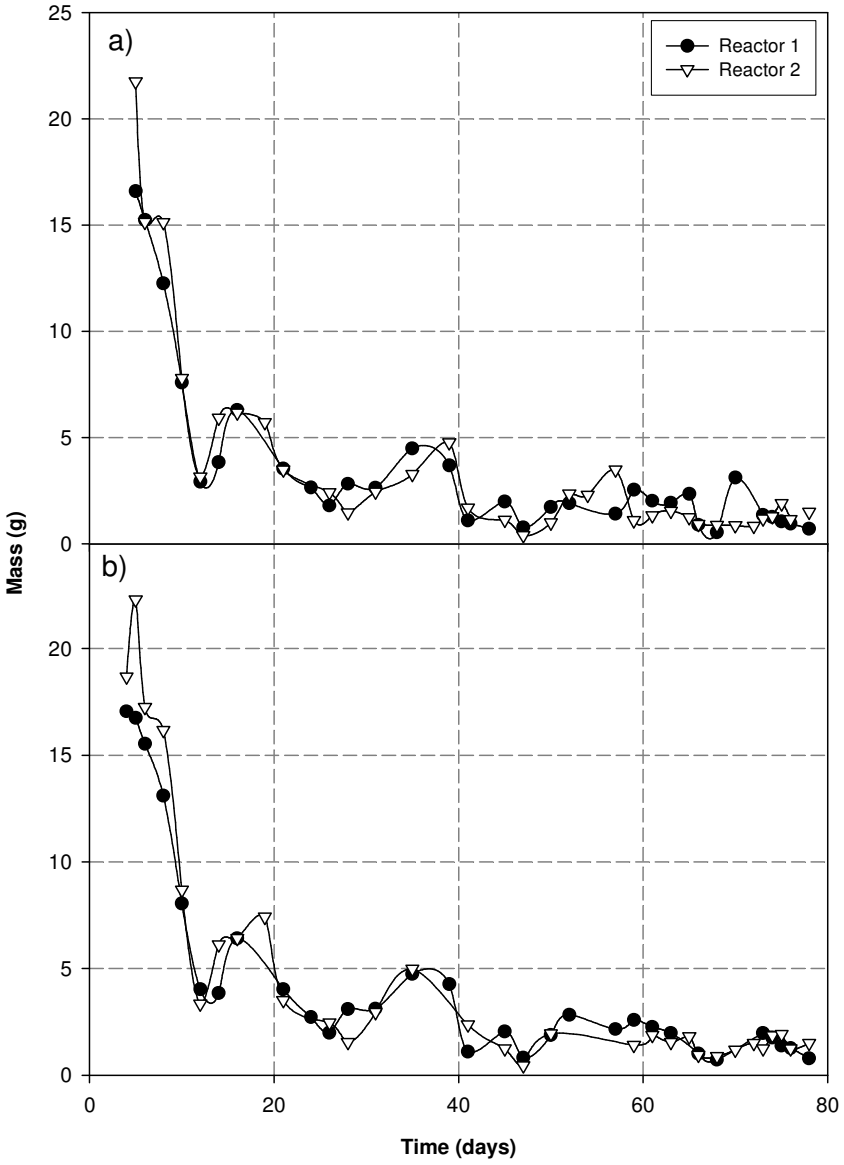

Figure 4.9. Daily mass variations of **a)** sCOD and **b)** tCOD values in the leachate of LBRs throughout operation

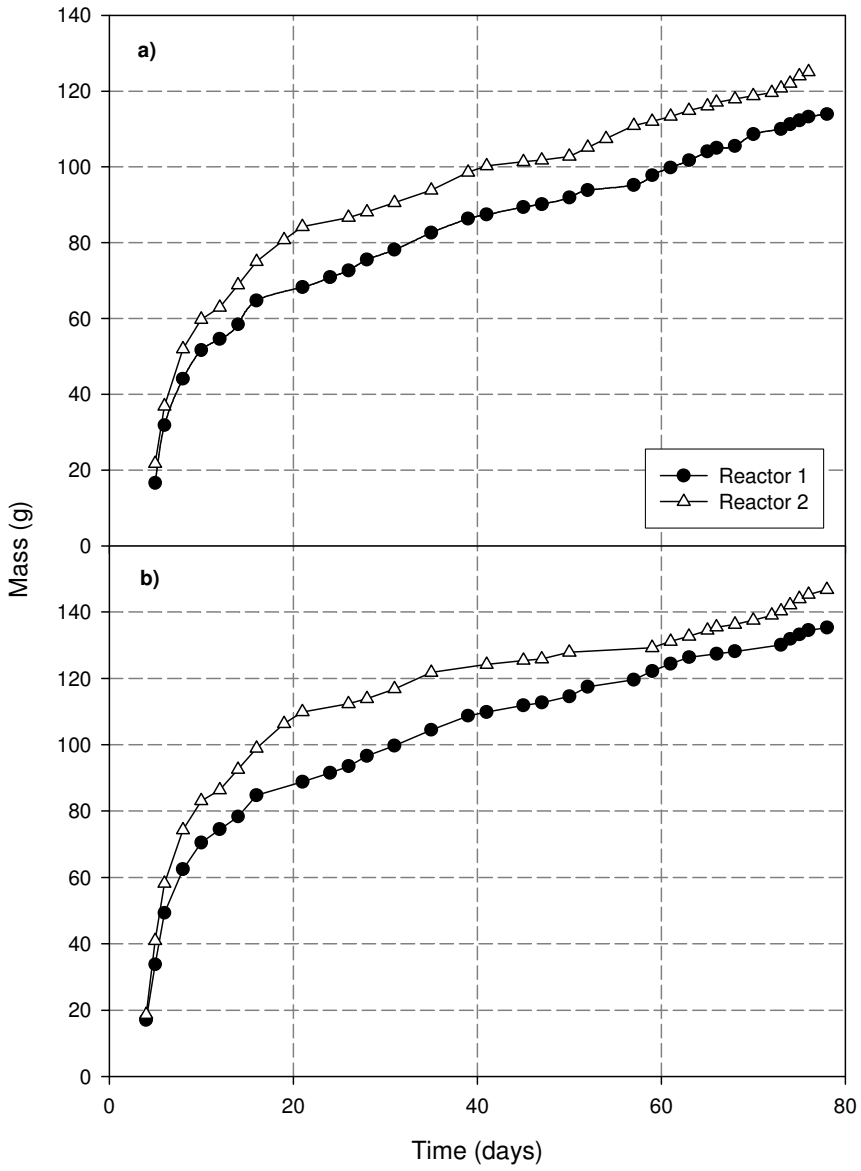

Figure 4.10. Cumulative mass variations of **a)** sCOD and **b)** tCOD values in the leachate of LBRs throughout operation

As it is seen in the Figure 4.9, the similar decrease trend in the sCOD and tCOD mass values were observed in both LBRs. The daily sCOD and tCOD values in terms of mass in both LBRs decreased rapidly in the initial 20 days and continued to decrease throughout the operation of LBRs.

If no significant COD removal was observed in the LBRs during this experiment, this would indicate that the end products remained as solubilised compounds in the

effluent. In other words, an important fraction of solubilised organics would not be used by microorganisms for growth and the acidogenesis reaction would not proceed in the LBRs.

The cumulative sCOD and tCOD mass values in the leachate of LBRs increased rapidly, especially in the initial 10 days, and they continued to increase during 20 days of operation and after 20 days, they increased slightly, as it can be figured out from the Figure 4.10. The cumulative sCOD values in terms of mass also show that the amount of sCOD in the leachate of Reactor 2 was about 10 g greater than that of Reactor 1 at the end of 80 days (Figure 4.10.a), which might have occurred due to the higher amount of water addition to the Reactor 2 and consequently, higher amount of particulate COD conversion to sCOD took place in the Reactor 2. Water addition helps the solubilization of particulate organic solids.

The Figure 4.10.a and Figure 4.10.b are also important to understand the sCOD and tCOD ratios of effluents in both LBRs. According to that, it can be concluded that 80-85% of the tCOD in the leachate were originated from the sCOD, most of the organics in the leachate was in soluble state, and the remaining COD except sCOD was due to the particulate organic solids that were escaped from the LBRs. This conclusion also shows that the most of the particulate solid organics in the LBRs did not wash-out or remained in the LBRs, but they were almost completely solubilised.

Eastmann and Ferguson (1981) stated that the acidogenic process is mainly regulated by the hydrolytic step and the kinetics of the acidogenesis process could be determined firstly by the hydrolysis rate, not by the bacterial growth kinetics. Therefore, the efficiency of hydrolysis process is very important for the next stage, which is acidification. The only parameter that might be used to obtain information on the development of the solubilisation of the particulate organic matter fed to the fermenter is possibly the sCOD/initial COD ratio (Traverso et al., 2000). By observing sCOD mass values in the leachate samples collected from the LBRs; the efficiency of the LBRs, in other words, solubilization efficiency, can be calculated in terms of sCOD/initial COD ratio. This parameter is very important for the efficiency of LBRs, in other words, for the hydrolysis process. Therefore, the ratios of the

amount of daily and cumulative sCOD mass values in the leachate to the initial COD mass value of OFMSW were calculated and they are exhibited in the Figure 4.11 and 4.12, respectively.

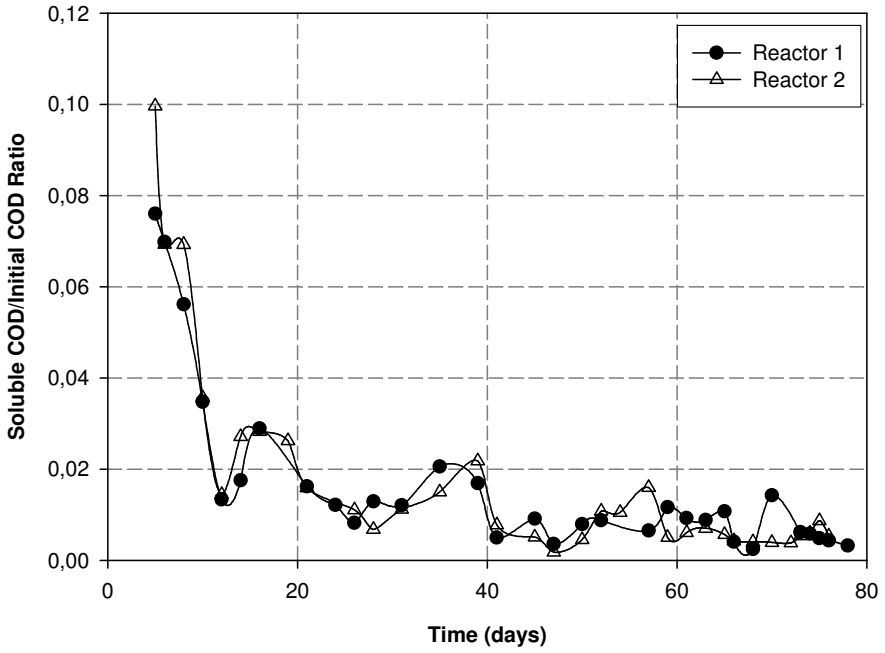

Figure 4.11. Daily sCOD/initial COD ratio in the LBRs in time

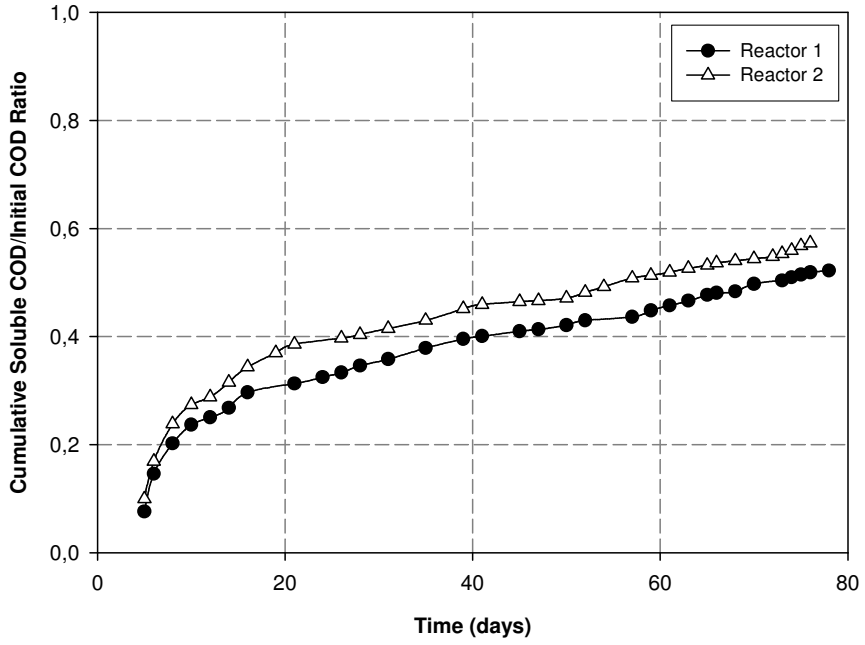

Figure 4.12. Cumulative sCOD/initial COD ratio in the LBRs in time

As it can be seen from the Figure 4.11, the hydrolysis process was realised effectively in both LBRs in the initial 20 days. When the cumulative values are evaluated, 30% and 40% of the initial COD mass were hydrolysed in the Reactor 1 and in the Reactor 2, respectively, in the initial 20 days. Hydrolysis process increased slightly to 50% and 60% during the operation of LBRs (Figure 4.12). The Figure 4.11 and Figure 4.12 prove that the hydrolysis efficiency in the Reactor 2 was higher and the previous results are confirmed. The high hydrolysis efficiency in the Reactor 2 might be related to the higher leaching efficiency (higher amount of water passing through the bed) due to the larger opening area of the screen in the Reactor 2 and/or the higher amount of water added daily to the Reactor 2, especially after 40 days, and consequently, to the high dilution rate.

In addition, it can be observed from the Figure 4.12 that about 40% of the initial COD mass of the OFMSW was effectively converted to sCOD in the first 30 days in both LBRs. In a similar study of Lai et al. (2001), the value of sCOD/initial COD ratio was found as 30-36% in the LBRs fed with unsorted coarsely shredded MSW. Therefore, it can be concluded that the hydrolysis process was efficient in the initial 30 days and the particulate organic matter was successfully solubilised in both LBRs.

Hydrolysis yield (%), which is equaled to the difference between the input particulate COD and the remaining particulate COD in the digester, over the input particulate COD (%100) (Raynal et al., 1998). In this experiment, the hydrolysis yields are calculated from the ratio of cumulative sCOD mass removal and the initial COD mass of feedstock. In the Table 4.1, the hydrolysis efficiencies of LBRs in the Set-1 are exhibited.

Table 4.1. Hydrolysis yield values for the LBRs in Set-1

	Reactor 1	**Reactor 2**
Hydrolysis yield (%)	52% (in 80 days)	57% (in 80 days)

As it can be seen from the Table 4.1, the hydrolysis efficiencies in the Reactor 2 were higher than those in the Reactor 1, due to the high amount of water addition to the Reactor 2 and lower HRT in the Reactor 2.

In conclusion, it was observed that lower HRT and higher amount of water addition resulted in better performance in the Reactor 2 in terms of higher hydrolysis yield due to the solubilisation of organics with higher amount of water addition.

4.2.4. The Volatile Fatty Acids (VFAs) Variations

Since that the efficiency of using high-rate methane digester such as UASB, anaerobic filter, anaerobic contact process, etc. are proven technologies in terms of high biogas production, special attention was given to the first phase of AD, which is acidification. Anaerobic acidogenesis is known as the first step in the AD of soluble organic materials to methane and CO_2. Many kinds of organic acids and alcohols are produced in the acidogenesis phase.

Although the proper operational conditions for the acetogens/methanogens have been extensively studied in the literature, little information is available for the acidogenic phase, which results in the VFA production. It is known that product formation by a mixed acidogenic population is a very complex process and is greatly influenced by many factors: reactor configuration, HRT, influent organic concentration, OLR, pH, temperature, oxidation-reduction potential and nutritional requirements.

VFAs can be used in denitrification, dephosphatation or methanisation. They are essential as energy and carbon sources for the microorganisms involved in the biological removal of nitrogen in wastewater treatment. Moreover, VFAs produced as a result of degradation of organic wastes can be used in the production of biodegradable plastics such as polylactate polymers, an environmentally friendly alternative to non-biodegradable plastics derived petrochemicals.

The concentration of VFA is an important parameter because of the degree of stability in the anaerobic acidogenesis. The organic matter degradation in the initial phase of the fermentation caused high VFA concentrations. In other words, as COD values decreased, VFA concentration values increased subsequently. Throughout this experimental study of LBRs, a significant population of VFA and COD degrading microorganisms, namely acetogens, were able to consume VFA rapidly without any VFA accumulation.

As a result of the acidification process in the LBR, organic acids (VFAs) and alcohols, which are very valuable products for chemical industries, food industries and petrochemical industries in the production of basic organic chemical products such as aromatic petrochemicals, organic industrial gases, synthetic organic dyes and pigments, organic insecticidal, herbicidal, fungicidal, and pesticidal preparations, natural food colorings, were produced. They are also used as raw material in polyester fibers and PET bottles, vinyl acetate, pharmaceuticals, synthetic fibers, paints, and cosmetics and dyes. Their applications include automobile paint, photogravure ink, urethane, electrical insulation varnish and food packaging. The end products of the acidogenic reactors are not only easily biodegradable matters for the methanogenic reactor, but they can also be used as intermediate products such as acetic acid, butyric acid, formic acid, ammonia and hydrogen gas in the fuel and food industry. Therefore, it is required that much attention should be given to the acid-phase digestion.

Most common VFAs that can be produced from many wastewaters are acetic acid (HAc), butyric acid (Buty) and propionic acid (HPr). HAc is an important industrial chemical, which is widely used. It is often used as raw material to prepare other valuable products. The largest use of HAc is in the production of vinyl acetate monomer, which is applied in paints and adhesives. In the form of vinegar, HAc solutions are used directly as a condiment, and also in the pickling of vegetables and other foodstuffs. In addition, the major esters of HAc are commonly used solvents for inks, paints and coatings. HAc production is mainly based on natural gas, which is a non-renewable resource and due to the high rate of consumption, natural gas can hardly support the HAc industry.

Buty is used in the preparation of various butyrate esters. Low molecular weight esters of butyric acid, such as methyl butyrate, are generally used in the food and perfume industry due to its pleasant aroma and taste.

HPr is mainly used in animal feeds and food for human consumption, since it inhibits the growth of mold and some bacteria. It can also be used as chemical intermediate in pesticide production and in pharmaceuticals. The esters of HPr can also be used as

solvents or artifical flavorings (Wikipedia, 2006).

In order to determine the feasibility of the acidification process as a first step of a two-phase anaerobic system, the main topics considered were the solubilisation of suspended solids and generation of acids (Guerrero et al., 1999). Therefore, VFAs production was observed in the LBRs in addition to TS and VS concentrations. In addition, the composition of organic acids in the medium influences the quality of the products of fermentation. Thus, it is important to control the product spectrum during anaerobic acidogenesis.

The variations of individual VFAs in the leachate (acetic acid, propionic, iso-butyric, butyric, iso-valeric, valeric, isocaproic, caproic and heptanoic acids) and ethanol concentrations were measured and the concentration variations of individual VFAs and ethanol are exhibited in the Figure 4.13 and 4.14.

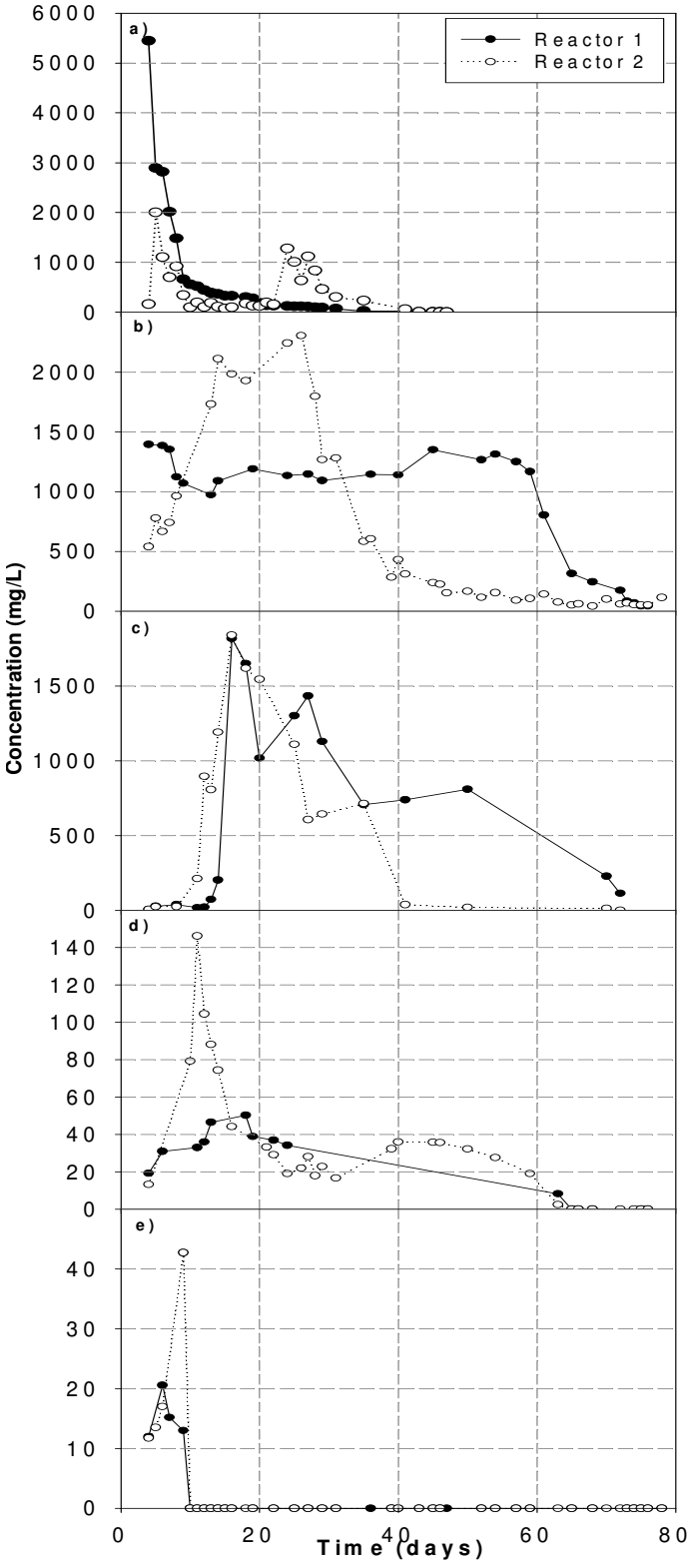

Figure 4.13. Daily concentration variations of **a)** Ethanol, **b)** Acetic acid, **c)** Butyric acid, **d)** Propionic acid and **e)** Isobutyric acid in the leachate

The main trends observed in individual VFA productions are related to the energetics of the transport processes and the free diffusion terms of the undissociated acids. The reactor pH has been identified as an important variable in glucose fermentations. The pH will have a strong impact on transport energetics of undissociated organic acids that will dissipate the proton motive force and freely diffuse into the cell at low pH values. At high pH values, acetate is predicted as the main product. The acetate production decreases at lower pH values, since the concentration of the undissociated form of the acid increases, resulting in more energy requirements for outwards transport of acetic acid. Butyrate replaces acetate as main product at decreasing pH-values since the production of one butyrate incorporates one acetate and consequently, less acid molecules need to be transported per glucose converted. At lower pH values (<5.6), the butyrate decreases as well, and ethanol becomes the dominant product. At these low pH values, any acid transport to the outside of the cell becomes energetically very expensive (Rodriguez et al., 2005).

In a perturbation study using a glucose-fed methanogenic CSTR, build-up of hydrogen dramatically changed the distribution of glucose metabolic intermediates, and the fermentation of glucose quickly shifted from a butyrate-type fermentation to the propionate-type one (Yu et al., 2004). Glucose fermentation can result in a number of alternative fermentation products apart from organic acids, the most of which (in anaerobic digesters) are lactate and ethanol. However, lactate is subsequently degraded very quickly and is therefore seen primarily during transient overload conditions in the acidification reactors. Ethanol is produced as an alternative to acetate at low pH (pH<5.0) (Batstone et al., 2002).

As it can be seen from the Figure 4.13.a, in addition to the production of VFAs, it was observed that high amount of ethanol were produced in both LBRs. The concentration of ethanol in both LBRs was high in the initial days; however it decreased as the VFA concentrations tend to increase in the LBRs. In the initial 4-5 days of operation, when the first GC analysis performed, it was observed that the ethanol concentrations in the Reactor 1 and in the Reactor 2 were 5500 mg/L and 2000 mg/L, respectively. After that, the ethanol concentration started to decrease rapidly and there was a great amount of decrease observed at the end of 10^{th} day in

both LBRs. The concentration of ethanol in the Reactor 1 continued to decrease throughout the operation, whereas the ethanol concentration in the Reactor 2 behaved differently. It increased after the 20th day and it reached to about 1500 mg/L at the 25th day. Then, it decreased rapidly at the end of 30th day. This increase and decrease in the ethanol production can be related to the decrease and increase in the acetic acid production, respectively. As it can be observed in the Figure 4.13.a and 4.13.b, as the concentration of ethanol in the Reactor 1 peaked at the 5th day, the production of acetic acid was lower with respect to ethanol. During the operation time, the acetic acid concentration stayed almost constant until the 60th day, whereas the ethanol concentration decreased. Similarly, the acetic acid concentration was low in the Reactor 2 at the 5th day, when the ethanol concentration was high. However, as the amount of ethanol decreased in time, it was observed that the acetic acid production increased. The second peak concentration of ethanol achieved at the 25th day in the Reactor 2 can be related to the the decrease in the butyric acid concentration rather than the acetic acid. The inverse proportion between the ethanol and acetic/butric acid concentrations can be explained with the pH values. The differences in by-products of acidification and their concentrations are related to the environmental conditions (pH, temperature, pressure of H_2, etc.) as well as the type of acidogenic culture (Rodriguez et al., 2005). Especially, the pH is a very important parameter in defining of the pathways in the acidogenesis fermentation. The optimum pH values for the fermentation of specific VFAs and alcohols can be different. For example, butyric acid-type fermentation occurred optimally at pH>6, propionic acid-type fermentation occurred mainly at pH about 5.5 and ethanol-type fermentation occurred generally at pH<4.5 (Maharaj and Elefsiniotis, 2001). The acetate is produced mainly at normal pH values and at low hydrogen pressure; the butyric acid is produced mainly at low pH values and at high hydrogen pressure values (Rodriguez et al., 2005). Although the specific acid productions proceed at various environmental conditions, it is known that they reached to the maximum levels when it is approached to the optimum conditions. Ethanol was one of the key acidogenic products, representing 10–12% of the effluent products at pH 4.0–5.5, and 4–5% at pH 6.0–6.5 (Yu and Fang, 2002). This concurred with a previous finding that pH 5.0 or less favored the production of ethanol.

The operational pH for the inhibition of the methanogenic activity affects the main fermentation pathway. In this study, the main products were ethanol, acetic acid and butyric acid, in the pH ranges 3.0-3.5, 3.5 and 3.5-4.0 respectively (Figure 4.8.a and Figure 4.13.a, b, c). It was understood that these pH values are optimum only for ethanol, not for the acetic and butyric acids. However, despite the optimum pH values attained for ethanol production in the study, the ethanol was produced only in the initial 5 days and it decreased rapidly during the initial 10 days. The acetic and butyric acids were produced mainly after 10^{th} day. This trend can also be explained with the increased pH values observed. These results indicate that the pH plays an important role in determining the type of anaerobic fermentation pathway in the acidification processes.

The specific VFAs production depends on the required energy during the transport and the free diffusion of acids. For example, the main product is acetate at high pH values, as the pH decreases, the acetate decreases and the acetic acid production increases and consequently, high amount of energy is required with the transport of the acetic acid outside the cell wall (Rodriguez et al., 2005). In the environment, as the low molecular weight VFAs increased rapidly, the pH gradient inside and outside the cell is unbalanced and this situation results to the inhibition of cell. The microorganisms convert the fermentation pathways from VFAs production to alcohol production in order to get away from the inhibition. In other words, this change operates in the way of detoxification mechanism. The intermediary products in biowaste digestion are mainly VFA and the production of alcohols is negligible (Ten Brummeler et al., 1991).

As it was mentioned before, when the LBRs were started to operate, the tap water was added to the LBRs in the initial 2 days; however, no leachate was collected from the LBRs. During this time, the production of VFAs might increase with the rapid hydrolysis and acidification proceeded. Furthermore, the effluent pH values were recorded as 3 at the end of 5^{th} day in both LBRs (Figure 4.8.a). The high VFA concentrations and ethanol concentrations could result from the detoxification mechanism of microorganisms and the fermentation mechanisms could be converted to the ethanol. Besides, this situation can also be explained as the inhibition of acid

producer bacteria and the dominance of ethanol producer bacteria. The metabolic change towards ethanol can also be explained with the high ethanol concentrations (2000-5500 mg/L) observed in the initial 5 days, when the first analyses were performed (Figure 4.13.a). The microorganisms could be converted to their previous fermentation pathways with the VFA production in the initial days and washing of ethanol in the LBRs as a result of the collection of leachate/water addition after the 2nd day of operation or the acid producer bacteria could become active again. These results can also explain the situation that almost no ethanol production in the Reactor 1 during the acetic acid production.

By comparing the operational stability and pH values between ethanol-type, propionic acid-type and butyric acid-type fermentation, the main fermentation type was found to be ethanol type fermentation in this experimental set-up. As a result of the fact that the low pH (smaller than 4.5) was observed in the Reactor 1 during the experiment, it can be concluded that ethanol-type fermentation occurred mainly and the ethanol concentration was expected to be high in the Reactor 1. Ethanol was the main solvent produced, with a concentration of 6000 mg/L, accounting for 64-69% of the total concentrations of VFAs. The liquid products were also strongly dependent on the fermentation pH. The main VFAs were HAc and Buty at pH 3.5-4.0 in this experiment. Low pH favored HAc production and high pH favored Buty production (Wu and Lin, 2004). In this study, low pH values observed during the operation cause higher HAc and Buty production.

According to Figure 4.13.b, the acetic acid was the major organic acid that was produced as a result of acidification in the LBRs, and the peak acetic acid concentrations in the Reactor 1 and in the Reactor 2 were 1500 and 2300 mg/L, respectively, between 10 and 25 days. The difference between the LBRs was that the acetic acid production in the Reactor 2 peaked in the initial 25 days and then it started to decrease and continued to decrease until the end of 40th day. On the contrary, there was almost a constant concentration of acetic acid production in the Reactor 1; however, it started to decrease at the end of 60th day. This difference can be related to the high amount of decrease/removal of the fermented organic solids at the end of 40th day in the Reactor 2, in which higher hydrolysis efficiency was

observed. Furthermore, much water added to the Reactor 2 after 40th day caused an increase in the dilution rate and decreased the hydrolysis and acidification rate in the Reactor 2 after 40th day.

The second major acid was butyric acid, which attained the peak concentration of 1800 mg/L between 15 and 20 days in both LBRs (Figure 4.13.c). Although it was not produced as much as compared to the acetic acid and butyric acid, the other acid that was mainly produced was the propionic acid, which reached to peak concentrations of 45 and 150 mg/L in the Reactor 1 and in the Reactor 2, respectively. The concentration of propionic acid reached to the peak concentrations in the first 20 days (Figure 4.13.d). The concentrations of acetic acid, propionic acid and isobutyric acid in the Reactor 2 were greater than those in the Reactor 1. This might have resulted from the higher pH values due to the high amount of water addition to the Reactor 2 and the higher hydrolysis efficiency in the Reactor 2 and consequently, the acidogenesis step proceeded much faster in the Reactor 2 with respect to the Reactor 1. The concentrations of other organic acids that were observed in the analysis of leachate (isovaleric, valeric, caproic, isocaproic and heptanoic) were smaller as exhibited in the Figure 4.14, when compared to acetic acid, butyric acid, propionic acid and isobutyric acid in the Figure 4.13.

For all HRT, the acetic acid was present in the reactors as well as butyric and propionic acids in smaller concentrations for complex substrates (Guerrero et al., 1999). These VFAs observed in the study of Guerrero et al. (1999), known as short-chain VFAs, were also found as major acids in this study as the major products of the acid-phase of AD.

The propionate production increased with the decrease of pH, as reported by many researchers, from 12% at pH 6.5 to 38% at pH 4.0. In the acidogenesis of primary sludge, the propionate increased steadily with the decrease of pH from 7.0 to 5.0 (Eastman and Ferguson, 1981). On the other hand, in the acidogenesis of glucose over the pH range of 4.5 to 8.0, the propionate production increased at lower pH. Another study showed that the propionate production increased substantially with decreasing pH from 6.0 to 4.5, despite the optimum pH for the growth of propionate-

producing bacteria being above pH 6.0 (Rodriguez et al., 2005). In contrast, the fractions of acetate and butyrate in the effluent products both decreased with pH, from 34% both at pH 6.5, to 18% and 6%, respectively, at pH 4.0. These results clearly show that pH has a significant effect of the distribution of effluent products (Yu and Fang, 2002). This trend was also valid in this study. As it is seen from the Figure 4.13.d, the concentrations of propionic acid in LBRs reached the maximum values in the initial days, when the pH values were low. However, at the same time, the acetic acid and butyric acid concentrations were low. As the propionic acid decreased in the LBRs with the increase in pH values, the acetic acid and butyric acid concentrations in the LBRs increased.

At lower pH values (<5.5), ethanol is predicted as the main fermentation product (Rodriguez et al., 2005). In this study, ethanol was observed as the main alcohol produced due to low pH values. However, acetate and butyrate were the major VFAs produced during the experiment due to low pH values.

There are three main acidogenic fermentation pathways through butyrate, propionate and ethanol. Butyrate fermentation is characterized by the production of butyrate and acetate, plus carbondioxide and hydrogen. Propionate fermentation, on the other hand, produces propionate, acetate and some valerate, with no significant gas production. Ethanol fermentation occurs only at low pH of 4.5, producing ethanol, acetate, hydrogen and carbondioxide (Cohen et al., 1984; Ren et al., 1995). Therefore, in this study, the main acidogenic pathways can be seen as ethanol and butyrate fermentation, however, since the propionic acid was also observed, the three types of fermentation co-existed in the LBRs, probably due to the complex nature of the OFMSW. Due to the pH conditions observed during the operation period, ethanol fermentation might be simulated mostly, resulting in ethanol, acetic acid, hydrogen and/or carbondioxide production in the LBRs.

Individual acids potential of OFMSW was calculated taking into account of the organic acid values achieved in the LBRs. For this reason, the following calculations were carried out.

Unit prices of acetic acid, butyric acid and propionic acid were calculated, by using Turkey's 2004 export statistics (TURKSTAT, 2006), as 425.9, 2407.1 and 3613.5 US dollars per m^3 of each product, respectively. Unit price of EtOH was taken as 132,12 US dollars per m^3 (Renewable Fuels Association, 2005).

It was achieved that 5989 mg EtOH in Reactor 1 and 5190 mg EtOH in Reactor 2, 8006 mg HAc in Reactor 1 and 11848 mg HAc in Reactor 2, 6181 mg Buty in Reactor 1 and 5203 mg Buty in Reactor 2, 195 mg HPr in Reactor 1 and 479 mg HPr in Reactor 2 were produced per 2.25 kg of OFMSW. As a consequence, when the gain from 1 kg of OFMSW was calculated according to the highest production in the LBRs, the following results were obtained:

- EtOH: 4.5×10^{-4} \$ / kg of OFMSW
- HAc: 2.1 x x 10^{-3} \$ / kg of OFMSW
- Buty: 6.9 x x 10^{-3} \$ / kg of OFMSW
- HPr: 7.7×10^{-4} \$ / kg of OFMSW

The results indicated that the most profitable product from the hydrolysis and acidification of OFMSW is Buty.

In addition to the major acids observed in the LBRs, the production of trace amounts (below 40 mg/L) of heptanoic, isovaleric, valeric, caproic, isocaproic acid production were realized in both LBRs, however, at the end of 10 days, the production of these acids was completely over (Figure 4.14).

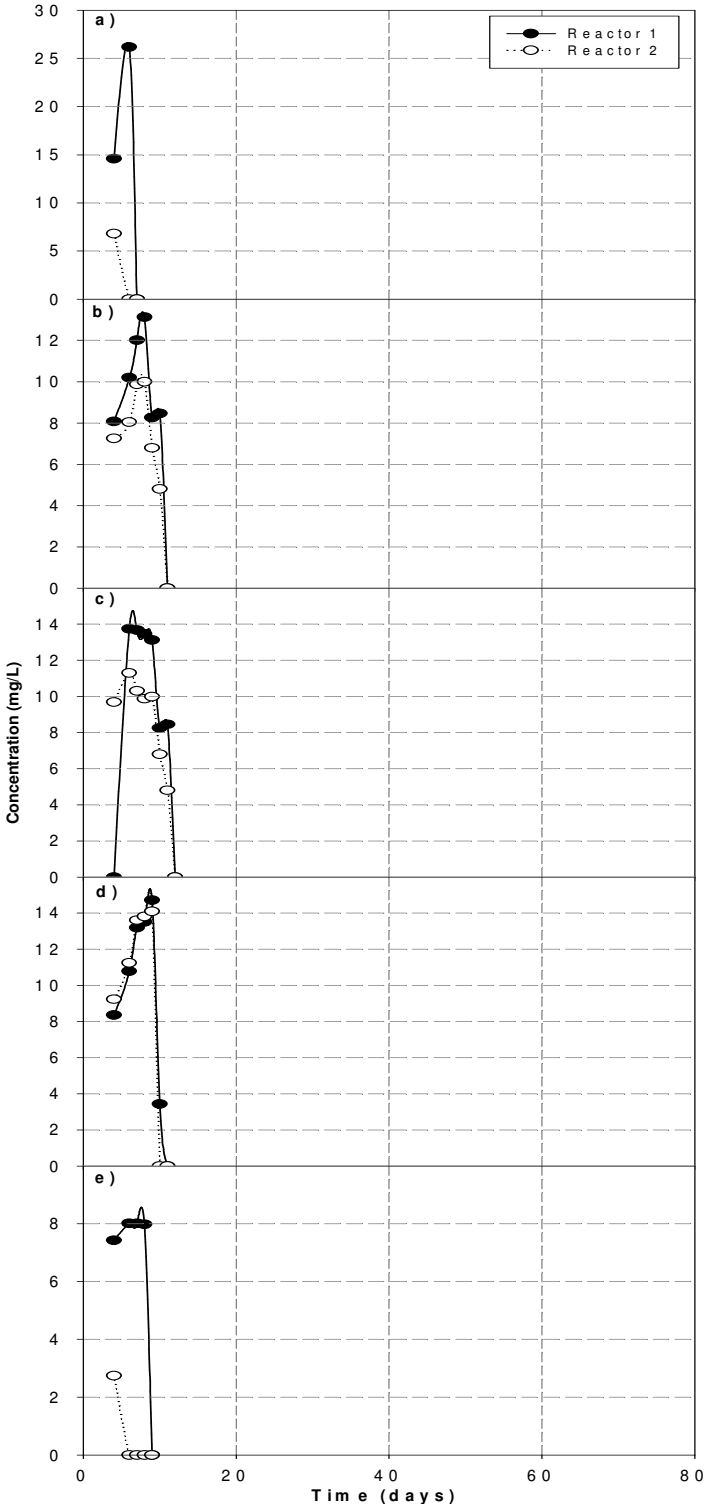

Figure 4.14. Daily concentration variations of **a)** Heptanoic acid, **b)** Isovaleric acid, **c)** Valeric acid, **d)** Caproic acid and **e)** Isocaproic acid in the leachate

According to the graphs of other organic acids in the Figure 4.14; heptanoic, caproic, valeric, isovaleric and isocaproic acids were observed in the initial 10 days at low concentrations in both LBRs. They started to decrease rapidly and they disappeared in the following days. The concentrations of heptanoic, isovaleric, caproic and valeric acids range between 0 and 25 mg/L. This amount is low with respect to the concentration of other organic acids produced. The least amount of organic acid observed in this experiment was isocaproic acid, which reached only about 3 mg/L in the Reactor 2 and 8 mg/L in the Reactor 1. The concentrations of these trace amount of acids were lower in the Reactor 2 than those in the Reactor 1, whereas the concentrations of the major organic acids in the Reactor 2 were higher than those in the Reactor 1.

The variations in the production of specific acids in terms concentration throughout operation time is exhibited in the Figure 4.13 and Figure 4.14. According to these figures, there was an increase in all types VFAs in the initial 25 days, and a decrease starting from 25^{th} day.

The acetic, propionic, butyric and isobutyric acids are known to produce as a result of fermentation of carbonhydrate, protein and lipids. The VFAs of high molecular weight such as isovaleric, valeric and caproic acids are generally produced as a result of protein fermentation (Yu and Fang, 2002). Yu and Fang studied the fermentation of cheese whey and they found that H_2, acetic, propionic and butyric acid production is the result of the carbonhydrate fermentation; ethanol, propanol, buthanol, isobutyric acid and VFAs of high molecular weight are produced due to the protein fermentation.

In this study, the OFMSW, which was composed of fruit, vegetable and kitchen waste in proportion of 3:2:1, respectively, was rich in terms of carbonhydrate and also protein. According to the literature, it can be concluded that the VFAs of high molecular weight were produced due to the protein fermentation in the initial 10 days, since their production was finished at the end of the initial 10 days; whereas the propionic and mainly the acetic and butyric acids were produced as a result of fermentation of protein and mainly carbonhydrate, found in the composition of

OFMSW. That the acetic and butyric acids and the trace amount of isobutyric, isovaleric and valeric acids were mainly produced during the acidification of the mixture of domestic and high amount of glucose containing industrial wastewaters proves that the main types of fermentation in this study are protein and carbonhydrate fermentation (Maharaj and Elefsiniotis, 2001).

In the study of Yu and Fang (2001), the acidification products were VFAs (mainly acetate, propionate and butyrate), alcohols (mainly ethanol, propanol and butanol) and hydrogen. The production of hydrogen and the three main VFAs, namely acetate, propionate and butyrate, corresponded to carbonhydrate acidification. The three alcohols, plus i-butyrate and higher molecular-weight VFAs, corresponded to protein acidification (Yu and Fang, 2001). In the study of Yu and Fang (2001), the batch and continuous experiments were conducted to treat dairy wastewaters. The VFAs were mostly acetate, propionate, and butyrate, plus smaller quantities of lactate, formate, i-butyrate, valerate, i-valerate and caproate; whereas the alcohols were mostly ethanol, propanol and butanol, plus trace amount of methanol. Ethanol was the main alcohol produced, reaching 67 mg/L on the 6^{th} day. Methanol and propanol were produced at much lower concentrations in the study of Yu and Fang (2001).

For municipal and combined municipal-starch rich industrial wastewaters, acetic acid was the dominant VFA produced followed by propionic acid. The higher concentration values of n-butyric acid were observed in combined municipal-industrial reactor because of the increased carbonhydrate concentration coming from starch industry wastewater. Small amounts of i-butyric, i-valeric and n-valeric acids were also observed (Maharaj and Elefsiniotis, 2001). In this LBR study, high concentrations of butyric acid were observed, which may result from the carbonhydrate concentration coming from OFMSW.

Parawia et al. (2004) found that acetic acid and propionic acid were the most abundant VFAs of potato waste acidogenesis, followed by butyric acid, iso-butyric acid, valeric acid, iso-valeric acid and caproic acids. They observed that acetic acid, propionic acid, butyric acid and iso-butyric acids formed directly from the fermentation of carbonhydrates and proteins, as well as during the anaerobic

oxidation of lipids. Furthermore, they observed that the high production of butyric acid was mainly attributed to the large amount of carbonhydrates present in the substrate. In this LBR study, since these acids indicated above were produced, it can be speculated that carbonhydrates and proteins fermentation were mainly realized in the LBRs and the high production of butyric acid can be mainly attributed to the large amount of carbonhydrates present in the composition of OFMSW.

Acetate, propionate, butyrate and i-butyrate could be formed directly from the fermentation of carbonhydrates, proteins and lipids. The higher molecular-weight VFA, including valerate, i-valerate and caproate are largely associated with the fermentation of proteins; acidogenesis of non-proteinaceous substrates produced little of these three VFAs (Yu and Fang, 2002). The i-Butyrate and i-valerate are produced from the fermentation of branched aminoacids and are usual intermediates undetectable or present in very low levels in a steady-state methanogenic reactor degrading carbonhydrates (Yu et al., 2004). Since, isobutryric acid and isovaleric acid productions were produced in less amounts, it can be thought that fermentation of branced aminoacids were not dominant in the LBRs of this study.

In this study, the main products are also acetate, butyrate, propionate and i-butyrate (isobutyrate), which indicate the fermentation of carbonhydrates, proteins and lipids. However, acetic and butyric acids were the dominant species. The other acid components of tVFA as i-butyric, i-valeric, valeric, caproic and heptanoic were present in trace amounts. The fact that the higher molecular-weight VFAs such as heptanoic acid, isovaleric acid, valeric acid, caproic acid and isocaproic acid were found in less amounts, may result from the acidogenesis of less-proteinaceous OFMSW. The OFMSW used was composed of fruit waste, vegetable waste and kitchen waste in the ratio of 3:2:1, respectively. The variations in the VFA types produced in the LBRs were resulted from the high amount of carbonhydrate fermentation (results in acetate, butyrate and propionate) and less amount of protein fermentation (results in iso-butyrate and higher molecular weight-VFAs).

In conclusion, ethanol and individual VFAs production in the LBRs show that the acidification process took place throughout the experiment, especially between 5th

and 25th days.

The acidogenic fermentation of OFMSW and the potential of VFA production in the LBRs were examined and the variation of daily total VFA (tVFA) concentrations of leachate that was produced during 80 days is exhibited in terms of acetic acid (HAc) in the Figure 4.15. The variation in the net tVFA production is expressed as acetic acid for comparison purposes. However, ethanol is not considered in the calculation of tVFA.

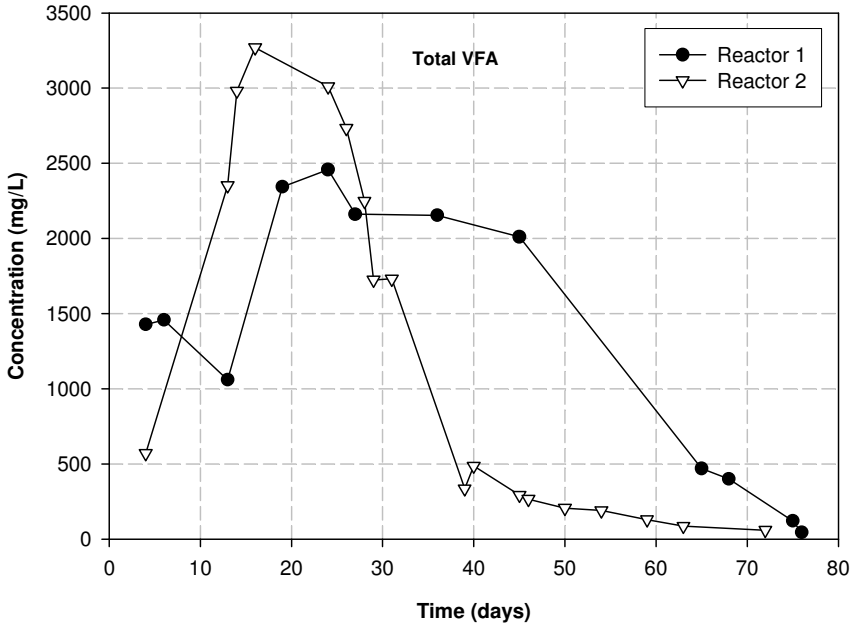

Figure 4.15. Daily concentration variations of tVFA (mg/L, in terms of HAc) in leachate throughout operation

The amount of added water/collected leachate, the COD analyses and the related calculations show that there was an efficient hydrolysis taking place in the Reactor 2 compared to the Reactor 1 (the hydrolysis efficiency in the Reactor 2 was high) and the hydrolysis reaction proceeded mainly in the initial 5 days. Consequently, the efficiency of the acidification process was expected to be higher in the Reactor 2. The daily tVFA concentrations show that the tVFA concentration in the Reactor 2 reached to its maximum value of 3250 mg/L in the initial 16 days (Figure 4.15). At the end of 16 days, the concentration of tVFA in the Reactor 2 started to decrease and it decreased to below 500 mg/L at the end of 40 days. The tVFA concentration in

the Reactor 1 increased much less than that of Reactor 2 and it reached to its maximum level in the 24th day, and after that it decreased much slowly and decreased to below 500 mg/L at the end of 65th day. The increases and decreases in the acids production are also supported by the amount of water addition, the effluent pH values and the hydrolysis efficiency in the LBRs (Figure 4.4, Figure 4.8.a and Figure 4.12).

As it can be seen from the Figure 4.15, the hydrolysis process in the leaching bed type of reactors accelerated the acidification process and consequently, the production of VFAs reached at maximum concentration of 2457 mg HAc/L in the Reactor 1 on the 24th day and 3269 mg HAc/L in the Reactor 2 on the 16th day. The concentration of tVFA in the Reactor 2 was slightly higher than that in the Reactor 1. This might have resulted from the higher pH values of the Reactor 2 with respect to those of Reactor 1 and also the higher hydrolysis efficiency observed in the Reactor 2 due to the high amount of water addition.

The concentration of tVFA values changed between 0.25 and 2.5 g/L in both LBRs during the 30-day operation period in both LBRs. These results suggest that a 30-day period was required to achieve an acceptable performance, measured by the amount of tVFA production in the leachate.

The addition of readily biodegradable compounds contained in the waste improved the reactor performance with respect to VFA production (Banerjee et al, 1999). In this LBR study, since the average net tVFA production in the LBRs reached to the maximum value in 25 days, the addition of readily biodegradable compounds in the OFMSW caused high hydrolysis efficiency, high acidogenesis efficiency and high tVFA production. According to the Figure 4.15, it can also be concluded that the optimum retention time should be 25 days for the maximum tVFA concentration in both LBRs, since the maximum tVFAs concentrations in terms of HAc were observed in the initial 25 days and the concentrations started to decrease after 25 days.

Since there might be dilution due to the water addition to the LBRs, the amount of tVFA production was calculated in terms of mass to eliminate the effect of dilution and the variations in the amount of daily and cumulative tVFA (mg, in terms of HAc) versus time is exhibited in the Figure 4.16 and 4.17, respectively.

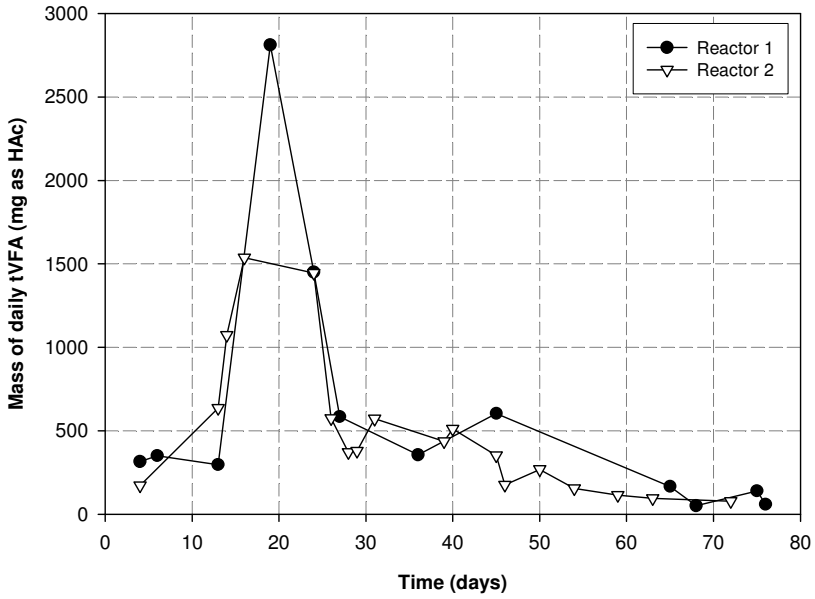

Figure 4.16. Daily mass variations of tVFA (mg, in terms of HAc) in leachate throughout operation

As it can be seen from the Figure 4.16, the hydrolysis process in the LBRs accelerated the acidification process and the amount of daily tVFA show that the acid production started in the initial 5 days in both LBRs. The tVFA production rate increased at the end of 10^{th} day and consequently, the production of daily VFAs in terms of mass, which reached the maximum value of 2812 mg HAc in the Reactor 1 at 19^{th} day and 1537 mg HAc in the Reactor 2 at 16^{th} day. After 20^{th} day, the acid production continued with a slower rate, and it reached to 500 mg between 30^{th} and 40^{th} days and it continued to decrease in both LBRs. However, it decreased much more rapidly in the Reactor 2 after 40^{th} day due to the higher amount of water addition into the Reactor 2 after 40^{th} day (Figure 4.16).

When the amount of cumulative tVFAs are examined (Figure 4.17), the acid production in both LBRs started slowly in the initial 5 days (approximately 100 mg), and it was observed that it increased rapidly after 10^{th} day and reached to 6000 mg at

the end of 30th day in both LBRs. After 30 days of operation, the production of tVFA continued slowly and it reached to 7000 and 9000 mg in the Reactor 1 and Reactor 2, respectively, at the end of experiment.

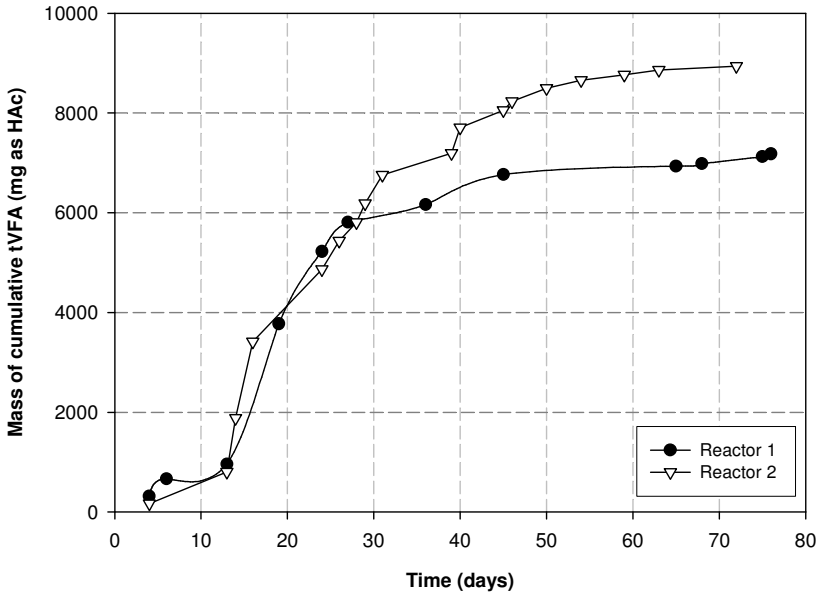

Figure 4.17. Cumulative mass variations of tVFA (mg, in terms of HAc) in leachate throughout operation

The Figure 4.16 and Figure 4.17 show that the acid production proceeded dominantly in both LBRs in the initial 25-30 days. When it is considered that the hydrolysis took place mainly in the initial 5 days, it can be concluded that it is sufficient to operate the LBRs, which were set for the fermentation of OFMSW, for about 25-30 days. The amount of tVFA production in the Reactor 1 and Reactor 2 decreased after 30th day. It reached to 7000 and 9000 mg in the Reactor 1 and Reactor 2, respectively, at the end of 80 days.

The cumulative mass of tVFA in the Reactor 2 was higher than that of Reactor 1. This might have resulted from the higher pH values observed in the Reactor 2 and the higher amount of water addition to the Reactor 2.

As it was stated before, although the composition and the amount of OFMSW in both LBRs were the same, the Reactor 2 exhibited 10% higher hydrolysis efficiency compared to the Reactor 1. For that reason, it was expected that the extent of

acidogenesis process, which was the following process of hydrolysis, therefore, was mainly related to the hydrolysis process, and the amount of tVFA production in the Reactor 2 was high. The graph of cumulative tVFA mass shows that the tVFA production in the initial 30 days was similar in both LBRs and the difference between the LBRs developed after 30^{th} day. It was found very important that the high hydroysis efficiency in the Reactor 2 during the operation produced the same amount of acid as in the Reactor 1 in the initial 30 days.

In the same manner, it can be thought that the the Reactor 2 would have a similar acidogenesis efficiency as in the Reactor 1, since the tVFA production were the same in both LBRs in the initial 30 days. However, when the acidogenesis process is investigated or the acidogenesis efficiency is calculated, not only the organic acid production but also the various alcohols (ethanol, methanol, buthanol, propanol, etc.), ketones (glycerol, acetone etc.), CO_2 and H_2 should also be analysed. In this study, since the potential of organic acid production is mainly focused, no such analysis was performed. Therefore, when theLBRs are compared, they should not be compared in terms of the acidogenesis efficiency, but in terms of acid production. As it was emphasized before, the acid production in the Reactor 2 in the initial 30 days was similar that in the Reactor 1. However, the Reactor 2 exhibited a higher performance in terms of tVFA production throughout the 80 days of operation time, which might have resulted from the higher hydrolysis efficiency in the Reactor 2.

Although the amount/composition of OFMSW was the same in the Reactor 1 and in the Reactor 2, these LBRs showed a totally different behaviour in terms of the hydrolysis efficiency, cumulative tVFA, acetic acid and ethanol concentrations and the trend/time of the specific VFAs production. The Reactor 2 exhibited a higher hydrolysis performance compared to the Reactor 1 and consequently, the specific acid production was completed in a shorter time. The most important difference between the two LBRs in terms of operation was that the dilution in the LBRs took place with the cumulative volume of 45 L water in the Reactor 2, whereas it was 25 mL water in the Reactor 1 due to the different sizes of opening area on the screen in the LBRs. The higher amount of water addition can increase the dilution rate and the hydrolysis process, and consequently, the conductivity of water through the LBRs

and the performance of the LBRs in terms of organic acids production. It was concluded that the leaching property of the LBRs and the dilution rate are very important issues for the optimum hydrolysis conditions of the LBRs. In addition, the increase in the dilution rate can be an important parameter affecting the amount of acidification products. Although the Reactor 1 and the Reactor 2 contained the same amount and composition of OFMSW, the ethanol production in the Reactor 1 was extremely high compared to the Reactor 2. However, the Reactor 2 showed a higher acetic acid concentration compared to the Reactor 1.

Two important operating parameters give an idea about the hydrolysis process. These parameters were: the pH of the leachate and the VFA concentration. It can be speculated that at higher pH values and under conditions of less variations in pH values, higher concentration of VFAs might be reached. This was the compass for the Set-2 in this study.

Due to the lower pH of OFMSW, these wastes were buffered by the addition of sodium hydroxide solutions (Mata-Alvarez et al., 1992a; Rodriguez-Iglesias et al., 1997). Potential exists to improve the performance of LBRs even further by changing the pH and by finding suitable mixes of dry biomass feedstocks. No chemical addition such as sodium hydroxide solutions was intended in this study; therefore the different proportions of cow manure was mixed with OFMSW and added into the LBRs in the Set-2 in order to increase the pH values to improve the acidification in the LBRs and to observe the effect of buffering capacity of manure on the VFA production. In the Set-2, the pH values were increased with the addition of cow manure due to the high buffering capacity of manure. Buffers reduce the variation in the pH values of an end-product. The pH variation is detrimental to consistent quality. Buffering capacity is the ability of the buffer to resist changes in pH. The closer the buffered pH is to the pKa, the greater the buffering capacity. The animal manure addition provides the increase of pH of the media, since it gives NH_4 to the media as it acidifies due to the high N content.

Acidogenesis was indicated by the low pH values, high net VFA production and negligible gas generation. Methanogenesis was successfully suppressed, mainly due

to low reactor pH (Banerjee et al., 1999). If the pH is allowed to fall below 6, methanogenic bacteria cannot survive (Davis and Cornwell, 1998). Since the pH values in the LBRs (Figure 4.8.a) were recorded as below 6, this indicates that methanogenesis was almost totally inhibited in the LBRs.

Acidification yield (%) was calculated from the tVFA and the tCOD of input (Raynal et al., 1998). In other words, the degree of acidification in the LBRs was calculated by taking the ratio of tVFA in terms of COD and the initial COD of the feedstock. Only tVFAs were included as the acidification products. However, the acidification yield should be calculated not only from the organic acid production, but also from the alcohols, ketones, CO_2 and H_2 production.

Table 4.2. Acidification yield values for LBRs in Set-1

	Reactor 1	**Reactor 2**
Acidification yield (%)	3.4% (in 80 days)	4.4% (in 80 days)

The low acidification degrees achieved in this study might be due to the consideration of only tVFA production. However, higher acidification degrees could have been achieved in this study, if gaseous products were included to the calculations.

4.3. Results of Experiments of Set-2

As it was stated in the previous sections; four identical LBRs were operated, comprising of OFMSW and manure in different ratios in the Set-2 in order to increase pH values by buffer supplementation as cow manure. The Reactor 1 consists of totally OFMSW; the Reactor 2, consisting 75% of OFMSW and 25% of manure; the Reactor 3, having 25% of OFMSW and 75% of manure and the Reactor 4 contains manure totally.

4.3.1. Water Addition and Leachate Collection

During the operation of LBRs, the volume of water added to the LBRs was determined according to the volume of leachate collected from the LBRs, as

it was stated in the previous sections. In other words, the daily volume of water addition to the LBRs during 40 days of operation time was set equal to the daily volume of leachate collection from the LBRs on the previous day. Therefore, the graph of daily volume of tap water addition to the LBRs throughout the operation of LBRs is not exhibited here.

The daily volume of leachate collection from the LBRs was recorded and the graph of daily volume of leachate collection and the cumulative leachate collected from the LBRs during the operation of LBRs are shown in the Figure 4.18.a and Figure 4.18.b, respectively.

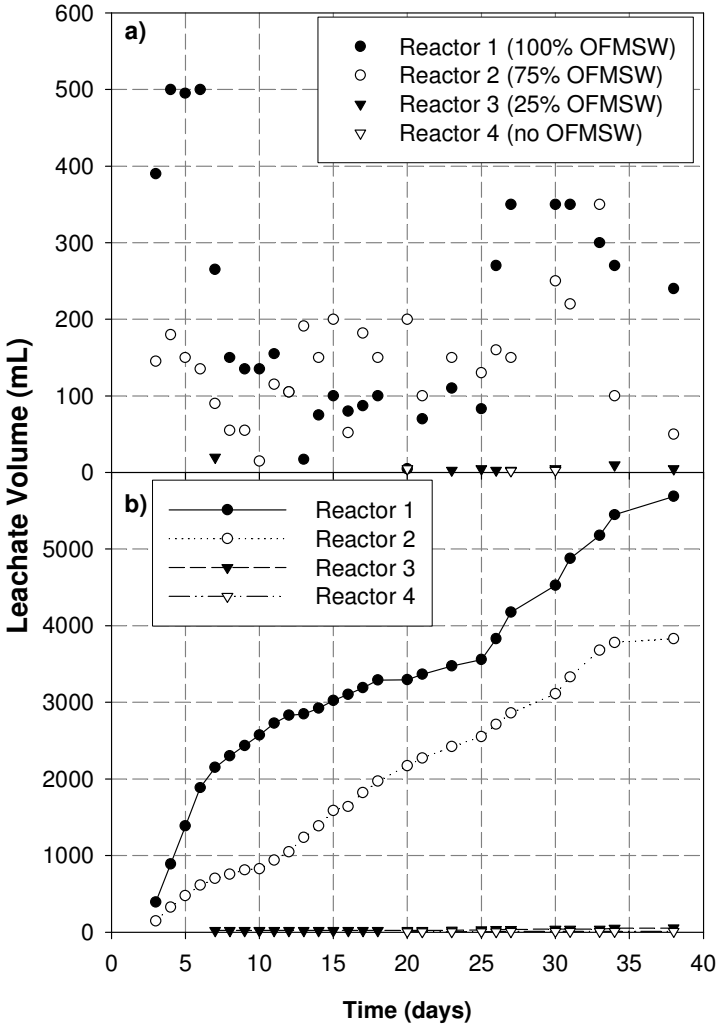

Figure 4.18. Volume of **a)** Daily leachate collection from LBRs and **b)** Cumulative leachate collection from LBRs

As it can be seen from the Figure 4.18.a, the daily leachate collected from the Reactor 1 was higher than all other LBRs. During the 40 days of operational period, leachate was collected from all LBRs; however, no significant leaching took place in the Reactor 3 and 4, possibly due to the clogging problems in the LBRs. Since, the Reactor 3 contains 75% of manure and the Reactor 4 was fed only with manure, clogging of the screen due to the large particle size of manure is the most possible reason for reduced leaching. The minimum amount of leachate was collected from the Reactor 4, which was fed only with cow manure. The large particle size of manure resulted in the clogging of the screen in the LBRs and as a result, the leaching in the Reactor 3, which was fed 75% of cow manure, and the leaching in the Reactor 4 were hindered.

According to the Figure 4.18.b, the cumulative leachate collected from the Reactor 1 and Reactor 2 throughout the operation time increased, whereas it remained constant for the Reactor 3 and Reactor 4 due to non-leaching. Therefore, it is expected that hydrolysis process might have proceeded in the Reactor 1 and Reactor 2 due to the much water addition and leachate collection in the Reactor 1 and Reactor 2. The cumulative volume of leachate collected from the Reactor 1 (6000 mL) was also higher than that from the Reactor 2 (4000 mL), which might have also resulted from the addition of high-solids manure into the Reactor 2. The manure addition made the leaching through the LBRs difficult. As it can also be seen from the Figure 4.18.b, the leaching started in the 7^{th} day in the Reactor 3, whereas it started in the 20^{th} day in the Reactor 4.

During the hydrolysis in the LBRs, some materials in the feedstock were likely to be limited by low hydrolysis (or acidogenic) rate related factors and hence required a longer SRT to achieve better conversion efficiencies. To maintain a stable high-solids hydrolysis process; solids content, chemical nature, pH, VFAs and moisture content have been considered to be the important environmental factors affecting the hydrolysis efficiency of the high-solids organic waste.

4.3.2. The Total Solids (TS) and Volatile Solids (VS) Variations

The variations in the TS and VS concentrations in the LBRs, which consist of different proportions of OFMSW and manure, were observed. According to the values recorded throughout the experiment, the TS and VS concentrations in leachate throughout the operation of LBRs are exhibited in the Figure 4.19.

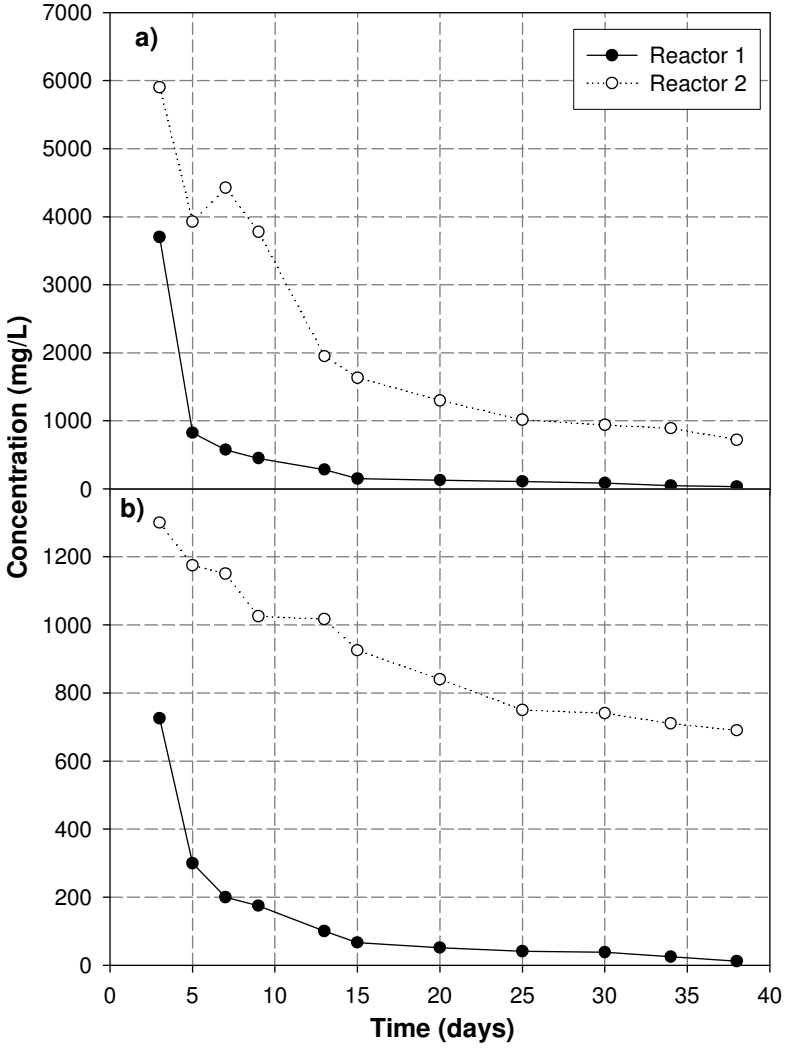

Figure 4.19. Concentration variations of **a)** TS and **b)** VS throughout the operation of LBRs

According to Figure 4.19.a, the TS concentrations started to decrease rapidly from 6000 mg/L to 1500 mg/L in the Reactor 2 and 4000 mg/L to 200 mg/L in the Reactor 1 in the initial 15 days and after 15th day; they decreased slowly and the concentrations reached to 1000 mg/L in the Reactor 2 and 100 mg/L in the

Reactor 1 at the 25th day. After 25th day, no excessive decrease in the TS concentrations was observed in both LBRs. At the end of 40th day, the TS concentrations in the Reactor 1 reached to about zero, whereas less amount of decrease in the TS concentrations took place in the Reactor 2 throughout the experiments due to the existence of high-solids manure in the Reactor 2.

According to Figure 4.19.b, the VS concentrations also started to decrease rapidly from 1300 mg/L to 900 mg/L in the Reactor 2 and 700 mg/L to 50 mg/L in the Reactor 1 in the initial 15 days and they decreased slowly after 15th day and the VS concentrations reached to 750 mg/L in the Reactor 2 and 20 mg/L in the Reactor 1 at the 25th day. After 25th day, no excessive decrease in the VS concentrations was observed in both LBRs. At the end of 40th day, the VS concentrations in the Reactor 1 reached to about zero, whereas less amount of decrease in the VS concentrations took place in the Reactor 2 throughout the experiments due to the existence of high-solids manure in the Reactor 2. The initial concentration of TS and VS in the Reactor 2 was higher because of high TS and VS content of feedstock in the Reactor 2 resulting from manure.

These observations suggest that solid organic materials started to hydrolyze rapidly and wash-out in the initial 15 days, since the solid concentrations in the leachate decreased rapidly. This trend occurred due to the fact that the solids changed state, in other words, they were dissolved in water and collected as dissolved solids in the leachate from the LBRs. The values of TS and VS concentrations in the Reactor 1 reached to almost zero at the end of 40 days. As a result, the solid organic materials were completely converted to soluble organic materials during 40 days in the Reactor 1, which suggests that the leaching process significantly solubilized solids contained in the feedstock in the initial 40 days in the Reactor 1. However, the decrease in TS and VS concentrations continued in the Reactor 2, which shows that the hydrolysis process continued and the solid organics were not completely converted to soluble organics during 40 days.

The cumulative TS and VS values of the leachate throughout operation were calculated in terms of mass and they are exhibited in the Figure 4.20 and Figure 4.21.

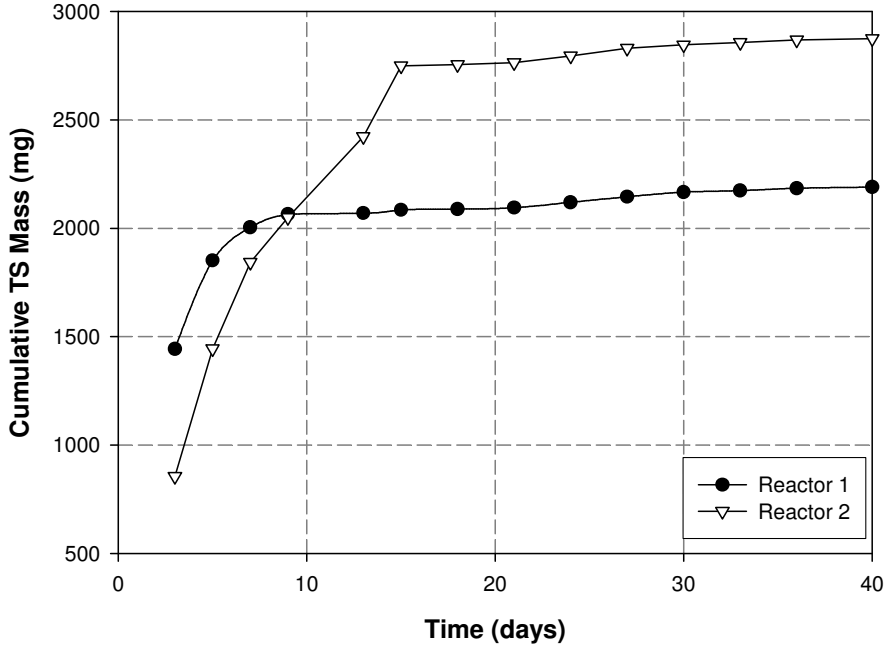

Figure 4.20. Cumulative mass variations of TS in leachate in time

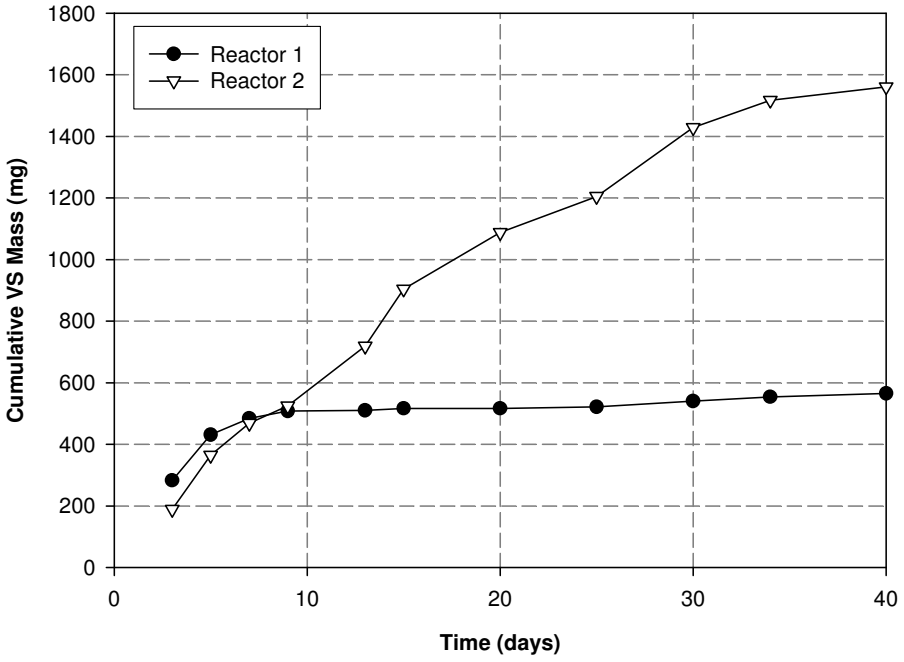

Figure 4.21. Cumulative mass variations of VS in leachate in time

The similar conclusion can be figured out from the Figure 4.20 and 4.21 as in the Figure 4.19. The solid particles were removed from the Reactor 1 in the initial 15 days, and after 15^{th} day, there was almost no solids washing-out in the Reactor 1. Particularly, the increase of TS and VS masses in the initial 15 days, can be interpreted as washing of the small particulates and their removal from the LBRs or this situation can be explained as the particulates formation due to the hydrolysis in the initial 15 days, when the hydrolsis mainly took place and the particulates from the LBRs were removed.

As it can be figured out from the Figure 4.20 and Figure 4.21, the amount of TS and VS removal and TS and VS removal rate in the Reactor 2 was higher compared to the Reactor 1. This might have resulted from the higher amount of washing of high-solid particles from the Reactor 2 due to the high-solids of manure. As a result, the solid organic materials were completely converted to soluble organic materials during 40 days in the Reactor 1, which suggests that the leaching process significantly solubilized minerals contained in the feedstock during 40 days in the Reactor 1. However, the increase in the amount of TS and VS cumulative masses continued in the Reactor 2, which shows that the hydrolysis process continued and the solid organics were not completely converted to soluble organics at the end of 40 days. The removal of TS and VS in the Reactor 2 would probably continue after 40 days.

4.3.3. The pH, Total COD (tCOD) and Soluble COD (sCOD) Variations

The use of COD alone as a process control parameter is not nearly as useful as pH alone. The combination of COD and pH is useful in controlling the system. The COD is a useful indicator of VFAs at the end of the treatment process and pH is a good indicator of when VFA concentration is high enough to feed the reactor (Hanson et al., 2001). Therefore, the variations of pH, tCOD and sCOD profiles of leachate in the LBRs over time are observed and they are shown in the Figure 4.22.

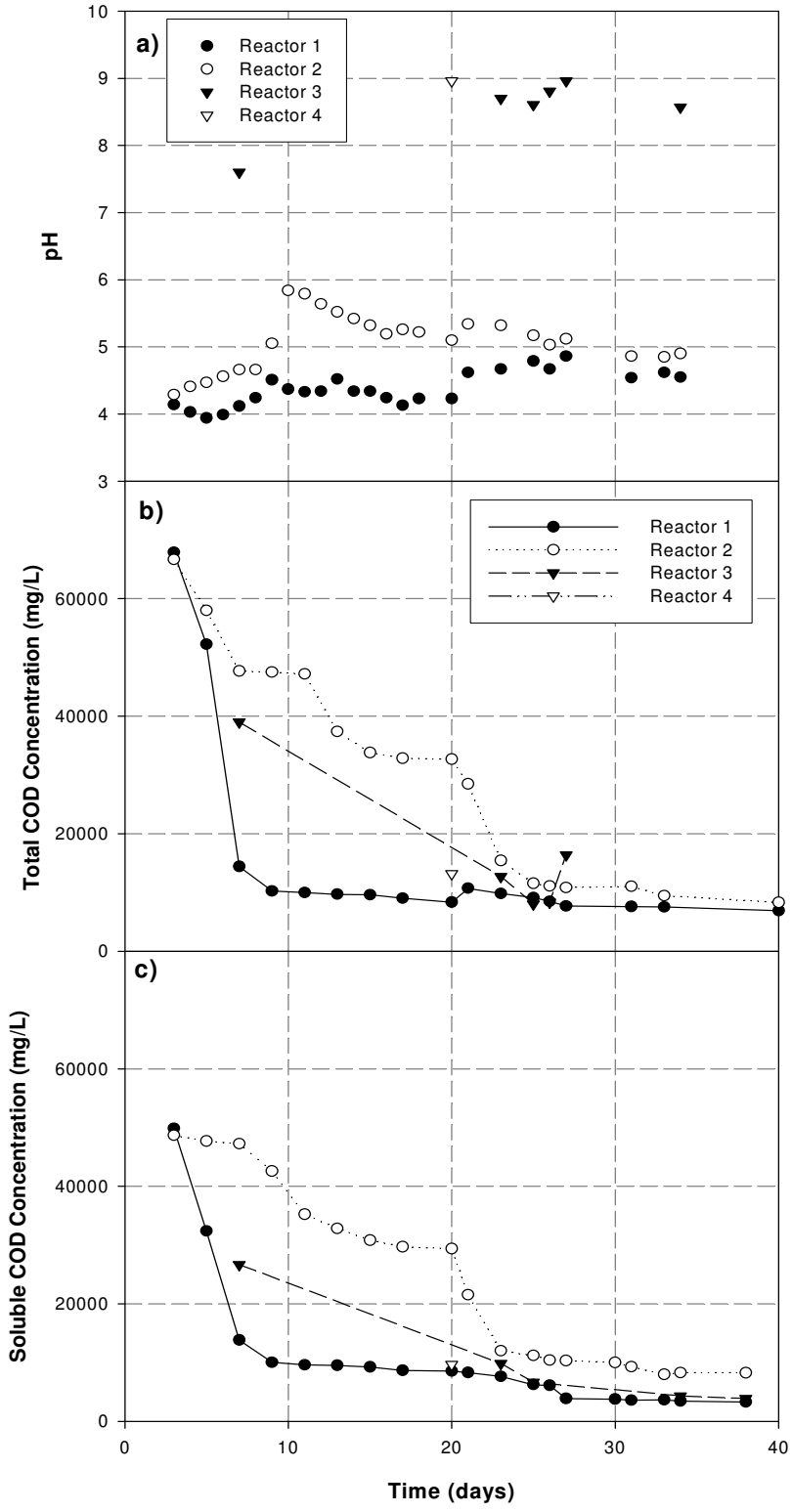

Figure 4.22. Daily variations of **a)** pH, **b)** Total COD and **c)** Soluble COD concentrations of leachate

As it is seen in the Figure 4.22.a, the pH of leachate from the LBRs increased slightly with time. However, the pH values in the Reactor 2 decreased slightly after 10^{th} day. The increase in the pH values might have resulted from the addition of tap water throughout the operation of LBRs. The LBRs might also tend to buffer themselves towards a higher pH value during the acidogenesis stage. In addition, the pH values of the LBRs fed with different proportions of cow manure, namely Reactor 2, 3 and 4 were higher with respect to those of the Reactor 1, which was fed only with OFMSW. The pH values of all LBRs except Reactor 1 were higher due to the fact that cow manure was added into the LBRs except Reactor 1 and the pH of manure was higher with respect to that of the OFMSW. The higher pH values in the Reactor 2 resulted from the manure addition, which has a high buffering capacity. The highest pH value observed belongs to the Reactor 4, which was fed with totally manure. The pH values were not low according to the optimum pH value, which is between 4 and 6.5 for acidification (Speece, 1996). The higher pH values in the Set-2 with respect to those observed in the Set-1 might be due to the pH value of feedstock composition, which consists of OFMSW and manure in different proportions. However, the higher pH values in the Reactor 1, fed with OFMSW only, of Set-2 depend also on the nature of the OFMSW. The initial pH of the OFMSW used in the Set-2 as feedstock was slightly larger, which was 5.18±0.2, than that in the Set-1.

Co-treatment of MSW and cow manure was conducted to evaluate the feasibility of producing methane gas from combined segregated municipal and agricultural waste using a two-phase anaerobic process. In the study of Hanson et al. (2001), without cow-manure added, the pH was rapidly reduced and then just as rapidly climbed back up. It appears that this represents mostly food waste and perhaps a little of the grass waste with very little degradation of the paper. The test with the cow-manure added shows a quick pH depression, followed by a period with an elevated pH. This is followed by a long period with a depressed pH. The first period of low pH is believed to be associated with degradation of the food and grass waste. The period of elevated pH is believed to be an accliamation or growth period for the microorganisms that degrade the paper waste. As a result, it was concluded that a depression in the pH is an indication of VFA production. The pH and VFA curves should be well correlated (Hanson et al., 2001). In the literature, it is also stated that

pH control gives the best performance with rapid decline in the COD and tVFAs concentrations (Reinhart and Townsend, 1998). Therefore, in this LBR study, the pH control was provided with the manure addition to the LBRs. In addition, the fact that the pH values were depressed after 10^{th} day in the Reactor 2 shows the indication of VFA production in the Reactor 2 after 10^{th} day.

According to the Figure 4.22.b and 4.22.c, it can be observed that tCOD and sCOD decreased with time as it was expected. The tCOD concentrations decreased rapidly from 70000 mg/L to 10000 mg/L in the initial 25 days in the Reactor 2, whereas they decreased more rapidly from 70000 mg/L to 10000 mg/L in the initial 10 days in the Reactor 1. In the same manner, the sCOD concentrations decreased rapidly from 50000 mg/L to 10000 mg/L in the initial 25 days in the Reactor 2, whereas they decreased more rapidly from 50000 mg/L to 10000 mg/L in the initial 10 days in the Reactor 1. The decrease in tCOD and sCOD in the leachate in time shows that there was a liquefaction/hydrolysis in the LBRs and the initial COD of the solid waste at the beginning of the experiment passed into the leachate by the addition of water in time. This value decreased with time due to the washing of the waste by addition of water in time. As the water passed through the LBR, it helps to hydrolyse the organic matter. Therefore, the sCOD values in the leachate increased in time. Hydrolysis started rapidly in the initial days with the addition of water to the LBRs. In addition, the decrease in tCOD and sCOD concentrations in the Reactor 1 proceeded more rapidly, which suggests higher hydrolysis rate in the Reactor 1. This might have resulted from the fact that much tap water was added to the Reactor 1 throughout the experiment, as it can be seen from the Figure 4.18.b and the high initial COD value of the feedstock containing OFMSW and manure in the Reactor 2, which was 318,09 g COD, whereas it was only 220 g COD in the Reactor 1.

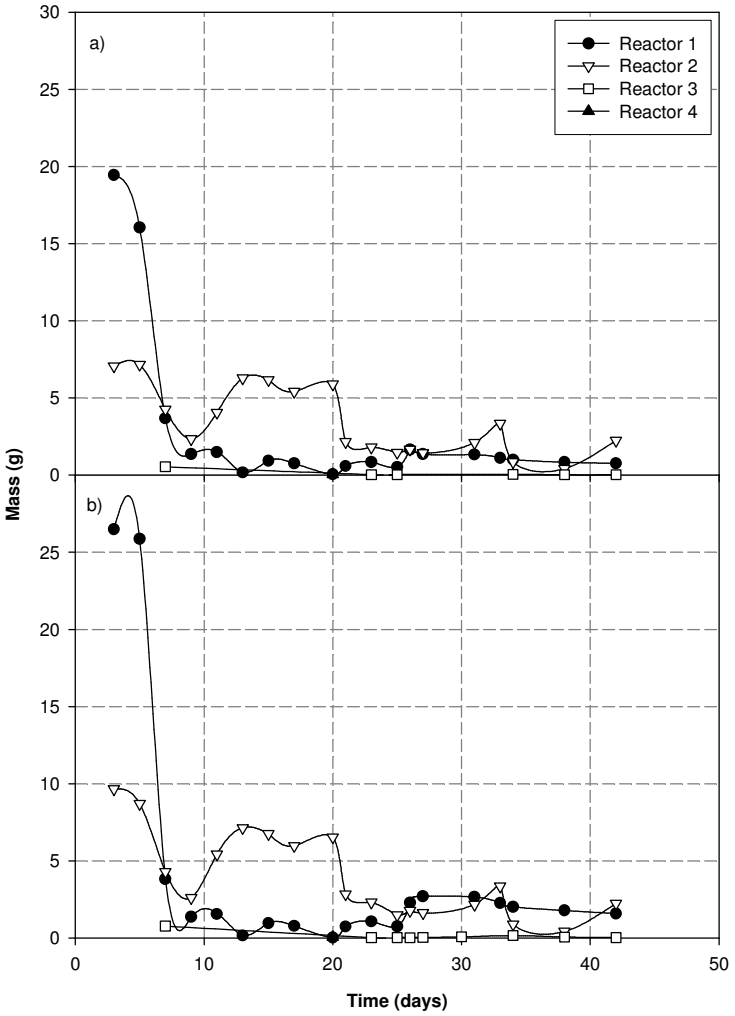

Figure 4.23. Daily mass variations of **a)** sCOD and **b)** tCOD values in the leachate of LBRs

As it is seen in the Figure 4.23, the rapid decrease trend in the daily sCOD and tCOD mass values were observed in the Reactor 1 in the initial 10 days, whereas the decrease trend in the daily sCOD and tCOD mass values were observed in the Reactor 2 throughout the operation of LBR.

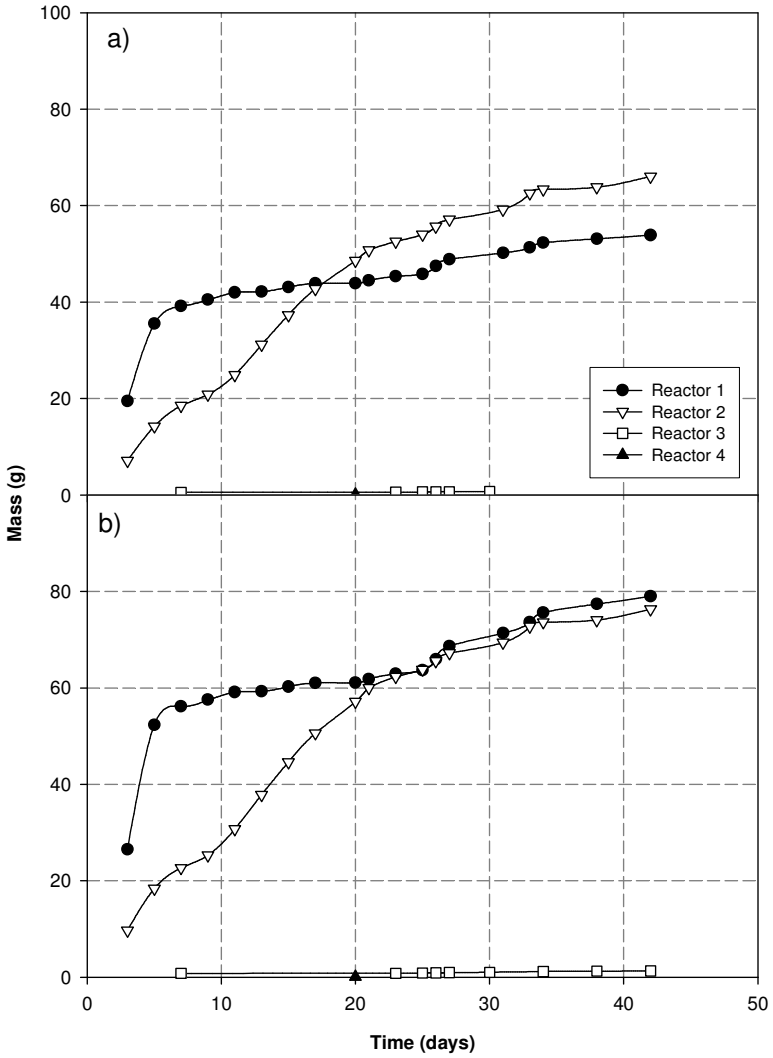

Figure 4.24. Cumulative mass variations of **a)** sCOD and **b)** tCOD values in the leachate of LBRs

The cumulative sCOD and tCOD mass values in the leachate of LBRs increased rapidly, especially in the initial 10 days, and after 10 days, they increased slightly (Figure 4.24. a and Figure 4.24.b). When the cumulative sCOD values in terms of mass are compared, it can be concluded that in the Reactor 2, whose initial sCOD mass value was lower than that in the Reactor 1, the amount of hydrolysed organic solids was higher at the end of 40 days. The cumulative sCOD values also show that the amount of sCOD in the leachate of Reactor 2 was about 10 g greater than that of Reactor 1 at the end of 40 days (Figure 4.24.a). However, both the initial tCOD mass value and the cumulative tCOD mass value were higher in the Reactor 1

than those in the Reactor 2. The mass values of sCOD and tCOD in the Reactor 1 and Reactor 2 increased due to the water addition and leaching in the LBRs (Figure 4.24).

The amount of cumulative sCOD masses in the Reactor 1 increased rapidly in the initial 10 days, however, this value increased slightly in the Reactor 1 after 10^{th} day. On the other side, the amount of cumulative sCOD masses in the Reactor 2 rapidly increased during the experiment (Figure 4.24.a). This might have realized due to the less amount of water addition to the Reactor 2, and consequently, due to the low hydrolysis efficiency in the Reactor 2. The cumulative tCOD values in terms of mass in the Reactor 1 increased rapidly in the initial 10 days, whereas this value increased continuously during the operation of Reactor 2 (Figure 4.24.b).

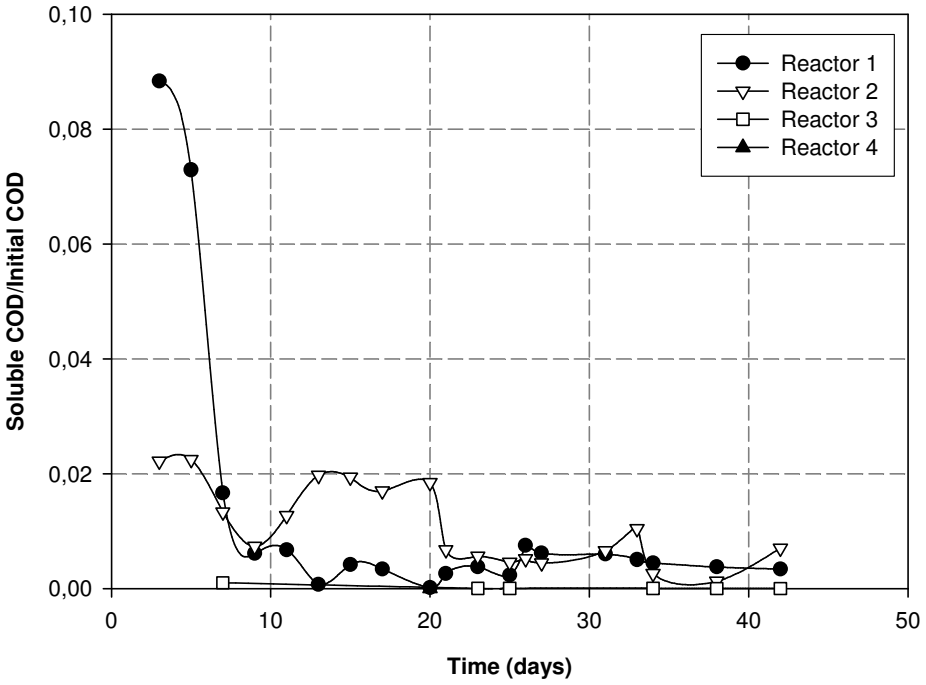

Figure 4.25. Daily sCOD/initial COD ratio in the LBRs in time

As it can be seen from the Figure 4.25, the hydrolysis process was realised effectively in the Reactor 1 in the initial 10 days due to the rapid decrease of sCOD/initial COD ratio. However, the decrease in the sCOD/initial COD ratio was lower in the Reactor 2. As a result, the hydrolysis process continued in the Reactor 2

during the operation, since the decrease in the sCOD/initial COD ratio continued.

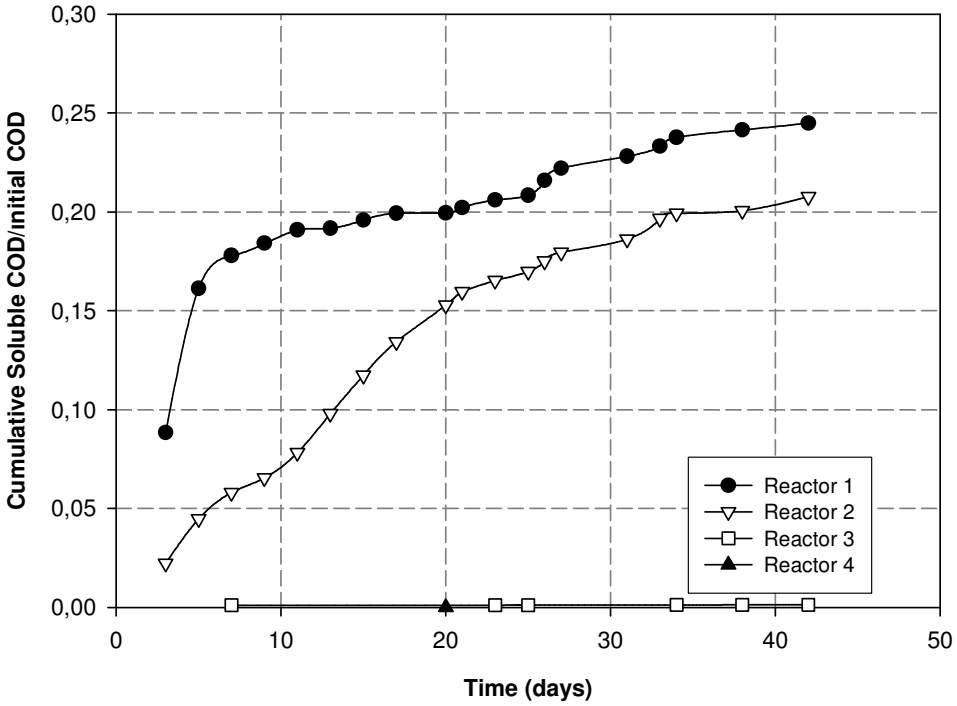

Figure 4.26. Cumulative sCOD/initial COD ratio in the LBRs in time

When the cumulative values are evaluated, the 20% and 15% of the initial tCOD were hydrolysed in the Reactor 1 and in the Reactor 2, respectively, during the initial 20 days (Figure 4.26). Hydrolysis efficiencies of the Reactor 1 and the Reactor 2 increased slightly to 25% and 20%, respectively, during the operation of LBRs. The Figure 4.25 and Figure 4.26 prove that the hydrolysis efficiency in the Reactor 1 was higher due to the much water addition and the previous results are confirmed. The higher hydrolysis efficiency in the Reactor 1 might be related to the higher leaching efficiency (passing through the bed) due to the much water addition and/or the smaller size of particles of feedstock (containing only OFMSW). The hydrolysis process would probably continue in the Reactor 2 after 40th day. In the Table 4.3, the hydrolysis efficiencies of LBRs in the Set-2 are exhibited.

Table 4.3. Hydrolysis yield values for LBRs in Set-2

	Reactor 1	**Reactor 2**
Hydrolysis yield (%)	25% (in 40 days)	20% (in 40 days)

The OFMSW composition added to the LBRs was changed in this study in order to investigate the effect of feedstock composition on the hydrolysis of OFMSW. The paper was added into the OFMSW in the ratio of 5.8 wt %, which was used in LBRs of Set-2, to investigate the effect of cellulose on the hydrolysis. The overall hydrolysis yields in the LBRs of Set-1 were found as 40% (in 40 days) in the Reactor 1 and 45% (in 40 days) in the Reactor 2, whereas these values were found as 25% (in 40 days) in the Reactor 1 and 20% (in 40 days) in the Reactor 2 of Set-2. These results show that the hydrolysis yields were higher in the LBRs of Set-1, which might have mainly resulted from the effect of different feedstock composition (OFMSW without paper in the Set-1), particle size, the amount of water addition and the use of different type of culture (acidogenic culture in the Set-1).

4.3.4. The Volatile Fatty Acids (VFAs) Variations

The anaerobic conversion of organic matter to fermentation products is an important biotechnological process. The prediction of the fermentation products is until now a complicated issue for mixed cultures. A shift from acetate to butyrate as main product when either hydrogen pressure increases and/or pH decreases is predicted as well as ethanol formation at lower pH values. The hydrogen production yield depends stoichiometrically on the range of fermentation products formed. Solvent fermentations for the production of alcohols have been of much interest in the past and recent years due to their potential application as sustainable additives to gasoline. Experimental investigations have repeatedly demonstrated the dependency of the products formed on the operational conditions (Rodriguez et al., 2005)

Although the proper operational conditions for the acetogenic/methanogenic phase have been extensively studied, little information is available for the acidogenic phase. The lack of such knowledge is one of the major barriers for the widespread of the two-phase process (Yu and Fang, 2001).

The variations of VFAs in the leachate (acetic acid, propionic, iso-butyric, butyric, iso-valeric, valeric, isocaproic, caproic and heptanoic acids) and ethanol were measured throughout the experiment and the variations of individual VFAs are exhibited in the Figure 4.27 and 4.28.

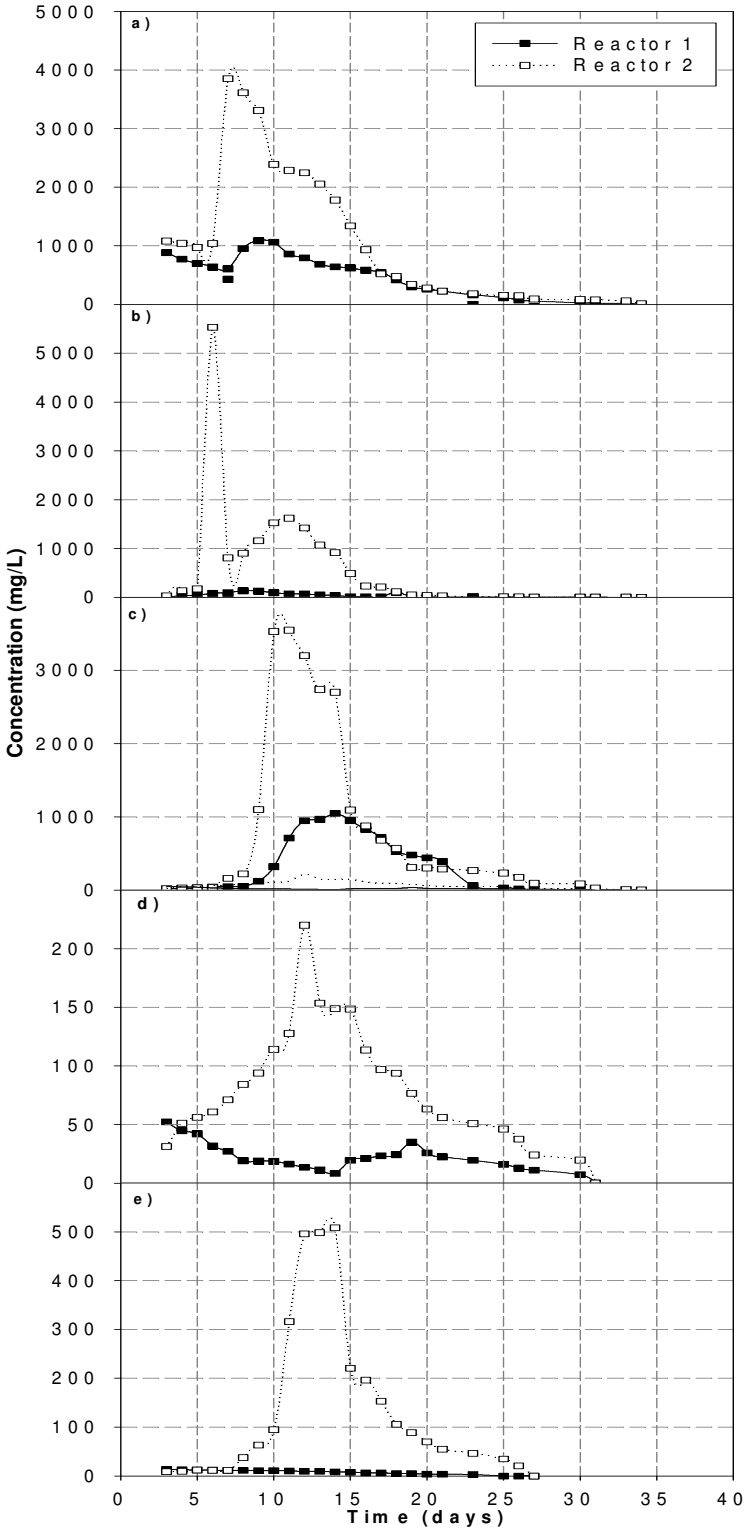

Figure 4.27. Daily concentration variations of **a)** Acetic acid, **b)** Ethanol, **c)** Isobutyric acid, **d)** Butyric acid and **e)** Isovaleric acid in the leachate samples

According to Figure 4.27.a, the acetic acid was one of the major organic acids that were produced as a result of acidification in the LBRs, at maximum concentration of about 4000 mg/L in the Reactor 2, whereas it was observed at maximum concentration of 1000 mg/L in the Reactor 1 between 5^{th} and 10^{th} days. The other major acid was isobutyric acid in the LBRs, which attained the peak concentration of 4000 mg/L in the Reactor 2 and 1000 mg/L in the Reactor 1 between 10^{th} and 15^{th} days (Figure 4.27.c). The butyric acid concentration reached to above 200 mg/L in the Reactor 2 in the initial 13 days and it started to decrease after 13^{th} day, whereas the same value decreased slightly from 50 mg/L to zero in the initial 30 days in the Reactor 1 (Figure 4.27.d). The isovaleric acid concentration increased to the peak concentration of 500 mg/L in the Reactor 2 in the initial 15 days; however, the concentration of the same acid was very low in the Reactor 1 throughout the experiment. The concentration of acetic acid, isobutyric acid, butyric acid and isovaleric acid in the Reactor 2 was greater than those in the Reactor 1. This might have resulted from the different initial COD values of feedstock in the LBRs and also from the higher pH values observed in the Reactor 2 throughout the experiment. The initial COD value in the Reactor 1 (220 g) was lower than that in the Reactor 2 (318 g). The acetic acid, isobutyric acid, butyric acid, isovaleric acid and ethanol disappeared after 25^{th} day. This may exhibit that the acidification process was completed in the initial 25 days.

At high pH values, the acetate is predicted as the main product. The acetate production decreases at lower pH values, since the concentration of the undissociated form of the acid increases, resulting in more energy requirements for outwards transport of acetic acid. Butyrate replaces acetate as main product at decreasing pH values, since the production of one butyrate incorporates one acetate and consequently, less acid molecules need to be transported per glucose converted (Rodriguez et al., 2005). In this experiment, the acetic acid and isobutyric acid were the most dominant VFAs in the LBRs, not the butyric acid, due to the increasing pH values.

The concentrations of ethanol were also high in the Reactor 2, which might have also resulted from the composition of feedstock; in addition to the higher pH values in the

Reactor 2 (Figure 4.27.b). However, the ethanol concentration was was very low in the Reactor 1.

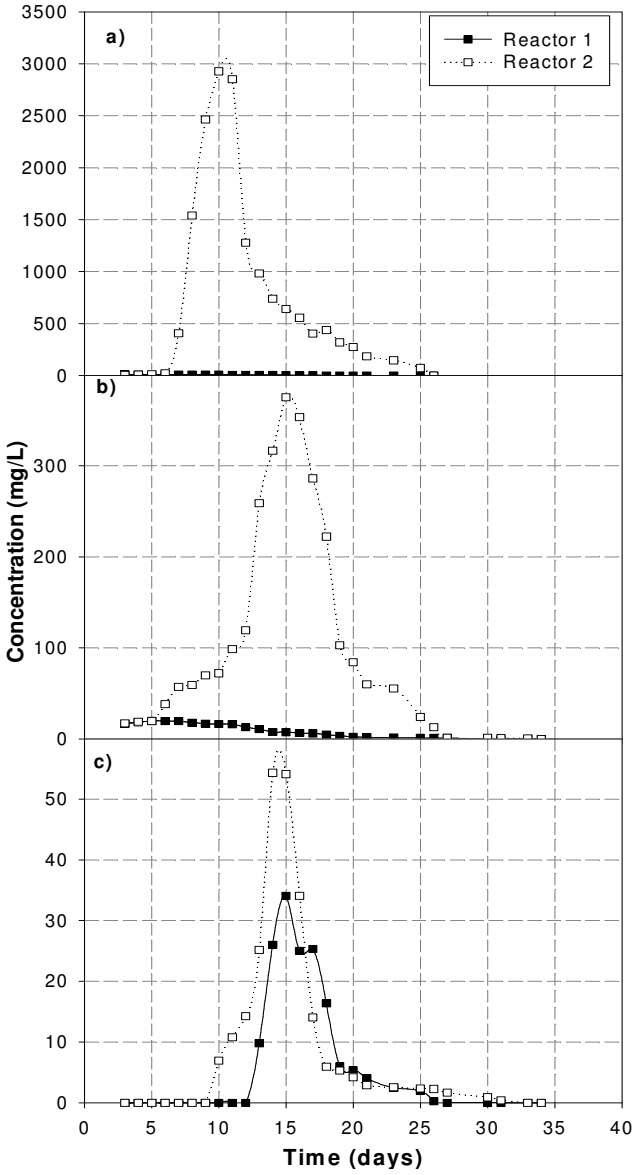

Figure 4.28. Daily concentration variations of **a)** Isocaproic acid, **b)** Caproic acid, **c)** Heptanoic acid in the leachate samples

According to the graphs of other organic acids in the Figure 4.28, the isocaproic, caproic and heptanoic acids were also produced in the LBRs. However, they started to increase and then, decrease rapidly, which exhibited the same trend with the other organic acids as shown in the Figure 4.27 and they disappeared after 30^{th} day. The least amount of organic acids observed in this experiment were heptanoic acid and

isocaproic acid, which was only about 60 mg/L in the Reactor 2 and about zero in the Reactor 1, respectively.

The highest concentrations of VFAs that was produced in this experiment were acetic acid and isobutyric acid, according to the Figure 4.27. The concentrations of other organic acids that were observed in the analysis of leachate (isovaleric, caproic, butyric and heptanoic) were smaller when compared to acetic acid, isobutyric acid and isocaproic acid in the Reactor 2, as shown in the Figure 4.27 and 4.28. However, isocaproic acid, isovaleric acid and caproic acid were in trace amounts in the Reactor 1. The difference between the individual VFAs might have resulted from the nature of the feedstock, which was totally different in the LBRs and the different pH values observed in the LBRs. The concentration of isocaproic acid, caproic acid and heptanoic acid were also greater in the Reactor 2 with respect to the Reactor 1, which might have resulted from the higher pH values of Reactor 2 throughout the experiment, as it was stated previously. The propionic acid and valeric acid were the acids, which were not produced in the LBRs of Set-2 throughout the experiment.

Horiuchi et al. (2002) observed that, under the conditions of pH from 5-7; the main soluble products were butyric acid and acetic acid, while the propionic acid concentration was rather low, in chemostat cultures supplemented with glucose. The main products at pH 8 were acetic acid and propionic acid. It is found that the high production of butyric acid observed at low pH was caused by the high hydrogen content (Butyric acid works as a hydrogen acceptor). Moreover, the reduction of hydrogen production in the acid reactor at pH 8, caused a change in the organic products in the acid reactor. It is observed that the molecular hydrogen produced during the production of acetic acid and butyric acid from glucose, was consumed during the production of propionic acid. Thus, at pH 8, propionic acid concentration in the acid reactor remarkably increased, resulting in a lower production of hydrogen. However, although the hydrogen content in the reactor was the key factor for regulating the acidogenesis, the results suggested that the microbial population in the acid reactor depended on the culture pH rather than the partial hydrogen pressure. Furthermore, Horiuchi et al. (2002) found that the change in the product formation occurred by the change of the dominant microbial populations in the acid reactor.

The change in the dominant population occurred because the optimal pH was different for the bacterial groups producing each organic acid. It was also found that the shift in products was reproducible and reversible, and was not affected by the dilution rate and the pH control was effective for selective production of various organic acids from organic wastes. The different organic acids produced in the LBRs of Set-2 might have resulted from the use of mixed anaerobic culture type, instead of acidogenic culture.

Similarly, Yu and Fang (2003) observed that pH had a more significant effect on acidogenesis than that of temperature. They found that gelatin degradation efficiency substantially increased with the pH between 4 and 7, however, the degree of acidification incraesed between 4 and 6.5, but dropped when the pH increased to 7. They found that the optimum pH for the overall acidogenic activity was 6. Moreover, they indicated that operation at pH of 4-5 favored the production of propionate and hydrogen, whereas, the operation at pH 6-7 encouraged the production of acetate, butyrate and i-butyrate.

Dinamarca et al. (2003) found that during the anaerobic acidogenesis of the organic fraction of urban solid waste, it was not necessary to control the pH, since the presence of proteins and other compounds provided adequate buffering capacity and that the pH control was thus, not necessary for those type of residues. The pH of the system fluctuated between 6.5 and 8.2 in the non-pH-controlled reactor. In this experimental study, the buffering capacity was provided with the manure addition to the LBRs in order to control the pH values in the LBRs and to see the effect of pH control on the products spectrum.

The different variations of VFA types in the LBRs resulted from the high amount of protein fermentation (results in iso-butyrate and higher molecular weight-VFAs) in the Reactor 2 due to the manure addition into the Reactor 2.

In the Set-2, it was achieved that 197 mg EtOH in Reactor 1 and 1162 mg EtOH in Reactor 2, 2760 mg HAc in Reactor 1 and 3116 mg HAc in Reactor 2, 1343 mg Buty in Reactor 1 and 1344 mg Buty in Reactor 2, were produced.

As a result, when the gain from 1 kg of OFMSW and 0.75 kg of OFMSW and 0.25 kg manure was calculated, the following results were obtained:

For 1 kg OFMSW:

- EtOH: 3.3 x 10^{-5} $ / kg of OFMSW
- HAc: 1.1 x x 10^{-3} $ / kg of OFMSW

For 0.75 kg of OFMSW and 0.25 kg manure:

- EtOH: 1.9 x 10^{-4} $ / kg of feed
- HAc: 1.3 x x 10^{-3} $ / kg of feed

The results indicated that the products from the hydrolysis and acidification of OFMSW and manure under the studied conditions is more profitable than the products from the hydrolysis and acidification of only OFMSW and the most profitable product from the hydrolysis and acidification of OFMSW and manure is HAc, rather than ethanol.

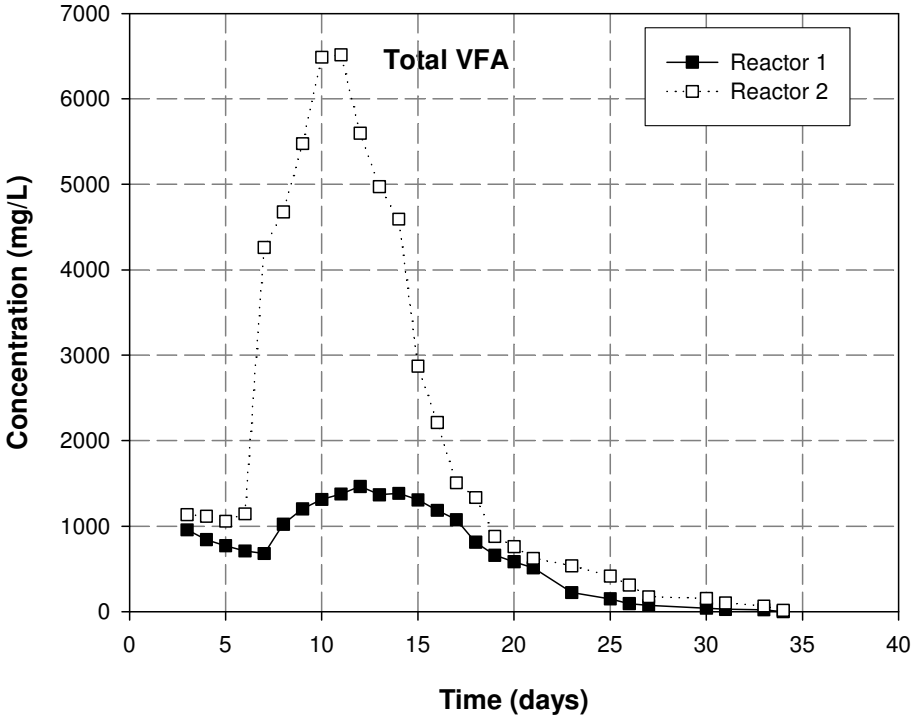

Figure 4.29. Daily concentration variations of tVFA of leachate samples in terms of HAc

As it can be seen from the daily tVFA concentrations in the Figure 4.29, the acidification process in the leaching bed type of reactors accelerated the production of tVFA, which reached a maximum concentration of 6517 mg HAc/L at 11^{th} day at pH value of 6 in the Reactor 2, which was fed with manure and OFMSW. The tVFA concentrations in the Reactor 1 peaked to 1500 mg/L at 13^{th} day at pH value of 4.5. Ethanol was not taken into consideration in the tVFA calculation. The concentration of tVFA in the Reactor 2 was larger than that in the Reactor 1. This might have resulted from the higher pH values observed in the Reactor 2 with respect to those in the Reactor 1 and also the greater initial COD value of feedstock in the Reactor 2, due to the manure addition into the Reactor 2. It can be concluded that when reagents with high buffering capacities such as manure are used to resist changes in the pH values, higher amount of VFAs production can be achieved. The decrease in tVFA concentrations might be due to consumption of acids in the cell growth.

According to the tVFA results, it can also be concluded that the optimum operation time should be 15 days for the maximum tVFA concentration in the LBRs of Set-2.

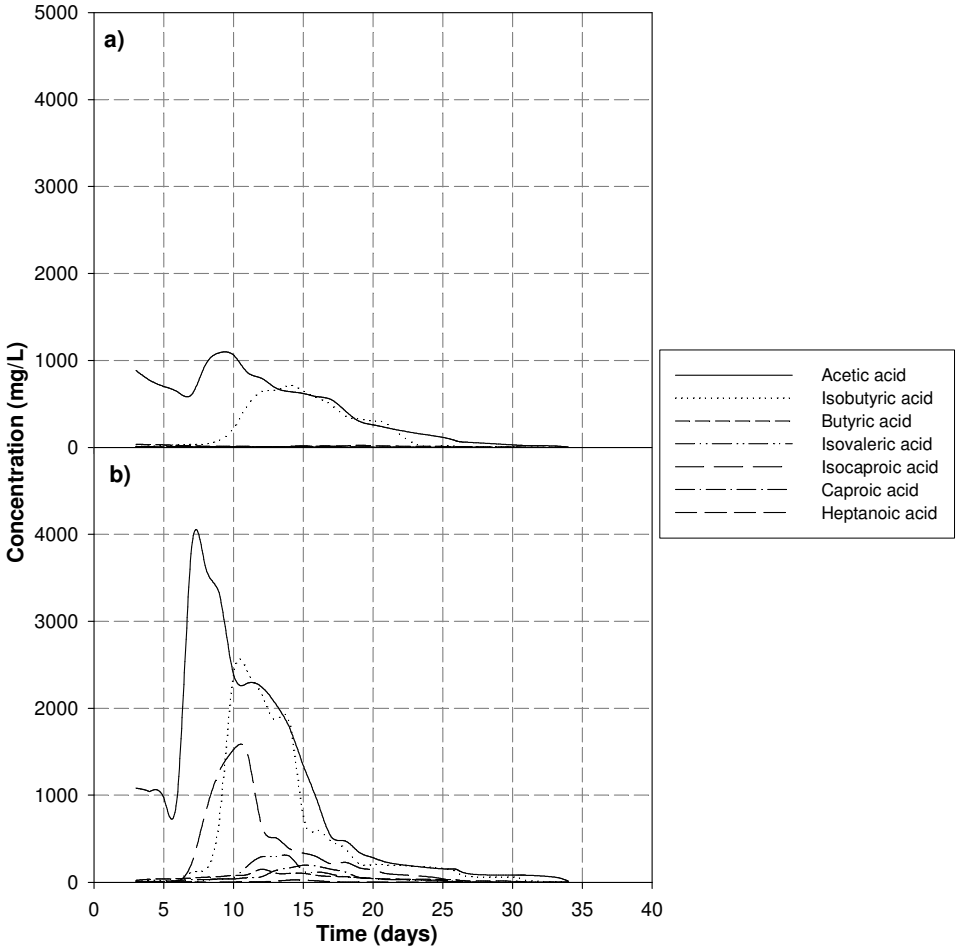

Figure 4.30: Daily concentration variations of tVFA of leachate samples in terms of HAc in **a)** Reactor 1 and **b)** Reactor 2

The Figure 4.30 shows that the major VFAs were acetic acid and isobutyric acid in both LBRs throughout the experiment. There was an increase in all types VFAs on days between 5 and 15 and a decrease afterwards. According to the trends of graphs, it can be concluded that the acidification process proceeded in higher amounts in the Reactor 2, which was fed with OFMSW and manure, according to the Reactor 1, which was fed only with OFMSW.

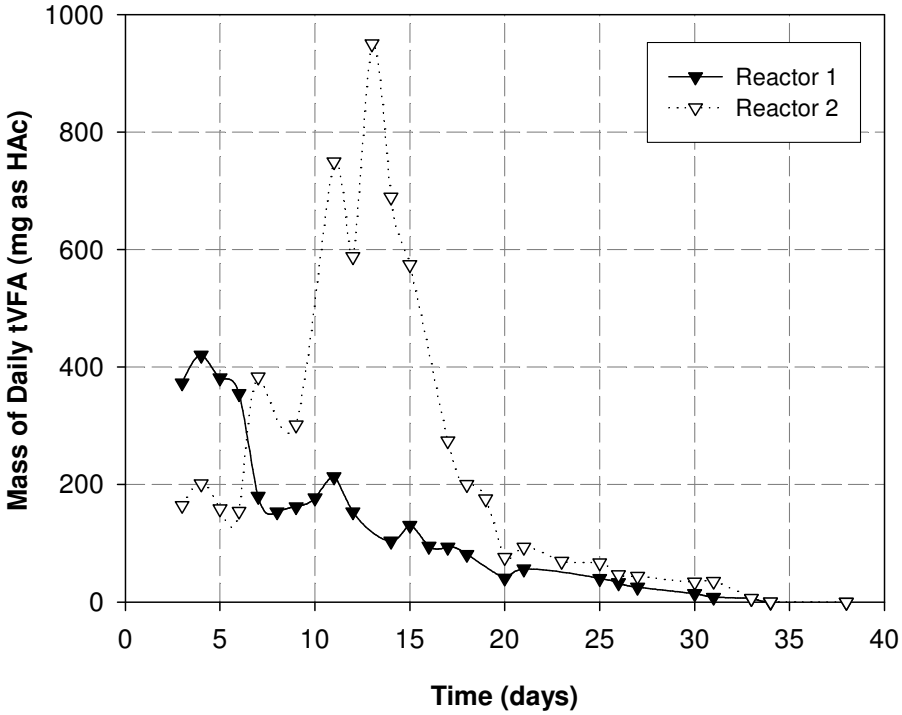

Figure 4.31. Daily mass variations of tVFA of leachate samples in terms of HAc

Since there might be dilution due to the water addition to the LBRs, the amount of tVFA mass production in terms of HAc are exhibited in the Figure 4.31 and Figure 4.32. As it can be also seen from the Figure 4.31, the amount of daily tVFA mass variations show that the acid production started in the initial 3 days in both LBRs and the amount of production increased until the end of 13th day in the Reactor 2. The acidification process in the leaching bed type of reactors accelerated the production of VFAs, which reached a maximum mass of 420 mg HAc at 4th day in the Reactor 1, which was fed with only OFMSW and a maximum mass of 950 mg HAc at 13th day in the Reactor 2, which was fed with manure and OFMSW. After 13th day, the acid production decreased and it reached to 100 mg at the end of 20th day and it decreased much more at the end of 40th day in the Reactor 2. However, the amount of tVFA mass in the Reactor 1 decreased slightly from 400 mg to zero in the initial 30 days. The decrease of tVFA mass in the Reactor 1 was much more rapid that that in the Reactor 2 due to the much water addition to the Reactor 1 and the higher hydrolysis efficiency observed in the Reactor 1 (Figure 4.31). The tVFA production in terms of mass in the Reactor 2 peaked at 13th day, when the pH value was 6.

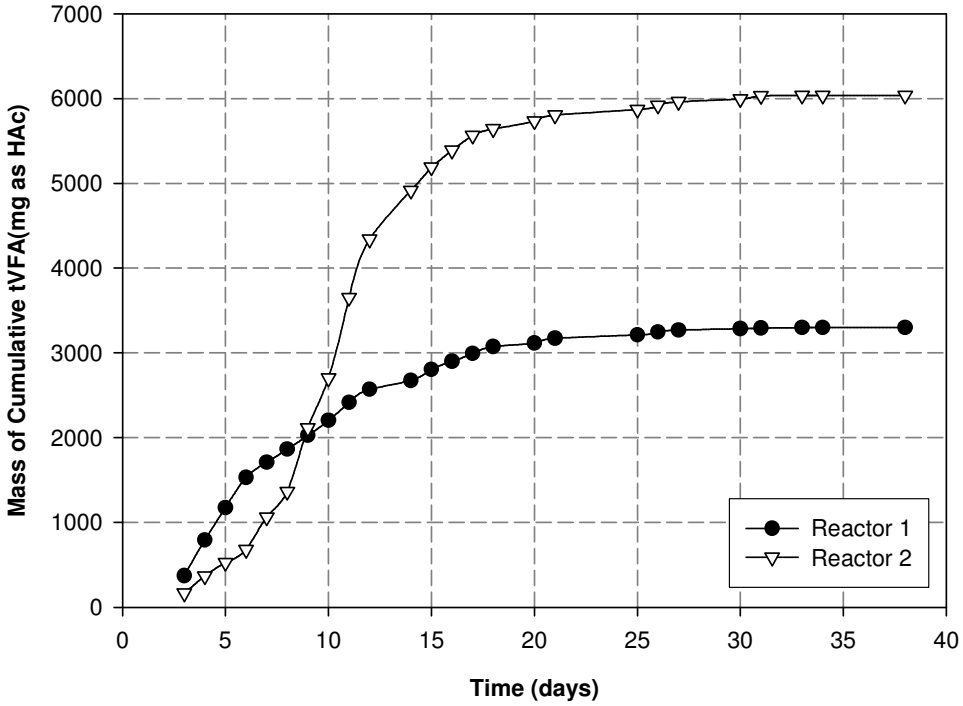

Figure 4.32. Cumulative mass variations of tVFA (mg, in terms of HAc) in leachate throughout operation

When the amount of cumulative tVFA masses are examined (Figure 4.32), the acid production in both LBRs started slowly in the initial 3 days and it was observed that it increased rapidly after 3th day and reached to 6000 mg in the Reactor 2 and 3000 mg in the Reactor 1 at the end of 20th day. After 20th day of operation, the production of tVFA continued slowly until the end of experiment. The cumulative mass of tVFA reached in the Reactor 2 was larger than that in the Reactor 1. This might have resulted from the higher pH values observed in the Reactor 2 with respect to those in the Reactor 1 and also the higher initial COD value of feedstock in the Reactor 2, due to the manure addition into the Reactor 2.

The highest VFA production was achieved in the LBRs of Set-1 seeded with acidogenic culture, since the microorganisms might have adapted to acidifying conditions and they might have been enriched before by pre-acidification stage.

The amount of cumulative tVFA production in the Reactor 1 of Set-2 was lower than those in the LBRs of Set-1, although all of the LBRs contain only OFMSW. However, since the hydrolysis efficiency in the Reactor 1 of Set-2 was lower due to the paper addition to the OFMSW used in the Set-2, the acidogenesis efficiency and consequently, the tVFA production were lower in the Reactor 1 of Set-2.

Anaerobic digestion of OFMSW was investigated in two thermophilic (55ºC) wet digestion treatment systems. Initially OFMSW was co-digested with manure with a successively higher concentration of OFMSW, at a HRT of 14–18 days and an OLR of 3.3–4.0 g-VS/l/d. Adaptation of the co-digestion process to a OFMSW: manure ratio of 50% (VS/VS) was established over a period of 6 weeks. This co-digestion ratio was maintained in one of the reactors, while the ratio of OFMSW to manure was slowly increased to 100% in the other reactor over a period of 8 weeks. Use of recirculated process liquid to adjust the organic loading was found to have a beneficial stabilization effect. The pH rose to a value of 8 and the reactor showed stable performance with high biogas yield and low VFA levels. VS reduction of 69–74% was achieved when treating 100% OFMSW. Addition of higher ratios of OFMSW and AD treatment solely of OFMSW was achieved after dilution with tap water and with recirculation of process liquid. Both the co-digestion process and the treatment of 100% OFMSW with recirculation of process liquid showed stable operation despite fluctuations in the feed volume. Recirculation of process liquid showed a beneficial effect on the process performance with a stabilization of the pH (Hartmann and Ahring, 2005b).

It was observed that addition of potato-processing wastewater to primary sludge at 1:1 ratio improved VFA production at the conditions studied (18-30 h HRT and 22-30 ^{o}C) (Banerjee et al., 1999). In this LBR study, the addition of manure to OFMSW at 1:3 ratio improved the VFA production.

Acidogenesis of municipal primary sludge and a wide variety of industrial wastewaters were also evaluated in various studies, in terms of process optimization. Eastmann and Ferguson (1981) determined that pH strongly affected soluble organic carbon production and VFA distribution in the acidogenesis of domestic primary

sludge in mesophilic, completely mixed digesters. No lipid degradation has been observed in this study.

The effect of SRT on the acidogenic phase of primary sludge using a completely-mixed reactor and an UASB reactor was investigated. The percentage of VFA distribution was slightly affected by changes in SRT, while organic matter degradation seemed independent of SRT, for the ranges from 10 to 20 days of SRT, at a constant HRT of 12 hours. It was also confirmed the significant effects of HRT, in addition to pH, on the utilization percentages of carbonhydrates, lipids and proteins, and the slight effects of SRT only on protein dissimilation, in acidogenesis of primary sludge (Demirel and Yenigün, 2002).

The acidification of glucose over the temperature range of 20ºC to 60ºC in a CSTR was investigated, and concluded that product distribution mostly depended on sludge loading and temperature, particularly in the thermophilic range. The rapid temperature drops affected starch degradation significantly at temperature levels between 30ºC and 15ºC. This study confirmed temperature effects on acidogenesis of simple, soluble substrate types. For complex-type substrates determined the distinct effects of temperature on the acidogenesis of primary sludge and starch-rich industrial wastewater in completely mixed reactors (Demirel and Yenigün, 2002). Maharaj and Elefsiniotis (2001) found VFA production feasible even at 8ºC, using diluted primary sludge and a mixture of diluted primary sludge and starch-rich industrial wastewater.

It was showed that mixing, seeding and solids concentration are the additional significant parameters governing VFA production for performance optimization of the acidogenic primary sludge fermentation systems (Demirel and Yenigün, 2002).

The final distribution of the VFA generated depends mainly on the nature of the substrate and the operational conditions, especially pH (Guerrero et al., 1999). This statement is also approved in this study with the higher VFA production in the Set-2, in which the manure was co-digested with OFMSW to use the effect of buffering capacity of manure on the pH values in the LBRs. The optimum pH value, which is

between 4 and 6.5 for acidification (Speece, 1996), was reached with the co-digetion of manure and OFMSW in the Set-2. As a result of these high and steady pH values due to buffering capacity of manure, higher VFA production in the Reactor 2 of Set-2 were obtained.

Table 4.4. Acidification yield values for LBRs in Set-2

	Reactor 1	**Reactor 2**
Acidification yield (%)	1.5% (in 40 days)	2% (in 40 days)

The acidification yields achieved in the LBRs were low, which might have resulted from the consideration of only tVFA production. However, higher acidification degrees could have been achieved in this study, if gaseous products were included to the calculations.

When the variations in the VFA types produced in the LBRs of Set-1 and Set-2 are compared, it is observed that in the LBRs seeded with acidogenic seed in the Set-1, more different types of VFA were produced. Similarly, this variation was due to the enriched acidogens present in the LBRs and adaptations to acidic conditions from the pre-acidification stage.

Throughout the experiments in this study, both COD solubilisation and VFA production were observed for both sets. The VFA production was attributed to both particulate COD solubilisation and fermentation.

Co-digestion with animal manure improves C/N ratio and organic acid production due to high buffering capacity of manure. In the Set-2, co-digestion of MSW with animal manure in the Reactor 2 resulted in sufficient nutrient value and bacterial diversity to improve the biodegradability of cellulose and increase the efficiency of organic acid production from the combined wastes. A lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria. However, the measurement of ammonia has not been performed in this study.

CHAPTER 5

CONCLUSIONS

In this study, hydrolysis and acidification of the high-solids OFMSW in the LBR were examined and the potential production of VFAs was investigated. In addition, it was attempted to reconstruct the hydrolysis and acidification profile of OFMSW by measuring especially sCOD and tVFA values at various periods of decomposition in the LBRs. An attempt was made to determine the stage of decomposition of the OFMSW at which hydrolytic and acidogenic activities begin, peak and decline. It was envisaged that such analyses would determine the feasibility of LBRs for the efficient digestion of OFMSW.

The main conclusions drawn from this study are as follows:

- The higher hydrolysis efficiency, achieved in the LBRs of Set-1, was resulted mainly from the non-cellulosic OFMSW and high amount of water addition. It was concluded that the feed composition and the amount of water addition were found to be important factors affecting the hydrolysis efficiency.
- The mass of tVFA production was higher in the LBRs of Set-1 with respect to that in the LBR of Set-2, containing only OFMSW with paper. The higher tVFA production in the Set-1 resulted from the higher hydrolysis efficiencies in the Set-1. The acidogenic process was found to be mainly regulated by the hydrolysis step, since the most of the organic matter in the OFMSW is in the particulate form. However, it was observed that cow manure addition resulted in higher amount of tVFA production in the LBR of Set-2 due to buffering capacity of manure, in spite of lower hydrolysis yields.
- In order to increase the efficiency of acidification processes, the pH values should be at the optimum ranges. The rapid acidified OFMSW cause a pH

decrease in the LBR to below the optimum range. This problem can be solved with mixing of OFMSW and high N content solid wastes such as animal manure, as in the Set-2 of this study. The animal manure addition provides increase of pH of the media, since it gives NH_4 to the media as it acidifies due to the high N content. The increase in the pH values in the Set-2 was provided with cow manure addition due to the high buffering capacity of manure, and as a result, the VFA production in the LBR was improved.

- The hydrolysis was mainly realized in the initial 5 days and the acid production was greatly achieved in the initial 25-30 days. Therefore, it was concluded that it is sufficient to operate the LBRs, which are used for the fermentation of OFMSW and in which, the maximum VFA production was aimed, for 25-30 days. At the end of 25-30 days, the continuity of operation/VFA production can be achieved by the addition of OFMSW to the LBRs. The LBRs will find an important place among the simple reactors used for the organic acid and alcohol production.
- The main individual VFAs produced as a result of hydrolysis and acidification of OFMSW were found as HAc and Buty and the main alcohol produced was EtOH in the LBRs of Set-1, whereas the main VFAs were HAc and isobutyric acid in the LBRs of Set-2. These variations in the by-products of acidification resulted from the nature of feed and pH variations in the LBRs. The pH parameter was found to be the most important parameter affecting product formation and product spectrum in the acidogenesis phase.
- It was understood that leaching property of the LBR and dilution rate are the important factors in order to operate the LBRs under the optimum conditions in terms of hydrolysis and acidification. The high amount of water addition increases the dilution rate and hydrolysis/acidification processes.
- The LBRs were found as alternative reactors for the degradation of high-solids OFMSW and the solubilization of concentrated solid wastes, which are difficult to operate in the CSTRs, especially in terms of mixing and not amenable to fermentation in the CSTRs in a short time, this resulted in rapid hydrolysis and acidification, consequently, high COD removal and high VFA production.

In conclusion, this study showed that co-digestion with animal manure is more successful than the digestion of MSW alone in terms of tVFA production.

The LBRs represent commercially viable reactors to convert OFMSW to organic acids and alcohols as useful by-products. The overall results of AD of OFMSW in the LBRs suggest that LBR system is a biologically and economically feasible and promising technology to treat these wastes with high efficiency in term of hydrolysis yield and organic acids production. This efficiency is possible by leaching of the liquid throughout the bed of LBRs. This study showed that rapid rates of MSW degradation can be achieved through employing a leach-bed process.

Recommendations for Future Work:

In order to have a better efficiency in the LBRs in terms of hydrolysis and acidification processes;

- ✓ The manure added to the LBRs can be shredded into smaller size particles by meat mincer in order to prevent clogging in the LBRs and to improve the hydrolysis process.
- ✓ The porous materials such as wood chips can be added to the LBRs to prevent the channeling in the LBRs and provide to keep water in the LBRs for longer time in order to to use less volume of water for th hydrolysis and acidification processes.
- ✓ High COD conversion to sCOD and the production of high VFAs in the LBRs will probably result in high amount of CH_4 in the methanogenic reactors used as second reactors in two-phase systems.

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APPENDIX A. FIGURES OF LBRs IN THE SET–1

Figure A.1. Experimental set-up of LBRs under mesophilic conditions

Figure A.2. Inside view of LBRs during operation

APPENDIX B. FIGURES OF LBRs IN THE SET–2

Figure B.1. Components of LBRs design

Figure B.2. Leachate collection component of LBRs design

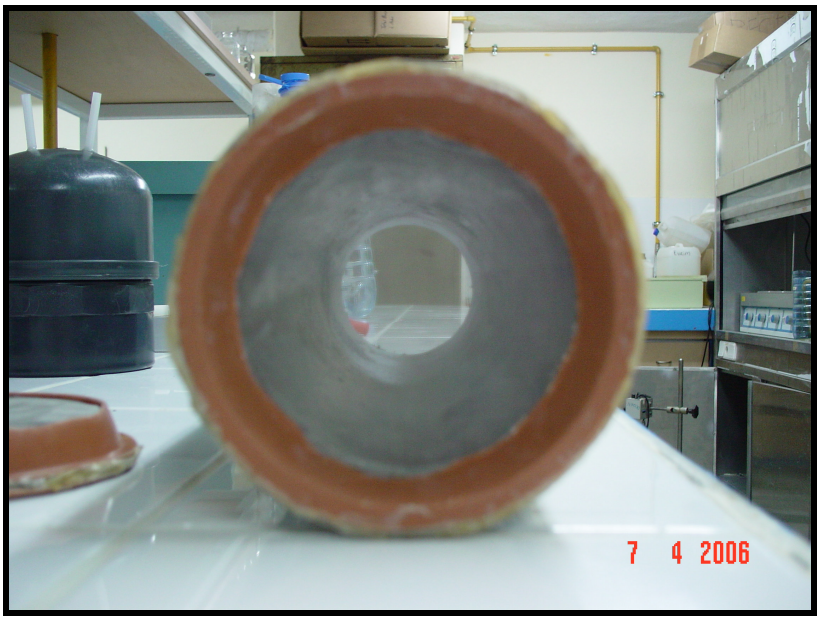

Figure B.3. Stainless steel mesh of pore size of 155 µm

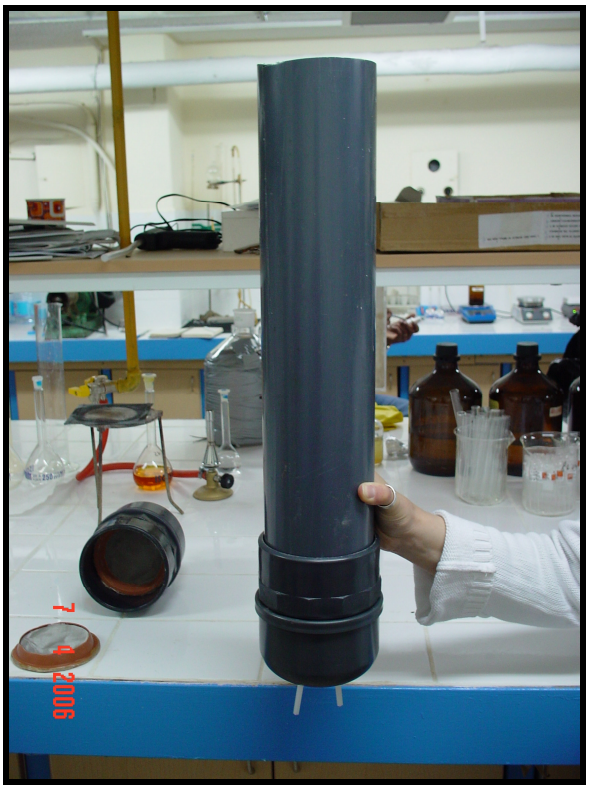

Figure B.4. LBRs used in the experimental study