III THEORETICAL CONSIDERATION

3.1 The anaerobic Waste treatment Process

In the anaerobic waste treatment process, microorganisms are used under anaerobic conditions to stabilize organic wastes by conversion to methane and carbondioxide. The most significant advantage of anaerobic treatment over aerobic treatment is that the growth of excess micro-organisms is minimized, thus decreasing the requirements for biological sludge disposal facilities and for the biological nutrients, nitrogen and phosphorus. In addition, the methane gas produced can serve as a source of fuel.

The process has been used in the past mainly for the stabilization of concentrated municipal and industrial sludge which know as "Conventional-process". The anaerobic contact processes or anaerobic activated sludge process was developed about 1950's for treatment of low strength waste, less than 4000 mg/l BOD. A newer anaerobic contact process which has been evaluated by YOUNG & McCARTY (1969). termed the "Anaerobic Filter process", is ideally suited for the treatment of a soluble waste.

3.1.1 Conventional process

The typical conventional anaerobic treatment process normally used for treating high-strength domestic and industrial waste especially domestic waste solids. It can classify to, low-rate and high-rate system. A low-rate system, the tank is not mixed and, in some cases, is not heated. Raw waste (especially sludge) is added at the top and withdrawn at the bottom. Stratification develops in the system due to a lack of mixing, much of the reactor volume is wasted, and many operational problems result. In this type of reactor, acidification takes place in the top and middle layers while methane fermentation is confined to the lower layer this leads to areas of low and high pH in the system, which restrict optimum biological activity. The high-rate system differs from low-rate system in that the contents are well mixed, either continuously or intermittently, and the digester is heated. This procedure avoids all of the difficulties inherent in low-rate systems. Consequently, this system operates well

CONVENTIONAL PROCESS

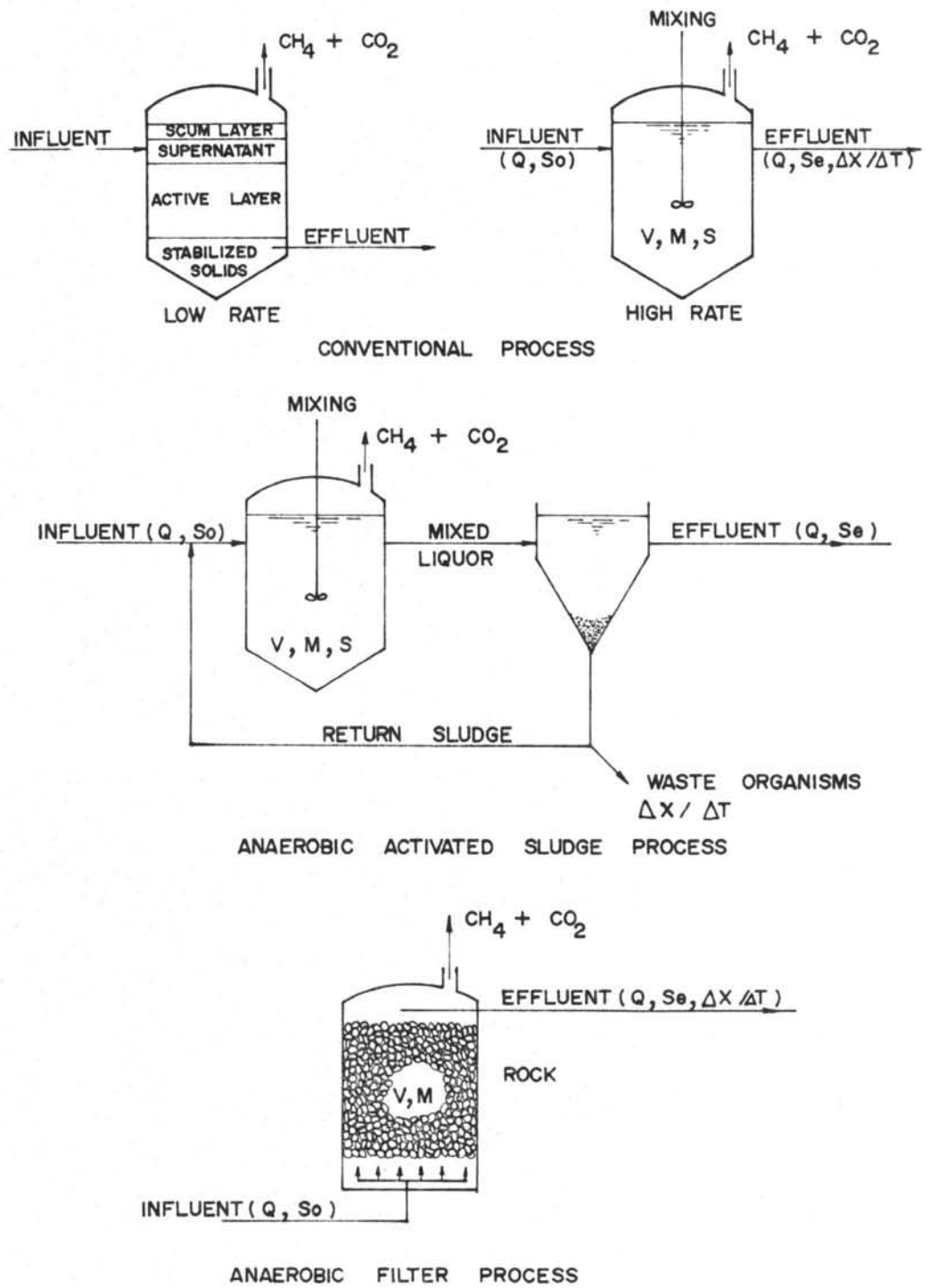ANAEROBIC ACTIVATED SLUDGE PROCESS

ANAEROBIC FILTER PROCESS

FIGURE 5. SCHEMATIC DIAGRAM OF THREE ANAEROBIC WASTE TREATMENT PROCESS

at lower hydraulics retention time and higher organic loading rates.

Modification of the conventional process have not been directed toward obtaining economical treatment.

3.1.2 Anaerobic contact process   The anaerobic contact process was developed by recycle of biological solids to the reactor, so may be called, the "anaerobic activated sludge process. Here, the waste is passed through a contact unit (Figure 5). The biological solids are retained in the system independent of waste flow, thus permitting the long solids retention times necessary for satisfactory anaerobic waste treatment (McCARTY, 1964). With good separation of the biological solids, anaerobic contact processes can be successfully operated with an average retention of the waste flow as little as 12 hours. In this manner the required volume of the reactor is greatly reduced and the econimics become more favorable. Table 3 shows the performance of the anaerobic activated sludge process studied by many investigators.

Although these anaerobic contact process have been used successfully for treating low-strength wastes, they are most effective for treating wastes which contain a significant concentration of suspended solids. With such wastes, the biological growth becomes attached to the solid particles so that it settles and is more readily separated from the effluent stream.

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With soluble wastes, the biological solids often remain dispersed or only lightly flocculated and a significant fraction may be lost with the effluent. Settling of these solids can only be accomplished with degasification or the addition of some inert solid material to promote flocculation (SCHROEPFER et. al., 1955). Rates of recycle from the solids separation unit as high as four times the normal waste flow rate is often required to maintain a satisfactory treatment efficiency (SCHROEPFER et.al. 1959).

Table 3 Summary of Anaerobic Contact Process Performance

| Waste | Hydraulic Detention Time Days | Digestion Temperature °C | BOD$_5$ | | | | Reference |
| | | | Raw Waste mg/l | lb/1000 cu.ft./day | | Percent Removed | |
				Added	Removed		
Maize starch	3.3	23	6,280	110	97	88	HEMANS et. al., (1962)
Whiskey distillery	6.2	33	25,000	250	237	95	PAINTER et. al., (1960)
Cotton kiering	1.3	30	1,600	74	50	67	PETTET et. al., (1959)
Citrus	1.3	33	4,600	214	186	87	McNARY et. al., (1954)
Brewery	2.3	-	3,900	127	122	96	NEWTION et. al., (1962)
Meat packing	1.3	33	2,000	110	104	95	PETTET et. al., (1959)
Meat packing	0.5	33	1,380	156	142	95	STEFFEN et. al., (1962)
Meat packing	0.5	35	1,430	164	156	95	SCHROEPFER et. al., (1955)
Domestic	1.0	22	510*	31*	26*	83*	RAO et. al., (1971)

* COD basis.

Although heating greatly improves the rate of waste stabilization in anaerobic contact processes, a waste strength of about 6000 mg/1 BOD is required to produce a sufficient quantity of methane to increase the waste temerature by as little as 10°C (McCARTY 1964).

Consequently, anaerobic contact processes are better suited for the treatment of either concentrated or naturally warm wastes; and, in general, they have not proved satisfactory for wastes containing less than about 2000 mg/1 BOD at temperature below 30°C (McCARTY 1964)

3.1.3 Anaerobic filter   The anaerobic filter consists of a bed of media suitably sealed from the atmos here to maintain an oxygen free environment. The filter media are curshed stone or pebble gravel similar to those used in aerobic trickling filter. The waste to be treated is distributed across the bottom of the filter and flows upward through a bed of media anaerobic microorganism become attached to the filter media and trapped in the void spaces. The waste comes in contact with a large biological mass as it passes through the filter and is stabilized by the metabolic activity of these microorganisms.

Table 4 sumarized the anaerobic filter performance reported by many investigators. However, the filter has also been applied successfully as a treatment process for reasons other than organic removal. In studies by TAMBLYN (1970) and SEIDEL (1970), the anaerobic filter was used as a reactor for the biological denitrification of highly nitrified subsurface dranage waters and aerobic activated slu'ge effluents. With methanol as a carbon source, nitrate removal exceedin 90 percent were achieved with detention times that range from 0.5 to 2.0 hr. Also, Mc HARNESS et. al., (1975) conduct the investigations successfully on field studies of nitrification with submerged filters.

YOUNG and Mc CARTY (1969) compared the anaerobic filter with other existing biological processes and pointed out a number of distinct advantages in using the former:

1. The anaerobic filter is ideally suited for the treatment of soluble wastes

Table 4 Summary of Anaerobic Filter Process Performance

Waste	Theoretical Detention Time, Hours	Raw waste COD mg/l	Loading lb COD per 1,000 cu.ft. per day	percent Removal	Reference	
Synthetic	6-12	2,000	107-224	74-88	Mc CARTY	(1968)
Synthetic	4.5-72	1,500-6000	26.5-212	63.2-99.2	YOUNG et.al.,	(1969)
Brewery	-	6,000-24,000	50-100	90	LOVAN et.al.,	(1971)
Starch	22	8,800	237	64	TAYLOR	(1971)
Domestic	-	170* - 240*	-	65-75	RAMAN et.al.,	(1972)
Metrecal	18	10,000	427	70-93	EL-SHAFIE et.al.,	(1973)
Pharmaceutical	12-48	1,000-16,000	13.8-220	93-98	JENNETT et.al.,	(1975)

* BOD Basis

2. No effluent or solids recycle is required with the anaerobic filter. The biological solids remain in the filter and are not lost with the effluent .

3. The accumulation of high concentrations of active solids in the filter permits the treatment of dilute wastes at minimal temperatures.

4 very low volumes of sludge are produced by the anaerobic filter. The effluent is essentially free of suspended solids, and sludge wasting in some cases is almost nonexistent.

The anaerobic filter then potentially approaches the "ideal" waste treatment process for low-strength soluble wastes.

3.2 The Kinetics of Biological Waste Treatment

An empirical expression which describes the net growth of microorganism in a continuous flow completely mixed both aerobic and anearobic biological waste treatment system are reported in the literatures (MONOD 1942, ECKENFELDER 1955) as follows:

$$\frac{dM}{dt} = a \left(\frac{dF}{dt}\right) - bM \tag{1}$$

where

$\frac{dM}{dt}$ = net growth rate of microorganisms per unit volume of reactor, mass/volume-time

$\frac{dF}{dt}$ = rate of waste utilization per unit volume of reactor, mass/volume-time

M = Microorganism concentration, mass/volume

a = growth yield coefficient, mass/ mass

b = microorganism decay coefficient, $time^{-1}$

The volumetric rate of waste utilization is related to both concentration of microorganisms in the reactor and concentration of the growth limiting substrate surrounding the organisms; which is first purposed by MONOD (1942).

$$\frac{dF}{dt} = \frac{k\ SM}{K_s + S} \tag{2}$$

where

S = waste concentration in the reactor, mass/volume,

k = max. rate of waste utilization per unit weight of microorganisms occuring at heigh waste concentration, $time^{-1}$ and ,

K_s = half concentration when $\frac{dF}{dt}$ is equal to $\frac{k}{2}$, mass/volume.

Combining Equation 1 and 2 leads to the following expression

$$\frac{dM/dt}{M} = \frac{ak\ S}{K_s + S} - b \tag{3}$$

and, $\frac{dM/dt}{M}$ is equal to the net growth per unit weight of microorganism per unit time, and may be designated as net specific growth rate, U

so, $$U = \frac{akS}{K_s + S} - b \tag{4}$$

The reciprocal of net specific growth rate is the solids retention time, SRT or mean cell resident time Θ

SRT, $$\Theta_c = \frac{M_T}{(\Delta M / \Delta T)_T} \tag{5}$$

where,

M_T = Total weight of active microbial solids in the system, mass $(\Delta M / \Delta T)_T$ = Total quantity of active microbial solids withdrawn daily, including those solids wasted and those lose in the effluent, mass/time.

The efficiency of a waste treatment process is defined is:

$$E = \frac{100(S_o - S_1)}{S_o} \tag{6}$$

where

E = treatment efficiency, percent

S_o = influent waste concentration, mass/volume

S_1 = effluent waste concentration, mass/volume

There are two efficiencies of interest the specific efficiency, E_s, and the gross efficiency, E_g. Specific efficiency refers to the

removal of some spcific component or group of componets in the waste
stream. With anaerobic treatment, one may be interested in the removal
of one or more volatile acids or lipid material. Gross efficiency
refers to the removal of waste as measured by some nonspecific or gross
parameter e.g., carbonaceous organic material measured as volatile solids
or chemical oxygen demand (COD).

Treatment dfficiency depend on the SRT and process failure
due to kinetic stress will occur when the SRT is reduced to a value at
which the mocroorganisms are washed from the system at a rate greater
than their max. net specific growth rate(Figure 6).

When the influent waste concentration is large enough to
be non-growth limiting, i.e., $S = K_s + S$, the minimum value of SRT at
which process failure can express from equation 3 as,

$$\frac{1}{SRT_M} = ak - b \qquad (7)$$

where,

SRT_M = minimum value of SRT., day.

With the conventional process, the SRT is equal to the
hydraulic detention time (V/Q). With the anaerobic activated sludge
and the anaerobic filter process, however the removal of excess
microorganisms and the removal of effluent from the system can be
carried out independently of each other so that a long SRT required
for efficient treatment can be maintained while operating at a
relatively short hydraulic detention time.

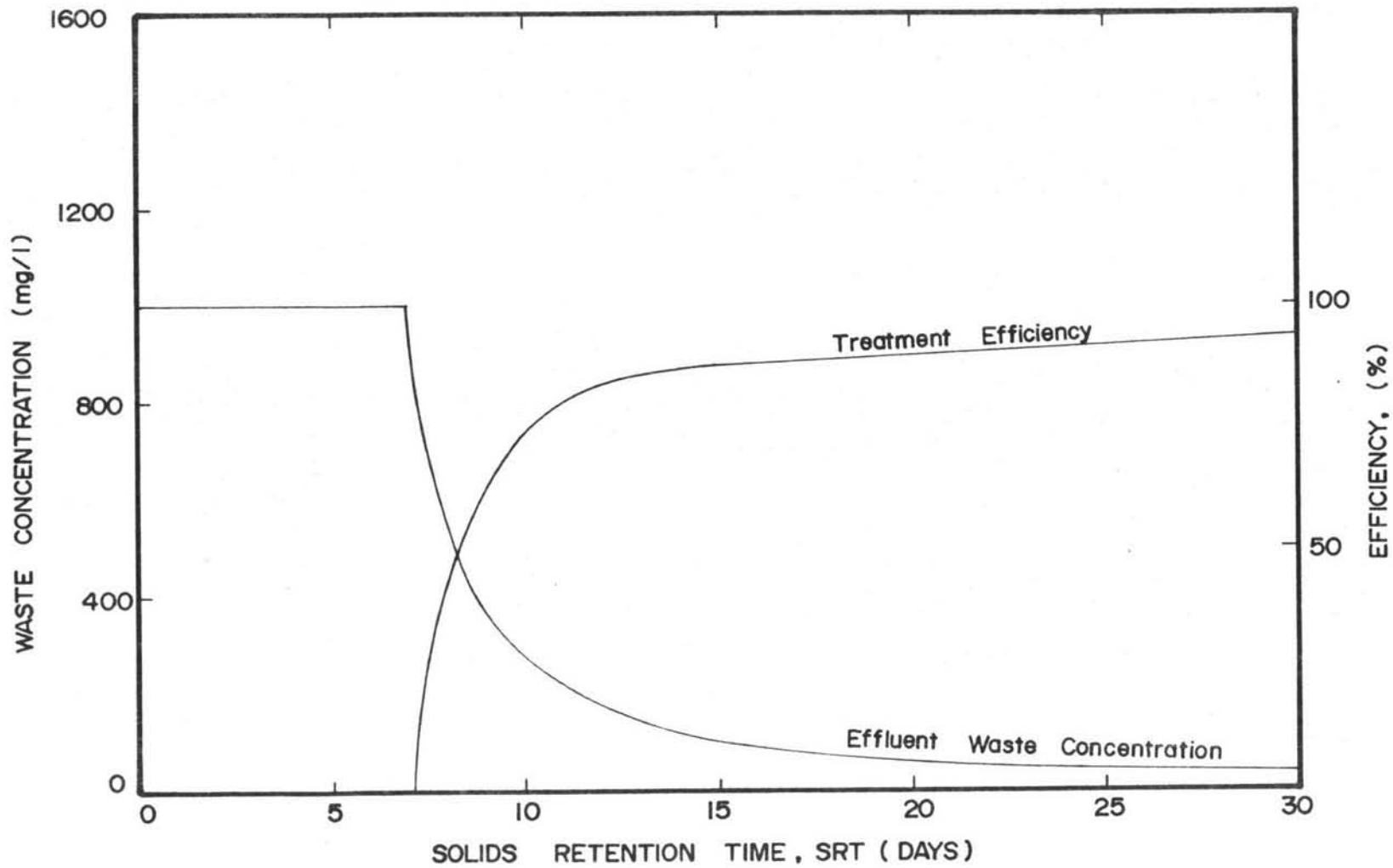The minimum values of SRT which are reported in the litetatures
are summarized in Table 5.

FIGURE 6. RELATIONSHIP BETWEEN SOLIDS RETENTION TIME, EFFLUENT WASTE CONCENTRATION AND TREATMENT EFFICIENCY.

Table 5 Minimum Values of Θ_c for Methane Fermantation of Various Substrates

Energy Substrate	SRT$_m$ (days)				Reference
	35°C	30°C	25°C	20°C	
Acetic acid	3.1	4.2	4.2		LAWRENCE (1969)
Propionic acid	3.2		2.8		LAWRENCE (1969)
Butyric acid	2.7		-		LAWRENCE (1969)
Long chain fatty acids	4.0		5.8	7.2	O'ROURKE (1968)
Hydrogen	0.95		-	-	SHEA (1968)
Sewage sludge	4.2		7.5	10	O'ROURKE (1968)
Sewage sludge	2.6		-	-	TORPEY (1955)

3.3 Biology and Biochemistry of the Anaerobic Filter

Anaerobic treatment of organic wastes can be described from kinetic viewpoint as a two step process involving (1) hydrolysis of complex organic material and organic acid production; (2) methane fermentation, as shown in Figure 7.

```
|←——————————————— First Stage ———————————————→|←Second stage→|
┌─────────────────┐      ┌─────────────┐ Volatile ┌──────────────────┐
│ Complex hydrolysis│──→ │ Soluble  Fermentation│ fatty   fermentation  CO₂ │
│ Organics enzymatic│     │ Products acid formers│ acids   methane      CH₄ │
└─────────────────┘      └─────────────┘          formers └──────────┘
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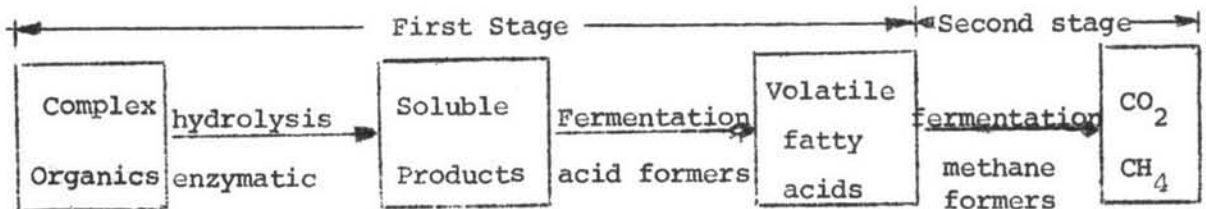
Figure 7 Two Stages of Methane Fermentation of Complex Organics

In the first stage complex organics are converted to less complex soluble organic compounds by enzymatic hydrolysis. These hydrolysis products are fermented to simple organic compounds,predominantly volatile fatty acids, by a specific group of facultative and anaerobic bacteria collectively called "acid formers". In the second step the simple organic compounds are fermented to methane and carbondioxide. The second step has generally been assumed to be accomplished by a group of substrate-specific, obligate anaerobic bacteria called the "methane formers". In the first stage, there is no reduction in COD, and hence essentially no reduction in BOD, because no inorganic oxidizing agent, such as oxygen is added and also no reduced organics are removed from the waste stream. The real COD and BOD reduction in anaerobic process accurs during the second stage of methane fermentation, by conversion of volatile acid to methane and carbondioxide (SPEECE & Mc CARTY, 1962)

3.3.1 Production of volatile acids   In this stage the "acid formers" elaborated extra-cellular enzymes hydrolyze the complex organic solids to soluble organic intermediates which the bacteria can utilize. The cellulose and starches are hydrolyzed to the simple sugars, while the proteins are broken to the amino acids. Only the fatty acids are not attacked by the extracellular enzymes. The bacteria begin to

metabolize the soluble organics and producing mainly saturated fatty acids, carbondioxide, ammonia (during protein degrodation) and cell matter as end-products.

Studies have shown that during acidogenesis of the waste there are no reduction in the COD of the nonacidic soluble organics called constant COD (or BOD) stage of digestion (SPEECE & Mc CARTY 1962). Instead, there is a small increase in COD, possibly because of the addition of degradation products of organic solids (GHOSH, et.al., 1975)

Volatile acids which have been found to occur in digesting sewage sludge include formic, acetic, propionic, butyric, valeric, caproic and isovaleric (POHLAND and BLOODGOOD 1963, KALPOVSKY 1951, LIUBIMOV and KAGAN, 1958). In the fermantation of many substances such as glucose, cellulose, glycerol, several amino acids, etc, pyruvic acid is a key intermediate which may be subsequently attacted to yield a variety of compounds. Details of the major metabolic pathways leading to pyruvic acid are shown in literature (WOOD, 1962).Figure 8 shows the variety of compounds that may arise from pyruvate. The boxed compounds are the possible end products. The volatile acids, gases, and alcohols formed may be utilized as substrates by the methane bacteria although it has been demonstrated (HEUKELEKIAN and BERGER, 1951) that alcohols are probably of minor importance in the digestion of sewage sludge as currently practiced.

Volatile acids may also be formed in the fermentation of some amino acids without passing through pyruvic acid as an intermediate. As an example, leucine and valine can be oxidized via Strickland reactions to the branched-chain volatile acids isovaleric and isobutyric respectively. Other amino acids, such as glycine, proline, etc., can serve as acceptors for the hydrogens produced. The oxidation of leucine to isovaleric acid is of special interest since this could account for the isovaleric acid
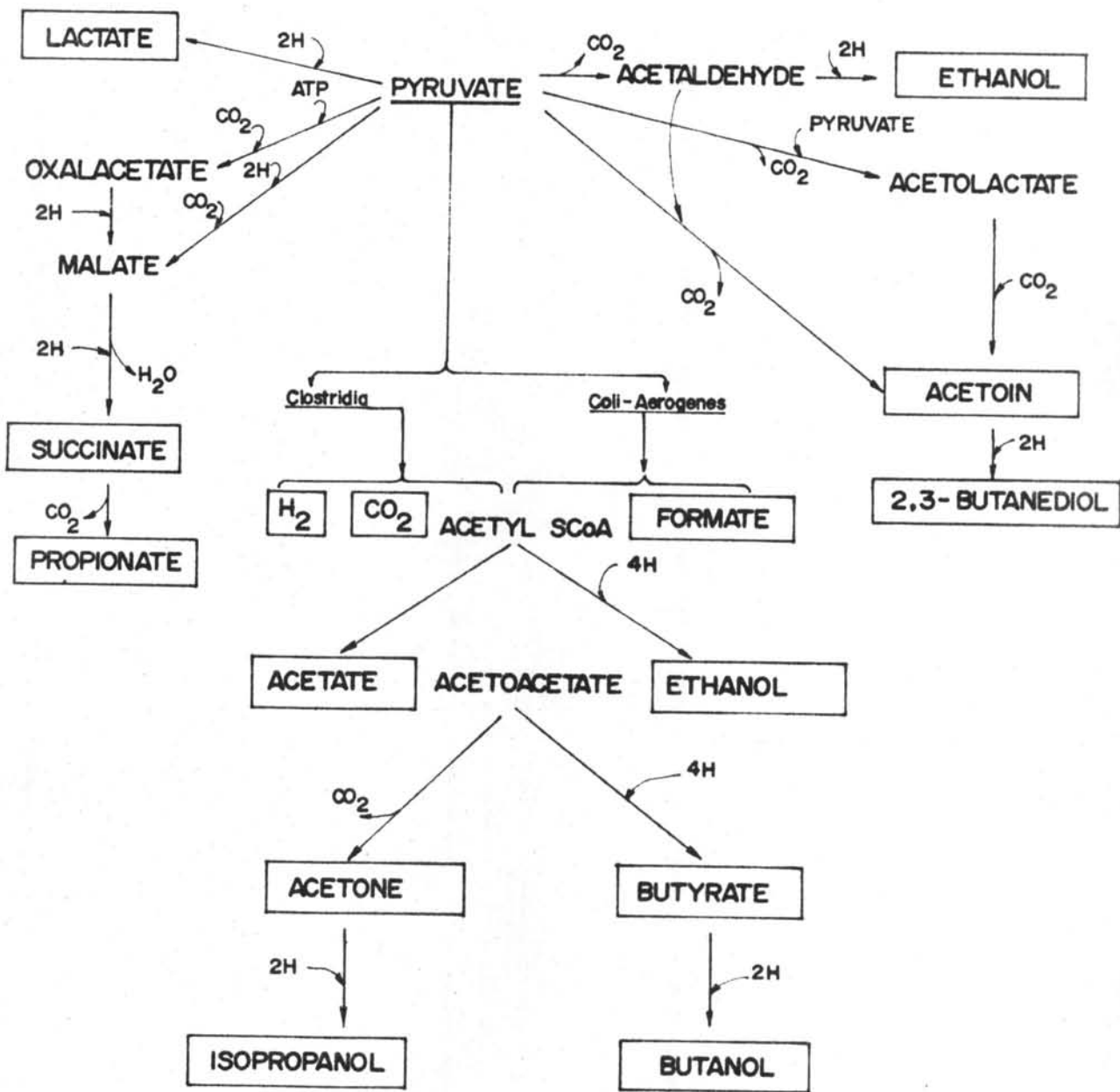
FIGURE 8 – FERMENTATION PRODUCT FORMATION FROM PYRUVATE

Volatile acids are also produced from fats. The fat is first hydrolized to glycerol and long chain fatty acids such as stearic, oleic, palmitic, etc.. The glycerol can then be converted to pyruvic acid vai glycolysis which in then will be to volatile acids or other products as previously described. JERIS and Mc CARTY (1962) have shown, using palmitic and octanoic acid labeled with carbon-14, that degradation is by beta-oxidation with acetic acid, carbon dioxide, and methane as products,the acetic acid could then be further degraded to methane and carbondioxide by another species of methane bacteria.

Volatile acids can also be formed from inorganic compounds but the importance of this in sewage sludge digestion has not been established. Equation 8 (THIMANN, 1963) shows the production of acetic acid from hydrogen and carbon dioxide by Clostridium aceticum.

$$2 CO_2 + 4 H_2 \longrightarrow CH_3COOH + 2H_2O \tag{8}$$
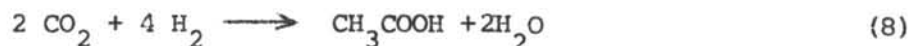
The accumulation of volatile acids in this stage which results from the fermentation may be the cause of a decrease in pH and a change in oxidation reduction potential. The additional unionized volatile acid the low pH (< 6.4) usually lead to the process being "stuck" the efficiency of which may be reduced to zero.

Kinetics of volatile acid production in anaerobic fermentaion process was first intensively investigated by ANDREWS and PEARSON (1965). From kinetics models, shown in Equations 1 & 2, they presented the kinetic coefficients of acid production bacteria as growth yield coefficient (a) = 0.54 mg V.S.S./mg COD utilized, specific organism decay coefficient (b) = 0.87 day^{-1} and maximum growth rate (k) $\geq$ 1.33 day^{-1}.

3.3.2 Methane fermantation stage   In the second or methane fermantation stage of anaerobic treatment, each of the organic acids produced in the first stage conversion of complex organics undergoes methane fermantation at a rate specific to that acid. It is only by this second stage reaction that any significant waste stabilization

occurs. The COD of the organic acids utilized is almost entirely converted to methane gas with only a small fraction converted to biological solids (SPEECE & Mc CARTY, 1962, LAWRENCE 1971).

The methane bacteria occur as sacinae, rods, and occi, only a most unusual representative, Methanococcus vanniellii is highly motile and has very fragile walls and large cell forms (STADTMEN &- BARKER 1951). They are obligate anaerobes with great sensitivity to oxygen, slow growing and can grow over a wide range of temperatures (COOLHAAS, 1928). To date only six species of methane bacteria have been obtained in pure culture. M. vanniellii (STADTMAN & BARKER - 1951), Methanobacterium ruminantium (SMITH & HUNGATE, 1958), Methano- bacterium Mobillis (PAYNTER, 1968), Methanobacterium formicicum (KLUYVER, 1947), Methanobacterium omelianskii (LANGENBERG & BRYANT,1968) and M. thermoautotrophicus (ZEIKUS & WOLFE, 1972). A partial and abbreviated scheme showing the interrelationship between the methane bacteria and other representatives of the anaerobic carbon cycle is listed in Figure 9.

JERIS & Mc CARTY (1962), conducted an experiment on the biochemistry of methane fermentation using C^{14} tracers. They concluded that, during methane fermentation the medium and long-chain organic acids are first converted to short-chain volatile acids, particularly acetic and propionic by beta-oxidation scheme, during which a small amount of methane is produced by the mechanism of carbondioxide reduction. The carbohydrates glucose, starch, and cellulose yield essentially two moles of acetic acid for each mole of glucose degraded, while leucine yields essentially two moles of acetic for each mole of leucine degraded.
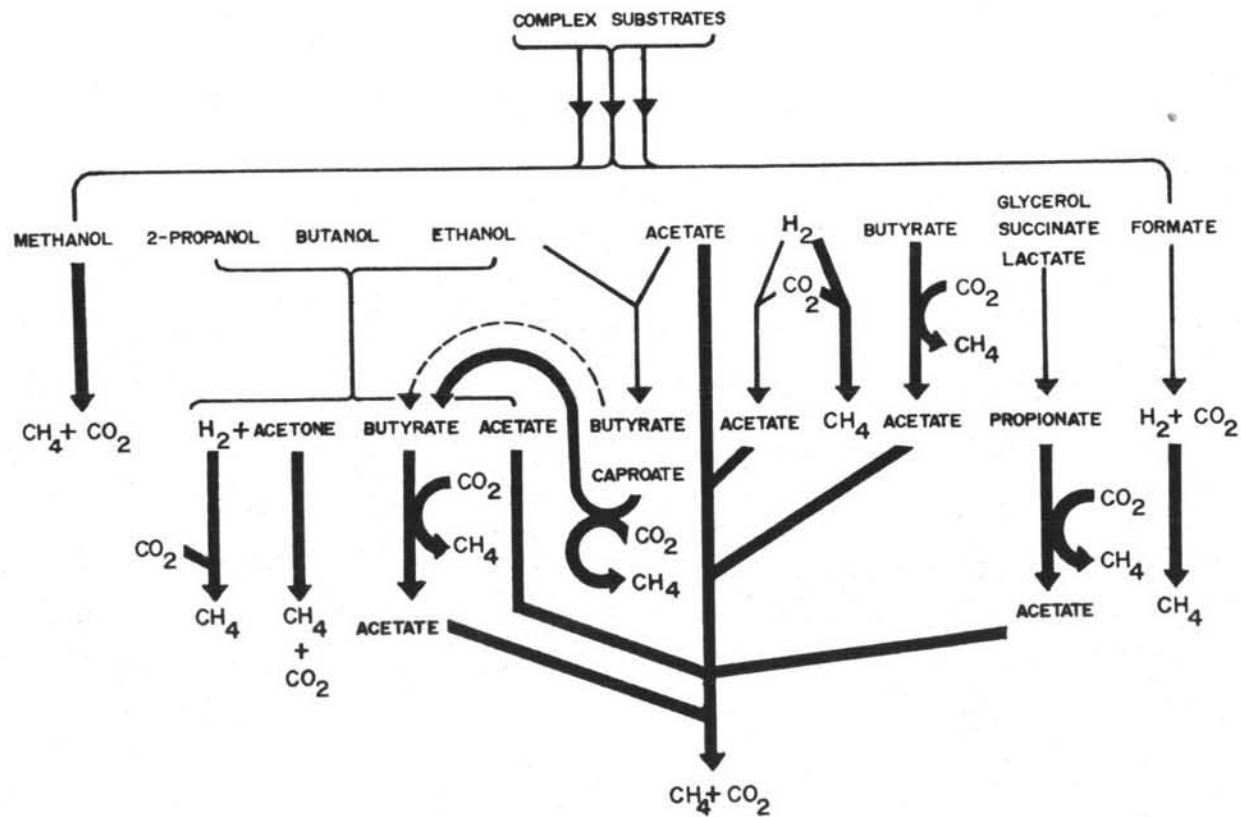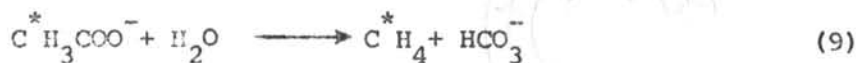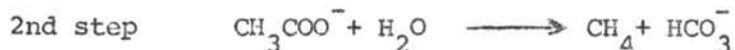
FIGURE 9. INTERRELATIONSHIP BETWEEN THE METHANE BACTERIA AND OTHER SUBSTANCES OF THE ANAEROBIC CARBON CYCLE

When the complex organic matters are metabolized to intermediate short-chain organic acids, methanogenic bacteria undergo stabilization to stable end products. According to BARKER (1956), acetic acid is fermented to methane and carbondioxide in single step, while both propionic and butyric acids are fermented in two steps. In the first step these acids are fermented to acetic and methane by species of methanogenic bacteria. The resulting acetic acid is then fermented by different methanogenic species to methane and carbondioxide. The stoichiometry of these fermentations is shown by the following equations.

Acetic Acid

$$\overset{*}{C}H_3COO^- + H_2O \longrightarrow \overset{*}{C}H_4 + HCO_3^- \tag{9}$$

Propionic Acid

1st step
$$CH_3CH_2COO^- + \frac{1}{2}H_2O \longrightarrow CH_3COO^- + \frac{3}{4}CH_4 + \frac{1}{4}CO_2 \tag{10}$$

2nd step
$$CH_3COO^- + H_2O \longrightarrow CH_4 + HCO_3^-$$

Overall
$$CH_3CH_2COO^- + \frac{3}{2}H_2O \longrightarrow \frac{7}{4}CH_4 + \frac{1}{4}CO_2 + HCO_3^- \tag{11}$$

Butyric Acid

1st step
$$CH_3CH_2CH_2COO^- + HCO_3^- \longrightarrow 2CH_3COO^- + \frac{1}{2}CH_4 + \frac{1}{2}CO_2 \tag{12}$$

2nd step
$$2CH_3COO^- + 2H_2O \longrightarrow 2CH_4 + 2HCO_3^-$$

Overall
$$CH_3CH_2CH_2COO^- + 2H_2O \longrightarrow \frac{5}{2}CH_4 + \frac{1}{2}CO_2 + HCO_3^- \tag{13}$$
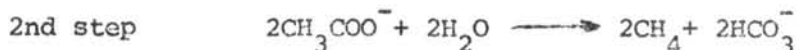
70 percent of the methane formed in a digester proceeds through an acetic acid intermediate step by direct cleavage into methane and carbondioxide (JENSE & Mc CARTY,1967). The methyl carbon of acetic acid, marked with an asterisk in Equation (9),together with its three hydrogen atoms, are converted intact into methane gas. The carbobyl carbon shown without an asterisk, is converted to carbondioxide. The remaining methane is formed from the reduction of carbondioxide. Hydrogen, which is removed from organic compounds by enzym-
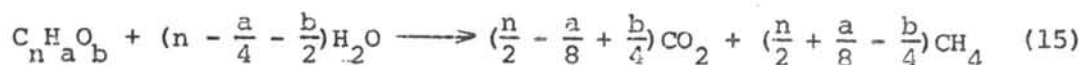-es,

reduces carbondioxide to methane gas. The carbondioxide here function as a hydrogen or electron acceptor. The chemical reaction is shown in Equation (14) (Mc CARTY 1964).

$$CO_2 + 8H \longrightarrow CH_4 + 2H_2O \tag{14}$$

It should be noted that some species of the methane bacteria can produce not only methane and carbondioxide but also other volatile acids as illustrated in Figure 10. In this case of organisms utilizing volatile acids with four or more carbon atoms a net increase in acidity can result. This increase in acidity can be substantial in the case of the long-chain fatty acids and illustrates the need for the estabishment of a balance population of methane bacteria in a reactor since a decrease in numbers or activity of some species, especially those utilizing acetic acid, could result in a gross increase in volatile acids with possible process failure.

The method of predicting methane production from waste chemical composition was first proposed by BUSWELL (1952):

$$C_nH_aO_b + (n - \frac{a}{4} - \frac{b}{2})H_2O \longrightarrow (\frac{n}{2} - \frac{a}{8} + \frac{b}{4})CO_2 + (\frac{n}{2} + \frac{a}{8} - \frac{b}{4})CH_4 \tag{15}$$

McCARTY (1964) gave the following useful relationship between the COD destroyed and the methane produced.

One pound BOD_L or COD stabilized = 5.62 cu.ft. CH_4 (STP) (16a)

or One gram BOD_L or COD stabilized = 0.351 lit. CH_4 (STP) (16b)

The mode of substrate utilization can be described by Equation (2) and the value of the coefficients are summarized in Table 6.
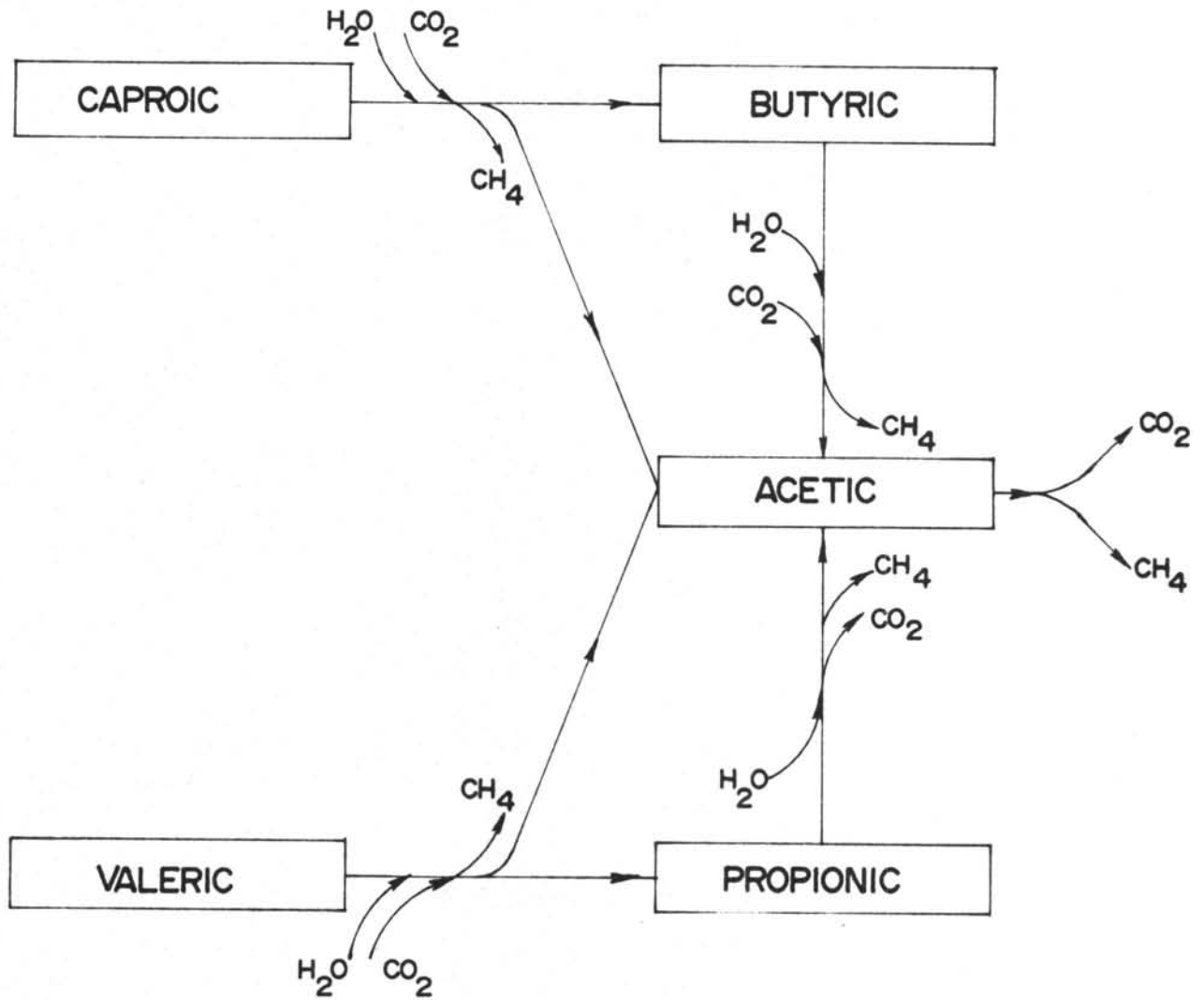
Figure 10. PRODUCTION OF METHANE AND CARBON DIOXIDE FROM
VOLATILE ACIDS.

Table 6 Average Values of Substrate Utilization Coefficient (LAWRENCES,1971)

Substrate	Temp. °C	K_S (mg/l)		k (mg/mg-day)	
		as COD	as HAc	as COD	as HAc
Acetic	25	930	869	5.0	4.7
	30	356	333	5.1	4.8
	35	165	154	8.7	8.1
Propionic	25	1145	613	7.8	9.8
	35	60	32	7.7	9.6
Butyric	35	13	5	8.1	15.6
Long chain fatty acids	20	4620	--	3.85	--
	25	3720	--	4.65	--
	35	2000	--	6.67	--
Complex waste	20	10610	--	3.85	--
	25	5790	--	4.65	--
	35	2224	--	6.67	--

* HAc = Acetic Acid.

3.3.3 The rate-limiting step   The rate-limiting step can be defined as that step in the process which will cause process failure to occur under imposed conditions of kinetic stress.   The first case is due to reducing the value of mean cell resident time, Θ_c (or SRT), until the limiting value of Θ_c is reached (Equation 7), at which the removal rate of microorganism is greater than their maximum growth rate, so a waste treatment efficiency equal to zero. The other case is due to a built-up in the concentration of long and short chain fatty acids, the predominate precursors of methane as reported by ANDREW (1965), SAWYER (1955) and TORPEY (1955).

BUSWELL (1963) suggested that the propionate anion is toxic to the methanogenic bacteria and hence may limit the process, but Mc CARTY (1969) indicated that, when the proper environmental contitions are maintained, propionic acid is converted at a greater rate than acetic acid and is stabilized to methane at approxidately the same rate. (values of k and K_s are shown in Table 6).

3.3.4 Biological solids production   Equation (1) describes the net growth-rate of microorganism in a continuous flow completely-mixed system.   The values of growth yield coefficient, a, and microorganism decay coefficient vary considerably from one type of waste to the other.   Thus, the growth cannot be predicted from a knowledge of the waste strength alone, as it is also related to waste composition (McCARTY, 1964).   The two extremes in growth are represented by fatty acid wastes, which produce the lowest growth, to carbohydrates, which produce the highest.   Other types of waste can be expected to vary between these two extremes, (McCARTY 1964, SPEECES & McCARTY 1962) . Growth yield and decay coefficient reported in the literatures are listed in Table 8.

Table 7 Growth Yield and Decay Coefficient of Various Substrate.

Substrate	a (mg/mg)	b (day^{-1})	References
Acetic acid	0.040	0.019	IAWR.& McC.
Propionic acid	0.042	0.010	"
Butyric acid	0.047	0.027	"
Glucose & Starch	0.46	0.088	SPEECE&McC.
Amino & Fatty acid	0.054	0.038	"
Nutrient broth	0.076	0.014	"

Mc CARTY (1964) also showed that the quantity of waste converted
to biological suspended solids decreases with increasing SRT.   When
cells are maintained for long periods of time, they consume themselves
for energy, with the result that the net growths are becoming less.
In the case of anaerobic filter, because of very long solids retention
time, (100 to 600 days), the net systhesis is very small requiring
no   sludge wasting over 300 days of operation. (YOUNG & Mc CARTY, 1969,
JENNETT & DENNIS, 1975).

3.3.5 Environmental condition for optimum performances

3.3.5.1 Nutrient requirements   SPEECE and Mc CARTY
(1962) conducted an intensive study on nutrient requirements of these
microorganism. As these authors indicated, the nitrogen requirements
for all substrate were equal to the net synthesis divided by 9.4
and the phosphorous requirements were approxidately one-seventh of
the nitrogen. Mc GARTY (1964) recommended the minimum requirements of
the nitrogen and phosphorous to be 0.011 pounds and 0.002 pounds
pounds of BOD_L, respectively.

SANDERS & BLOODGOOD (1964) investigated the effect of nitrogen-to-carbon ratio on anaerobic decomposition. They concluded that the minimum nitrogen-to-carbon ratio in the daily organic loading was approximately 0.0620, and the higher ratio did not appear to improve decomposition.

3.3.5.2 pH and alkalinity   Tight pH control is required for this process because methane bacteria are extremely sensitive to slight changes in pH. The usual pH range required is from 6.6 to 7.4. In general, it has to maintain the pH as close to 7.0 as possible (Mc CARTY,1964).

Alkalinity in a digester is normally composed of organic-ammonium salts such as ammonium bicarbonate (NH_4 HCO_3) and ammonium acetate ($CH_3COO. NH_4$). The dynamic nature of buffer destruction and formation in the digester is illustrated by the following equation .

$$C_6H_{12}O_6 \longrightarrow 3CH_3COOH \tag{17}$$

$$3CH_3COOH + 3NH_4HCO_3 \xrightarrow{\text{acid formers}} 3CH_3COONH_4 + 3H_2O + 3CO_2 \tag{18}$$

$$3CH_3COONH_4 + 3H_2O \xrightarrow{\text{methane formers}} 3CH_4 + 3NH_4HCO_3 \tag{19}$$
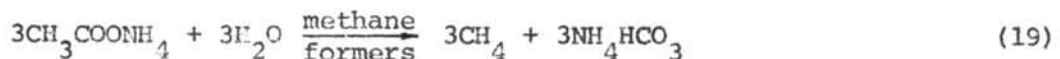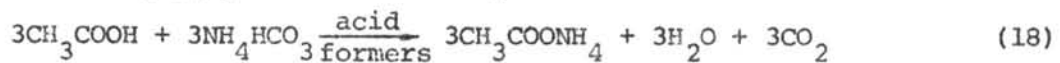
Equation (17) represents the breakdown of glucose to acetic acid by acid forming bacteria. The acid is neutralized, as shown in Equation (18), by the bicarbonate buffer. If sufficient buffer is not present, the pH would drop and the conversion of acetate to methane as shown in Equation (19), would be inhibited. During the reaction in Equation 19, the buffer consumed in the reaction in the Equation 18 is reform-
-ed

BONTA and POMEROY (1934) showed that the pH of the system is directly proportional to the bicarbonate alkalinity and the percentage of CO_2 in the gas, the correlation may be expressed as ,

$$pH = 5.14 - \log (\text{percent } CO_2) + \log HCO_3^- \text{ (as mg/1 } CaCO_3) \tag{20}$$

Mc CARTY (1964) illustrated the relationship between pH and bicarbonate concentration (Fig.11) which indicates that the bicarbonate alkalinity should be maintained at a minimum level of 1000 mg/l as $CaCO_3$ to ensure adequate pH control .

The rate of change of the volatile acids to alkalinity ratio may be described quite satisfactority the digestion environment. In any event, increases in the ratio above 0.3 to 0.4 indicate stress and process failure will occur when a ratio of 0.8 is reached (WPCF manual of practice No. 16).

Steady state acetate fermentation at pH levels as low as 4 by using anaerobic filter was reported by CLARK & SPEECE (1970), as well as, LOVAN & FOREE (1971), because of a high concentration of bacterial solids to affect the reduced unit activity caused by non-optimum pH levels.

3.3.5.3 Temperature   BABBITT and BAUMANN (1958) stated that digestion ceases at temperatures below 50°F (10°C). The effective ranges of temperatures suitable for mesophilic bacteria were found to be from 30 to 38°C (85-100°F) by Mc CARTY (1964), from 29 to 40°C (80-104°F) by ECKENFELDER and O'CONNOR (1964), and from 32 to 35°C (90-95°F) by SCHLENZ (1951). However, higher rates of treatment are achieved at thermophilic temperature about 50°C but it is impractical due to the cost of external heat requirement. Mc CARTY (1964) stated ~ that the waste COD must be equal to or greater than 5000 mg/l to significantly increase the temperature of the inffuent waste without a supplemental fuel requirement.

The study of methane fermentation kinetics by LAWRENCE & Mc CARTY (1969) showed that the value of maximum rate of waste utilization (k) is relatively unaffected by temperature, but the variation of k in their study may have been caused by shifts in population predominance. The effects of fermentation temperature on
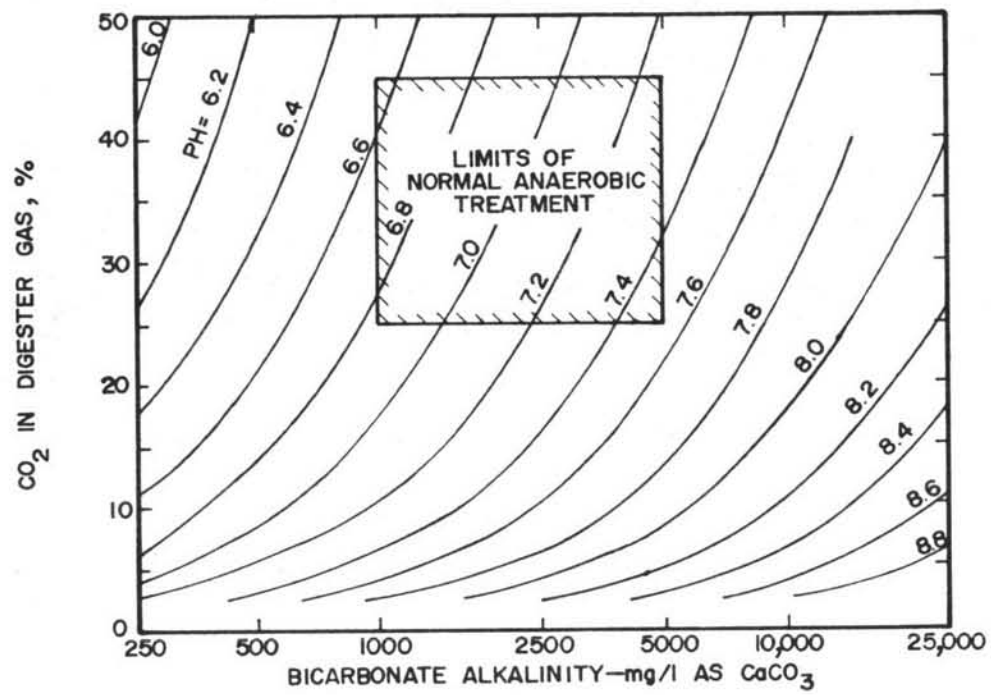
FIGURE II. RELATIONSHIP BETWEEN pH AND BICARBONATE CONCENTRATION NEAR 95° F

half velocity coefficient (K_S) for acetic acid was given. The resulting equation in the form of ARRHENIUS equation, which describes this relationship is :

$$\log \frac{(K_S)_2}{(K_S)_1} = 6980 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{21}$$

where,

T_2 & T_1 = fermentation temperature , °KELVIN.

O'ROURKE (1968) developed the equations to define the temperature dependency of k and K_S for a complex over the temperature range of 20° - 35°C

$$(k)_T = (6.67 \text{ day}^{-1}) 10^{-0.015(35-T)} \tag{22}$$

$$(K_S)_T = (2224 \text{ mg/l COD}) 10^{0.046(35-T)} \tag{23}$$

where,

T = fermentation temperature, °C .

Figure 12   (LAWRENCE 1971) shows the effect of temperature on effluent quality as a funtion of θ_c (min. SRT) for a complex waste The principal effect of temperature is that treatment efficiency at a given value of θ_c decreases with a decrease in temperature. In the case of anaerobic filter, a large value of solids retention time is maintained, so, a lower temperature to achieve a given level of treatment is possible (Mc CARTY 1969).

3.3.5.4 Toxic materials   KUGELMAN and CHIN (1971) reviewed the effect of toxic materials in anaerobic process. They indicated that toxicity in general is due to an excess quantity of any material, even for a substance normally considered as a nutrient. It was also indicated that a quantitative definition of the concentration at which a substance starts to exert a toxic effect is difficult to define because this could be modified by antagonism, synergism and acclimation. In addition, the degree of stress on the process as defined by the organic loading and biological solids retention time can significantly affect toxicity.
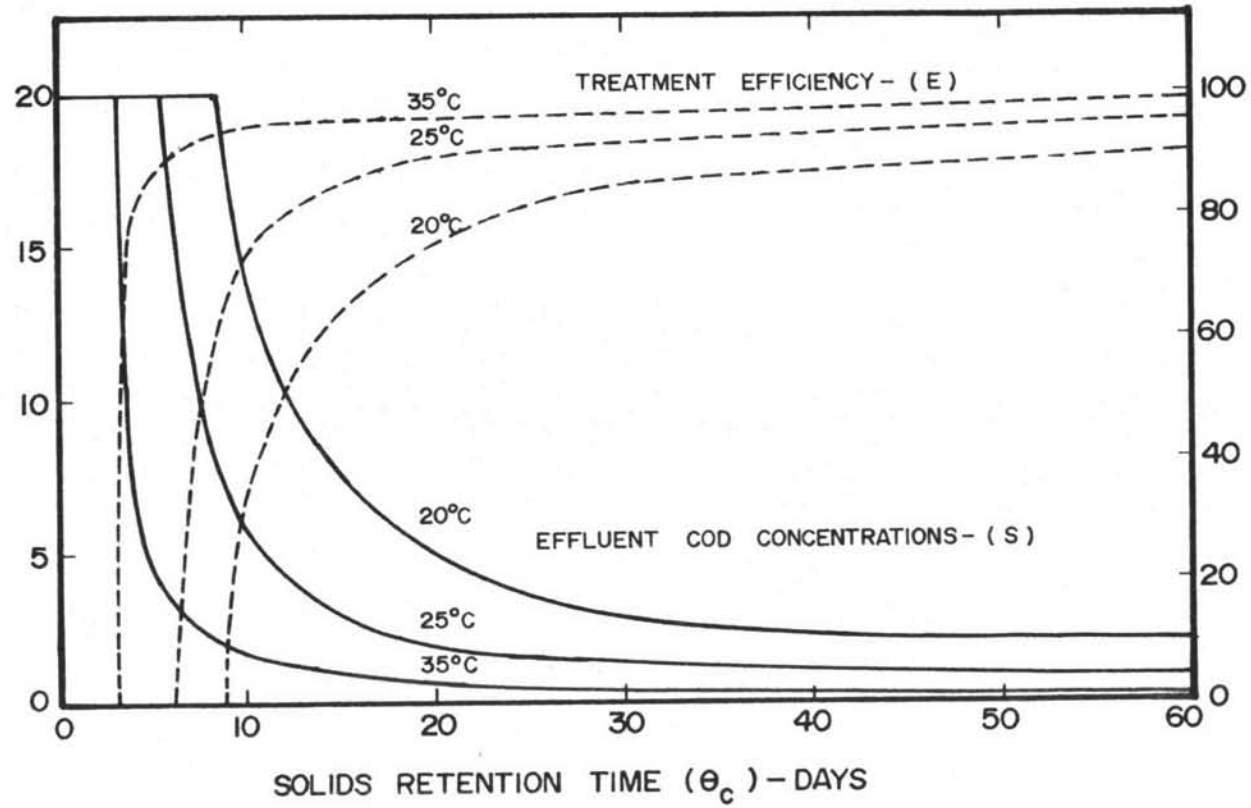
FIGURE 12. PREDICTED EFFECT OF FERMENTATION TEMPERATURE ON EFFLUENT BIODEGRADABLE

COD CONCENTRATION AND TREATMENT EFFICIENCY FOR A COMPLEX WASTE

Many investigators (Mc CARTY & MCKINNEY 1961, KUGELMAN & Mc CARTY 1965, Mc CARTY 1964) reported their results on toxicity in anaerobic process, some information is given in table 8

Table 8 Threshold Toxic Concentrations of Various Substances Situation in Anaerobic Process

Substance	Moderately Inhibitory (mg/l)	Strongly Inhibitory (mg/l)
Sodium	3500-5500	5000
Potassium	2500-4500	12,000
Calcium	2500-4500	8,000
Magnesium	1000-1500	3000
Ammonia Nitrogen	1500-3000	3000
Free Ammonia		150
Heavy Metals (soluble)		1
Sulfides		200

Mc CARTY (1964) proposed the possible methods to control toxic materials in anaerobic process by; (1) removal of toxic material from waste (2) dilution below toxic threshold, (3) formation insoluble complex or precipitate, (4) antogonizing the toxicity with another material.

3.4.3 <u>Biological Solids transport</u>   The biological solids

in the anaerobic filter can increase only up to some maximum concentration
as limited by the available volume, and the rate of bacterial decay
and removal. The removal can be brought about by hydraulic lifting
and by flotation due to gas bubbles attached to the flocculated
biological solids. However, the prospective hydraulic detention times
for the anaerobic filter process are sufficiently long so that the
settling velocity of flocculated solids should normally be greater
than the upward liquid velocity. The effect of gas flotation is
also limited since a flocculated particle with the attached gas bubble
would tend to rise only as far as the filter stone immediately above
it. Also much of the biological mass may be trapped between the filter
stone or attached to the stone surface so that it would not directly
affected by the hydraulic flow rate.

The most significant factor causing the transport of biological
solids is expected to be the scouring and mixing action of the gas
flowing through the filter from one interstitial space to another.
Since both the gas and the liquid waste flow upward through the filter,
the net transport of biological solids at any horizontal cross-section
would be expected to be upward.