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# Anaerobic acidogenesis of wastewater sludge

SAMBHUNATH GHOSH, JOHN R. CONRAD, AND DONALD L. KLASS

THE ANAEROBIC DIGESTION PROCESS has been popular in the waste treatment field for decades because it is characterized by (a) the capability of stabilizing large volumes of dilute organic slurries at low cost, (b) low biomass production, (c) a high kill rate of pathogenic organisms, and (d) the capability of producing solid residues suitable for use as soil conditioners. Perhaps a more attractive feature of this process is its ability to convert the organic carbon in the feeds to a product gas stream high in methane, a commodity in short supply today. It is this aspect of the process that has prompted several investigators to advocate its application for the simultaneous stabilization and gasification of municipal, industrial, and agricultural wastes.<sup>1-6</sup> Thus, it has been estimated that, in a city of 1 million people, 10 to 20 million standard cu ft/day (0.28 to 0.56 million cu m) of substitute natural gas (SNG) may be obtained by digesting municipal refuse alone. This quantity of SNG may satisfy 5 to 9 percent of the community's gas demand and would be a welcome relief from the impending shortage of natural gas. Industrial and agricultural wastes would represent even larger sources of SNG. In view of these developments, we may expect to witness increasing application of the anaerobic digestion process not only for waste treatment but also for the simultaneous production of supplemental fuel gas. The need for improving anaerobic digestion technology is therefore greater now than ever before.

Despite its many advantages, the anaerobic digestion process has not yet reached its full potential. This is attributed to several factors:

1. Variable performance and operation;

2. Lack of knowledge about the physical, chemical, and biochemical interactions;
3. Use of conventional mode of digester operation and design; and
4. Use of empirical design procedures not firmly based on fundamental characteristics of the digesting system.

Despite its biochemical complexity, the anaerobic digestion process is essentially diphasic. The ultimate stabilization of a given type of waste substrate is contingent on the growth and metabolism of two groups of organisms that are very different from each other in terms of physiology, nutritional requirements, growth kinetic capabilities, and sensitivity to environmental stresses. Efficient operation of the conventional anaerobic process requires that the acid-forming organisms grow in harmony with the methane formers, because any loss in the "balance of activities" of these two groups of organisms, particularly in favor of the relatively fast growing acid formers, leads to an upset in the digestion process. These considerations have led engineers to design single-phase digesters that provide for the growth of the sensitive and slow growing methane formers. Thus, conventional methods of digester design and operation provide for the simultaneous enrichment of the acid and the methane formers under identical environmental conditions. Available data indicate that the full metabolic potential of the acid and the methane phases may not be reached under these conditions. It is also probable that such design practices have been instrumental in causing decreased process efficiencies and even process failures.

## PROCESS DESCRIPTION

**Process configuration.** Recognizing the substantial difference in the metabolic characteristics of the acid and the methane formers, some researchers have envisioned controlled anaerobic stabilization by phase separation of the two groups and culturing in isolated environments.<sup>7-11</sup> Optimum environments could then be provided for both groups of organisms, and the substrate loading rates to each group could be controlled, thereby enhancing process efficiency and reliability. This procedure would facilitate process monitoring and automated control techniques.

The benefits of phase separation have been recognized for some time. As early as 1958, Babbit and Baumann<sup>7</sup> suggested that the inhibitory effects of intermediate products produced during the early stages of anaerobic sludge digestion could be overcome by separating the process into two or more stages. In this context, it is important to emphasize that conventional stage digestion should not be confused with the proposed two-phase process. In the former, both acid and methane formers are harbored in a primary stage with provisions for accelerated or high-rate digestion. The secondary stage following the first stage is little more than a holding tank to permit possible polishing and residual solids separation for ultimate disposal and/or recycle.

In contrast to the two-stage digestion process, the two-phase digestion system consists of two separate completely-mixed biochemical reactors in series, one for acid fermentation and the other for methane fermentation. The environment in the first reactor is controlled to promote the growth

and proliferation of the acid formers, while the second reactor receives the products from the first and is designed to provide an environment optimum for the methane formers. Solids recycle may be practiced around each reactor much in the same way as it is in the anaerobic contact process. The respective sizes of the reactors and possible recycle rates for each phase would be based on the growth kinetic requirements of each group of organisms. Because the volatile acids are the primary products of the first phase, pH control in the second phase may be necessary when the buffer capacity has been exceeded. Such control in the methane reactor could be provided by external neutralization of the influent or by recycle of supernatant from the second phase. A physical model of a complete two-phase process is depicted in Figure 1.

## ADVANTAGES AND DISADVANTAGES

The two-phase digestion process has several potential benefits compared with the conventional standard and the high-rate processes. These are:

1. Capability of maintaining the optimum environment for each group of digester organisms;
2. Substantial reduction in total reactor volume and the consequent savings in capital and operating costs;
3. Higher rates of solids stabilization and increased production rate and methane content of the final product gases;
4. Decreased heat requirement and increased thermal efficiency;
5. Suitability for incorporation into exist-

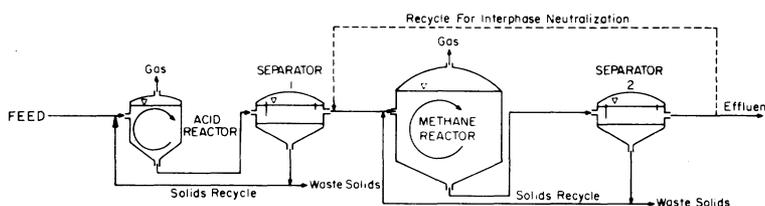


FIGURE 1.—Physical model of the two-phase anaerobic digestion process.

ing treatment plants with minimum capital investment; and

6. Reduction of the nitrogen content of the system effluent by simultaneous liquefaction and denitrification of waste feeds in the acid digester.

The potential disadvantages of the two-phase process include the need for skilled operation and increased instrumentation for monitoring and control. The cost of operating a two-phase digestion system may not be higher (it may even be lower in many instances) than that of the conventional process, because the higher cost of control instrumentation and the probable higher labor cost may be offset by decreased heat requirements and lower capital costs.

#### PHASE SEPARATION TECHNIQUES

The objective of physical separation of the acidogenic and the methanogenic phases is to maintain appropriate densities of dominant cultures of the acid and methane formers in separate reactors, preferably in the exponential growth phase, to maximize the rates of acidification and gasification by exerting independent controls as dictated by the metabolic and biokinetic properties of both groups of organisms. Thus, phase separation should not be construed as a total elimination of all species of methane formers from the acid digester and vice versa; indeed, such complete elimination is probably undesirable.

Phase separation may be accomplished by the dialysis technique suggested by Hammer and Borchardt<sup>8</sup> and Schaumburg and Kirsch,<sup>9</sup> by selected inhibition of each group of organisms through addition of inhibitors (for example, oxygen, nitrates, sulfates, or metals), or by balancing the potential.<sup>10</sup> However, operational difficulties with dialysis membranes and the uncertainties associated with the determination and control of inhibitor concentrations and potential make these techniques unattractive. By comparison, the method suggested by Pohland and Ghosh<sup>12, 13</sup> and Ghosh<sup>14</sup> seems to be more practical and adaptable to existing single-phase diges-

tion systems. This method uses the principles of population dynamics outlined by Ghosh and Pohland<sup>11</sup> and involves the application of biokinetic selection pressure or kinetic control on each of the digestion phases by operational adjustment of the dilution rate and the recycle ratio. Thus, by proper manipulation of these operating parameters, it is possible to preclude any significant growth of the methane bacteria and at the same time achieve maximum acidification of the system feeds in the first digester. The latter achievement would impede the growth of the acid formers but will enrich the methane bacteria in the second reactor. Further enrichment of the two cultures is possible by biomass recycle around each phase.

#### OBJECTIVES

The feasibility of phase separation by kinetic control was demonstrated by Pohland and Ghosh<sup>12, 13</sup> with a simple soluble substrate (glucose). However, the application of this technique to two-phase digestion of wastewater sludge has not been demonstrated. Furthermore, little or no information is available on the biokinetic properties of acidogenic organisms grown on wastewater sludge, which is essential for further development of the two-phase digestion process. In view of these observations, the objectives of the research reported herein were to:

1. Study the feasibility of maintaining dominant cultures of acidogenic organisms with wastewater sludge feeds by kinetic control;
2. Compile information on the biokinetic characteristics of acidogenic organisms, which is essential for operating an acid-phase digester receiving sludge substrates; and
3. Develop guidelines and criteria for operating acid-phase digestion with wastewater sludge feeds.

#### THEORETICAL CONSIDERATIONS

In order to evaluate the biokinetic characteristics of the acidogenic organisms and to be able to describe and project the be-

havior of the acid-phase digester under various operating modes, it was necessary to use a number of process kinetic equations reported earlier by Ghosh.<sup>14</sup> These equations were derived from mass balances around the acid digester and were based on the growth kinetic model proposed by Monod. Thus, substrate [volatile solids (vs)] and biomass balances for the acid formers yielded the following relationships describing steady-state substrate and biomass concentrations as functions of the digester detention time.\*

$$S_1 = \frac{K}{\hat{\mu}^{\theta-1}} \quad (1)$$

where:

- $S_1$  = steady-state substrate concentration for acid formers, g/l,
- $K$  = saturation concentration, g/l as vs,
- $\hat{\mu}$  = maximum specific growth rate, 1/hr,
- $\theta$  = theoretical detention time, hr.

$$x = \frac{L\theta - S_1}{U_p + U_e + m\theta} \quad (2)$$

$$\theta_c = \frac{K + S_o}{\hat{\mu} + S_o} \quad (3)$$

$$Y = \frac{1}{U_p + U_e} \quad (4)$$

where:

- $x$  = biomass concentration, g/l,
- $L$  = substrate loading, g/l/hr or pcf/day,
- $U_p, U_e$  = substrate utilization coefficients for growth and energy, respectively,
- $m$  = maintenance coefficient for acid formers, 1/hr,
- $\theta_c$  = critical detention time, hr,
- $S_o$  = influent substrate concentration, g/l, and
- $Y$  = true yield coefficient.

Similarly, mass balances of the acidic products of acidogenesis gave the following equations for the steady-state concentra-

\* Symbols used in this paper are defined when they first appear and are arranged alphabetically in the section entitled "Notation."

tion of a volatile acid:

$$A_1 = A_o + \alpha_i x (U_e + m\theta) - x_m (U'_p + U'_e + m'\theta) \quad (5)$$

where:

- $A_1, A_o$  = concentrations of volatile acids at steady state and influent, respectively,
- $\alpha$  = true product yield constant,
- $x_m$  = concentration of methane formers,
- $U'_p, U'_e$  = substrate utilization coefficient for methane formers, and
- $m'$  = maintenance coefficient for methane formers.

Neglecting the growth of methane bacteria in the acid-phase reactor,

$$A_1 - A_o = \alpha_i x (U_e + m\theta); \quad (6)$$

and

$$A_1 = A_o + \frac{\alpha_i (U_e + m\theta) (L\theta - S_1)}{U_e + U_p + m\theta} \quad (7)$$

A corresponding formula that expresses steady-state gas production rate in terms of mass per unit time is

$$G'_1 = \frac{\alpha_g V [(L\theta - S_1) (x) U_p]}{\theta} \quad (8)$$

where:

- $G'_1$  = steady-state gas production rate from acid fermentation, g/hr, and
- $\alpha_g$  = true yield of gas product.

A general equation describing the rate of formation of any product, liquid or gas, in terms of mass of the product per unit time per unit volume of the acid digester is

$$P' = \frac{\alpha (U_e + m\theta) (L\theta - S_1)}{\theta (U_e + U_p + m\theta)} \quad (9)$$

where:

- $P'$  = steady-state formation rate of acidogenesis product at given detention time, g/l/hr.

The biokinetic constants,  $\hat{\mu}, K, U_p, U_e, m, \alpha_i, \alpha_g,$  and  $Y,$  may be determined from the following linear equations obtained by re-

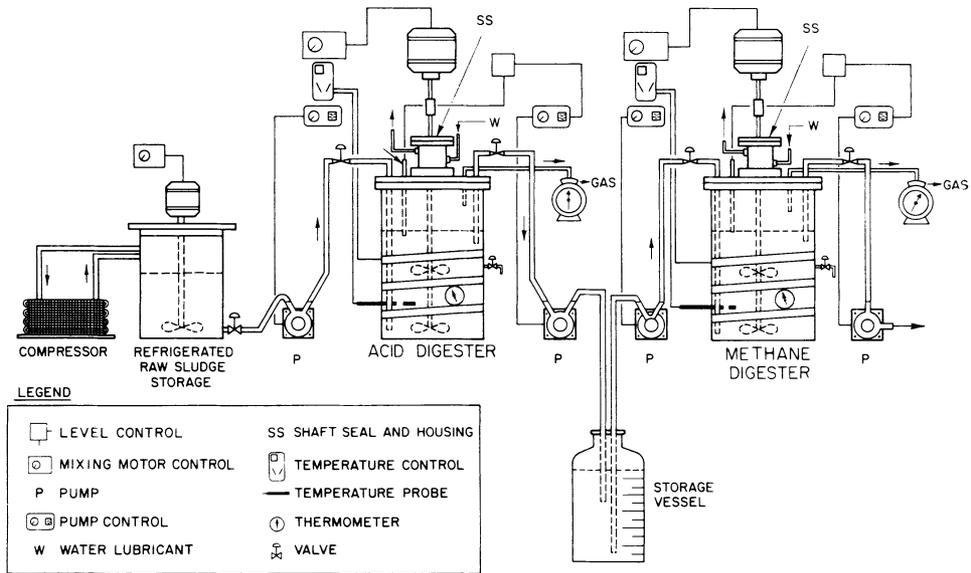


FIGURE 2.—Laboratory two-phase sludge digestion system.

arranging Equations 1, 3, 7, and 8:

$$\theta = \frac{1}{\hat{\mu}} + \frac{1}{S_1} \left( \frac{K}{\hat{\mu}} \right) \quad (1a)$$

$$\frac{L\theta - S_1}{x} = U_p + U_e + m\theta \quad (3a)$$

$$\frac{L\theta - S_1}{A_1 - A_o} = \frac{1}{\alpha_i} + \frac{x(U_p)}{A_1 - A_o} \quad (7a)$$

$$\frac{\theta G'_1}{(L\theta - S_1)} = \alpha_o V - \frac{\alpha_o V U_p(x)}{L\theta - S_1} \quad (8a)$$

The critical detention time for any given organic (vs) loading is given by the formula

$$\theta_c = \frac{L + \sqrt{L + 4K\hat{\mu}}}{2\hat{\mu}L} \quad (10)$$

#### MATERIALS AND METHODS

To demonstrate the feasibility of phase separation by kinetic control involving operational adjustment of the dilution rate, continuous culture experiments were performed by using activated sludge feeds obtained from the Stickney Plant of the Metropolitan Sanitary District of Greater Chicago. The sludge was fed to a custom designed, chemostat-type, 10-l digester maintained at 36° to 37°C, the usual op-

erating temperature for mesophilic field digestion. A schematic diagram of the laboratory two-phase digestion system is presented in Figure 2. With this arrangement, feed sludge stored in a refrigerated reservoir at about 5°C was pumped to the acid digester, the effluent of which was then fed to the second-phase methane digester. Temperature, mixing, flow-through rate, and culture volume were controlled independently for the acid and the methane digesters. The acid digester was allowed to settle down and operate at the pH corresponding to the natural buffering capacity of the liquefying sludge, and no external pH control was exerted. The pH of the methane digester varied between 6.96 and 7.37, and no external pH control was necessary.

The experimental work consisted of a number of steady-state, continuous-flow runs. The acid digester was subjected to detention times ranging from 11 to 28 hr. This range was selected on the basis of earlier digestion work at the Institute of Gas Technology (IGT) and information compiled on the kinetics of methane fermentation of acetate substrate. The acid digester was operated with vs loadings of 2.2 to 2.7 pcf/day (1.47 to 1.80 g/hr/l).

TABLE I.—Anaerobic Acidogenesis of Wastewater Sludge: Data on ORP, pH, Volatile Acids, Ammonia Nitrogen, and Filtrate COD

Detention Time (hr)	ORP (mV)	pH	Volatile Acid Concentration (mg/l)								NH <sub>4</sub> -N (mg/l)		Filtrate COD (mg/l)	
			Influent				Effluent				Influent	Effluent	Influent	Effluent
			HAc	HPr	HBut	HVal	HAc	HPr	HBut	HVal				
12.72	-258	5.74	1,806	764	585	478	2,396	839	890	900	—	—	5,240	4,880
13.20	-264	5.79	1,873	600	376	438	2,193	755	668	776	488	600	7,245	8,069
13.20	-257	5.83	2,322	740	649	465	2,645	855	820	604	331	490	5,337	6,680
13.44	-176	5.66	1,229	369	186	312	2,555	716	663	823	333	551	—	—
14.16	-231	5.69	2,207	560	560	557	2,803	930	868	929	—	—	—	—
15.36	-225	5.86	1,698	509	272	186	2,741	927	645	796	284	539	4,343	4,867
15.36	-236	5.66	3,317	974	651	669	2,860	1,015	1,176	1,115	196	201	6,042	6,561

The methane digester was operated at a constant detention time of 6.46 days (155 hr). A constant portion of the acid reactor effluent was used as the feed. The overall detention time and the organic loading of the two-phase system, which was operated continuously for a period of over 4 months, varied between 6.9 and 7.6 days and 0.15 to 0.28 lb vs/day/cu ft, respectively.

The progression of digestion was monitored by analyzing the influent and the effluent streams for pH, alkalinity, oxidation reduction potential (ORP) (with re-

spect to the calomel electrode), ammonia nitrogen, filtrate chemical oxygen demand (COD), gas production, gas composition, solids, volatile acids, and total dehydrogenase activity. Dehydrogenase activity was measured by using the technique outlined by Ghosh.<sup>15</sup> Active biomass concentration of the acidogenic organisms was estimated from the measured dehydrogenase activity by using the following formula:

$$x = 4.4 + 2,144a \quad (11)$$

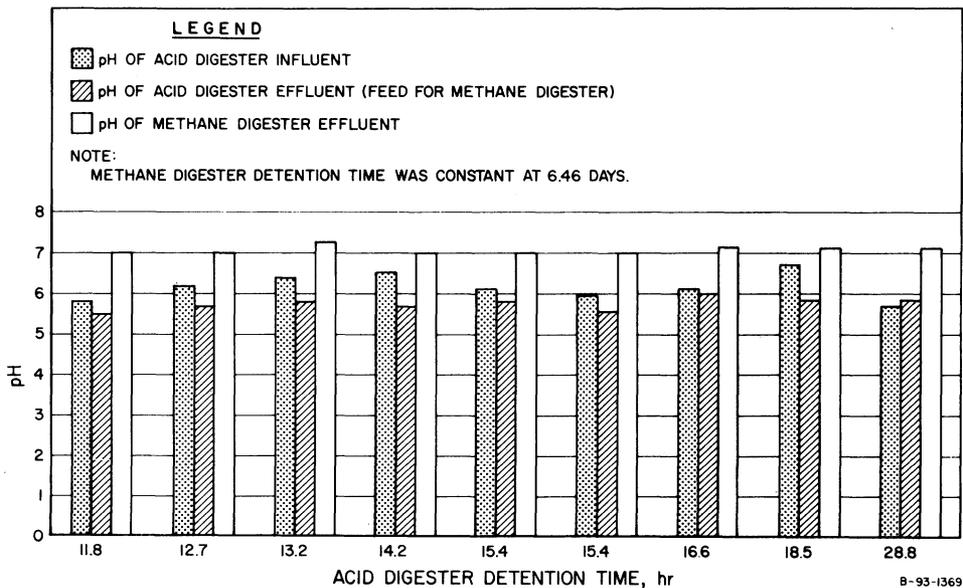


FIGURE 3.—Comparison of influent and effluent pH's for acid and methane digesters.

TABLE II.—Anaerobic Acidogenesis of Wastewater Sludge: Data on VS Loading, and Dehydrogenase Activity

Detention Time (hr)	VS				VS Reduction (%)	VS Loading (lb/day/cu ft)	Dehydrogenase Activity, Absorbance ( <i>a</i> )	Active Biomass Concentration* of Acid Formers (mg/l)
	Influent		Effluent					
	Concentration (g/l)	(%)	Concentration (g/l)	(%)				
11.40	—	—	—	—	—	—	0.4067	875
12.72	22.680	69.7	17.268	66.0	15.6	2.67	0.6200	1,350
13.20	20.436	73.4	18.240	68.4	21.6	2.32	0.2633	565
13.20	21.616	68.4	19.420	66.9	6.6	2.44	0.4251	915
13.44	18.968	—	17.348	—	—	2.11	0.1966	425
14.16	21.348	69.2	18.992	66.8	10.4	2.25	0.4466	962
15.36	22.056	69.8	18.672	67.2	9.1	2.14	0.4921	1,055
15.36	21.108	67.3	19.108	66.6	3.1	2.05	0.3738	805
16.80	17.400	66.8	15.000	62.2	18.2	1.54	0.6190	1,315
18.24	25.100	71.0	17.300	67.5	15.2	2.05	1.4345	3,080

\* Active biomass concentration (*x*) was estimated from the measured dehydrogenase activity (*a*) according to the formula  $x = 4.4 + 2,144a$ .

All analytical tests, except that involved in the measurement of dehydrogenase activity, were performed according to "Standard Methods."<sup>16</sup> However, samples for solids analysis were centrifuged, and the solids were washed before proceeding with the test for determining the vs concentration and percentage vs.

## RESULTS AND DISCUSSION

**Evidence of phase separation.** Operating data (Table I) on the acid-phase di-

TABLE III.—Gas Production from Continuous Acid-Stage Digestion of Wastewater Sludge

Detention Time (hr)	Gas Production Rate (ml/hr)	Gas Composition (mole %)		
		CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>
11.40	105	40.7	50.1	9.2
12.72	122	37.7	52.1	10.2
13.20	114	33.0	44.3	22.7
13.92	164	32.2	56.0	11.8
13.68	188	35.9	55.2	8.9
14.16	236	30.3	58.2	11.5
14.88	217	19.3	58.2	22.5
15.36	152	30.6	51.9	17.5
15.84	164	35.2	54.1	10.7
16.80	142	31.8	45.1	23.1
17.76	189	28.7	57.1	14.2
18.24	171	35.8	54.5	9.6
19.44	107	43.5	48.0	8.5
26.40	293	—	—	—
28.80	252	—	—	—

gester showed that biochemical transformations occurring in this reactor gave rise to a 15 to 120% increase in total volatile acid (as acetic) and a 20 to 90% increase in ammonia nitrogen in the effluents over concentrations of these parameters in the reactor influents. These increases were accompanied by concomitant decreases in vs (Table II), pH (Figure 3), and an increase in alkalinity from about 300 mg/l as CaCO<sub>3</sub> in the influents to about 700 mg/l in the effluents. Total gas production from the acid digester ranged from 100 to 300 ml/hr (Table III), or 2.4 to 7.2 l/day, whereas the methane production rate varied from 0.9 to 1.7 l/day (Table IV). The specific rate of vs destruction by the acid digester organisms varied from 0.152 to 0.451/day. By comparison, the methane digester, which used the acid digester effluent as the substrate, effected a 65 to 100 percent conversion of influent volatile acids (Figure 4), an increase in effluent pH and alkalinity over those of the influents (Figure 3), large methane production rates ranging from 37 to 70 l/day (Figure 5), and a specific vs destruction rate of about 0.045/day. These and other performance comparisons of the acid and the methane digesters (Table V) indicated the following:

TABLE IV.—Gas Yields from Acid Digester

Detention Time (hr)	Methane Production Rate (l/day)	Gas Yields			
		Total Gas		Methane	
		(ml/g VS reduced)	(standard cu ft/lb VS reduced)	(ml/g VS reduced)	(standard cu ft/lb VS reduced)
12.72	1.10	23	0.34	9	0.13
13.20	0.90	15	0.22	5	0.07
14.16	1.71	58	0.86	18	0.27
15.36	1.12	44	0.58	13	0.19
16.80	1.08	21	0.31	7	0.10
18.24	1.47	34	0.51	12	0.18

1. Hydrolysis of sludge solids and volatile acid production were the major reactions in the acid digester.
2. Activity of methanogenic organisms in the acid digester was insignificant.
3. Despite the large detention time, little destruction of vs occurred in the methane digester.
4. Gasification of the influent volatile acids was by far the major biochemical transformation that occurred in the methane digester.

In view of these observations, it is evident that under the operating conditions

used in this study, the acidogenic organisms were enriched in the first-phase acid reactor. The second-phase methane reactor contained dominant cultures of methane formers.

**Substrate for acid formers.** To analyze the acid digestion data, it was necessary to identify the nature of the substrate that supported the growth and activity of the acid formers. The influent slurry was composed of a soluble and a solid fraction, either one of which might have served as the substrate. However, as pointed out in the previous section, acid production

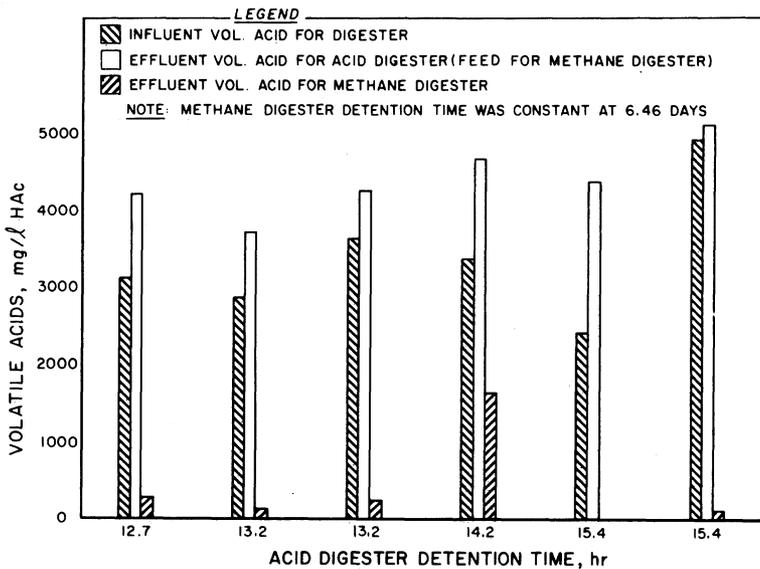


FIGURE 4.—Comparison of influent and effluent volatile acids for acid and methane digesters.

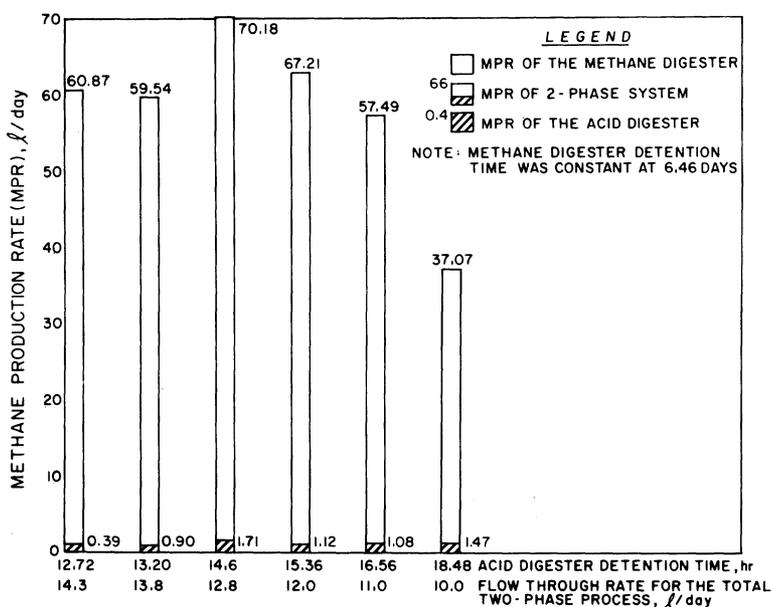


FIGURE 5.—Comparison of methane production rates of the acid digester and the two-phase digestion system.

was directly proportional to the extent of vs reduction, from which it may be inferred that the volatile fraction of the sludge solids served as the substrate for

the acidogenic organisms. This postulate was supported by soluble COD balances that indicated little or no assimilation of soluble organics by these organisms. A sample

TABLE V.—Comparison of Operating and Performance Characteristics of the Acid and Methane Digesters

Parameters	System Feed	Acid Digester	Methane Digester	Two-Phase System
Temperature (°C)	2-5	37	37	37
Detention time (day)	—	0.47-1.20	6.46	6.86-7.66
Loading (lb VS/day/cu ft)	—	1.54-2.67	0.18	0.20
[lb volatile acid (as HAc)/day/ cu ft]	—	0.04	—	—
pH	5.75-6.78	5.66-5.86	7.12	7.12
Ammonia nitrogen (mg/l)	196-486	490-600	766	766
Average alkalinity (mg/l CaCO <sub>3</sub> )	298	790	4,127	4,127
Gas composition (mole%)				
CH <sub>4</sub>	—	19-44	69.7	65.9
CO <sub>2</sub>	—	73-33	29.0	32.3
N <sub>2</sub>	—	8-23	1.3	1.8
Gas production rate (l/day)	—	2.5- 5.7	88.8	91.3-94.5
Methane production rate (l/day)	—	0.9- 1.7	61.9	62.8-63.6
Gas yield (standard cu ft/lb VS reduced)	—	0.2- 0.9	17.7	15.7
Methane yield (standard cu ft/lb VS reduced)	—	0.1- 0.3	11.9	10.7
VS reduction (%)	—	8.5-31.1	29.3	40.2
Specific rate of VS conversion (mass/day/unit mass VS added)	—	0.152-0.451	0.045	0.055
Effluent volatile acid (mg/l HAc)	—	3,717	134	134

soluble COD balance presented in Table VI further illustrates this point.

Table VI shows that during acidogenesis of the sludge feed there was no reduction in the COD of the nonacidic soluble organics. Instead, there was a small increase in this parameter, possibly because of the addition of degradation products of organic solids, which suggests that the acid formers were unable to use these compounds as substrates. Also, the COD balances indicated that the increase in soluble COD during acidogenesis could be accounted for by the increase in the volatile acid COD. From these observations, it was deduced that the volatile solids fraction of the activated sludge feeds served as the substrate for the acidogenic organisms.

**Kinetics of acidogenesis.** Several parameters are important in the design and operation of the acid-phase reactor of a two-phase digestion system. These include effluent vs concentration, volatile acid concentration in the digester effluent, rate of formation of the products of acidogenesis, and the true product yields. As shown in the previous section on theoretical considerations, these parameters are dependent on the operating conditions and the biokinetic characteristics of the acidogenic organisms. The biokinetic constants of the acidogenic cultures were determined by analyzing the steady-state data on acid-phase digestion in terms of Equations 1a, 3a, 4, 7a, and 8a. In these analyses, vs were considered the substrate for the acid formers. The techniques for determining the maximum specific growth rate ( $\hat{\mu}$ ), the saturation constant ( $K$ ), the true growth yield constant ( $Y$ ), and the maintenance coefficient ( $m$ ) are similar to those used by other investigators and need not be elaborated here. Equations suitable for determining product yield constants, however, are not generally encountered in the literature. A sample plot of Equation 7a is therefore included in Figure 6 to illustrate the method of estimating the volatile acid yield constant.

The kinetic constants of the acidogenic organisms, determined as outlined above for sludge substrate and mesophilic di-

TABLE VI.—Soluble (Filtrate) COD Balance Around Acid Digester at a Detention Time of 13.2 hr

Parameter	Value (mg/l)		
	Influent	Effluent	Effluent-Influent
Total soluble COD	5,337	6,680	1,343
Volatile acid COD	3,249	4,550	1,301
COD of other soluble organics	2,088	2,130	42

gestion conditions, are listed in Table VII along with the values of these constants determined by Ghosh<sup>14</sup> for glucose substrate. Examination of Table VII reveals the following:

1. The maximum specific growth rate of the acid formers is one order of magnitude larger with the soluble glucose substrate than with activated sludge. Also, a comparison of the saturation constants indicates that the acid formers have little affinity for activated sludge as a substrate. The lower growth rate and decreased affinity of these organisms for sludge substrate is probably caused by the rate-limiting nature of the hydrolysis step involved in the overall conversion of sludge solids to volatile acids.
2. Comparison of the maximum specific growth rate and the saturation constants of acidogenic organisms with the corresponding constants of 0.23 to 0.36 day and 0.9 to 2.5 g acetate/l determined at IGT for the methane formers indicates that methanogenesis of wastewater sludge is the rate-limiting step in the overall digestion of wastewater sludge.
3. As with the soluble substrate, glucose, the yield of acetic acid was highest with sludge feeds. However, the yield of propionic acid from sludge was less than that from glucose, and no valeric acid was detected during acidogenesis of glucose. This acid was produced in the same quantity as butyric acid during acidification of wastewater sludge.

## LEGEND

$A_0$ INFLUENT VOLATILE ACID, g/l	$U_p$ SUBSTRATE UTILIZATION COEFFICIENT FOR SYNTHESIS
$A_1$ EFFLUENT VOLATILE ACID, g/l	$x$ BIOMASS CONCENTRATION, g/l
$S_0$ INFLUENT VOLATILE SOLIDS, g/l	$\alpha_{HBut}$ BUTYRIC ACID YIELD CONSTANT
$S_1$ EFFLUENT VOLATILE SOLIDS, g/l	

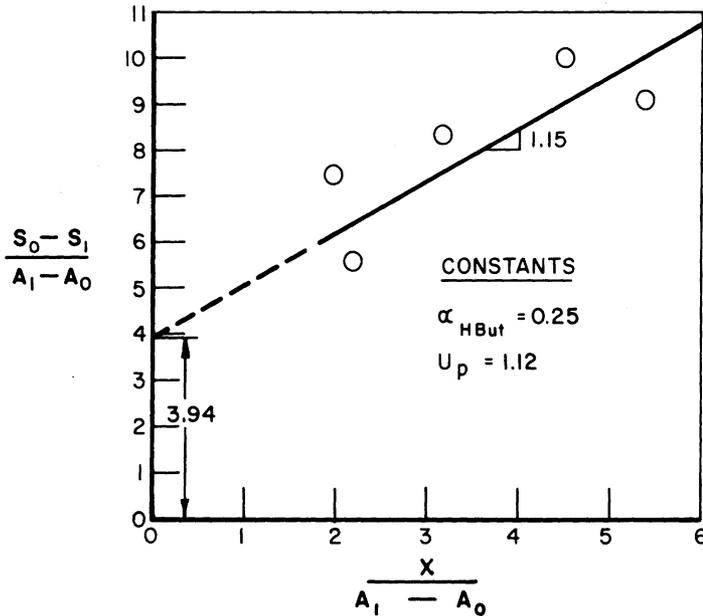


FIGURE 6.—Sample plot for determining volatile acid yield constant using butyric acid data.

A few comments on the method of determination of biomass yield are in order. The yield constant,  $Y$ , reported herein was based on active biomass concentrations

TABLE VII.—Biokinetic Constants of Acidogenic Organisms under Mesophilic Conditions with Activated Sludge and Glucose Substrates

Kinetic Parameter	Substrate	
	Sludge (This Study)	Glucose <sup>14</sup>
Maximum specific growth rate, $\hat{\mu}$ (1/hr)	0.16	1.25
Minimum generation time (hr)	4.33	0.56
Saturation constant, $K$ (g/l)	26.0 as VS	0.023 as glucose
Maintenance coefficient, $m$ (1/hr)	0.033	0.256
Substrate utilization coefficients		
For synthesis, $U_p$	1.12	4.63
For energy metabolism, $U_e$	1.35	1.16
True yield coefficient, $Y$	0.40	0.17
Product yield coefficient $\alpha$ for		
Acetic acid, $\alpha_{HAc}$	0.28	0.73
Propionic acid, $\alpha_{HPr}$	0.11	0.19
Butyric acid, $\alpha_{HBut}$	0.25	0.17
Valeric acid, $\alpha_{HVal}$	0.25	None detected
Gas, $\alpha_g$	0.071	0.054

estimated from measured dehydrogenase activities of acidogenic cultures at several detention times. This procedure was used because a direct determination of organism concentration was not possible with wastewater sludge. Furthermore, in computing observed biomass yields (which have direct bearing on  $Y$ ) at the experimental detention times, it was assumed that the concentration of acidogenic organisms in the feed sludge was negligible in comparison with that prevalent in the acid digester. This assumption was made because storage of the feed sludge at 5°C would not be conducive to the survival or growth of the acid formers outside the acid digester. Such an assumption was also necessary because no reliable method of measuring the concentration of acid formers in whole sludge is presently available. The point is that this assumption, coupled with the use of an indirect method of estimation of biomass concentration,

introduced an inherent error in the estimated value of the biomass yield constant. Because it is not possible to determine precisely the magnitude of this error, a complete mass balance of identifiable substrates and products of acidogenesis indicated that this error may be as high as 50 percent.

**Operating characteristics of the acid digester.** Data compiled during this work show that the pH and ORP of the acid reactor contents changed little despite variation of organic loading and detention time. It seems that mesophilic cultures of acidogenic organisms favor a pH and ORP ( $E_c$ ) of about 5.7 and  $-240$  mV compared with 7.0 and  $-400$  mV for methane formers.

Another important observation was that a considerable amount of denitrification of the sludge feeds occurred concurrently with the acidification reactions. Occurrence of substantial denitrification in the acid reactor probably contributed to enhanced enrichment of methanogenic bac-

teria in the methane digester and higher methane content of the off-gases from this digester.

For a given temperature, pH, and mixing regime, the substrate conversion efficiency and the rate of product formation are dictated by two important operating variables: detention time and loading. The high saturation constant of the acid formers for sludge substrate indicates that an unduly large detention time (and the resulting low growth rate) is not conducive to efficient acidogenesis. Thus, the curves of product formation shown in Figure 7 indicate that little additional product formation is achieved by increasing the acid digester detention time above 24 hr. Also, if a critical detention time is about 3 days for the methane bacteria, use of detention times between 2 and 3 days would impede the enrichment and effective separation of acidogenic organisms.

An important consideration in the design and operation of an acid digester is

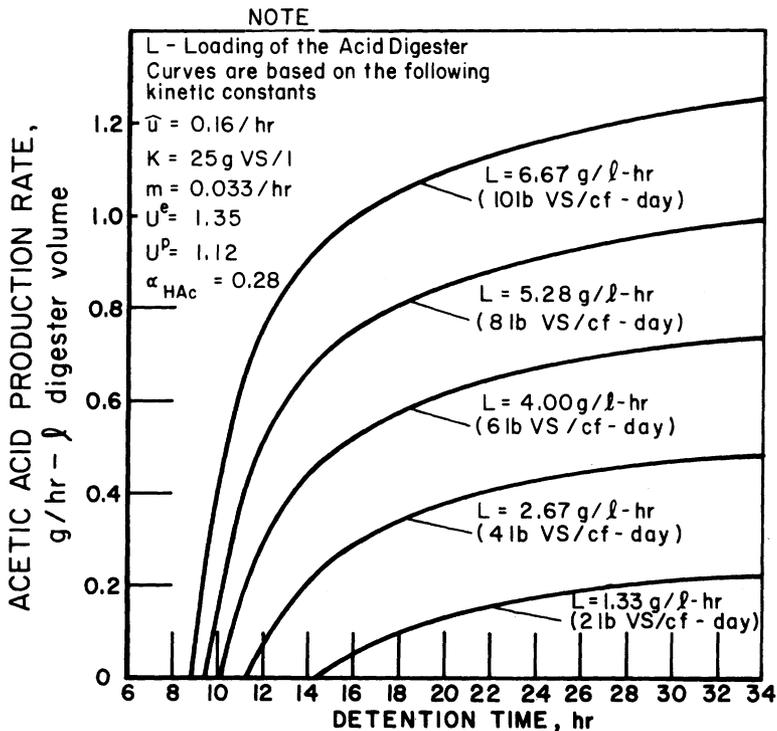


FIGURE 7.—Sample theoretical curves for volatile acid production rate from the acid-phase digester.

the critical detention time at which organism washout occurs. As defined by Equation 10, the critical detention time is determined by the biokinetic constants and the loading. Figure 7 shows that under mesophilic conditions, critical detention times may range from 8.9 to 14.4 hr for vs loadings of 10 to 2 pcf/day (6.67 to 1.33 g/hr/l).

Theoretically, the rate of formation of product acids (in terms of mass of acid produced per unit time per unit volume of acid digester) increases with the organic loading. However, digester operation with loadings above 4 lb vs/day/cu ft (65 kg/day/cu m) (which corresponds to a feed solids concentration of about 9 percent total solids) may not be practical because of problems encountered in pumping and mixing of sludge having consistencies of 9 percent total solids or higher.

Based on these considerations, it seems that efficient acidogenesis of sludge may be accomplished under mesophilic conditions if the detention time and the digester loading lie between 20 and 24 hr and 2 to 5 lb vs/day/cu ft (32 to 81 kg/day/cu m), respectively.

#### ENGINEERING SIGNIFICANCE

Experimental data accumulated during this research indicated that phase separation is desirable for an overall improvement of the anaerobic digestion process. Operation of the laboratory system served to demonstrate several attractive features of the two-phase process. Notable among them are:

1. Feasibility of steady-state operation of both phases for extended periods.
2. Capability to effect a 40 percent vs reduction with activated sludge feed, high gas and methane yields of 15.7 and 10.7 standard cu ft/lb vs (0.97 and 0.66 cu m/kg) reduced, respectively, all at an overall detention time of about 7 to 7.5 days. By comparison, digestion of this same sludge in a single-phase laboratory digester for 21 days resulted in a vs reduction of 33 percent, and gas and methane

yields of 13.5 and 7.8 standard cu ft/lb vs (0.83 and 0.48 cu m/kg) reduced, respectively. High-rate digestion (14-day detention time) of this sludge at the Metropolitan Sanitary District of Greater Chicago exhibits gas yields similar to those observed in the laboratory two-phase system, but a reduced vs reduction efficiency of about 34 percent is realized in the field-scale, single phase digesters.

3. The effluent from the two-phase system contained less than 140 mg/l volatile acid, 770 mg/l ammonia nitrogen, and 4,130 mg/l alkalinity, as compared with 600 mg/l volatile acid, 1,500 mg/l ammonia nitrogen, and 7,900 mg/l alkalinity observed in the single-phase laboratory digestion unit.

In view of these observations, it seems that substantial improvement in solids stabilization, gas production, and effluent quality may be realized by resorting to a two-phase digestion system with a volumetric capacity even one-half of that of a single-phase, high-rate digester. Furthermore, information compiled thus far indicates that relative to single-phase operation, a two-phase system would be more reliable and stable.

To the authors' knowledge, little information is available on the acidogenesis of wastewater sludge, and it is hoped that this work will contribute toward establishing more rational methods of two-phase digestion design and operation. It should be emphasized that additional work remains to be done with laboratory and pilot systems to evaluate fully the feasibility of two-phase digestion.

#### SUMMARY AND CONCLUSIONS

In addition to its capability of stabilizing large volumes of dilute sludge at low cost, the anaerobic digestion process may play an important role in reclaiming the energy from the 2 to 3 billion tons of waste produced in the U. S. every year. Despite its worldwide application, this process has not yet reached its full potential, and significant improvement of the conventional

process design and operating methods is needed if anaerobic fermentation is to compete with other physical and chemical processes for waste stabilization and energy reclamation. The two-phase anaerobic digestion system has several advantages over conventional digestion methods and may be the process of choice in many applications. This paper has presented a general discussion on the theory and operating principles of the two-phase digestion process with special emphasis on the acidogenic phase of the total process.

Experimental data from a laboratory two-phase digestion system that received activated sludge as feed and was operated by kinetic control for phase separation were presented. Results of the study showed that stable, steady-state operation of the two-phase process is possible with wastewater sludge for extended time periods. The data were analyzed in terms of several process kinetic models to determine the biokinetic characteristics of the acidogenic organisms and to develop operating and design guidelines for acid-phase digesters.

Overall, the study provided evidence that a two-phase digestion process may be operated at one-half of the detention time of a high-rate digester and still exhibit higher rates of solids stabilization and methane production. It was hypothesized that phase separation allows the two groups of digester organisms to attain their full metabolic potential and thus effectuate substantial improvement in overall digestion efficiency.

In particular, the following specific conclusions may be drawn from the work presented herein:

1. It is possible to separate enrichment cultures of acidogenic and methanogenic organisms in isolated environments or phases by kinetic control involving manipulation of dilution rates and imposition of limits on the microbial generation time.
2. Hydrolysis and acidification of wastewater sludge are the predominant reactions in the acid-phase digester.
3. The *vs* fraction of the feed sludge serves as the major substrate for the acid formers.
4. Under mesophilic conditions, acidogenesis of activated sludge occurs at a pH of 5.7 and an ORP,  $E_c$ , of  $-240$  mV.
5. With activated sludge substrate, mesophilic cultures of acid formers exhibited the following biokinetic properties: maximum specific growth rate, 0.16/day; minimum generation time, 4.3 hr; saturation constant, 26 g *vs*/l; maintenance coefficient, 0.033/hr; growth yield coefficient, 0.40; acetic acid yield constant, 0.28; propionic acid yield constant, 0.11; butyric acid yield constant, 0.25; valeric acid yield constant, 0.25; and gas yield constant, 0.071.
6. Comparison of the maximum specific growth rate and the saturation constant of methane and acid formers shows that methanogenesis is the rate-limiting step in the overall anaerobic digestion of wastewater sludge.
7. Acid-phase digestion may be conducted satisfactorily in a separate reactor at loadings and detention times ranging between 2 to 5 lb *vs*/day/cu ft (1.33 to 3.34 g/hr/l) and 10 to 24 hr, respectively.
8. Acidified activated sludge may be gasified efficiently in a methane digester at a detention time of 6.46 days. Reliable and stable operation of the methane digester was obtained during 4 months of operation. The two-phase system showed a *vs* reduction efficiency of 40 percent, gas and methane yields of 15.7 and 10.7 standard cu ft/lb *vs* (0.97 and 0.66 cu m/kg) reduced, respectively, and an effluent volatile acid concentration of 134 mg/l (as acetic). This type of performance is considerably better than that presently achieved in conventional digesters with detention times of 14 days or longer.

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**Authors.** Sambhunath Ghosh, John R. Conrad, and Donald L. Klass are, respectively, supervisor, Bioengineering Research, associate microbiologist, and assistant research director, the Institute of Gas Technology.

## NOTATION

- $A$ —concentration of any volatile acid, g/l  
 $a$ —absorbance of enzyme-reduced triphenyltetrazolium chloride at 483  $m\mu$  with a 1-cm light path  
 $e$ —subscript referring to substrate utilization coefficient for energy production in terms of mass of substrate assimilated for the production of energy for synthesis of unit biomass  
 $G'$ —steady-state gas production rate caused by acid fermentation, g/hr  
 $g$ —subscript referring to gaseous product of acidogenesis  
 $i$ —subscript referring to any acid product of acidogenesis  
 $K$ —saturation concentration, g/l as vs  
 $L$ —substrate loading, g/hr/l or pcf/day  
 $m$ —subscript denoting methane formers  
 $m$ —maintenance coefficient for acid formers, 1/hr  
 $m'$ —maintenance coefficient for methane formers, 1/hr  
 $P'$ —steady-state rate of formation of any product of acidogenesis at a given detention time,  $\theta$ , g/hr/l  
 $p$ —subscript referring to substrate utilization coefficient for growth in terms of mass of substrate assimilated for the synthesis of unit biomass  
 $S$ —substrate (vs) concentration for acid formers, g/l  
 $U$ —Substrate utilization coefficient for acidogenic organisms, dimensionless  
 $U'$ —substrate utilization coefficient for methanogenic organisms, dimensionless  
 $V$ —digester volume, l  
 $x$ —biomass concentration, g/l

- $Y$ —true yield coefficient, dimensionless  
 $\alpha$ —true product yield constant, dimensionless  
 $\theta$ —nominal (theoretical) detention time, hr  
 $\theta_c$ —critical detention time, hr  
 $\mu$ —maximum specific growth rate, 1/hr  
 $o$ —subscript denoting influent concentration  
 1—subscript denoting steady-state concentration in reactor

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