工學碩士 學位論文

Conditions for Enhanced Acidogenic Fermentation of Food Waste

음식물쓰레기의 고효율 산발효를 위한 환경인자

指導敎授　宋 永 彩

2002年　2月

韓國海洋大學校　大學院
土木環境工學科 禹 靜 熹

Table of Contents

List of Tables

List of Figures

ABSTRACT

전체 생활쓰레기 발생량 중 25.4%를 차지하는 음식물쓰레기는 큰 생분해도와 높은 염분 및 수분함량, 그리고 낮은 발열량 등의 고유한 특성 때문에 수거/운반 및 최종처분에 있어서 악취, 침출수, 유독가스 및 공중보건상의 여러 가지 문제의 근원이 되고 있다. 그러나, 재활용 자원으로서의 가치가 대단히 높아 퇴비화, 사료화 등의 방법으로 재활용하거나 혐기성소화를 이용한 유기산 및 메탄가스생성 등의 방법에 관한 연구가 활발히 진행되고 있다. 본 연구에서는 가수분해효소 및 산발효에 영향을 미치는 인자들을 보다 구체적으로 평가 및 검증하기 위하여 실험실 규모의 중온 산발효조 2기를 이용하였으며, 음식물쓰레기의 산발효 반응에 있어서 가수분해 및 산발효속도, 산발효분율 그리고 산발효물의 조성과 농도에 대한 희석율과 유기물 부하율, 알칼리도의 영향에 대한 연구를 수행하였다. 희석율은 $0.33d^{-1}$ 일 때 가수분해 및 산발효 분율이 각각 55.2%, 54.6%로 가장 높았으며, 희석율 $1.0d^{-1}$에서는 가수분해효소 및 산발효균의 유실로 발효효율이 높지 않았으며, 희석율 $0.25d^{-1}$에서는 발효생성물이 축적되어 가수분해 및 산발효를 저해하는 현상이 관측되었다. 유기물부하율 $5.0 \sim 20g$ $VS/L \cdot day$의 범위에서 산발효효율을 평가한 결과 $10g$ $VS/L \cdot day$에서 가수분해 및 산발효분율이 50%, 41.1% 로 가장 높았다. 희석수에 공급된 알칼리도는 3,000mg/L에서 5,000mg/L 그리고 8,000mg/L as $CaCO_3$로 증가할 때 반응조내 평균 pH는 약 5.3, 6.3, 6.9로 증가하였다. 산발효조의 pH가 약 5.0까지 낮아짐에 따라 총 VFA농도는 증가하였으나, 낮은 pH와 높은 VFA농도에 의해 가수분해 반응은 저해되었다. 생성된 VFA의 주성분은 초산 등의 저급 지방산이었으나 pH가 낮아질 수록 고급지방산 성분이 많았다.

I. INTRODUCTION

In Korea, the food wastes comprising 25.4% of all municipal solid wastes are recyclable resources, so that many studies on the recycling methods such as aerobic/vermi composting, animal feed production and combustion have been performed[1,3,4,5,6,19].   However, application of the recycling technologies to food wastes has been limited because of the waste characteristics including great septicity, high salt and moisture content, and low caloric value.   Some technologies stabilizing food waste anaerobically accompanied by the production of methane or organic acids appear to be a good alternative to the waste management[7].   Yet, the optimum conditions of the anaerobic degradation for food waste are not well documented.   It is usually known that the rate-limiting step controlling the whole degradation process of particulate organics is a hydrolysis step that depends on acidogenesis step.   This means that efficient anaerobic digestion of food wastes could be possible if hydrolysis and acidogenesis of particle organic matters could be improved[8,9,10,11].   According to a recent anaerobic degradation model for particle organic matters, their efficient hydrolysis depended on concentration or activity of hydrolytic enzymes[7].   Moreover, the hydrolytic enzymes are produced by acidogens and are directly proportional to acidogenesis but inhibited by the hydrolyzed products.   It is therefore considered that acidogenesis affects the hydrolysis of particulate organics by thermodynamic equilibrium the hydrolytic and acidogenic products[12,13,14].

1

In this thesis, the effects of dilution rate, organic loading rate, alkalinity and SCOD on the products of hydrolysis and acidogenesis and their production rates were studied to elucidate factors affecting the anaerobic hydrolysis and acidogenesis of food wastes. The results obtained might contribute to development of anaerobic technologies for an efficient management of food wastes.

II. LITERATURE REVIEW

2.1 Food Waste

2.1.1 Food Waste Production and It's Management

In 1995 alone, the amount of domestic solid wastes generated in Korea reached 47,774ton/day which carried 31.6% of food waste (Table 2.1). However, since introduction of the new garbage disposal policy, Pay-as-you-throw」 system in 1996, the amount of food waste has been gradually decreased[1].

Table 2.1 Current status of MSW and food waste production in Korea

Year / Production	'95	'96	'97	'98	'99
MSW(ton/day)	47,774	49,925	47,895	44,583	45,614
Food waste (ton/day)	15,075	14,532	13,063	11,798	11,577
Percentage(%)	31.6	29.1	27.3	26.5	25.4
Production (kg/day·person)	0.34	0.33	0.29	0.25	0.25

Most of the food wastes were disposed through landfill in the year 2000, and about one third of them were recycled.   The amount of recycled food waste amounted to 3,928ton/day and, among the wastes, 2,400ton/day were used for animal feed production, 1,254ton/day for composting and 274ton/day for methane production and others[15].   However, due to a potential outbreak of the Creutzfeldt-Jakob disease, the food waste recycling for animal feed production has been dramatically declined, an alternative technology for food waste recycling becomes necessary.
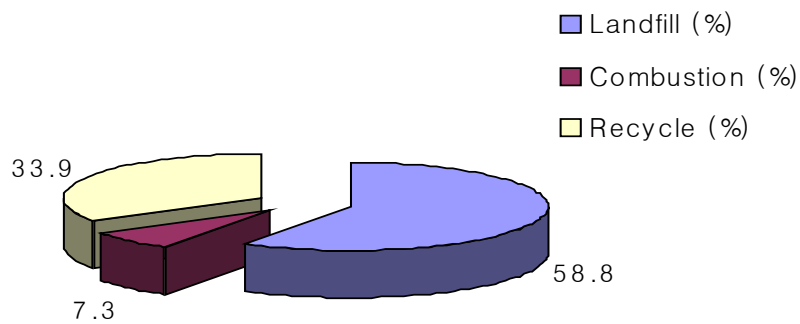
Fig. 2.1 Treatment and final disposal of food wastes in Korea

Several technologies could be used for the reduction and recycling of food wastes.   Drying, extinction and dewatering are common methods to reduce the quantity of food wastes.   On the other hand, animal feed production, composting through drying or fermentation, methane gas recovery and organic acid production using acidogenic fermentation are the typical recycling methods.   The moisture content of food wastes could be reduced

4

to less than 25% by heat-drying, and to less than 40% by fermentation or in composting. In the case of drying animal feed production, the moisture content could be reduced to less than 15%. Although both weight and volume of the waste are reduced to about one fifth, the salt contained in the wastes could be concentrated.   Therefore, the dried food wastes could only be used as a raw material for the assorted animal feed[15].

2.1.2 Characteristics of Food Waste

The food wastes are mainly produced from home, restaurants and feeding facilities, and commonly the wastes consist of vegetable (53.1%, w/w), fish(18.6%) and meat, and a little grain and fruit   residuals[2].   So, the moisture content of the waste is quite high(85%), and the salt content is 3%.   Also, food wastes are much putrescible due to high biodegradability of the main components such as carbohydrate, protein and fat.   These characteristics of the food wastes have caused problems during their collection from sources and their transportation to the processing facilities. The food wastes buried together with other solid wastes causes the second sanitary problems as the generations of malodor, leachate, hazardous gas and pathogens, and hinder the early stabilization of the buried wastes.
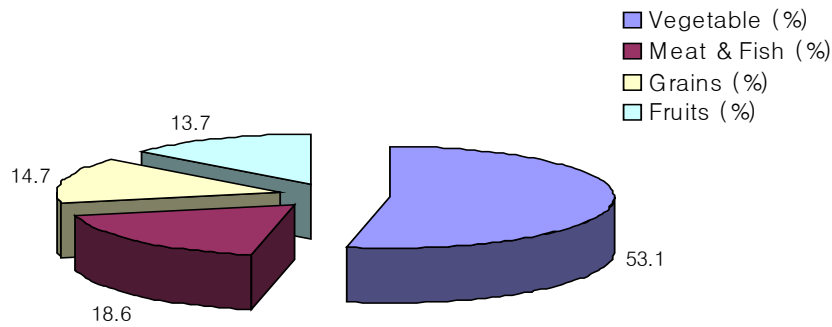
Fig. 2.2 Percentage of food waste main components

2.2 Anaerobic Digestion

Anaerobic digestion of organic matter could be briefly defined as a biological conversion process of organic matters to methane and carbon dioxide in oxygen free condition. However, the anaerobic degradation pathways and the roles of microorganisms in the pathways are not generally clear yet.   Anaerobic degradation process is simply described as a complex series-parallel reaction consisted of hydrolysis, acidogenesis, acetogenesis and methanogenisis[16].   The hydrolysis step of particulate organics in the anaerobic degradation is generally known as a rate-limiting step controlling the overall degradation process and the rate could be affected by temperature, pH, hydrolytic enzymes and organic acids[17, 18].

6

2.2.1 Anaerobic Degradation Pathway

In an anaerobic digestion process, organic matters are degraded by the biological reactions mediated with several anaerobic microorganisms. Fig. 2.3 shows the anaerobic degradation pathways of complex substrates. Anaerobic degradation that is a metabolic process of organic matter by anaerobic microorganisms is slower process than the aerobic degradation. Therefore, for the anaerobic treatment of high solid wastewater, longer retention times are needed to ensure sufficient hydrolysis reaction. In an anaerobic degradation, macroorganic matters such as carbohydrates, lipids and proteins are first hydrolyzed into soluble products including monosaccharides, fatty acids and amino acids. The hydrolytic reactions are performed by extracellular enzymes that are secreted from several acidogenic microorganisms, and the hydrolytic reaction steps are commonly considered as a rate-limiting step due to their slow reaction rates. It is well known that the hydrolysis steps are affected by pH, temperature, hydrolysis enzymes and organic acids[17, 18, 49]. The acidogenic bacteria oxidize or ferment to volatile organic acids, alcohol, carbon dioxide, hydrogen and ammonia the soluble monomers that are generated in hydrolysis step. Methanogenesis is the final step of anaerobic degradation that generates methane and carbon dioxide as the final products from hydrogen and acetic acid. It is known that about 70% of methane gas is generated from acetoclastic methanogens and 30% from hydrogenotrophic methanogens[20, 49].
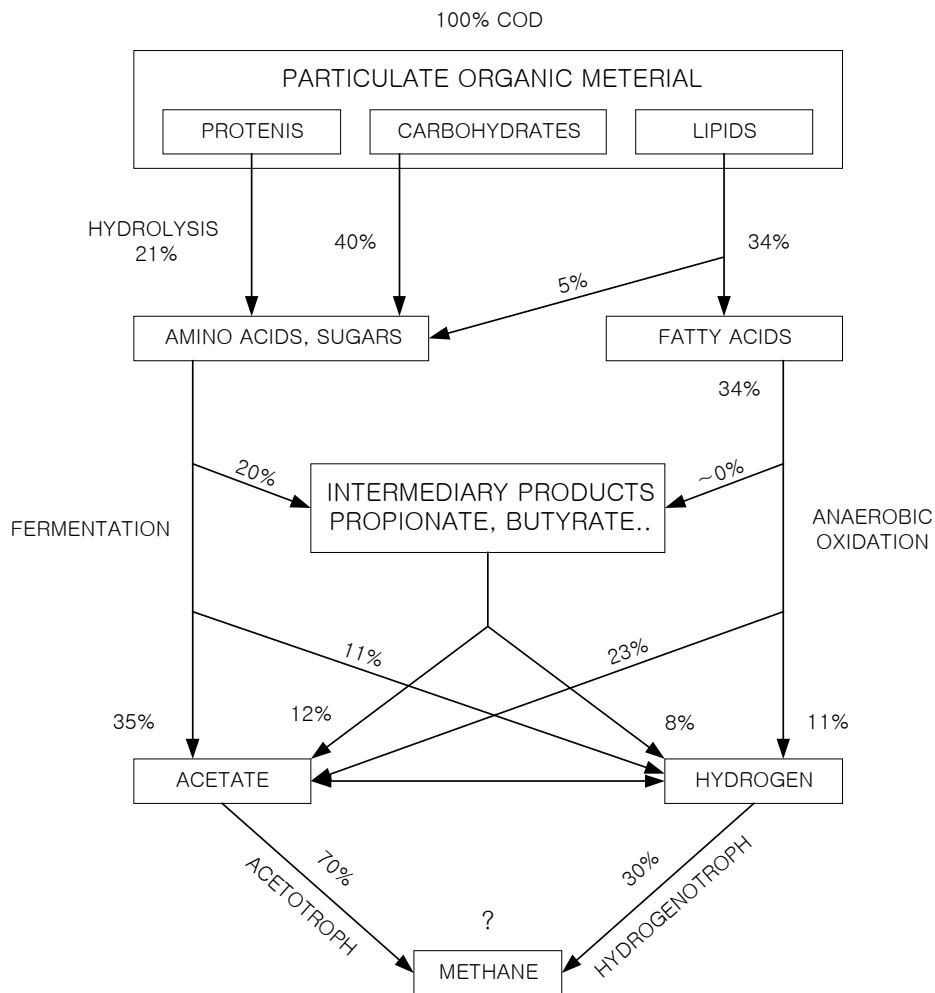
Fig. 2.3 Anaerobic degradation pathway of organic matters

2.2.2 Hydrolysis

Hydrolysis is an enzymatic reaction that is converted macromolecule organic material(carbohydrates, proteins, lipids) into monomer such as monosaccharides, amino acids, glycerol and long chain fatty acids(LCFAs). The hydrolytic enzymes are secreted by acidogenic microorganisms. According to Eastman and Ferguson(1981), in hydrolysis particulate organic matters are converted into soluble substrates, and the hydrolysis step is generally known as a rate-limiting governing overall anaerobic degradation process[14,21].
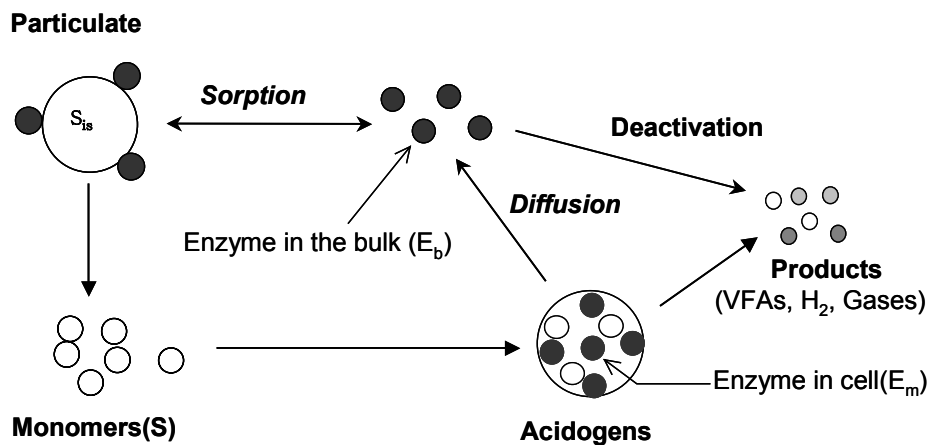
Fig. 2.4 A Model for hydrolysis

The hydrolysis rates of various organic materials are depended upon characteristics of substrates, anaerobic bacterial density, the hydrolytic

enzymes, and the concentration of generated final by-products as well as environmental conditions.   The rate of hydrolysis and acidification as well as the VFA quality could be improved if the environment conditions such as dilution rate, organic loading rate, pH, and external electron acceptor were controlled properly[7,22].

2.2.3 Acidogenesis

Acidogenesis is the reaction that converts the hydrolyzed monomers to short chain fatty acids(C2-C4), alcohol, carbon dioxide and hydrogen to obtain the carbon and energy sources for acidogens growth such as *Syntrobacter woliniiand and Syntrophomonas wolfei*.   The spontaneous acidogenic reactions could occur thermodynamically if the hydrogen partial pressure is maintained at low level because it makes the free energy change for the reaction to a negative value.   Here, the performance of acidogenic reaction depends on hydrogen partial pressure of the system[23].   It is well known that there is a symbiotic relationship between acetogens and methanogens.   The low hydrogen partial pressure could be obtained by the hydrogenotrophic methanogens through consuming hydrogen and carbon dioxide during production of methane.   The acetogenic bacteria convert ethanol, propionic acid, butyric acid to acetic acid and hydrogen.
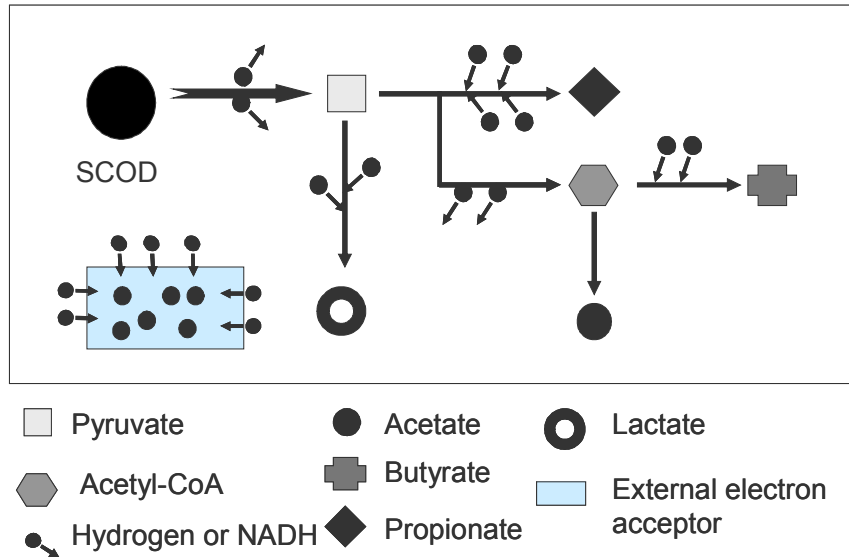
Fig. 2.5 A schematic representation of acidogenesis during anaerobic degradation process

2.2.4 Operational Parameter for Acidogenesis

Studies, undertaken over years to increase the understanding of VFA production, indicated that "acid phase" anaerobic digestion was greatly affected by the operational parameters such as SRT, HRT, temperature, pH, wastewater characteristics, reactor configuration, trace minerals, hydrolysis enzyme, oxidation-reduction potential(ORP) and VFA concentration[10,12, 24,25,26].

(1) HRT

HRT (Hydraulic retention time) is a major environmental factor in hydrolysis and acidification of anaerobic digestion. Generally, more VFA could be obtained at longer HRT, but the maximum production rate of VFA is obtained at shorter HRT. In an acidogenic digester operating at HRTs ranged from 6 to 15 hours, the VFA level increased until 12 hours of HRT, but the level of VFA was decreased at over 15 hours because of the methane produced by methanogenic bacteria. For particulate organic matter, acidogenesis is not affected by the growth of microorganism, but the rate of hydrolysis mainly[27]. Miron Y. et al.(2000) reported that acidogenic condition is more favorable when SRT is below 8 days because most of carbohydrate could be degraded. At 10 days of SRT, LCFAs could be oxidized partially, and methanogenic condition is favorable at over 10days of SRT. Eastman and Ferguson(1981) studied on the hydrolysis and

acidification of sewage sludge in short SRTs ranged from 9 to 72 hours at 35℃, and suggested that fat was not degraded in acid phase, and hydrolysis was a rate-limit step in acid phase of particulate matter. Lilley et al.(1990) reported that the reaction of VFA formation was 1st order and 17% of the influent COD could be converted into VFA at 20℃ and in less HRT than 10 days.

(2) Temperature

Acidogenic digester could be operated at two optimal temperature ranges which are the mesophilic condition of 30~38 and the thermophilic conditions of 55~60. When the acidogenic digester is operated at the mesophilic condition, the VFA loss to methane and the microbial decay rates are less than at the thermophilic acidogenesis, and the mesophilic acidogenesis is more cost effective because of the less heating energy requirement[28]. The phase separation of the acidogenic stage at both the mesophilic and thermophilic conditions was more effective than psychrophilic condition, and the acid compositions were more stable at mesophilic range[29]. Johannesburg, South Africa is a temperate climate zone but the average temperatures during the winter season could drop to a low temperature from 12 to 16℃, causing a decrease in VFA yields[27]. Banister(1998) found that VFA yields from NRAW(1% TS) decreased by 45% at 12℃ compared to the yield observed at 22~28℃ of acidogenic temperature at 6 days of HRT. Skalsky(1995) et al. reported that VFA

13

production at 14℃ was approximately 42% of 21℃.

(3) pH

pH is one of the important factors influcing the efficient anaerobic degradation of organic matter. Generally, metanogenic bacteria are more sensitive to pH than of the acidogenic bacteria. However, pH has so much influenced on the VFA formation or hydrolysis rate [28,30,31,32]. In a general two-phase anaerobic digestion, the optimum pH range for acidogenic digester is pH 5.0~6.0, and pH for methanogenic digester must be kept around pH 7.0[32]. Valerie Penaud et al(1997) are reported that the hydrolysis percentage of protein was 5.7% at pH 5.0 and 82% at pH 9.0, that increased with pH. However, the hydrolysis rate of carbohydrate was 80% at pH 7 and less than 50% in other ranges of pH. Therefore, the optimum pH for overall substrate solubilization was ranged from 8.5 to 9.0, and the maximum VFA concentration was obtained at pH 8. The VFA formation rate was 35~40% at over pH 5.0, and the maximum conversion rate was appeared at pH 6.3. The amount of VFA produced at pH 3.6 was half of the pH 5.0. The values of pH in acidogenic reactor have an influence on the composition of VFA. They reported that the HAc in produced VFA was 83% at pH 7.0, but decreased to 60% and 33% at 6.5 and 6.3, respectively. The acidogenic system has some buffering capacity, and the pH could be maintained at 5.0~ 7.0 even if the system pH was not

controlled by addition of acidic or alkaline material.   However, the pH value depends on the acidogenic conditions including substrate characteristics[30,31,28].

(4) VFA Concentration and Hydrolysis Enzyme

Many investigators have shown that VFA concentration is one of the most important parameter in anaerobic digestion[25,26].   There are many studies on the inhibitory effect of VFA on the acidogenesis, and the pH drops in the anaerobic digester are mainly originated from the produced VFA.   It is also believed that the intensity of VFA inhibition depends on pH determining the content of undissociated acid[33, 34].   Wang and Wang(1983) reported that the inhibitory effect of the undissociated acetic acid on the acidogenesis was higher than of the dissociated acetate ions. They argued that the inhibitory effect at the lower pH than 6.0 was mainly originated from the undissociated acid, but at over 6.0 of pH, from the dissociated acid ion.   In the hydrolysis of particulate materials, Denals A. et. al (1996) reported that the influent PCOD in the first reactor, introducing a wastewater containing 90% of PCOD, can be removed up to 50% within 4 hours with one tenth of returned biomass from the second reactor in two stage reactor system.   This indicates that the slowly degradable particulate material could be hydrolyzed at higher ratio of biomass to substrate.   Also, Llabres-Luengo et al (1988) proposed the hydrolysis kinetic model that the hydrolysis rate was proportional to the substrate volatile solids and the biomass and inversely to the VFA concentration.   They concluded that the

15

VFA inhibition governed the hydrolysis kinetics, but did not distinguish the effects of pH and VFA[22,35].

2.2.5 Anaerobic Digestion of Organic Wastes

In the last ten years, the comprehension on anaerobic microorganism has been much increased, and the improvements in the process control and the optimization of anaerobic system have been made.   In particular, there was significant technological improvement for the start up and the stability in the anaerobic digestion system.   Moreover, some novel high rate anaerobic systems were developed, and have been used for sewage sludge and organic solid waste as well as lots of industrial wastewaters from sugar, starch, alcohol, paper and food industries.

Raynal(1998) studied on the influences of HRT, pH, load for vegetable and fruit peeling (potato peelings, green salad leaves, green peas mixed with carrots, apple pomace) with two-phase anaerobic digestor at 35℃, and determined the feasibility and performances of a two-stage fermentation process applied to the degradation of vegetable solid wastes including multiple liquefaction reactors and a central methanizer.   On average, hydrolysis yields were high up to 80%(except for apple pomace), and the acidogenic effluents were degraded in a methanation reactor to an extent of 80%.   Overall organic matter removal reached 87% in 4g COD/L·day of

loading rate, and 17days of HRT.   It has been considered that anaerobic digestion is available to treat vegetable solid wastes with a high hydrolytic yield.

Adrie Veeken et. al(2000) performed a study about anaerobic hydrolysis rate of MSW(Municipal Solid Wastes) at fixed VFA concentrations ranging from 3 to 30g COD/L and fixed pH values between 5 and 7.   In this experiment, it was found that the hydrolysis rate constant was pH dependent but was not related to the total VFA and undissociated VFA concentrations. On the other hand, neither VFA(total or undissociated) nor starting material had a statistically reliable effect on the hydrolysis rate of biowaste within pHs of 5 - 7 and VFA concentrations of 3 ~ 30g COD/L.   These findings imply that the pH is the primary variable in controlling the hydrolysis rate of the anaerobic solid state fermentation process, not the VFA concentration. However, the severe inhibition was always accompanied by not only high VFA concentrations, but also low pHs (5.0~5.5)[38].   According to de Baere et al. (1985), the maximum concentration of organic acids that can be attained in anaerobic digestion is 30 g/L.   Also, ten Brummeler et al. (1991) found that hydrolysis of biowaste were severely inhibited under VFA concentrations up to 33 g/L.   Veeken and Hamelers (2000) also reported that a complete inhibition of anaerobic hydrolysis of biowaste was obtained at VFA levels of 40~50 g VFA-COD/L.

Hang-sik Shin et al. (2000) studied the acidogenic performance of food waste by rumen microorganisms in the leaching bed reactor and then compared with that by mesophilic acidogens.   When a rumen microorganism was used as the inoculum, the maximum acidification

efficiency was 71% in dilution rate 3.0 d^{-1} and the first order kinetic constant was 0.1149 d^{-1}.   While, the maximum efficiency in the reactor inoculated with mesophilic acidogens was 59.8% in dilution rate 4.5 d^{-1} and the first order kinetic constant was only 0.0677 d^{-1}.   This indicates that the performance of acidogenic system could be enhanced by use of rumen microorganisms as an inoculum.

Recently, researches have been focused on the anaerobic co-digestion of organic solid waste and sewage sludge[6,39,40,41,42,43].   The co-digestion has some economical benefits including the use of the existing facilities to treat other waste and the improvement of the performance making up the deficient organic loading rate of the existing process[48,46]. Therefore, the substrates applying co-digestion are gradually expanded from organic solid waste including food wastes and sewage sludges to the various industrial wastes[39,44,40,42,45,46,43,47].

III. MATERIAL and METHOD

3.1 Food Waste and Seed Sludge

The food waste used in the study was obtained from a dining hall in Korea Maritime University, and the impurities including plastic bags, chopsticks were removed. The waste was macerated after dilution with tap water(1:1 as weight), and then screened with a sieve of 4mm opening. The initial characteristics of the prepared food waste such as pH, TS, VS, TCOD, SCOD, alkalinity and TKN were measured, and then was stored in a 4 °C refrigerator up to a week(to prevent the denaturalization until feeding into the reactor). The seed sludge was obtained from an anaerobic digester of S municipal wastewater treatment plant in Busan metro-city, and used as the inoculum for the acidogenic reactor after the analysis of initial characteristics.

Table 3.1 Characteristics of food waste and seed sludge

Contents	pH	TS(mg/l)	VS(%)	TCOD (SCOD) (mg/l)	Alkalinity (mg/l)	TKN (mg/l)
Food waste	5.28	80,595.3	94.8	204,575.3 (91,500.8)	3,900	2,800
	Vegetable(40.1%), Grain(39.1%), Meat and fish (20.8%) (Wide daily variation)					
Seed sludge	7.46	30,046	43.9	21,320 (14,573)	2,187	130.8

Table 3.1 shows the average characteristics of the food waste and the seed sludge. The main composition of food waste greatly changed everyday, but the average contents of vegetable and grain were higher than those of meat and fish. The average pH of food waste and seed sludge was measured as 5.28 and 7.46 respectively, and VS/TS ratios were 94.8% for the food waste and 43.9% for the inoculum sludge.

3.2 Experimental Apparatus

Two sets of lab-scale acidogenic system were used in this study and the schematic diagram is shown in the Fig.3.1. The acidogenic reactor was a continuous stirred reactor type and was made of acrylic acid resin with 13L of the working volume. On the upper plate of the reactor, an air sealed feeding hole was made to feed the food waste and to minimize the inflow of air. The reactor was coiled a heating conduction line on the surface of the reactor, and then set a temperature sensor in the reactor content to maintain the reaction temperature at 35±2 °C during the experiment. A peristaltic pump was installed between dilution water tank and lower part of the reactor, and used to supply dilution water into the reactor. A water displacement gas chamber making the collection and the quantification of the biogas possible was connected to the cover of the reactor by a rub tube.
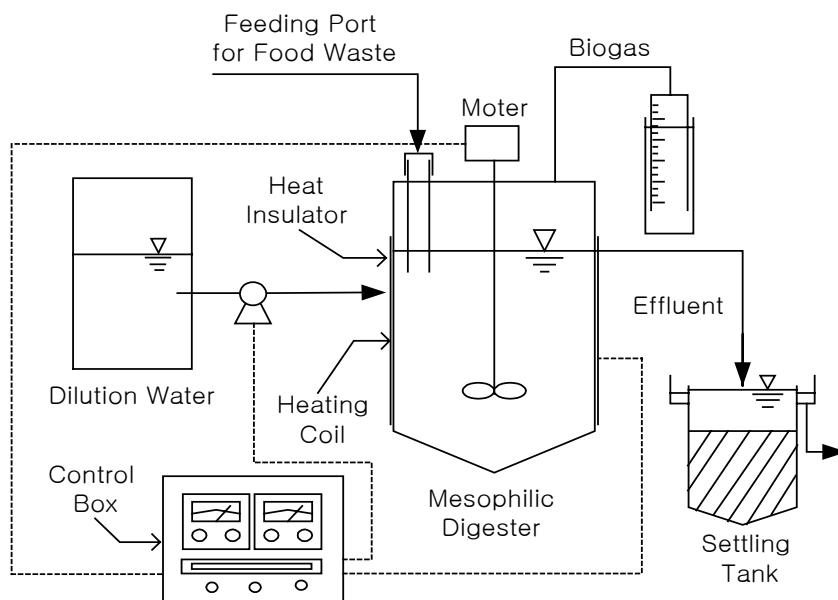
Fig. 3.1 Schematic diagram of a lab scale acidogenic digestor

Fig. 3.2 Photograph of the lab scale acidogenic digestor

3.3 Operation Methods

Prior to the start-up of the acidogenic system, 30% of the effective reactor volume was loaded with the seed sludge. The pre-treated food waste was intermittently added by hands to the acidogenic reactors once a day, and the dilution water containing alkalinity was continuously added to the reactor with a peristaltic pump to prevent the accumulation of VFAs and other products as well as the rapid pH drop during the acidogenisis. The fermented content was taken from sampling port everyday and total VFA, pH and SCOD were measured to monitor the stability of acidogenic reactor. When the system was approached to a steady state, the content of reactor was sampled several times by 2~3 hours of time intervals during a feeding cycle, and analyzed TS, VS, Total VFA, COD, alkalinity, pH, TKN, ammonia, etc.

The percentage of hydrolysis(%) was defined by the ratio of the produced SCOD(gr) and the added TCOD(gr) for a feeding cycle. Therefore, the equation of hydrolysis(*Hyd(%)*) is expressed in grams of COD(g), and as the production of hydrogen and methane are relatively small, the contributions of both components were neglected for the estimation. The equation is as following.

$$Hyd \ (\%) = \left[\sum_{i=1}^{n} Q_i S_{si} \Delta t_i \ \middle/ FS_0 \right] \times 100$$

Where, Ssi and Qi are the SCOD in the effluent and the flow rate of dilution water at time ti and F, and S_0 indicated the volume and the TCOD of the feeding waste[3].

The percentage of acidification(*Ac(%)*) was estimated by the ratio of the produced total VFA and the SCOD(gr) of the monomer in the discharged dilution water.

$$Ac(\%) = \left[(\sum_{i=1}^{n} Q_i S_{ai} \Delta t_i - FS_{a0}) \middle/ (\sum_{i=1}^{n} Q_i S_{si} \Delta t_i - FS_{a0}) \right] \times 100$$

Where, Sai and Sa_0 are the total VFA in the effluent at time ti and the VFA of the feeding waste[3].

3.3.1 Effect of Dilution Rates for Acidification of Food waste

In order to test the effect of dilution rate on the food waste acidification, the flow rate of dilution water supplying into the acidogenic reactor was controlled to 1.0, 0.55, 0.33, and 0.25/day. The alkalinity and sulfate containing in dilution water was maintained to 8,000 mg/L as $CaCO_3$, and 350mg/L, respectively. In the previous study, the sulfate could be used as an electron acceptor and was an effective way to accelerate hydrolysis and acidogenesis. The organic loading rate by adding of food waste was kept at 5g VS/L·d through the dilution rate study.

24

3.3.2 Effect of Organic Loading Rate, Alkalinity on Acidification of Food waste

The effects of organic loading rate on the hydrolysis and acidogenesis were studied at the loading rates of food waste into the acidogenic reactor ranged from 5g VS /L·d to 20g VS/L·d. The dilution water supplied continuously into the acidogenic reactor contained 8,000mg/L of alkalinity and 350mg/L of sulfate, and the dilution rate was constant as 0.33/day.

In order to study the effect of pH on the hydrolysis and acidogenesis, the organic loading rate was maintained to 5g VS/L·d, and the alkalinity values of dilution water controlled to 3,000mg/L, 5,000mg/L and 8,000mg/L as $CaCO_3$. The sulfate concentration contained in the dilution water was kept to 350mg/L and the dilution rate was 0.33/d.

3.4 Analysis

The concentrations of TS, VS, TCOD, SCOD, Alkalinity, TKN and ammonia were determined according to Standard Methods basically. The pH was immediately measured after sampling with pH meter(Orion 370). The generated biogas was measured using gas collector of water displacement type. Total VFAs were determined according to a titration method proposed by Anderson and Yang(1992), and the compositions of VFAs were analyzed by HPLC with Aminex HPX-87H column(300×7.8mm, BIO-RAD) and 0.005M(or 0.008M)H_2SO_4 as the solvent. The sulfate, Ortho-P, nitrate were analyzed by Ion Chromatography, DX-500 equipped with CD-20.

VI. RESULTS and DISCUSSION

4.1 Effect of Dilution Rate for Hydrolysis and Acidogenesis

The influences of dilution rate on the hydrolysis and acidogenesis were studied at 1.0, 0.55, 0.33 and 0.25/day of the dilution rate through monitoring the characteristics of the reactor content during a feeding cycle. The characteristics of the reactor content including pH, VFA and SCOD were stable, indicating the steady state, in the 30th day after the start-up operation.

Fig. 4.1.1 and Fig. 4.1.2 show the pH and SCOD in acidogenic reactor depending on the dilution rates. The values of pH were around 6.7 and 6.8~7.1 at 0.25/d and 0.33/d of the dilution rate, respectively, but the value was a little increased with the increase of the dilution rate from 0.55 to 1.0/day. The peak value of SCOD was observed within 1-3hours after feeding of food waste, and then gradually decreased as shown in Fig. 4.1.2. The maximum values of SCOD were 6,021mg/L, 13,362mg/L, 18,271mg/L and 41,146mg/L at 1, 0.55, 0.33 and 0.25, respectively, indicating the value was inversely proportional to the dilution rate because of more accumulation of the hydrolysis products at lower dilution rate.
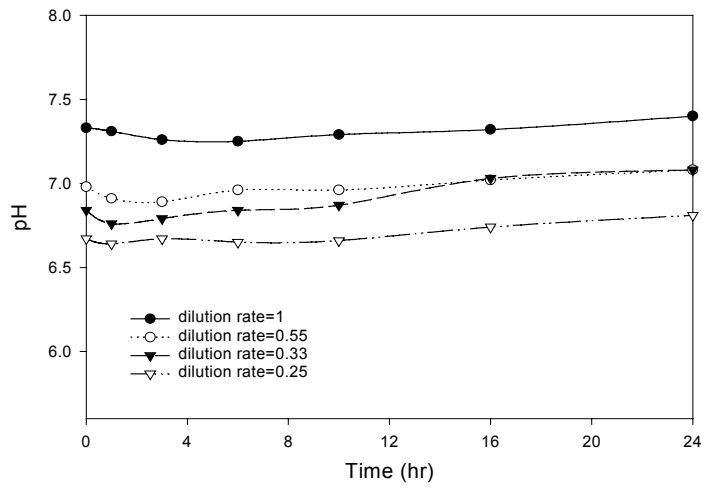
Fig. 4.1.1 Trends of pH during the acidogenesis of food waste under various
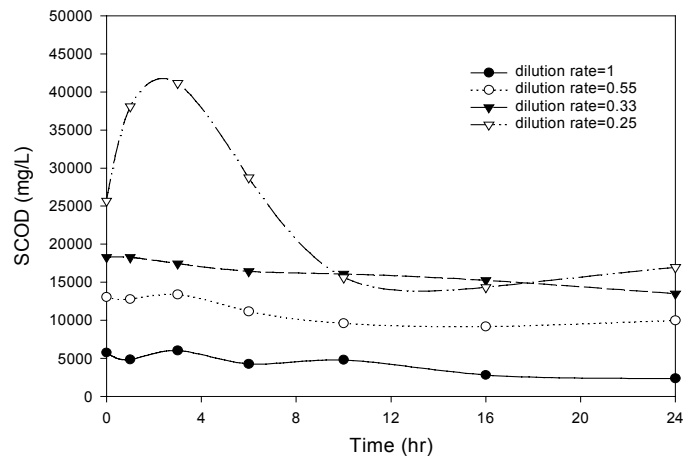
dilution rates

Fig. 4.1.2 Accumulation of SCOD from food waste hydrolysis under various

dilution rates

28

Fig. 4.1.3 shows the trends of VFA for 24 hours after feeding of food waste. The value of VFA was significantly affected by the dilution rate like that of SCOD.
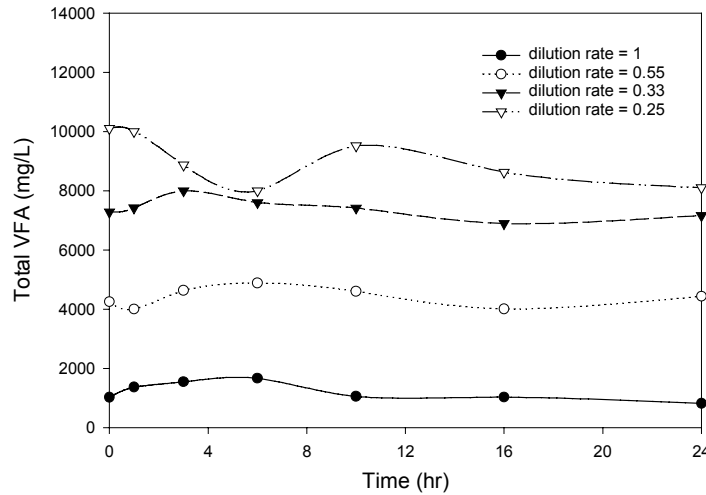

Fig. 4.1.3 Effect of dilution rates on VFA production in
acidogenic ferment

Fig. 4.1.4 illustrates the rates of hydrolysis and acidification. The percentage of hydrolysis was no more than 25.5% at 1.0/d of dilution rate, but increased to 55.2% at 0.33/d of the dilution rate. However, the percentage decreased to 42.6% when the dilution rate was decreased to 0.25/d. These results showed that the production of hydrolytic enzyme from acidogens was inhibited by the high concentration of hydrolyzed products at 0.25/d of the dilution rate as shown in Fig.4.1.2. However, the percentage of acidification of hydrolyzed products increased from 34.5% to

59.3% when the dilution rate decreased from 1.0 to 0.25/d, respectively. This resulted from the washout of acidogens at higher dilution rate such as 1.0/d, which was led to lower production of hydrolytic enzyme. Furthermore, the average pH at 1.0/d of the dilution rate was 7.3 that was a little higher than the optimal values for acidogens reported in literature.
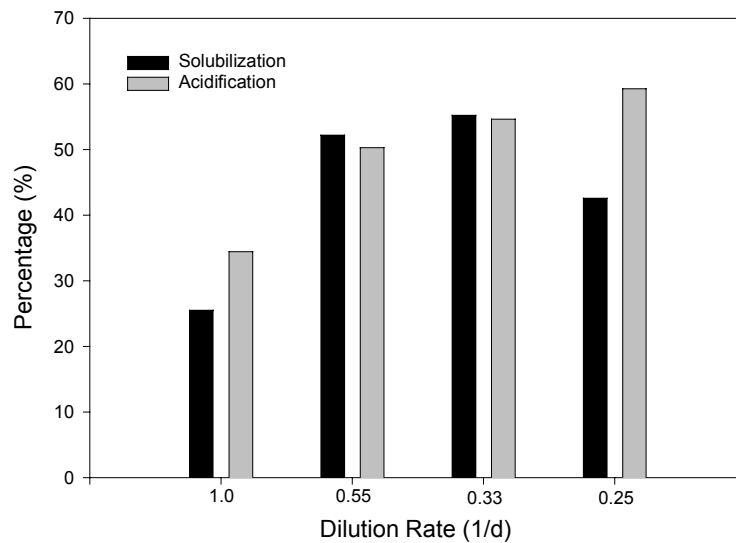

Fig. 4.1.4 Comparison of hydrolysis and acidification of food waste under various dilution rates

Therefore, it was concluded that the optimum dilution rate for the hydrolysis and acidification of food waste are 0.33/d.   Sarada, et al. (1995) reported that 4days of HRT for acid formation was a little more suitable than 8days, and Ghosh et al. (1978) also reported that the HRT of acidogenic process for cellulosic waste was optimized at 4~6days.   Andrews et al. (1965) reported

that the production of VFA was increased with the increase of HRT until 2.4 days.　Therefore, it was considered that the optimum HRT of acidogenesis depends on the characteristics of substrate.
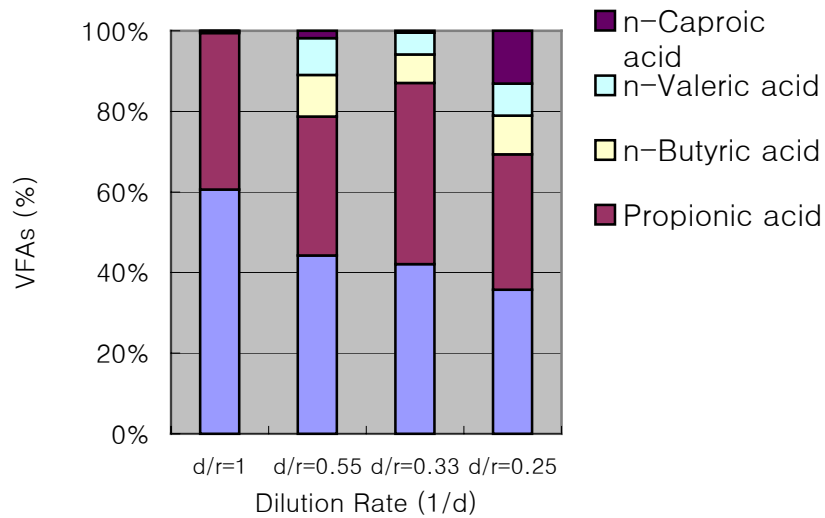

Fig. 4.1.5 Effect of dilution rate on the VFA composition

Fig. 4.1.5 and Fig. 4.1.6 show the VFAs composition(%) and concentration according to the dilution rate.　The major components of VFA were short chain fatty acids including acetic acid and propionic acid at 1.0/d of the dilution rate.　However, the percentage of the long chain fatty acids such as valeric acid, caproic acid gradually increased when the dilution rate decreased from 0.55 to 0.25.　The concentration of VFA increased with the increase of the dilution rate and showed the highest as

31

9,028mg/L as HAc at 0.25/d of the dilution rate as shown in Fig. 4.1.6. Akashah, et al. (1997) reported that the content of propionic acid and valeric acid in acidogenic digester decreased with the increase of the dilution rate[50].
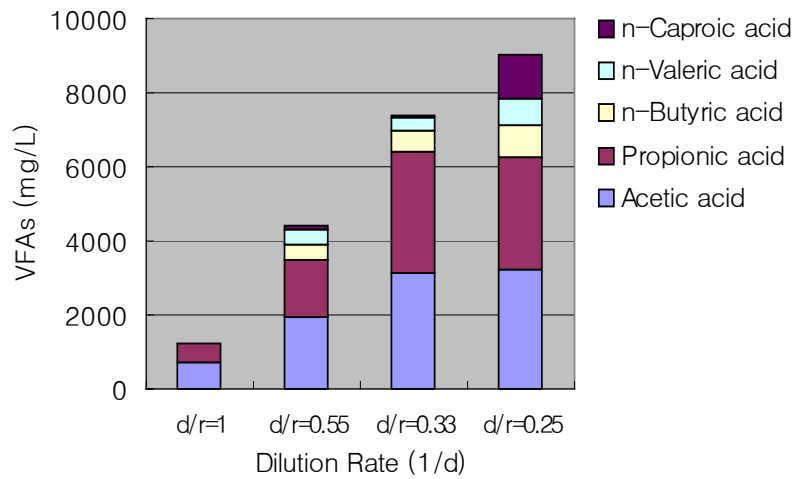

Fig. 4.1.6 Accumulative levels of VFA components under
various dilution rates

4.2 Organic Loading Rate

The acidogenic reactor was run at various organic loading rates from 5g VS/L·d to 20g VS/L·d.　The dilution rate and alkalinity were maintained at 0.33/d and 8000mg/L as $CaCO_3$, respectively.　The hydrolysis and acidogenic performance of the reactor was reached to the steady state in 30th days.　The effect of organic loading rate on the hydrolysis(%) and acidification(%) of food waste was summarized in Fig. 4.2.1.
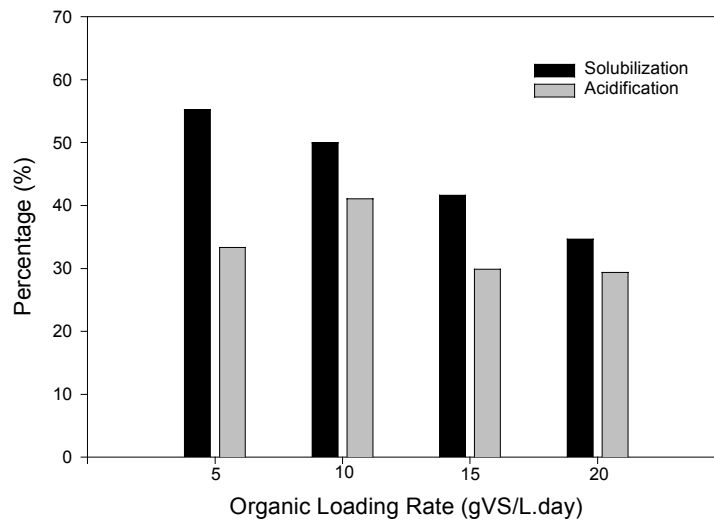

Fig. 4.2.1 Comparison of hydrolysis and acidification under various organic loading rates

When the organic loading rate was 20g VS/L·d, the percentage of hydrolysis was no more than 34.7%, but it was increased to 55.2% at 5g VS/L·d of the organic loading rate. The content of VFA in the hydrolyzed products, SCOD also increased from 29.4% to 41.1% according to the decrease of the organic loading rate from 20g VS/L·d to 10g VS/L·d but it was decreased about 17% at the loading rate 5g VS/L·d. These results indicate that the performance of hydrolysis and acidogenesis was significantly dependent on the organic loading rate.

Fig. 4.2.2 shows the SCOD behaviors from various organic loading rates. The SCOD was showed from 14,624mg/L to 18,271mg/L at 5g VS/L·d of organic loading rate, and at 10g VS/L·d of organic loading rate, it was the highest as 31,584mg/L at about 3 hours after the feeding, and then gradually decreased. At 15g VS/L·d and 20g VS/L·d of the loading rate, the highest SCOD appeared in an hour, then gradually decreased from 46,604mg/L to 38,192mg/L and from 51,198mg/L to 37,364mg/L, respectively. At 10g VS/L·d of the loading rate, about 11,000mg/L of the SCOD was higher than for 5g VS/L·d, and over 15,000mg/L of the SCOD at 15g VS/L·d of the loading rate was higher than for 15g VS/L·d. However, the value of SCOD at 20g VS/L·d of the loading rate was not much different from that at 15g VS/L·d. It means that the hydrolysis at over 20g VS/L·d of organic loading rate might be inhibited by the high concentration of hydrolyzed products. Also, as shown in Fig 4.2.1, the percentage of hydrolysis was highest at 5g VS/L·d of the loading rate of which SCOD value was lowest. This implied that the hydrolysis could be stimulated by the shortage of the hydrolysis products.
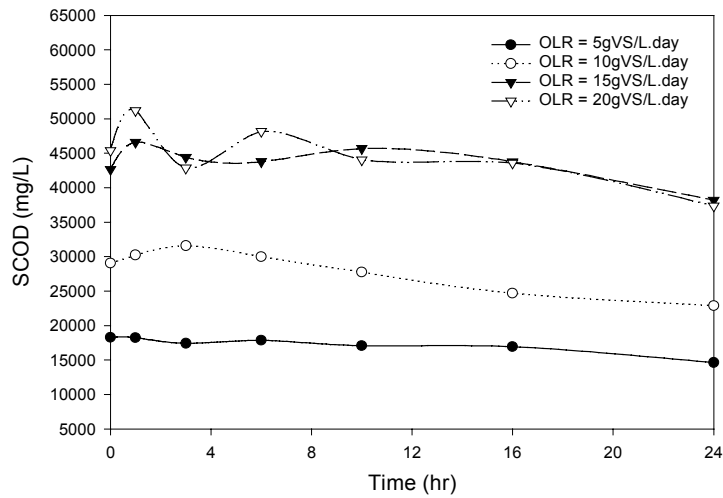
Fig. 4.2.2 Effect of organic loading rate on the hydrolysis of particulate
food waste in acidogenic reactor

Fig. 4.2.3 and Fig. 4.2.4 show total VFA and pH depending on the organic loading rate. Total VFA rapidly increased between 1 and 3 hours after the feeding, but there are some differences according to the loading rates. The trends of pH were the reciprocal curves with the VFAs. When the total VFA began to decrease slowly after 3 hours, and pH increased slowly too. The highest values of the VFA at various organic loading rates were 4,746mg/L at 5g VS/L·day, 8,140mg/L at 10g VS/L·day, 8,204mg/L at 15g VS/L·day and 7,830mg/L at 20g VS/L·day of the loading rate.
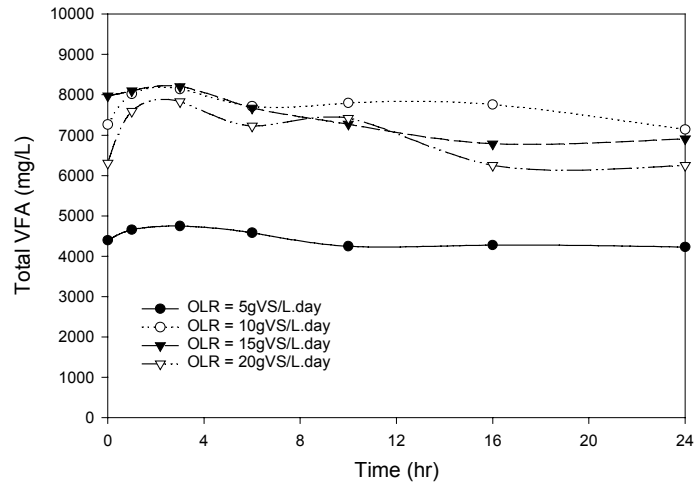
Fig. 4.2.3 Effect of organic loading rates on the acidogenesis
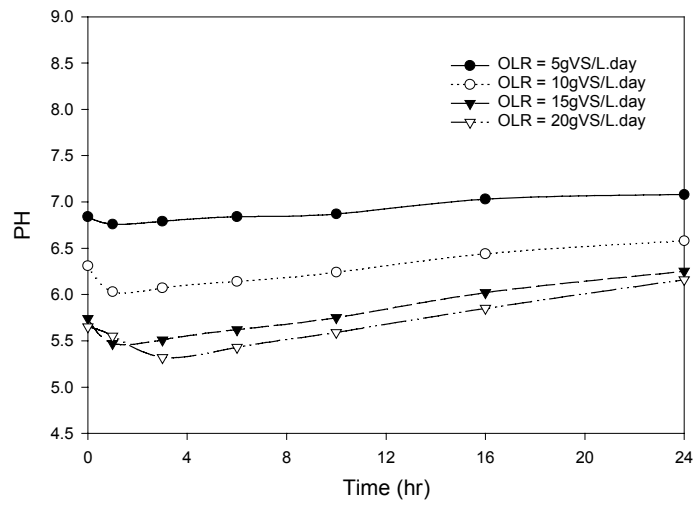
of hydrolyzed monomer

Fig. 4.2.4 Behaviors of pH in the acidogenic reactor at various

organic loading rates

In a previous study(Daigger, 1995; Banister et al., 1998), the higher VFA yields could be obtained by the decrease of solids concentration in the acidogenic reactor. This might result from the better mixing of the reactor or the reduction of inhibitory substance in the dilute reactor. In this study, the lower VFA was obtained at 15g and 20g VS/L·day of the loading rate in which the SCOD was higher than 10g VS/L·day. It could be also considered that the production of hydrolytic enzyme by acidogens could be inhibited by concentration of hydrolysis products, which inhibited acidification from low hydrolysis. These results were in agreement with the hypothesis of hydrolysis and acidification model mentioned in the introduction.
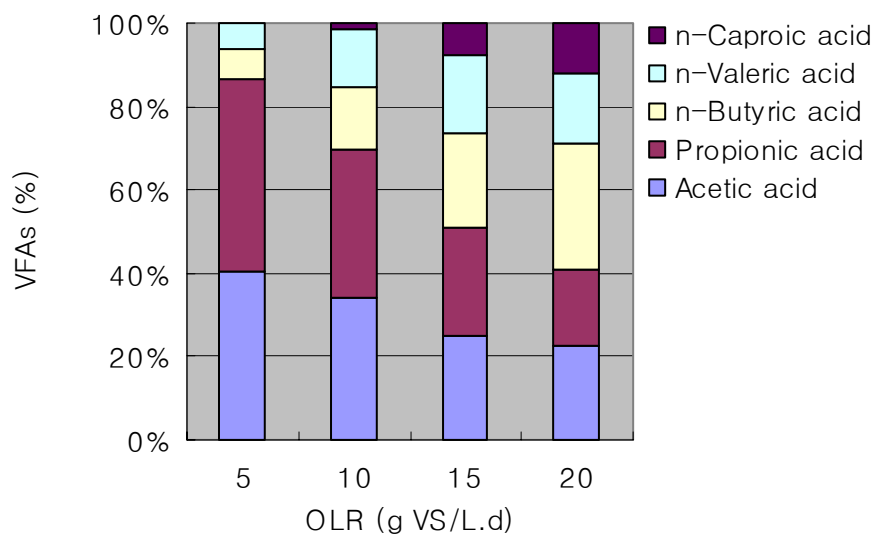
Fig. 4.2.5 Effect of OLR on the contents of VFA components from
acidogenesis of food waste

Fig. 4.2.5 shows the VFAs composition(%) according to the organic loading rate.　When organic loading rate was 5g VS /L·d, the major components were short chain fatty acids such as acetic acid and propionic acid.　However, according to the increase of organic loading rate up to 20g VS/L·d, the contents of caproic acid, valeric acid and butyric acid were increased.

4.3 pH and alkalinity

In order to investigate the influence of pH on the hydrolysis and acidogenesis and to determine the proper alkalinity requirement, the alkalinity of dilution water entering into the acidogenic reactor varied to 3,000mg/L, 5,000mg/L and 8,000mg/L as $CaCO_3$.

Fig. 4.3.1 and Fig. 4.3.2 show the pH and the total VFA, respectively, at various alkalinity.　At 3,000mg/L as $CaCO_3$ of alkalinity, the pH values rapidly decreased to 5.1 in about an hour after the feeding of food waste and then gradually recovered up to 5.5.　At 5,000mg/L as $CaCO_3$ of the alkalinity, the dropped and recovered pH values were 6.1 and 6.5 and at 8,000mg/L as $CaCO_3$, the values were 6.8 and 7.1, respectively.
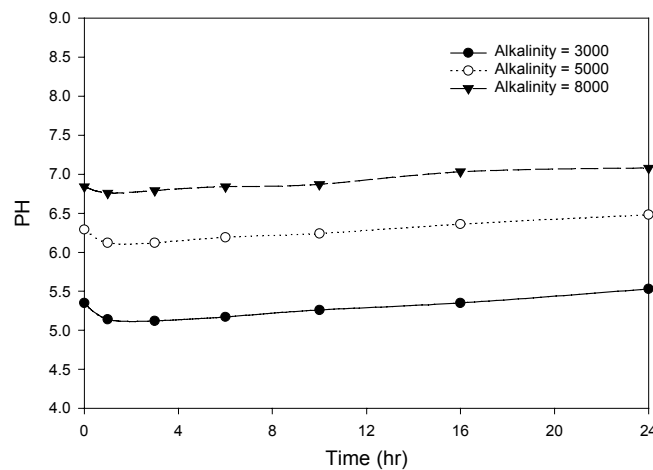
Fig. 4.3.1 Effect of alkalinity on the pH in the acidogenic reactor
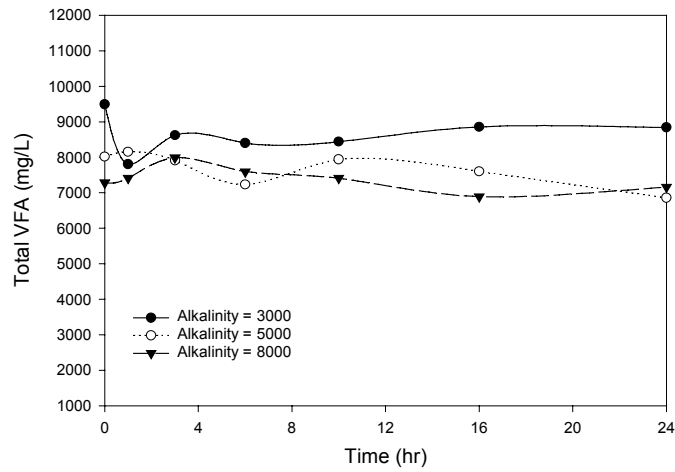
Fig 4.3.2 Behaviors of volatile fatty acids at various alkalinity

Fig. 4.3.2 shows the total VFA at various alkalinity contained in the dilution water for the feeding cycle. At 3,000mg/L as $CaCO_3$ of the alkalinity in the dilution water, total VFA was 7,806~9,486mg/L as HAc. However, when the alkalinity increased to 5,000mg/L and 8,000mg/L as $CaCO_3$, total VFAs were maintained at a little lower ranges as 6,860~8,152mg/L and 6,886~7,992mg/L as HAc, respectively. Mosey et al. (1983) reported that there were so many kinds of acidogens which could endure the environmental changes, and the optimum pH for acidogenesis was a weak acidic conditions[3,51].

Fig. 4.3.3 shows the SCOD behavior at various alkalinity of dilution water entering into the acidogenic reactor.　At 3,000mg/L as CaCO_3 of alkalinity, the SCOD was the highest as 14,244mg/L at the early stage after the feeding, and then gradually decreased to 12,906 mg/L.　At 8,000mg/L as CaCO_3 of the alkalinity, the trend of SCOD was similar to that of 3,000mg/L as CaCO_3.　However, the highest value of SCOD at the early stage was higher as 18,272mg/L and the final SCOD at the end of the feeding cycle was also higher as 14,624 mg/L than that of 3,000mg/L as CaCO_3.　This result indicates that the neutral range of pH is a little more favorable to soluble the particulate food waste than the acidic condition such as pH 5.1~5.5.
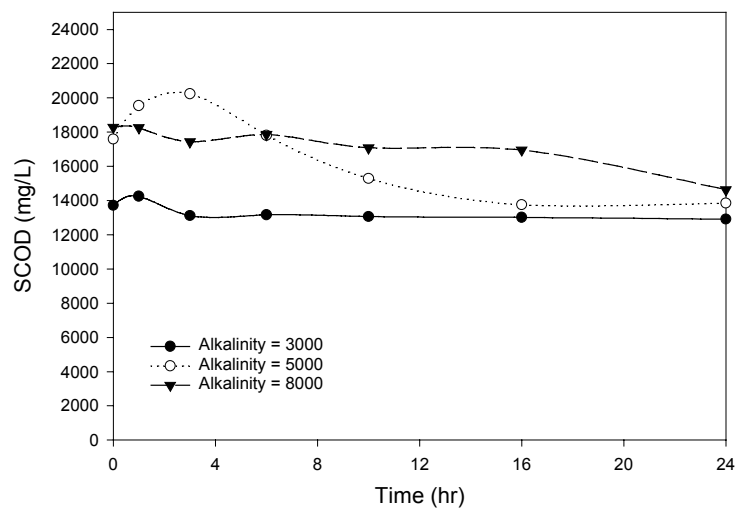
Fig. 4.3.3 Trends of SCOD with time at various alkalinity

The effect of pH and alkalinity on the hydrolysis and acidogenesis was summarized in Fig. 4.3.4. The percentage of hydrolysis increased from 32% to 55% according to the increase of the alkalinity from 3,000mg/L to 8,000mg/L as CaCO3. However, the VFA percentage of the SCOD was higher as 82.2% at 3,000mg/L of the alkalinity in the dilution water. Above results indicate that the proper requirement of alkalinity for the acidogenesis of food waste could be changed according to the purpose of the acidogenic reactor.

Fig. 4.3.4 Summary of alkalinity effect on the hydrolysis and acidogenesis of food waste

This is in agreement with the previous study about two-phase anaerobic digestion of vegetable residues (Raynal et al., 1998).   They observed that volatile fatty acids could rapidly be converted into methane at pH 6.5 and then the pH was increased.   Th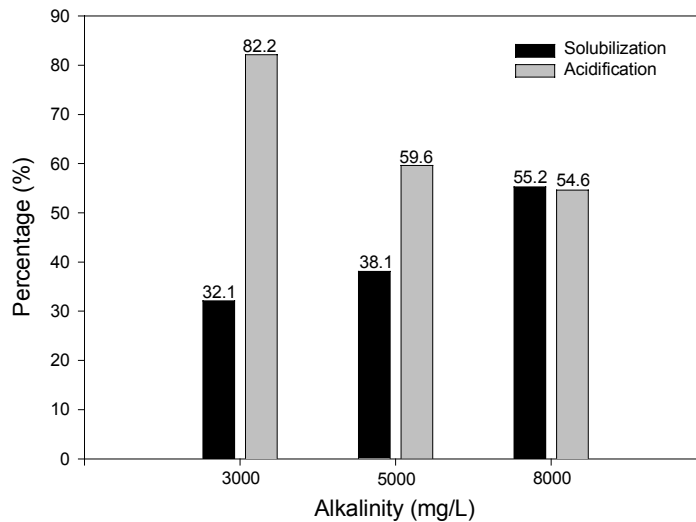e restriction of methanogenic activity in acidogenic reactor was achieved by lowering the pH to 5.5, and the level of VFA could be accumulated up to 11.47 g/L.   Veeken et al. (2000) reported that VFA levels were 3 and 10 g VFA-COD/L at pH 6.0 and pH 7.0, respectively.   The rate of the solubilization was almost equal to the rate of acidogenic fermentation and accumulation of the monomeric products was not observed[38,52].   In this study, the result showing the lowest hydrolysis rate at alkalinity 3000mg/L as $CaCO_3$ indicates that the hydrolysis could be inhibited by low pH and high VFA concentration.   In previous studies[11,36,37], the VFA levels inhibiting the hydrolysis was commonly 30~50g VFA-COD/L.   However, in this study, there were some differences as 18g VFA-COD/L, 14g VFA-COD/L and 12g VFA-COD/L at alkalinity 3,000, 5,000 and 8,000mg/L as $CaCO_3$.   This reflects the effects of pH on the hydrolysis of food waste.   Therefore, both VFA level and pH should be considered to better describe the hydrolysis and the acidogenesis of particulate matter.

Fig. 4.3.5 and Fig. 4.3.6 shows the effect of alkalinity on the composition of organic acids.   The dominant VFAs were acetic acid and propionic acid, but the compositions of VFA was significantly affected by the alkalinity.
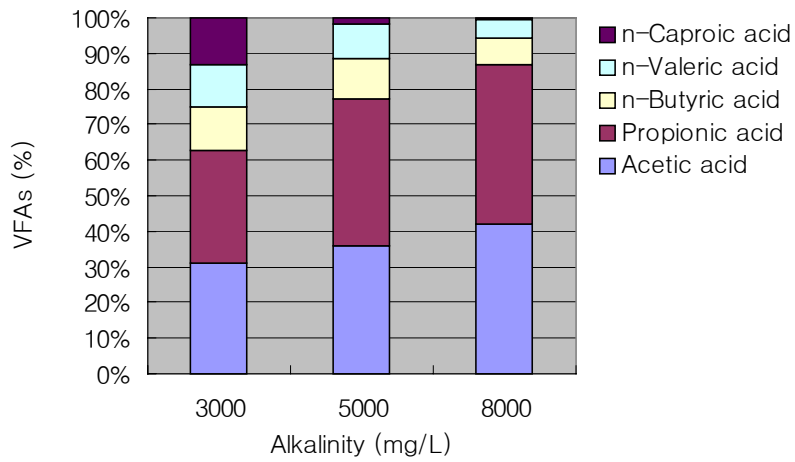
Fig. 4.3.5 Effect of alkalinity on the contents of VFA components

from acidogenesis of the food wastes

The total concentration of VFA was the highest at the lowest alkalinity as 3,000mg/L as $CaCO_3$, but the content of long chain fatty acids such as valeric acid and caproic acid were much in the fermented effluent. Conversely, when alkalinity was 8,000mg/L as $CaCO_3$, the total VFA was a little less than that of 3,000mg/L as $CaCO_3$, but the content of short chain fatty acids such as acetic acid and propionic acid were more than 85 percent of the whole VFAs. Above results indicate that the acidogenic pathway for might be significantly affected by pH (Valerie Penaud et al., 1996).

Fig. 4.3.6 Accumulative concentration of VFA components

at various alkalinity levels

V. CONCLUSION

A study to find out the influences of dilution rate, organic loading rate and alkalinity for acidification of food waste was performed and following conclusions were obtained.
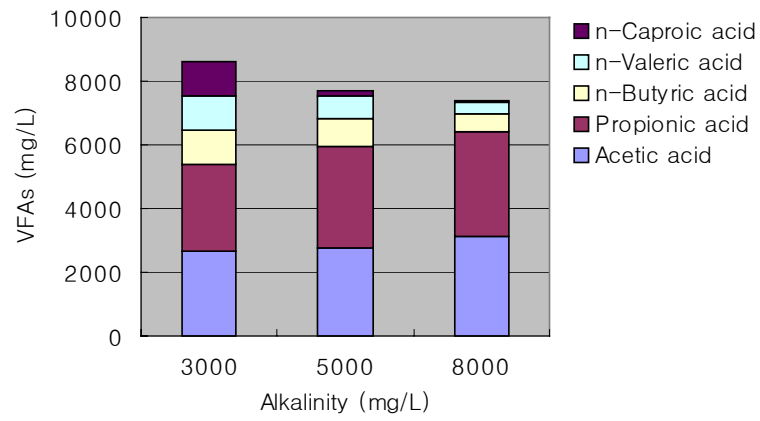
1. The proper dilution rate ensuring efficient hydrolysis and acidification was 0.33/d under 5g VS/L·day of organic loading rate and 8000mg/L as $CaCO_3$ of alkalinity.

2. The influences of products on the hydrolysis and acidogenesis process could be mitigated by the proper control of dilution rate.

3. The optimal organic loading rate for food waste acidification was 10g VS/L·day under 8000mg/L as $CaCO_3$ of alkalinity and 0.33/d of dilution rate.

4. The hydrolysis of organic particulates was improved at higher pH up to neutral point, but the percentage of acidification was higher at lower pH about 5.3.

5. The major components of VFAs produced from food waste were the short chain acids such as acetic acid, propionic acid and butyric acid. However, the contents of valeric and caproic acids were increased according to the decrease of pH from 6.9 to 5.3.

REFERENCE

1. 환경부, 2000, 전국폐기물 발생 및 처리현황.

2. 환경부, 1997, 음식물쓰레기 관리정책 및 기술동향과 감량화·자원화 실천사례.

3. Callander, I.J. and Barford, J.P., 1983, Recent Advances in Anaerobic Digestion Technology, Process Biochem., 18, pp. 24-30.

4. Geroge, T., Franklin, L. Burton, 1993, Wastewater Engineering Treatment, Disposal, and Reuse, Third Edition.

5. Nagase, M. and Matsuo, T., 1982, Interactions between amino acid-degrading bacteria and methanogenic bacteria in anaerobic Digestion, Biotech. Bioeng., 24, pp. 2227~2239.

6. Peres, C.S., Sanchez, C.R., Matumoto, C. and Schmidell, C., 1992, Anaerobic biodegradability of the organic components of municipal solid wastes(OFMSW), Wat. Sci. Tech., 25(7), pp. 285~293.

7. Song, Y.C., Kim, M.K., Paik, B.C., and Shin, H.S., 2001, Effect of Electron Acceptor on Enhanced Acidogenesis of Food Waste, Proceeding of the 7th Korea-Thailand Conference on Environmental Engineering, pp. 22-28.

8. Goel, R., Mino, T., Satoh, H., and Matsuo, T., 1997, Effect of Electron Acceptor Conditions on Hydrolytic Enzyme Synthesis in Bacteria Cultures, Wat. Res., 31(10), pp. 2597-2603.

9. Valerie, P., Jean, P.D., Michel, T., Rene, M., Bruno, V., and Pierre, C., 1997, Definition of optimal conditions for the hydrolysis and acidogenesis of a pharmaceutical microbial biomass, Process Biochemistry, 32(6), pp. 515-521.

10. SS Banister and WA Pretorius., 1998, Optimization of primary sludge acidogenic fermentation for biological nutrient removal, Water S.A., 24(1), pp. 35-41.

11. Veeken, A., and Hamelers, B., 2000, Effect of substrate-seed mixing and leachate recirculation on solid state digestion of biowaste, Water Sci. and Technol.

12. Banerjee, A., Elefsiniotis, P., and Tuhtar, D., 1998, Effect of HRT and Temperature on the Acidogenesis of Municipal Primary Sludge and Industrial Wastewater, Wat. Sci. Tech., 38(8~9), pp. 147~423.

13. Hammer, M.J., 1986, Water and Wastewater Technology, Wiley, New York.

14. Miron, Y., Zeeman, G., Jules, B., Van Lier and Lettinga, G., 2000, The Role of Sludge Retention Time in the Hydrolysis and Acidification of Lipids, Carbohydrates and Proteins during Digestion of Primary Sludge in CSTR Systems, Wat. Res., 34(5), pp. 1705~1713.

15. 음식물쓰레기 감량화.자원화 홈페이지, 2000.

16. Gujer, W. and Zehnder, A.J.B., 1983, Conversion Process in Anaerobic Digestion, Wat. Sci. & Tech., 15, pp. 127-167.

17. Eastman, J.A. and Ferguson, J.F., 1981, Solubilization of Particulate Organic Carbon During the Acid Phase of Anaerobic Digestion, J. WPCF., 53, pp. 352-366.

18. Noike, T., Endo, G., Chang, J., Yaguchi, J. and Matsumoto, J., Characteristic of Carbohydrate Degradation and Rate Limiting Step in Anaerobic Digestion, 1985, Biotech. Bioeng., 27, pp. 1482-1489.

19. Song, Y.C., 1995, High-rate methane fermentation of the organic solid waste., ph D Thesis, Dept. of civil engineering, KAIST.

20. Smith, P.H. and Mah, R.A., 1966, Kinetics of Acetate metabolism

During Sludge Digestion App. Microbial., 14, pp. 368-371.

21. Chiu, Y.C., Chang, C.N., Lin, J.G. and Huang, S.J., 1997, Alkaline and ultrasonic pretreatment of sludge before anaerobic digestion, Wat. Sci. Tech., 36(11), pp. 115~162.

22. Deanls, A.B., 6007 Hill Rd. N.B., Olympia, Wash. 98516. 1996, Anaerobic Treatment Process for the rapid hydrolysis and conversion of organic materials to soluble and gaseous components, United States Patent

23. Marek, R., 1996, An Extension of the Mosey Model, Wat. Res., 30(10), pp. 2440-2446.

24. Gene, F., Parkin, and William, F.O., Fundamentals of Anaerobic digestion of Wastewater Sludges, pp. 867-913

25. Ahring, B.k., Sandberg, M. and Angelidaki, I., 1994, Volatile Fatty Acid as Indicators of Process Imbalance in Anaerobic Digesters, Applied Microbial Biotechnology. 43, pp. 559-565.

26. Hill, D.T., Cobb, S.A. and Bolte, J.P., 1987, Using Volatile Fatty Acid Relationships to Predict Anaerobic Digester Failure, Transaction of ASAE, 30(2), pp. 496-501.

27. Eastman, J.A., 1977, Solubilization of Organic Carbon During the Acid Phase Anaerobic Digestion, Ph.D. Thesis, University of Washington.

28. Dinopoulou, G., Rudd, T. and Lester, J.N., 1988, Anaerobic Acidogenesis of a Complex Waste-water, Ⅰ. The Influence of Operation Parameters on Reactor Performance, Biotech. Bioeng., 31(9), pp. 958~968.

29. Zoetemeyer, R.J., Arnoly, P., Cohen, A. and Boelhouwer, C., 1982, Influence of Temperature on the Anaerobic Acidification of Glucose in a Mixed Culture Forming Part of a Two-Stage Digestion Process, Wat. Res.,

16, pp. 313~321.

30. Breure, A.M. and Van Andel, J.G., 1984, Hydrolysis and Acidification Fermentation of a Protein Gelatin in an Anaerobic Continuous Culture, Appl. Microbiol. Biotech., 20(1), pp. 40~45.

31. Bull, M.A., Steritt, R.M. and Lester, J.N., 1984, An Evaluation of Single- and Separated-Phase Anaerobic Industrial Waste-water Treatment in Fluidized Bed Reactors, Biotech. Bioeng., 26(9), pp. 1054~1065.

32. Droste, R.L., 1997, Theory and Practice of Water and Wastewater Treatment Plant, John Wiley&Sons, Inc., New York.

33. Anderson, G.K., Donnelly, T., and Mekeown, K.J., 1982, Identification and Control of Inhibition in the Anaerobic Treatment of Industrial Wastewater, Process Biochemistry, 17(4), pp. 28-32

34. Baronofsky, J.J., Schreurs, W.J.A., and Kashket, E.R., 1984, Uncoupling by Acetic Acid Limits Growth of and Acetogenesis by Clostridium thermoaceticum., Applied and Environmental Microbiology, 48(6), pp. 1134-1139

35. Llabres-Luengo, P., and Mata-Alvarez, J., 1988, The Hydrolytic Step in a Dry Digestion System., Biol. Wastes, 23, pp. 25-37

36. de Baere, L., Verdonck, O., and Verstraete, W., 1985, High rate dry anaerobic composting process for the organic fraction of solid Wastes., Proc., 7th Symp. on Biotechnology for Fuels and Chemicals, C. D. Scott, ed., Wiey, London, pp. 321-330

37. ten Brummeler, E., Horbach, H. C. J. M., and Koster, I. W.,1991, Dry anaerobic batch digestion of the Organic Fraction of Municipal Solid Waste, J. chem. Tech. Biotech., 50, pp. 191-209

38. Adrie, V., Sergey, K., Heijo, S., and Bert, H., 2000, Effect of pH and VFA on Hydrolysis of Organic Solid Waste, Journal of Env. Eng., pp.

1079-1081.

39. Callaghan, F.J., D.A.F. Wase, K. Thayanithy and C.F. Forster, 1999, Co-digestion of waste organic solids; batch studies, Bioresource Tech., 67, pp. 117~122.

40. LIN, C.Y., Bian, F.Y. and Chou, Jen., 1999, Anaerobic co-digestion of seepage and land fill leachate, Bioresource Tech., 68, 99, pp. 275~282.

41. Edelmann, W. and Engeli, H., 1993, Combined digestion and composting of organic industrial and municipal wastes in Switzerland, Wat. Sci. Tech., 27(2), pp. 159~168.

42. Lafitte-Troupue, S. and Forster, C.F., 2000, Dual anaerobic co-digestion of sewage sludge and confectionery waste, Bioresource Tech., 71, pp. 77~82.

43. Mogens Hedegaard and Volder Jaensch, 1999, Anaerobic Co-digestion of Urban and Rural Wastes, Renewable Energy, 16, 99, pp. 1064~1069.

44. Chanakya, H.N., Venkatsubramaniyam, R. and Jayant, Modak., 1997, Fermentation and Methanogenic Characteristics of Leafy Biomass Feedstocks in a Solid Phase Biogas Fermentor, Bioresource Tech., 62, pp. 71~78.

45. Malpei, F., Bonomo, L. and Rozzi, A., 1998, Anaerobic Biodegradability of Print pastes plus Primary sewage sludge, Bioresource Tech., 63, pp. 57~63.

46. Masoud Kayhanian and Dan Rich, 1996, Sludge management using the biodegradable organic fraction of municipal solid waste as a primary substrate, Water Environ. Res., 68, pp. 240~252.

47. Poggi-Varaldo, H.M., Valdes, L., Esparza-Garcia, F. and Fernaadez-Villagomez, G., 1997, Solid substrate anaerobic co-digestion of paper mill sludge, biosolids, and municipal solid waste, Wat. Sci. Tech., 35(2-3),

pp. 197~204.

48. Li, Y.Y. and Noike., 1989, The effect of Thermal pretreatment and time on the degradation of waste activated sludge in anaerobic digestion, Japan Journal of water pollution research., 12, pp. 112~121.

49. 송영채, 1991, 혐기성 유동상 반응조를 이용한 폐수처리, 한국 과학기술원 석사학위논문.

50. Akashah, M., Yoshida, M., Watanabe, M., Nakamura, M., Matsumoto, J., 1997, Hydrogen Gas Production from Glucose and its Microbial Kinetics in Anaerobic Systems, Wat. Sci. Tech. 36(6-7), PP. 279-286.

51. Mosey, F.E., 1983, New Development in the Anaerobic Treatment of Industrial Wastes, Effl. Water Tr. J., 23, pp. 85-93

52. Raynal, J., Delgenes, J.P. and Moletta, R., 1998, Two-Phase anaerobic Digestion of Solid Wastes by A Multiple Liquefaction Reactors Process, Bioresource Tech., 65, pp. 97-103

53. Shin, H.S., Han, S.K, Song, Y.C., Lee, C.Y., 2000, Enhanced Acidogenic Fermentation of food waste(I):Effect of Seed Inoculation., J. of Kowrec, 8(3), pp. 112-117

54. Ghosh, S., and Klass, D.L., 1978, Two Phase Anaerobic Digestion. Process Biochem., 13, pp. 15-24.

55. Lilley, Id., Wentzel, Mc., Loewenthal, Re., and Marais, GvR., 1990, Acid fermentation of primary sludge at 20℃, Res. Rep. W64, Depart. of Civil Eng., Univ. of Cape Town

56. Skalsky, DS., and Daigger, GT., 1995, Wastewater solids fermentation for volatile acid production and enhanced biological phosphorus removal., Wat. Env. Res. 67(2) pp. 230-237