A Comprehensive Dynamic Model for Animal Waste Methanogenesis

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ABSTRACT

DYNAMIC simulation of methane fermentation of animal waste has advanced with the development of a more accurate and comprehensive mathematical model that considers and describes two basic biological pathways of methane formation. Recent work in the field of microbology has shown that there are four major microbial cultures involved in methanogenesis, with the final pathways to methane formation involving acetic acid metabolism and the reduction of carbon dioxide with hydrogen. Digestion failure, often encountered using animal waste because of the high organic and nitrogen content, can only be predicted when the dynamic relationship of these four microbial groups are considered in a symbiotic manner. Work reported here describes a dynamic computer model that predicts digestor operating conditions for the four major animal types. Validation of the computer predicted operating conditions was performed using the steady-state data of 16 pilot and full-scale methane fermentation plants (four each of swine, dairy, beef and poultry). Upon validation of the model using these data, projected minimum detention times at specific loading rates for temperatures of 35 °C and 60 °C were determined. Relationships developed in this model provide some insight into the basic response, under dynamic conditions, of biological processes.

INTRODUCTION

Development of mathematical models that describe the anaerobic processing of animal waste has been pursued for approximately 8 years by various investigators. Some of the first work using dynamic models was reported by Hill and Barth (1974, 1975). This early work was followed by the development of a model for digestion of swine waste (Hill and Barth, 1977) and a description of the techniques used in modeling biological processes (Hill and Nordstedt, 1980). Other models that have contributed significantly to the understanding of animal waste digestion include the first order models of Morris (1976) and Grady et al. (1972) and most recently, the modified Contois model developed by Chen and Hashimoto (1979).

Each of these models has significant advantages. First order models allow the use of simple inputs. The models of Hill et al. (1974, 1977, 1982) use Monod kinetics, and are therefore highly accurate in predicting process optima and failure. The Contois model possesses properties of both first order and Monod models, sacrificing some of the accuracy of the Monod models, but retaining most of the simplicity of first order models.

Each of these models possesses disadvantages as well. First order models usually are developed for steady-state analysis, and therefore cannot predict transient or dynamic state behavior. The Contois model, while capable of predicting steady-state inhibition, is also severely limited due to the form of its kinetic growth equation in predicting dynamic response. Monod models require tremendously cumbersome parameter evaluation, with the final determination of these parameters often requiring computer iteration.

te Boekhorst et al. (1981) have recently described the state-of-the-art of computer simulation of anaerobic digestion of animal waste. They point out that anaerobic digesters utilizing animal wastes rarely operate at true steady-state, but instead are actually a quasi-steady state process. It is the dynamic model that possesses the capability of predicting this quasi-steady state response and can therefore lead to process optimization and better design.

Until recently, the understanding of the microbial processes involved in methanogenesis of sludges was lacking. Progressive work in this area has provided basic knowledge necessary to construct the mathematical dynamics that give the capability of going beyond prediction of general trends to the accurate, quantitative simulation of the dynamic response of digestor operation. Because it is the dynamic model that is needed for accurate process description, considerable effort was devoted to developing a two-culture Monod-based model that possessed a minimum amount of parameter determination, while not sacrificing accuracy or predictive ability (Hill, 1982; Hill et al., 1982).

These earlier dynamic Monod-based models were developed using the understanding of microbial methanogenesis at the time. This included a two microbial culture approach of acetogenesis followed by methanongenesis. This approach limited and biased model response. The model described here is a departure from the earlier Monod based models in that the stoichiometry, kinetics and interactions of four active microbial cultures are used. This new model uses the approach described by Hill (1982) for reducing the complex waste to an organic base consisting of biodegradable material and volatile fatty acids (VFA). Inhibition kinetics developed by Hill et al. (1982) are used in describing the growth of the four bacterial cultures. The final microbial process in the model is the methanogenic fermentation utilizing both known metabolic pathways
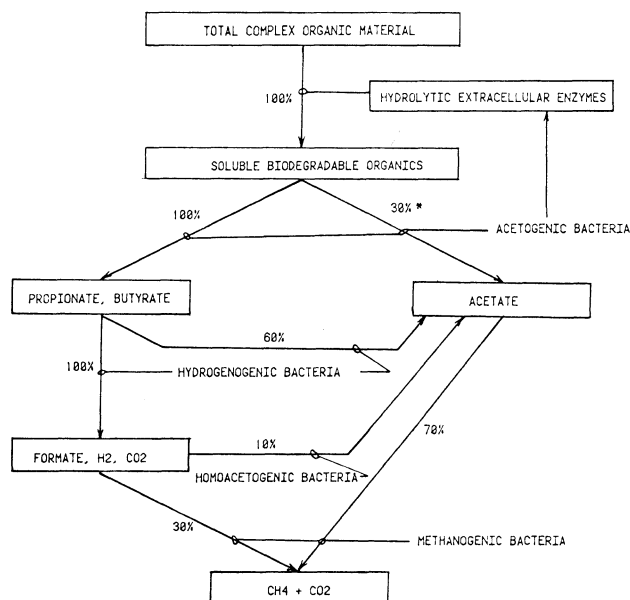
FIG. 1 Basic microbiology and mass flows of the model.

Waste type	Bo $\frac{\text{g VS des}}{\text{g VS added}}$ as $\theta \rightarrow \alpha$	Range	Value determined by model iteration
Beef (dirt)	0.50	0.4 to 0.6	0.60
Beef (confinement)	0.70	0.6 to 0.8	0.70
Dairy	0.40	0.3 to 0.5	0.36
Swine	0.90	0.8 to 1.0	0.90
Poultry (layer)	0.80	0.7 to 0.9	0.90
Poultry (broiler)	0.70*	0.6 to 0.8	0.70

* Estimate

of acetate metabolism and carbon dioxide (CO_2) reduction with hydrogen (H_2).

The result of this effort has been the development of a dynamic computer-based model that is highly accurate in predicting real process response to specific operating conditions. Development of the chemical stoichiometry and application of the previously developed kinetics (Hill et al., 1982) have shown a surprising correlation to actual results recently reported by various microbiologists in studying methanogenesis in organic sludge materials. Basic knowledge and understanding of anaerobic digestion developed in these associated fields of study is contained in this model. Of necessity, it is complex, and since it is Monod based, it requires iterative parameter determination. Simplifying assumptions have been kept to a minimum to preserve accuracy. However, this approach has led to the development of a dynamic model that has been validated quantitatively with field operating data.

NARRATIVE OF THE MODEL

The basic microbiology of the model is depicted in Fig. 1. Complex organic material enters the digestor and is converted by extra-cellular enzymes to soluble, biodegradable organic material. This basic technique has been described by Hill (1982) and uses a set of constants that are waste specific. The value of these biodegradability constants (B_o) are given in Table 1 for all four animal types along with the range of values as originally derived. The value for poultry broiler waste is an estimate, since no real data are available for determination of B_o. Also included in Table 1 are the values of B_o as determined by computer iteration using this model. Some variation is noted, but all are within the expected range. The second step in this conversion of raw waste to its organic base is the determination of the influent VFA concentration. This technique is also described by Hill (1982) and the values of the acid coefficients used for this model are the same.

Once in soluble organic form, the waste is acted upon by a culture of bacteria classified as "acetogens", which are capable of forming three major VFA's; acetate, pro-

pionate and butyrate (Smith, 1980). A second group of bacteria, called "hydrogenogens" utilizes the propionate and butyrate, forming acetate, formate, H_2 and CO_2 as the major end products. Smith (1980) has stated that as much as 70 percent of the organic material passes through this pathway in the eventual formation of methane.

The formate, H_2 and CO_2 enter a pool, where they are eventually utilized in the direct conversion to methane by methanogenic bacteria or in the conversion to acetate by a highly specialized group of bacteria known as "homoacetogens". This latter bacterial group has only recently (Ziekus, 1979; Ziekus, 1977; Wolfe, 1979) been implicated to a significant extent in the overall methanogenic process.

Two major metabolic pathways have been demonstrated to contribute significantly to the formation of methane (CH_4) and CO_2 (Bryant, 1976, 1979; McInerney and Bryant, 1978; Ziekus, 1979; Wolfe, 1979; Smith, 1980). Direct conversion of acetate to CH_4 and CO_2 has long been known to be a major pathway. Recent work of Smith (1980) and previous work (Smith and Mah, 1966; Kugelman and McCarty, 1965) has shown that this pathway contributes between 60 and 70 percent of the total CH_4 produced, with the remaining 30 to 40 percent being produced by the reduction of CO_2 with H_2.

Overall conversion of organic material to CH_4 is a closely coupled symbiotic relationship between these four types of bacteria, with the dynamic balance between the production and utilization of the intermediate products critical to the overall success of the fermentation. Should this dynamic balance be disturbed, VFA accumulation and digestor failure are imminent.

Material balances used in this model show that approximately 30 percent of the total acetate formed is produced by the acetogenic bacteria. Essentially all of the propionate and butyrate are also formed through this metabolism. Conversion of propionate and butyrate to acetate by the hydrogenogenic bacteria contributes the largest amount to the acetate pool, approximately 60 percent. This compares favorably to the findings of Smith (1980) that up to 70 percent of the organic material passes through this pathway. Conversion of formate, H_2 and CO_2 produces about 10 percent of the total acetate. The final material balance shows approximately 70 percent of the total methane coming from the metabolism of acetate and 30 percent from the reduction of CO_2 with H_2. Thus, the chemical stoichiometry and microbial kinetics used in this model produce mass balances that have been observed in microbiological

TABLE 2. VALUES OF KINETIC CONSTANTS USED IN MODEL

Culture	$\hat{\mu}$ day^{-1}	$\hat{K}D$ day^{-1}	K_S, g substrate L	K_{IG}, gVFA L	K_{ID}, gVFA L	Y, g organism g substrate
Acetogenic	*	†	5.0	9.0	16.0	0.07
Hydrogenogenic	*	†	1.0	9.0	16.0	0.07
Homoacetogenic	*	†	0.5	9.0	16.0	0.125
H2 Methanogenic	*	†	0.01‡	11.0	16.0	0.056
Acetate Methanogenic	*	†	0.01‡	11.0	16.0	0.042

*Temperature dependent (From Chen and Hashimoto, 1979)
†Numerically equal to $\hat{\mu}$
‡Units are L H_2/L digestor volume

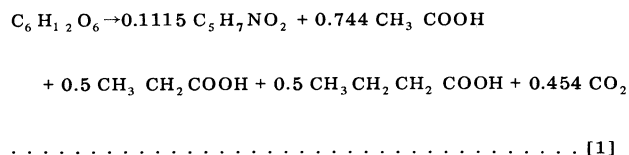studies using organic sludges as methanogenic substrates.
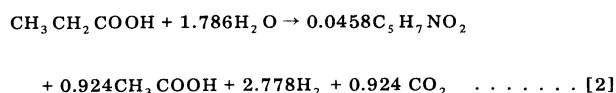
MATHEMATICAL RELATIONSHIPS

Stoichiometry

The basic stoichiometry developed for this model was taken from the work of Smith (1980) and Wolfe (1979). The final equations for the formation of bacterial mass, acetate, propionate, butyrate, H_2, CO_2 and CH_4 are presented according to the bacteria involved. The empirical chemical formula for bacterial mass is $C_5H_7NO_2$ (Loehr, 1974) with a molecular weight of 113 g/mole. Values of the yield coefficients (Y) for each bacterial culture were determined by computer iteration using the data of 16 pilot and full scale methane fermentation plants. These values are given in Table 2.

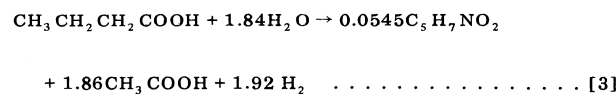The basic equations for the model are as follows:
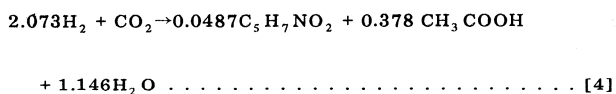
Acetogenesis

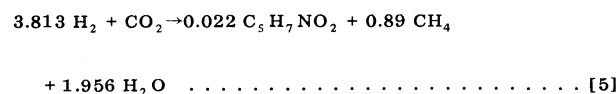$$C_6H_{12}O_6 \rightarrow 0.1115\ C_5H_7NO_2 + 0.744\ CH_3COOH$$

$$+ 0.5\ CH_3CH_2COOH + 0.5\ CH_3CH_2CH_2COOH + 0.454\ CO_2$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots [1]$$

Propionate Hydrogenogenesis

$$CH_3CH_2COOH + 1.786H_2O \rightarrow 0.0458C_5H_7NO_2$$

$$+ 0.924CH_3COOH + 2.778H_2 + 0.924\ CO_2 \quad\dots\dots\dots [2]$$

Butyrate Hydrogenogenesis

$$CH_3CH_2CH_2COOH + 1.84H_2O \rightarrow 0.0545C_5H_7NO_2$$

$$+ 1.86CH_3COOH + 1.92\ H_2 \quad\dots\dots\dots\dots\dots\dots [3]$$

Homoacetogenesis

$$2.073H_2 + CO_2 \rightarrow 0.0487C_5H_7NO_2 + 0.378\ CH_3COOH$$

$$+ 1.146H_2O \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots [4]$$

Hydrogen Methanogenesis

$$3.813\ H_2 + CO_2 \rightarrow 0.022\ C_5H_7NO_2 + 0.89\ CH_4$$

$$+ 1.956\ H_2O \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots [5]$$

Acetate Methanogenesis

$$CH_3COOH \rightarrow 0.022\ C_5H_7NO_2 + 0.945\ CH_4$$

$$+ 0.945CO_2 + 0.06\ H_2O \quad\dots\dots\dots\dots\dots\dots\dots\dots [6]$$
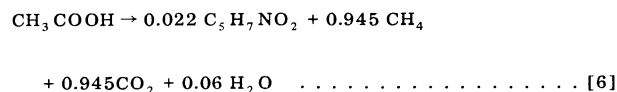
The acetogenic reaction (equation [1]) is based on the raw material glucose, which represents all the soluble organics, except VFA. Hill and Barth (1974) performed an elemental analysis of raw swine waste and determined its empirical chemical composition to be $C_6H_{13}NO_5$. Similar analyses of raw dairy, beef and poultry waste were performed for this study with the results showing that only the nitrogen and oxygen ratios change. The relative carbon and hydrogen ratios are similar. Glucose yield from this raw waste is 1 to 1 on a weight basis as well as a mole basis (Hill and Barth, 1974), thus the initial conversion of raw waste to soluble organics can be represented by:

$$C_6H_{13}NO_5 + H_2O + H^+ \rightarrow C_6H_{12}O_6 + NH_4^+ \quad\dots\dots\dots [7]$$
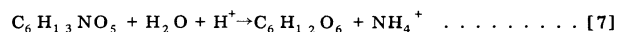
The nitrogen necessary for bacterial synthesis in equations [1] through [6] comes from the release of NH_4^+ in equation [7].

This basic stoichiometry (equations [1] through [7]) was used to calculate the yield and utilization coefficients for the material mass balances of the model. Hill and Nordstedt (1980) describe in detail use of these coefficients.

Mass Balances

Twelve mass balances are necessary to perform the simulation using the microbial pathways described in Fig. 1. These are: soluble organics (S); acetic acid (AC); propionic acid (PAC); butyric acid (BAC); H_2; CO_2; CH_4; and five bacterial cultures. The methanogenic culture is sub-divided into two cultures, one utilizing H_2 and CO_2 and the other utilizing acetate. This is necessary to maintain mathematics for H_2 utilization. Smith (1980) reported that all methanogenic isolates he characterized were capable of utilizing H_2 and acetate in the formation of methane. But, in order for H_2 utilization to be handled mathematically, it is necessary to maintain a separate sub-culture of methanogens utilizing H_2.

Detailed derivation of the mass balances are not given here since the techniques and procedures are detailed in a number of publications by Hill and his co-workers (1974, 1975, 1977, 1980) and in Andrews et al. (1971, 1975). Also, using the stoichiometry of the preceeding section to calculate material yield coefficients, the mass

balances can be obtained.

One unique feature in this model regarding the mass balances deals with one microbial culture (hydrogenogens) utilizing two substrates (propionate and butyrate). Total growth of this culture comes partly from butyrate and partly from propionate. No work could be located in the literature to help in apportioning this growth mathematically between the substrates. Accordingly, total growth is apportioned by the ratio of propionate and butyrate to the total present. For example, if butryate represents 60 percent of the total propionate and buytrate, then 60 percent of the total growth of the hydrogenogenic population was attributed to butyrate uptake and 40 percent to propionate uptake. This representation is new in mathematical modeling of biological processes, but the results of the simulations justify its use at present. Complete verification of its validity awaits further microbiological investigation.

Kinetics

Microbial growth in this model is based on the inhibition kinetics developed by Hill et al. (1982). Effects of high VFA concentration are expressed in both the growth and death kinetics of all four microbial cultures. No inhibition by high H_2 concentration on any of the bacterial populations is included in the model. This was shown to be the case by Smith (1980) in studies specifically designed to determine if H_2 concentration could be used as an indicator of digestor "health". He found no significant impairment of methane production at high H_2 concentration.

The utilization of two gases (H_2 and CO_2) in the formation of CH_4 also required a new technique in modeling. As previously mentioned, the methanogenic culture is sub-divided into two protions that utilize H_2 and CO_2 and acetate. For the hydrogen utilizing sub-culture, the Monod "half-velocity" constant is based on hydrogen concentration. Thus, the hydrogen mass balance is maintained in units of gas volume per liquid volume of digestor (L H_2/L). Hydrogen is rarely detected in digestor off-gas because its concentration must be maintained at a level below 5×10^{-5} atm due to energy relationships in metabolism (Smith, 1980). Thus, all hydrogen produced by hydrogenogenesis is assumed to be utilized in either homoacetogenesis or methanogenesis. The value of the H_2 half-velocity constant for these two cultures is the same, since no preference on H_2 utilization by either culture was assumed. Basic microbiological knowledge is lacking in dealing with these specifics. The value of this constant (0.01 LH_2/L-vol) was assigned based on maintaining the very low H_2 concentration in the digestor.

The remaining kinetics are standard Monod based, and have been described in numerous publications. Values of the kinetic constants used in this model are given in Table 2. Maximum specific growth rate ($\hat{\mu}$) is determined using the temperature dependent function of Hashimoto et al. (1979). Maximum specific death rate (K_D) is numerically equal to $\hat{\mu}$ as described by Hill et al. (1982). The values of K_s (Monod half-velocity constant) and Y for each culture were determined from experimental data and model output by computer iteration using the criteria of producing the best fit of volumetric methane productivity (γ_v). The growth inhibition coefficient (K_{IG}) and death constant (K_{ID}) are the values

reported by Hill et al. (1982).

Volatile Solids Reduction, Methane Productivity and Gas Quality

Imperative in the analysis of a digestor are the three critical parameters of volatile solids reduction, volumetric methane productivity and gas quality. These three parameters are closely tied together because the only means for removing VS is in the production of CH_4 and CO_2. Calculation of these three parameters in this model differs slightly from previously reported work and will be discussed briefly.

Methane productivity is calculated according to equations [5] and [6], and no empirical coefficients, such as those developed by McCarty (1964) or Metcalf and Eddy (1979) were used. The value obtained during simulation is 0.55 LCH_4/g VS destroyed, a value somewhat higher than the 0.50 calculated by McCarty but more closely in line with recent experimental data obtained for swine waste (0.56 LCH_4/g VS) by Fischer et al. (1979) and dairy waste (0.54 LCH_4/g VS) by Hills (1980).

Carbon dioxide productivity is calculated according to equations [1], [2] and [6] similar to CH_4 productivity. Gas quality is obtained by dividing CH_4 production by total gas ($CH_4 + CO_2$). Volatile solids reduction is calculated by the removal of mass as represented by CH_4 and CO_2 production in equations [1], [2], [5] and [6].

MODEL VALIDATION

The mathematical relationships developed in the mass balances, stoichiometry, and kinetics were coded in the IBM CSMP III* (1972) language and simulations using various operating conditions and waste types were performed. Validation data used are contained in Table 3. These data consisted of four experimental studies for each of the four animal types. Data of Burford et al. (1977) and Hashimoto et al. (1979) were used for beef validation; Fischer et al. (1975, 1979), Stevens and Schulte (1979) and Lapp et al. (1975) for swine; Converse et al. (1977, 1981) for poultry; and Converse et al. (1977a), Coppinger et al. (1978) and Bartlett et al. (1981) for dairy. Inputs to the model consist of four basic operating parameters: 1) VS concentration in the influent (VS_{IN}, g/L); 2) temperature of digestion (T, °C); 3) detention time (DT)(θ, Days); and 4) waste type (swine, beef, dairy, poultry).

For data comparison, the available literature was searched for a broad range of loading rates, DT's and temperatures for each waste type. These data were used to validate the model over a variety of operating conditions likely to be encountered in actual field units. A summary of the data of Table 3 shows that the model output was compared to experimental data for beef feedlot waste at two temperatures (35 and 55 °C), 4 detention times (20, 12, 6 and 5 days) and loading rates of 3.1 to 17.0 g VS/L-Day. For swine waste, a comparison of two temperatures (25 and 35 °C), three detention times (15, 18 and 20 days) and loading rates of 1.45 to 4.0 g VS/L-Day was made. The ranges of available data for poultry and dairy waste are not as broad as that for beef and swine, limiting the temperature comparison

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TABLE 3. DATA USED IN VALIDATING THE FOUR CULTURE MATHEMATICAL MODEL OF METHANE FERMENTATION

Waste type	Reference	T, °C	Θ, days	VS_in, g/L	γv, L CH₄ L-day	VS_RED, %	CH₄, %	γv, L CH₄ L-day	VS_RED, %	CH₄, %	Gas, L Gas L-day	VS_EFF, g/L
						Experimental		Simulated				
Beef-dirt	Burford et al. (1977)	35	20	62.0	0.69	—	—	0.69	41.0	65.6	1.0	36.8
Beef-conf	Hashimoto et al. (1979)	55	12	62.5	1.59	—	—	1.40	47.9	65.9	2.1	32.0
	Hashimoto et al. (1979)	55	6	68.4	2.73	—	—	2.88	45.8	65.8	4.4	37.1
	Hashimoto et al. (1979)	55	5	85.0	4.23	—	—	4.26	45.5	65.7	6.5	46.5
Swine	Fischer et al. (1975)	35	15	43.6	1.08	64.1	60.0	1.00	60.5	66.0	1.5	17.1
	Fischer et al. (1979)	35	15	60.0	1.36	63.0	60.0	1.37	61.5	66.0	2.1	23.0
	Stevens & Schulte (1979)	25	20	28.8	0.52	19.5	68.0	0.43	53.2	65.8	0.64	13.5
	Lapp et al. (1975)	35	18	36.0	0.71	—	66.0	0.68	60.7	66.0	1.0	14.1
Poultry (layer)	Converse et al. (1977)	35	31	59.5	0.74	41.1	55.6	0.72	64.7	67.5	1.06	21.0
	Converse et al. (1977)	35	42	81.9	0.77	44.8	63.0	0.73	65.2	67.3	1.08	28.5
	Converse et al. (1977)	35	44	69.1	0.58	44.3	61.5	0.59	65.0	67.8	0.87	24.2
	Converse et al. (1981)	35	36	65.1	0.66	61.5	58.5	0.67	64.9	67.3	1.0	22.8
Dairy	Converse et al. (1977a)	60	6.2	65.2	1.26	28.9	54.1	1.27	22.1	65.6	1.90	50.8
	Coppinger et al. (1978)	35	12	76.8	0.77	—	56.7	0.80	22.8	65.7	1.23	59.3
	Bartlett et al. (1981)	35	11	113.2	1.21	—	60.0	1.20	23.2	65.7	1.83	74.0
	Bartlett et al. (1981)	35	35	121.1	0.40	—	60.0	0.41	24.9	65.9	0.62	71.8

to 35 °C for poultry and a somewhat narrow loading range of 1.57 to 1.95 g VS/L-Day. Detention times studied for poultry waste were 31, 36, 42, and 44 days. Dairy waste digestion was compared at two temperatures (35 and 60 °C), detention times of 6.2, 11, 12 and 35 days and loading rates of 3.46 to 10.5 g VS/L-Day.

Also contained in Table 3 are the data for experimental VS reduction and gas quality and simulated VS reduction, gas quality, total gas production and VS in the effluent. These data are given (in the case of VS reduction) for comparison purposes and as information as to model output for the other variables. Comparison of VS reduction data shows close agreement with the swine data of Fischer et al. (1979), the poultry data of Converse et al. (1981) and the dairy data of Converse et al. (1977a). Since analytical sampling and testing procedures for VS can be quite variable, discrepancy in these data is not surprising. Variability due to sampling in determing volumetric methane productivity (γ_v) is much less than with VS determination and is the reason γ_v data were used in validating the model.

Table 4 contains the statistical data for the comparison of experimental γ_v and simulated γ_v. A correlation test was performed for all 16 data points taken as a whole and for each waste type taken as an individual group. The goodness of fit statistic (R) shows high correlation for beef, swine and dairy waste (0.99, 0.96 and 0.99 respectively) while poultry showed a 0.90 goodness of fit; somewhat lower, but quite acceptable. The narrowest range in experimental data also occurred with poultry waste. The overall goodness of fit was 0.99 with the largest error of 17.3 percent occurring with swine waste. Of the total 16 data comparisons, 14 were within

TABLE 4. GOODNESS OF FIT STATISTIC AND ERROR DATA FOR MODEL CORRELATION

Waste type	Total observations	R	Largest error, %	No. of OBS within 5%	No. of OBS within 10%
Beef	4	0.99	11.9	2	3
Swine	4	0.96	17.3	2	3
Poultry	4	0.90	5.5	3	4
Dairy	4	0.99	5.2	4	4
All observations	16	0.99	17.3	11	14

10 percent and 11 showed errors of less than 5 percent.

COMPUTER SIMULATIONS

Once this model was validated, a series of simulations were performed to determine the computer predicted minimum DT (before failure) for a given influent VS concentration at two temperatures of 35 °C and 60 °C for all four waste types. The procedure used in these simulations was to start the model at time 0 with a specific VS influent concentration, at the prescribed temperature, and at a DT sufficiently large to allow successful start up. Typically, this initial DT was 10 days. Upon attainment of the steady-state after start-up, DT was reduced by one day at 50-day intervals (of simulation time). Thus, the first 50 days were simulated using DT of 10 days; day 51 to 100 (of simulation time) used DT of 9 days; days 101 to 150 used 8 days; etc. The systematic reduction in DT was stopped when failure, as determined by γ_v, was evident.

Figs. 2 and 3 contain the simulated output for swine waste at 35 °C. The symbols used in these figures are:

CH₄   volumetric methane productivity, LCH₄/L-Day
PCCH4   gas quality, percent CH₄
ACT   total VFA concentration, g/L (as acetic)
VSRED   volatile solids reduction, percent
VSOUT   volatile solids concentration in effluent, g/L
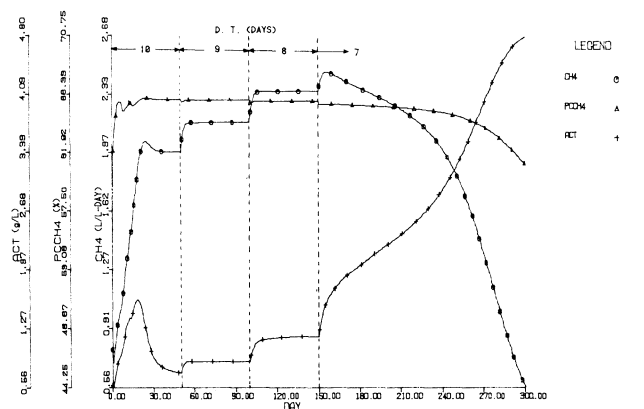Influent volatile solids concentration remained con-

FIG. 2 Methane productivity, gas quality, and acid level indicating failure for DT < 8 days.
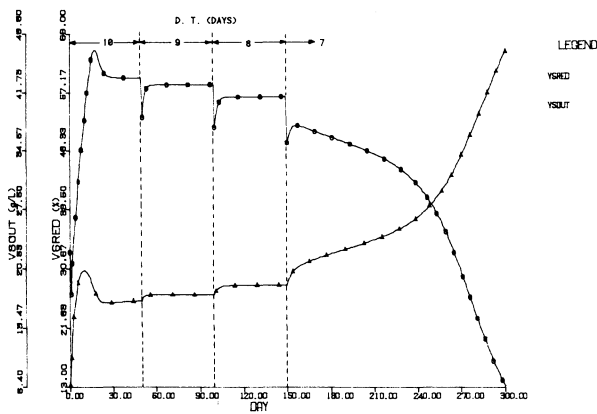
FIG. 3 VS reduction and VS concentration showing digester failure for swine waste at DT < 8 days.

tant at 60 g VS/L for this entire simulation. Since VS concentration was constant but DT varied, organic loading rate varied for these simulations. During the first 20 days CH4, PCCH4 and VSRED show increases due to the transient start-up period. At day 30, the steady-state is attained showing volumetric methane productivity of 1.98 LCH4/L-Day, VSRED of 59.4 percent and a gas quality of 65.9 percent CH₄. At day 50, the DT is reduced to 9 days and again steady-state is attained with CH4 being 2.16 LCH₄/L-Day, VSRED of 58.4 percent and a gas quality of 65.9 percent CH₄. At day 100, DT is reduced to 7 days (and remains constant for the duration of the simulation) failure is noted since CH4 drops to 0.56 LCH₄/L-Day, VSRED falls to 13 percent and gas quality is approximately 60 percent CH₄ on day 300. Also, during the period beyond day 150, total acids reach a concentration of 4.8 g/L (as acetic) and VSOUT increases constantly until a value of 46.2 g VS/L is reached at day 300.

Identical simulations were performed at 35 and 60 °C for beef, swine, poultry and dairy waste. A summary of the results of these simulations is given in Table 5. The VS loading concentrations for beef, poultry and dairy waste were 85, 70, and 66 gVS/L respectively and failure occurred at 7, 9 and 8 days for 35 °C operation. The 60 °C temperature produced failure at 4 days for all waste types. Data of Table 5 show that at 35 °C and DT slightly above minimum DT, beef waste may be loaded at approximately 1.5 times the rate of swine, poultry or dairy. At 60 °C, this rate decreases to approximately 1.3 times.

At the longer DT's (8 and 9 days) the model predicts that the percentage of CH₄ produced by acetic acid metabolism attains a steady-state value of approximately 70 percent. Upon an abrupt change in DT, this value falls to about 65 percent for approximately 10 days, then returns to a steady-state value less than the previous value. Upon failure the model predicts that essentially all CH₄ is produced by the acetate pathway (98 percent), with almost none coming from the H₂-CO₂ pathway.

Hydrogen production by the hydrogenogenic bacteria ccompletely ceased in the model upon failure, which explains why the H₂-CO₂ methane pathway was terminated. Methane produced during the failure period (which was a very small amount) came from the acetic acid originally in the influent waste.

CONCLUSIONS AND SUMMARY

Development of a totally accurate simulation model of

TABLE 5. COMPUTER PREDICTED MINIMUM DETENTION TIME (BEFORE FAILURE) FOR 35 °C AND 60 °C OPERATION

Waste type	Influent VS concentration, g/L	35 °C θ min, days	35 °C loading rate, gVS/L day	60 °C θ min, days	60 °C loading rate, gVS/L day
Beef	85.0	7	12.14	4	21.25
Swine	60.0	8	7.5	4	15.0
Poultry	70.0	9	7.78	4	17.5
Dairy	66.0	8	8.25	4	16.5

anaerobic digestion of any organic material is an impossibility. Microbial processes are much too precarious and temperamental and are influenced by many variables (such as mutation) which cannot be accounted for in mathematical simulation. This model, however shows the capability of accounting for enough variables so that, now, good quantitative simulations which are needed to develop operational design criteria of quasi-steady state biological processes are obtained.

The mass flow relationships of this model are closely correlated to the observations made in recent microbiological studies using organic sludges as methanogenic substrates. Approximately 30 percent of the acetate pool is formed initially by the acetogenic bacteria, 60 percent by the hydrogenogenic and 10 percent by the homoacetogenic. Of the total methane formed in a "healthy" digestor, approximately 70 percent comes from the metabolism of acetate and 30 percent from the reduction of CO₂ with H₂.

Response of this model on an operational level shows that quantitative simulations to within 5 percent of experimental data can be obtained in greater than 68 percent of the cases and to within 10 percent in greater than 85 percent of the cases. Of 16 experimental comparisons, the largest error encountered was 17.3 percent, which occurred using swine waste. Goodness of fit (R) was calculated as 0.99, 0.96, 0.90 and 0.99 for beef, swine, poultry and dairy waste, respectively. Goodness of fit for the entire data set was 0.99. Methane yield of 0.55 LCH₄/gVS obtained using the stoichiometry and kinetics developed for this model, is slightly higher than the theoretical yield reported by McCarty (1964).

Specific recommendations and conclusions which can be made using the simulations performed thus far are:

1 Swine waste digestion at 35 °C should be performed at DT's in excess of 8 days. Similar minimum DT's for beef, poultry and dairy wastes are 7, 9, and 8 days respectively.

2 Minimum DT before failure at 60 °C for all waste types is 4 days.

3 Maximum loading rates before failure were 12.2, 7.5, 7.8 and 8.25 gVS/L-Day for beef, swine, poultry and dairy waste respectively at 35 °C. Similar values at 60 °C were 21.25, 15.0, 17.5 and 16.5 gVS/L-Day.

4 Of the biologically formed acetate, approximately 30 percent is formed by the acetogenic bacteria directly from the raw waste; approximately 60 percent is formed by the hydrogenogenic bacteria from propionate and butyrate; and 10 percent is formed from H₂ and CO₂ by the homoacetogenic bacteria.

5 Kinetics and stoichiometry show that approximately 70 percent of the methane formed in a healthy digestor comes from acetic acid metabolism with the remaining 30 percent from CO₂ reduction with H₂.

6 During inhibition, the formation of hydrogen by the hydrogenogenic bacteria ceases completely, prohibiting methane formation from hydrogen.

FUTURE RESEARCH

The work planned using this model will now include simulation studies to determine recommended loading rates, detention times and temperatures for more efficient design of digestor systems for all four waste types. Studies of the dynamic behavior, to determine process stability when one or more operating parameters are suddenly changed, will be made. The uses of this model will lead to a clearer understanding of anaerobic digestion of animal manures, which is needed if full benefit of their energy conversion properties are to be recognized.

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