III THEORETICAL CONSIDERATION

3.1 Anaerobic Wastewater Treatment.Overview

Anaerobic wastewater treatments have been used for more than a century, or since septic tank was discovered. In the last twenty years, attempts and researchers have focused on anaerobic treatment. Many kind of anaerobic processes were introduced, all of them have scientific support as well as advantages and drawbacks. Despite the fact that the various anaerobic processes differ, they have the common feature of producing methane as an end-product. Although the technology of anaerobic processes has been shown to be applicable for industrial, agricultural and municipal wastes, the early digester designs were of the continuous stirred tank type in which effective contact between the waste requiring treatment and the active microbial flora was achieved by a lengthy retention time. Therefore, the digesters required a very large digestion volume. More recently, anaerobic treatment of large-volume industrial wastewaters has been facilitated by the development of advanced reactors that achieve separation between the hydraulic retention time (HRT) and the solids retention time (SRT). Such seperation allows the slowly growing microorganism to remain within the reactor independent of the wastewater flow, thereby allowing application of significantly higher volumetric loading rates.

3.1.1 Old-fashioned Anaerobic Treatment

These kind of anaerobic systems have been known since this was first developed. The main concern was with operation and not with mechanical equipment. Mixers and heater were only used if high performance was required. Some examples that reported successful treatment with slaughterhouse waste were as follow.

3.1.1.1 Anaerobic Lagoons

Anaerobic Lagoons are used extensively for first-stage treatment of wastewater from meat packing industry. They are simple basins with 3-6 metres depth and an average detention time of seven days. The gases produced in the lagoon will carry grease and solids to the surface. A crust forms over the whole lagoon and thus prevents the escape of odours. The formation of this cover can be accelerated by allowing paunch contents and grease to flow to the lagoon during the initial stage of operation. A loading rate of 240-320 kg BOD per 1,000 cubic metres per day is normally used with an average depth of 4.6 metres. BOD removal range is between 60-90% at a detention time from 5-50 days.

3.1.1.2 Conventional Anaerobic Treatment

A conventional digester can be classified as a standard-rate or high-rate digester. The standard rate digester is the anaerobic system without mixing and not heated, whereas the high rate digester contains stirrer and heater. In the standard rate reactor, stratification occurs due to lack of mixing.Acidification takes place in the tip and methane fermentation occupies the lower part. The high-rate type that maintains a well-mixed can be used either as a one-stage or two-stage reactor. The configurations of methane digester are shown in Fig. 3.1-Fig.3.3.

Steiner, Wildenauer and Kandler (1985) studied the efficiency of the process using 2 litres reactor with slaughterhouse wastes. The experiment was carried out on both mesophilic and thermophilic temperatures (35^{o}C and 55^{o}C). The wastewater contained 2.9% to 10.5% volatile solids. The result showed that by increasing organic loading, the reduction of COD and VS was decreased. The digestion failed with an organic loading of 8.8 kg VS/m^3.d which caused excessive enrichment of volatile solids. At this maximum organic loading of 8.8 kg VS/m^3.d, the detention time was observed to be around 7-12 h.

De Laclos and Pavia (1987) studied the methane fermentation with a slaughterhouse by-product waste. The digester used was a 15 litres one-stage reactor. The wastewater, which contained volatile solids of 45-65%, could be reduced to 55-65% volatile solids at a loading of 6-7 g VS/l.d. The detention time was 20 days at 40°C.

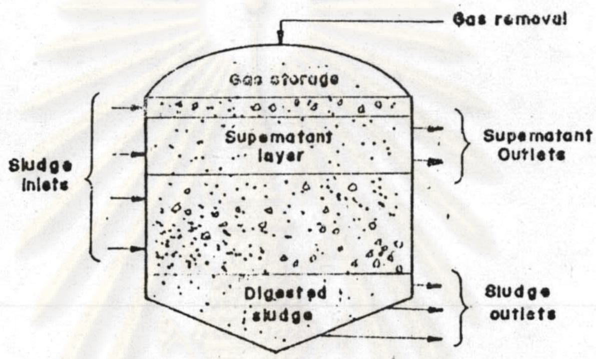


Figure 3.1 Standard-rate digester

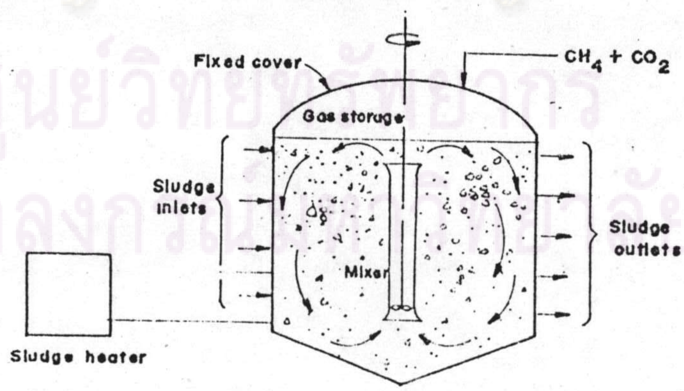


Figure 3.2 High-rate digester

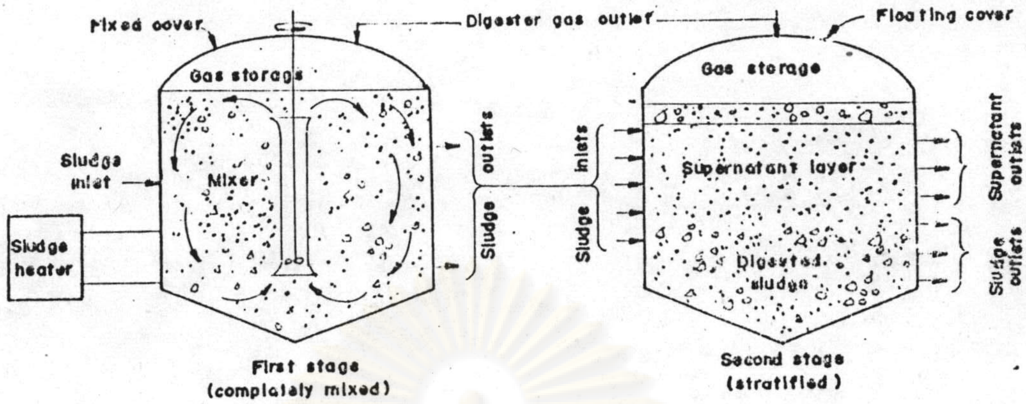


Figure 3.3 High-rate : 2 stage digester

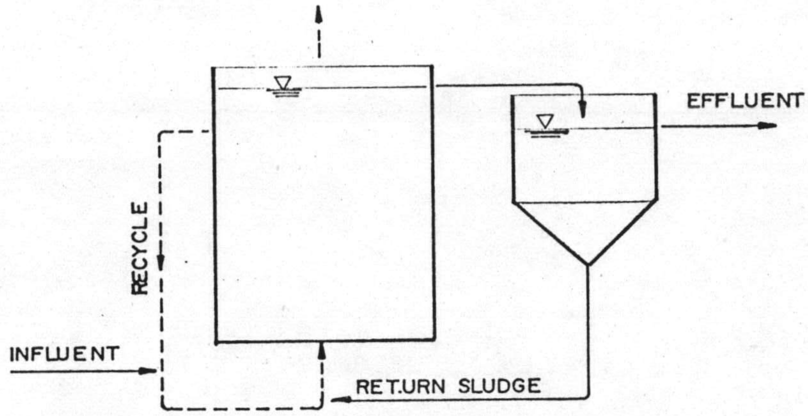
3.1.2 Advanced Anaerobic Treatment

The concept of advanced anaerobic systems was based on three fundamental aspects. Firstly to accumulate the biomass within the reactor by means of settling,and by attachment to solids (fixed or mobile). Such systems could ensure that the mean solids retention time becomes much longer than the mean hydraulic retention time. Secondly to improve contact between biomass and wastewater to overcome the problems of diffusion of substrates and products from the bulk liquid to biofilms or granule. And finally to enhance activity of the biomass due to adaptation and growth.

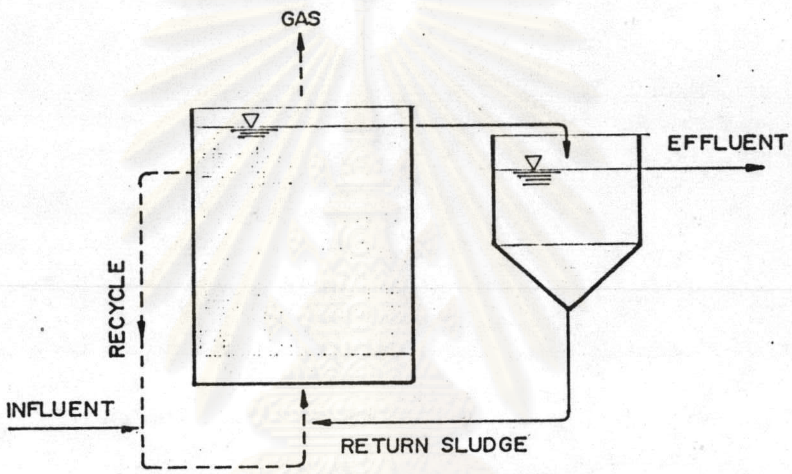
The multiplicity of reactor designs developed to implement this technology can be depicted as shown in Fig.3.4. Some examples of advanced anaerobic treatment were as follows :

3.1.2.1 Anaerobic Contact Process

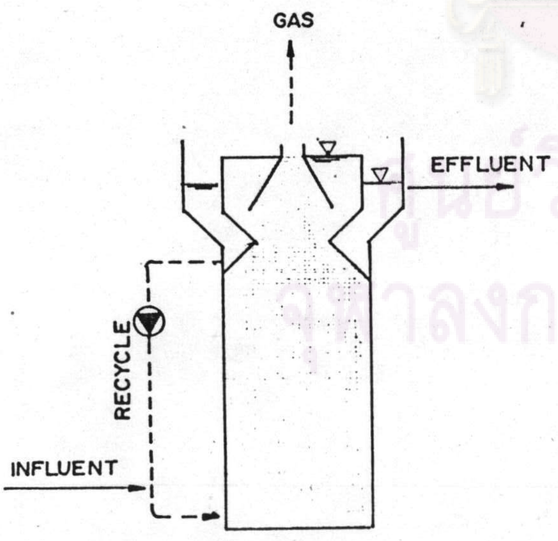
Employing the idea of the activated sludge system,the anaerobic contact process was developed by the recycling of



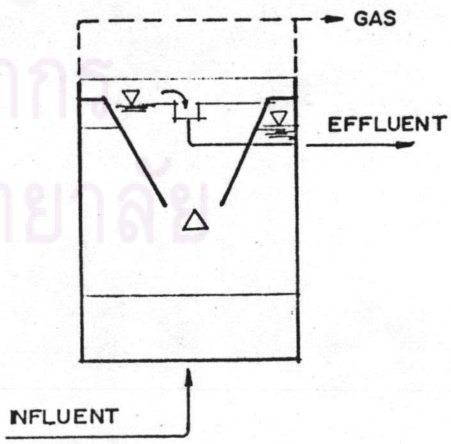
ANAEROBIC CONTACT PROCESS



ANAEROBIC FIXED-FILM REACTOR



FLUIDIZED BED REACTOR



SLUDGE BLANKET REACTOR

FIG. 3.4 PROCESS-DIAGRAM OF DIFFERENT TYPES OF REACTORS biological solids to the reactor. It is also referred to as anaerobic activated sludge. The seperation and recirculation of the biomass is of the utmost importance.

The influent wastewater is equalized by storage in a tank. After preheating to 32-35°C the wastewater is fed at uniform rate to a completely-mixed digester at the loading of1.5-3.0 kg BOD/m^3.d. Detention time in the digester is approximately 12 hours with a mixed liquor suspended solids concentration of 7,000-12,000 mg/l. Anaerobic contact process has been used successfully at Wilson Certified Foods, Albert Lea, Minnesota and also at Auckland Farmers Freezing Co-op in New Zealand. The BOD removal was said to be 85-93% (Lund 1971, Azad 1976, Gutteridge et al. 1978).

3.1.2.2 Fixed-bed Reactor

The reactor contains about 60-90% filling materials,sometimes with sludge recycle. The wastewater is fed through the bottom and distributed upward across the filter. The microorganisms become attached to the filter media, then absorb and stabilize the incoming wastewater. Fig. 3.5 shows the configuration of the fixed-bed reactor with settling tank.

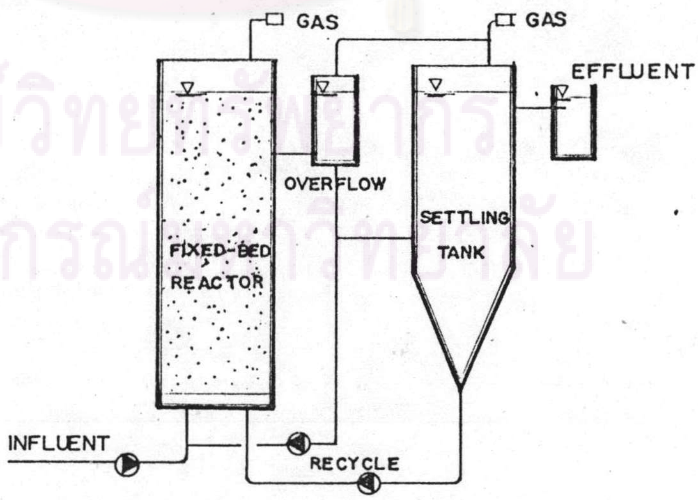


Figure 3.5 Fixed-bed reactor complete with settling tank for pilot scale research unit

3.1.2.3 Anaerobic Sludge Blanket Reactor

The anaerobic sludge blanket reactor is often called Upflow Anaerobic Sludge Blanket (UASB) process. The process is based on the formation of good sedimentation qualities in the lower part of the reactor as a sludge blanket. The sludge blanket process is not universally applicable, since pellets will not form in certain kinds of wastewaters. Fig. 3.6 shows the configuration of the UASB reactor with settling tank.

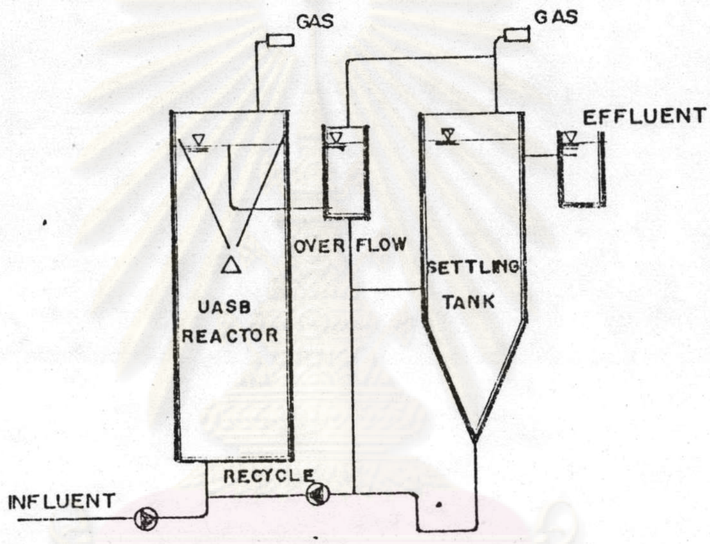


Figure 3.6 UASB reactor complete with settling tank for collecting the washed-out sludge of a pilot scale reactor

With the slaughterhouse wastewater, there has been some research attempting to find out the efficiency of the treatment and the proper environment required, as follows :

Sayed, de Zeeuw and Lettinga (1984) studied the 30 m^3 UASB flocculent-type pilot plant which was initially started up at 30°C and after 20 weeks operated at 20°C. The feed was in semi-continuous condition which consisted of higher load during the day time, lower feed at night and no feed at weekend. The total COD of slaughterhouse wastewater was 1,500-2,200 mg/l. The highest organic loading was

3.5 kg COD/m^3.d at a detention time of 7 h and COD reduction was 70%.

Sayed, Campen and Lettinga (1987) studied a one-stage continuously fed granular UASB system. With a reactor volume of 33.5 litres at 30°C and 20°C and the wastewater of 1,500-2,200 mg/l COD, the organic loads, were 11 and 7 kg COD/m^3.d. The process efficiency was 55% in term of total COD and 85% filtered COD, respectively.

Sayed and de Zeeuw (1988) observed the efficiency of UASB one-stage flocculent sludge reactor with a volume of 10.5litres. The wastewater from a slaughterhouse with BOD concentration ranging 1,925 to 11,118 mg/l was used and the continuous feed was employed. The result showed that the COD reduction range was 68%-82% at an organic loading of between 10-20 kg COD/m^3.d.

3.1.2.4 Anaerobic Fluidized Bed Reactor

The anaerobic fluidized bed reactor is filled with inert material, sand for example, which will be held in suspension by the upflow of the fluid. If necessary, recirculation of settled anaerobic sludge and flushed-out inert material is included. High hydraulic recirculation rate occurs by using an external pump to maintain fluidization.

Bull, Sterritt and Lester (1983) experimented on treating synthetic meat extract wastewater with COD of 1,250 mg/l. The flow rate varied in a range of 4-8 h. The reactor could tolerate these transient changes satisfactorily with no long term detrimental effects. Normal operation was regained within 9 h. A simulated working week experiment was carried out with a 48-h 90% influent flowrate reduction, followed by return to normal operation. The reactor could tolerate these conditions well, with full recovery made within a few hours.

3.2 Microorganisms Concept

Most of the advanced anaerobic reactors conceptual design were 'retained biomass systems' where the microorganisms are either present as an attached biofilm on a support medium within the reactor,or are encouraged to grow as readily settleable flocs or granules that could be either retained in the reactor (UASB, fluidized or expanded beds etc) or separately settled and returned to the main reaction tank (anaerobic contact plants). For modelling purposes,these reactors were usually divided into suspended-growth and attached biofilm systems (McCarty and Mosey, 1991).

3.2.1 Suspended-growth Microorganisms

Conceptually, the simplest suspended-growth reactors are the anaerobic contact and UASB reactors. They are both designed to selectively retain high concentrations of active biomass and their performance depends mostly on the effectiveness of the solid/liquid seperation device. This, in turn, is critically dependent on the settleability of their biomass (McCarty and Mosey,1991).

The microorganisms in RAUS reactors were, consequently, basically similar in concept design to UASB. Hence, it should be concluded that RAUS microorganisms were of a suspended-growth type.

3.2.2 Attached Biofilm Microorganisms

The clearest example is the anaerobic filter but some of the other reactors, including fluidized and expanded beds may also be considered as biofilms attached to a suspended support medium.

3.3 Biological and Biochemistry of Anaerobic Process

Anaerobic process performs through two kinds of microorganisms ; non-methanogenic bacteria and methanogenic bacteria. In the case of non-methanogenic bacteria the insoluble organic material is firstly digested and solubilized by extracellular enzyme released by bacteria. The reactions responsible for solubilization and size reduction are usually called hydrolytic. Fermentation then takes place, the oxidized end products are short chain volatile acids such as acetic, propionic, butyric,valeric and caproic acids. Their production is refered to as acidogenesis and the resposible organisms are called acid producing bacteria. Some of the acid-producing bacteria utilize volatile acids to produce acetic acid, CO_2 and H_2. The activity is called hydrogenogenesis.

The products of the nonmethanogenic phase are utilized by methanogenic bacteria to produce methane gas and carbon dioxide. The steps of anaerobic operations are shown in Fig. 3.7.

3.3.1 Nonmethanogenic Bacteria

Nonmethanogenic bacteria consist of facultative and obligate anaerobic bacteria. The end products of bacteria metabolism are as shown in Fig. 3.8.

3.3.2 Methanogenic Bacteria

Two distinct groups of bacteria are involved in the phase of methane production. One group obtains energy from the oxidation of molecular hydrogen whereas the other group oxidized acetate.

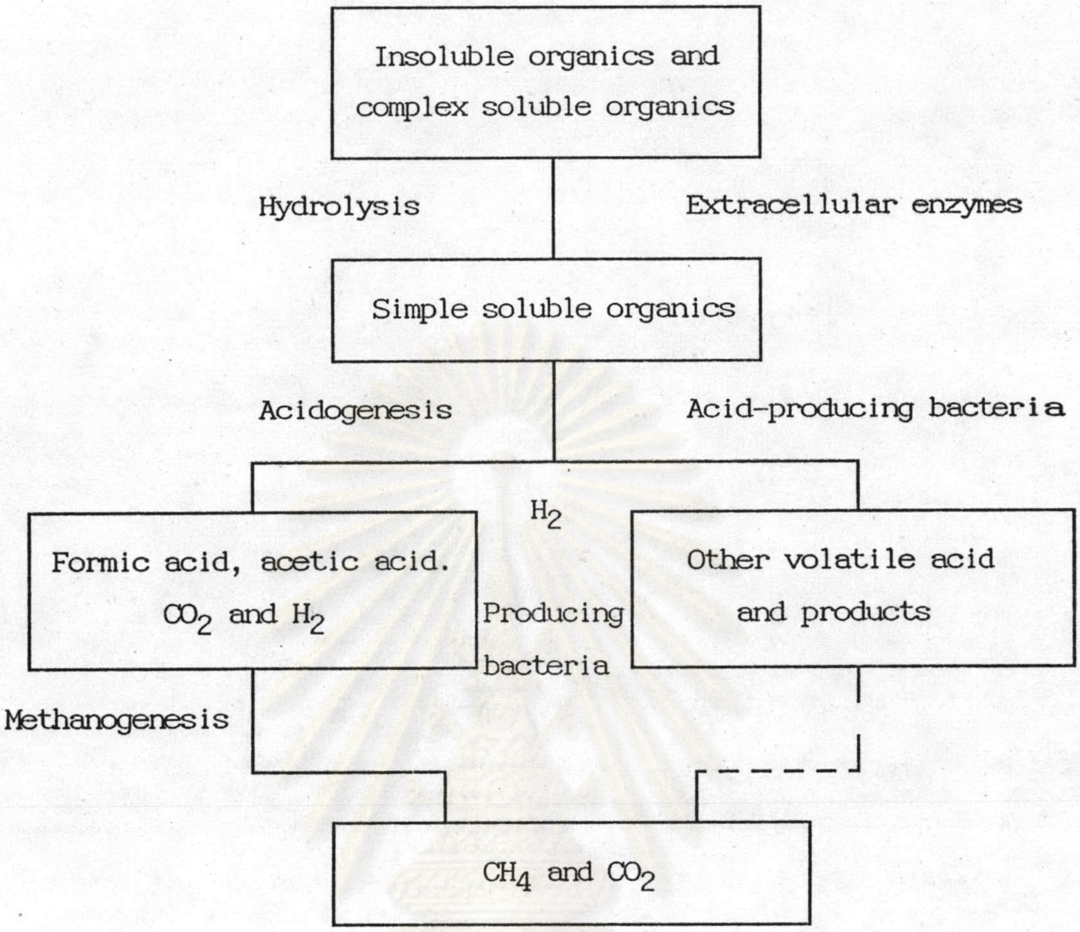


Figure 3.7 Anaerobic operations

The methanogenic bacterias that oxidize hydrogen are strictly obligate anaerobic. During their metabolism, they form methane gas in the process as follows :

$$4\,H_2 + CO_2 \longrightarrow CH_4 + 2\,H_2O$$

The proposed reaction for the group which oxidizes acetate is

$$CH_3COOH + 4\,H_2 \longrightarrow 2\,CH_4 + 2\,H_2O$$

Methanogenic bacteria appear to be extremely sensitive to certain environmental factors. Being obligate anaerobes, a small

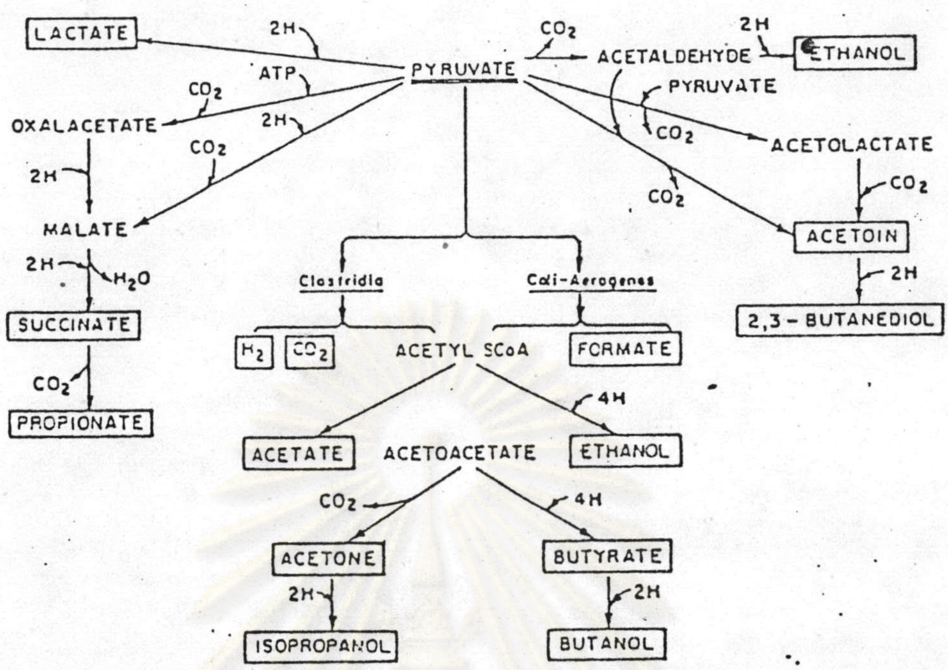


Figure 3.8 Fermentative product formation from pyrurate

amount of oxygen is inhibitory to these bacteria. It is essential that a highly reduced environment be maintained to promote their growth. The optimum digestion, as measured by methane production, occurred with an oxidation-reduction potential (ORP) between -520 and -530 mV (E_C-calomel reference electrode). When the effect of ORP on the treatment of swine wastes was studied by operating with an E_C of -435 mV, some methane production occurred but when the E_C reached -360 mV, methane production was completely inhibited. Maintenance of this low ORP is essential for the successful operation of methane fermentation. Not only oxygen, but any highly oxidized material, such as nitrites or nitrates, can exhibit inhibition of the methanogenic bacteria (Pfeffer,1979).

There are a number of materials that can exhibit toxicity to the methanogenic bacteria. Some alkali and alkaline earth-metal salts above certain concentrations exhibit degrees of inhibition and toxicity. The threshold levels vary depending on whether these metals act singly or in combination. Certain combinations have synergistic effects, whereas others display an antagonistic effect.

Ammonia, particularly when in the NH_3 form, is inhibitory when present in high enough concentrations. At concentrations between 1500 and 3000 mg/litre of total ammonia nitrogen and a pH greater than 7.4, NH_3 concentration can become inhibitory. At concentrations above 3000 mg/litre, the ammonium ion itself becomes quite toxic regardless of pH.

Other common forms of toxicity include those of sulphides, heavy metals and toxic organic materials. Concentrations of soluble sulphide varying from 50 to 100 mg/litre can be tolerated in anaerobic treatment with little or no acclimatisation, whereas concentrations up to 200 mg/litre can be tolerated with some acclimatisation. Low, soluble concentrations of copper, zinc and nickel salts are associated with most of the problems of heavy metal toxicity in anaerobic treatment. Also, there are many organic materials that exhibit inhibitory effects. These range from organic solvents to many common materials such as alcohols and long chain fatty acids in high concentrations.

3.4 Effect on Environmental Factors

The majority of the environmental factors which affect performance concern the feed composition, e.g. the presence of inhibitory or toxic feed compounds. Generally, every compound is inhibitory or even toxic above a certain concentration. On the other hand, low concentrations of these compounds often have a stimulating effect on the process. Obviously, knowledge about the toxicity level of most common compounds and the factors which influence the inhibition, is in dispensable. The influence of the most common environmental factors on the process are as follows :

3.4.1 Temperature

The temperature for anaerobic treatment ranges on two levels, mesophilic and thermophilic. Mesophilic levels range from 35 to 40°C (Pfeffer, 1979) 20 to 40°C (van Velsen and Lettinga, 1979) and thermophilic from 55 to 60°C(Pfeffer, 1979) 40 to 65°C (van Velsen and Lettinga, 1979). Although the rates of reaction in the thermophilic level were much faster than those in the mesophilic level, the economics of most sewage sludge digestion systems have dictated operation in the mesophilic or lower. This results from the fact that the methane requirements to maintain thermophilic temperatures in most digesters are excessive and uneconomical. In the mesophilic range, the optimum temperature was 37.8°C and the optimum thermophilic temperature appeared to be 55°C. However, a number of reports suggested that temperatures above 25-35°C offerred no improvement in digestion.

However, the study of Pfeffer (1979) found a marked improvement in gas production and substrate utilization with increasing temperatures. These data are shown in Fig. 3.9 The data show a substantial increase in the rate of gas production as well as a greater yield for the retention time studied with increasing temperature.

Cordoba et al. (1988) studied the temperature effect on upflow anaerobic filter by using a 40 mm. diameter reactor. The height to volume ratio equal to 10 and the ceramic saddle was used as packing media. The experiment were carried out at the temperature of 40, 30, 26, 20 and 16°C and organic loading up to 11 g COD/l.d. The observed data identitied that the highest efficiency removal was 95% at 40°C and the lowest was at 16°C.

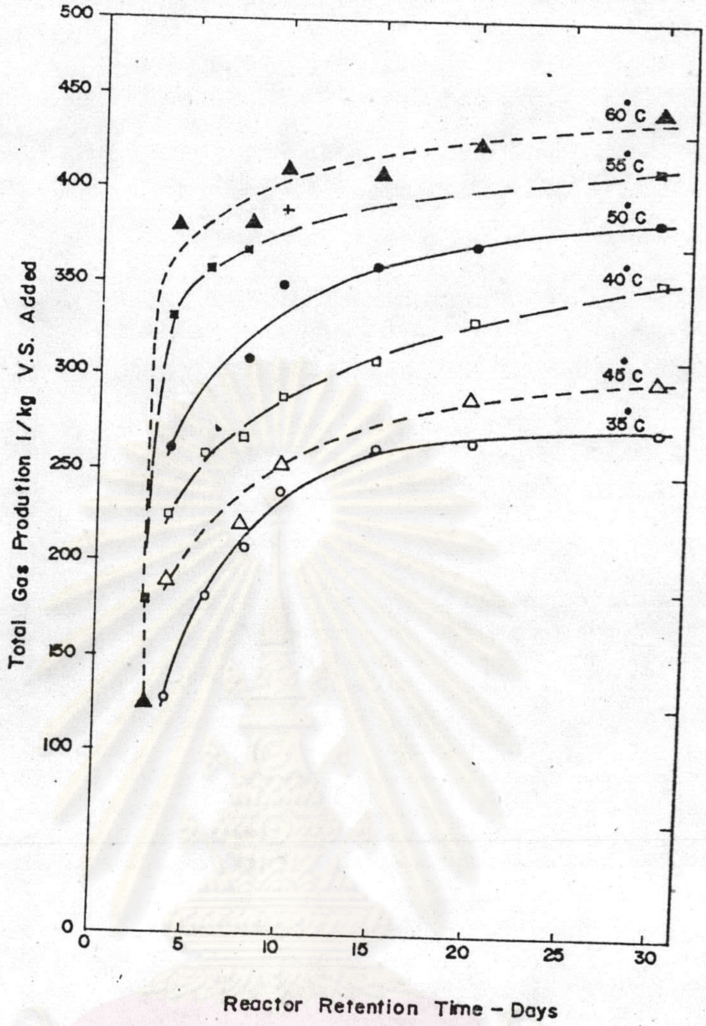


Figure 3.9 The effect of temperature and retention time on the production of gas from urban refuse.

Source : Pfeffer (1979)

3.4.2 Effect of pH

A pH around neutrality is optimum. The anaerobic reactors are most sensitive to pH changes during start-up. At this stage, a decrease in pH to 6.5 or lower can increase the time of start-up significantly. Once steady-state operation is achieved, reactors become quite resistant to the effect of pH changes, and rapid recovery has been observed in a 12-h period for pH levels as low as 5.4 (Young and Dahab, 1982).

McCarty (1964) reported that methane production proceeded very well as long as the pH was maintained between 6.6 and 7.6. The optimum pH range appears to be between 7.0 and 7.2. When the pH dropped below 6.6, significant inhibition of the methanogenic bacteria occured. At a pH of about 6.2, the acid conditions exhibit acute toxicity to these bacteria. It was interesting to note that this pH did not stop acid production. The fermentative bacteria would continue to produce acids until the pH drops to 4.5 or 5.0. When this happened, the digester was said to be 'stuck', or 'pickled'. The pH was low enough to inhibit the microbial population that was normally present in this system. Control should be exercised when the pH appears likely to drop below a value of 6.6. This could be done by the additon of alkali.

Bull et al. (1983) experimented on synthetic meat extract wastewater with anaerobic fluidized bed reactor. The result recommended that long term operation at low pH was considered inadmissible.

3.4.3 Nutrient Requirements

The bacteria responsible for waste conversion and stabilization in the anaerobic process require nitrogen, phosphorus and other materials in trace quantities for optimum growth. Therefore, another important environmental condition is the presence of the required nutrients in adequate quantities. If the nutrients are not present in the required quantities, they must be either added or supplemented.

Speece and McCarty (1964) calculated the nitrogen and phosphorus requirements based on an average chemical formulation of biological cells of $C_5H_9O_3N$. Nutrients must be adequate to satisfy the cell growth requirements. The nitrogen requirement is about 11% of the cell volatile solids weight and the requirement for phosphorus is equal to about one-fifth of the nitrogen requirements. Although these requirements should theoretically be based on the fraction of waste removed during treatment rather than on the waste added, it is good practice to base them on waste additions. Other elements having stimulatory effects at low concentrations include,but are not limited to, sodium, potassium, calcium, magnesium and iron. All of these preceeding elements may exhibit inhibitory effects at higher concentrations.

3.4.4 Volatile Fatty Acids

The adverse effect of high concentrations of VFA on methanogenic bacteria is paricularly important because VFA are intermediates in the anaerobic digestion process. The toxic effect of VFA at high concentrations is attributed either to the toxicity of the VFA themselves or to the decrease in pH brought about by the VFA.

The undissociated VFA are inhibitory, since the bacterial cell wall is far more permeable to undissociated molecules in comparison with their ionised state. Therefore, more VFA will be taken up by the organisms at low pH values. Once taken up, the VFA dissociate within the cell and cause a decrease of the pH, which will adversely affect the enzyme activity. This hypothesis may explain the strong inhibitory effect of VFA at low pH values (below pH 5.8).

3.4.5 Ammonia-nitrogen

The feasibility of methane fermentation of various types of waste depends largely on the ability of methanogenic bacteria to acclimatise to adverse environmental factors. In the digestion of some wastewater, i.e. manure, an important factor is ammonia-nitrogen,because exceptionally high ammonia-nitrogen concentrations (exceeding 3000 mg litre^{-1}) frequently occur in these types of waste. Moreover, upon digestion, ammonia-nitrogen may be released through the decomposition of N-containing compounds.

Evidently a minimum amount of ammonia is always required in order to achieve favourable conditions for growth. According to McCarty (1961) ammonia-nitrogen concentrations in the range of 200-1500 mg $litre^{-1}$ have no adverse effect on the methane formation. McCarty also stated that ammonia-nitrogen concentrations in the range of 1500-3000 mg $litre^{-1}$ were inhibitory at pH levels above 7.4, whereas ammonia-nitrogen concentrations in excess of 3000 mg $litre^{-1}$ were supposed to be toxic at all pH values.

3.4.6 Heavy Metals

Free heavy metal ions have a toxic effect on anaerobic digestion processes, even at very low concentrations. However, since the toxicity only seems to be concerned with the free metal ions,the degree of toxicity depends, among other things, on the presence of complexing or precipitating anions. In this respect, the presence or formation of sulphides is particularly important, because most heavy metal sulphides are extremely insoluble. Therefore, when the digester feed contains sufficient sulphur compounds, e.g. sulphates and proteins, very high concentrations of heavy metals are admissible in the digester feed. Investigations of McCarty revealed that heavy metals have no toxic effect when added as sulphates.However, when the heavy metals are added at the same concentration as chlorides they immediately become toxic. According to Mosey Zn, Cd, Pb and Cu do not inhibit the anaerobic process when the sulphide ion concentration exceeds $10^{-17.2}$ mol $litre^{-1}$. At unsufficiently high sulphide concentrations, the concentration of the free metal ions is determined by the solubility of other metal salts, e.g.hydroxides or carbonates.

As indicated by the presence of approximately 0.5% H_2S in the biogas, the piggery manure contained sufficient sulphur compounds to remove the toxic effect of heavy metals, especially Cu.

3.4.7 Aromatic Compounds

Upon the storage of complex wastes, aromatics may be formed by the microbial degradation of proteins, and if so they contribute to the formation of obnoxious odours. Phenol, p-cresol, ethyl phenol, indole and skatole were found to be the predominant aromatics which may occur in the manure, due to their use as disinfectants,especially p-cresol. With respect to the influences of aromatics on the digestion of sewage sludge, phenol is significantly inhibitory at concentrations between 0.1 and 0.4% of the TS, whereas concentrations above 0.4% of the TS are toxic.

3.5 Stabilization of Organic Material

Organic destruction in anaerobic treatment is directly related to methane production and vice versa. Buswell and Mueller developed the following equation 1 to predict the quantity of methane from a knowledge of the chemical composition of the waste :

$$C_nH_aO_b + (n - \frac{a}{2} - \frac{b}{4})H_2O \longrightarrow (\frac{n}{2} - \frac{a}{8} + \frac{b}{4})CO_2 + (\frac{n}{2} + \frac{a}{8} - \frac{b}{4})CH_4 \qquad (1)$$

McCarty (1964) showed that the theoretical methane production from the complete stabilization of 1 kg of BOD_L or COD was 0.348 m^3 at standard temperature and pressure.

3.6 Biological Solids Production

A major advantage of the anaerobic process is that the net production of biological solids is lower than in aerobic systems.This occurs partly because of the low net synthesis of anaerobic reactions and partly because of the long solids retention time (SRT) within the reactor. The effect of SRT on solids production in completely mixed digesters is illustrated in Figure 3.10. The interception of each line on the vertical axis of Figure 3.10 represents the gross yield, Y_0, of biological solids for the respective class of organic material. As the solids retention time increases,biological decay causes the net yield, Y_n, to decrease. While it is not possible to draw a direct analogy between the overall solids retention time in an anaerobic PBR and a completely mixed digester, the ratio of solids in inventory to the rate of solids lost per day gives a reasonable approximation of SRT.

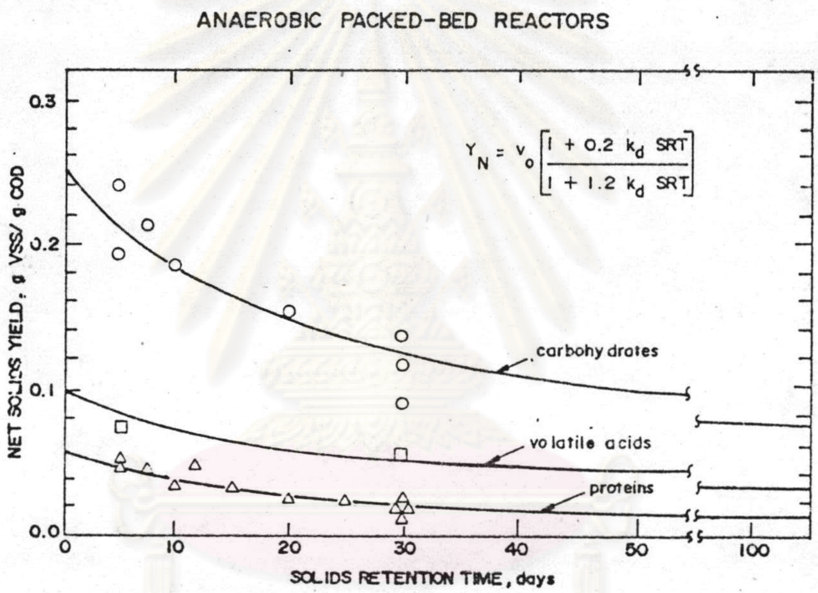


Figure 3.10 Net yield of biological solids as related to solids retention time for three types of organic wastes. (k_d = 0.04/day.)

3.7 Gas Composition

In the conversion of carbohydrates to carbon dioxide and methane, equal volumes of each gas are produced. This reaction is shown in Eqn. 1.

$$(C_6H_{10}O_5)_x + xH_2O \longrightarrow xC_6H_{12}O_6 \longrightarrow 3xCH_4 + 3xCO_2 \qquad (1)$$

However, all of the carbon dioxide is not released as a gas but enters into reactions with water and hydroxide ions. Microorganisms can deaminate biodegradable protein producing ammonia which reacts with water according to Eqn. 2.

$$NH_3 + HOH \rightleftarrows NH_4^{+} + OH^{-} \qquad (2)$$

The hydroxide produced by this reaction reacts with carbon dioxide to form bicarbonate ions as shown in Eqns. 3 and 4.

$$CO_2 + HOH \rightleftarrows H_2CO_3 \rightleftarrows H^{+} HCO_3^{-} \qquad (3)$$

$$H_2CO_3 + OH^{-} \rightleftarrows HCO_3^{-} + HOH \qquad (4)$$

Therefore, the protein content of the substrate will significantly affect the quantity of carbon dioxide actually released from the solution as well as the bicarbonate buffer capacity of the system.

The carbon dioxide incorporated in the bicarbonate ion is removed from the reactor in the liquid phase rather than the gas phase. There are two factors related to this washout of carbon dioxide ; the degree of alkalinity which will control the washout rate at a given retention time and the retention time, or the liquid through-put rate, which will also influence the washout rate. Therefore, for a given substrate, digestion at shorter retention times will produce a gas having a higher methane content.

With the above relationships, it is possible to calculate the actual bicarbonate ion concentration in a digestion system. The carbon dioxide-bicarbonate equilibrium can be combined with the solubility of carbon dioxide to predict the gas composition under various operating conditions. One must also include the effect of the vapour pressure of water. This increases substantially at thermophilic temperatures. These data are shown in Table 3.1. The added water vapour in the gas reduces the partial pressure of carbon dioxide which in turn changes the bicarbonate alkalinity equilibrium.

Temperature also influences the equilibrium constants for these equations. For a given pH, say 7.0, the ratio of bicarbonate ions to carbonic acid (carbon dioxide) increases. At 30°C this ratio is 4.9 while at 60°C it increases to 5.19, a relatively small increase. When the effect of temperature on the solubility of carbon dioxide, as described by Henry's Law, is considered the effect is compounded. Equation 6 shows this solubility relationship.

Table 3.1 Vapour pressure of water at various temperatures

Temperature (°C)	30	35	40	45	50	55	60
Vapour Pressure (mmHg)	31.8	42.2	55.3	71.9	92.5	118.0	149.4

Source : Pfeffer (1979)

$$K = \frac{P}{X} = \frac{\text{partial pressure (mmHg)}}{\text{mole fraction}} \qquad (6)$$

For a given mole fraction in solution, an increase in temperature will increase the partial pressure. Table 3.2 lists Henry's constant for carbondioxide at various temperatures. The temperature effect on this equilibrium results in a significant reduction in alkalinity. A decrease in the solubility of carbon dioxide by a factor of 0.85 in going from 30 to 60°C in conjunction with an increase in the vapour pressure of water by a factor of 4.7 produces a significant reduction in the carbon dioxide in solution. This effect is not offset by the change in the carbon dioxide-bicarbonate relationship with increasing temperature. Therefore, a much lower bicarbonate alkalinity will be associated with a given pH at the elevated temperatures. Since more carbon dioxide is lost in the gas phase, the caustic addition required to maintain a desired pH would be less.

Table 3.2 Henry's Constant for carbon dioxide at various temperatures

Temperature (^{o}C)	30	40	50	60
$K \times 10^{-7}$	0.139	0.173	0.217	0.258

Source : Pffefer (1979)