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KINETIC PROPERTIES OF SEPARATED SOLID-LIQUID FRACTIONS OF BLENDED SWINE WASTE SLURRY

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ABSTRACT

The kinetic properties ultimate methane yield (bo) and substrate inhibition coefficient (K) of separated solid-liquid fractions of blended surface-scraped swine waste were evaluated from data on batch digestion and semicontinuous high-rate digestion.

Results showed that the solid fraction had a lower Bo (0.373 li CH_4/gm VS added) than the liquid fraction (0.498 li CH_4/gm VS added) due to its higher concentration of refractory materials.

K was evaluated using Chen & Hashimoto's model for continuous well-mixed anaerobic systems at steady-state. The relationship between influent substrate concentration (So) and K was found to be exponential. Empirical equations derived at different combinations of organic loading rate (OLR), Hydraulic retention time (HRT) and temperature are as follows:

Solid Fraction:

$K = 0.429 + 0.00177 \exp(0.187\ So),\ r^2 = 0.997$

Liquid Fraction:

$K = 0.798 + 9.43\times10^{-8} \exp(1.808\ So),\ r^2 = 0.863$

The threshold substrate concentration where inhibition might start was approximately 30 gm VS/li for the solid fraction and 8 gm VS/li for the liquid fraction.

INTRODUCTION

Anaerobic digestion is a very complex process involving the dynamic interaction between an organic substrate and different species of facultative and obligate anaerobes. Due to its complexity, the process has never been completely and accurately modeled and simulated.

Kinetic models in anaerobic digestion are broadly classified into (Hill, 1983): (1) steady-state first order, (2) Monod-based, and (3) Chen and Hashimoto's kinetic model. Based on its accuracy in predicting operational optima and failure, the second model is most effective under dynamic conditions. However, the numerous parametric determinations required renders application of the model difficult and impractical. On the other hand, Chen and Hashimoto's kinetic model, with only two parametric determinations, has often been used in continuous steady-state digestion.

Kinetic models evolve through two stages: microbial kinetics and fermentation kinetics. Microbial kinetics relate microbial growth to substrate utilization, or both to substrate or cell mass concentration. The relationship between microbial growth and substrate utilization is expressed as follows (Hashimoto et all., 1980):

$$\mu = YF/X \qquad (1)$$

where:

μ = specific microbial growth rate (time^{-1})
Y = growth yield coefficient (mass micro-organisms/mass substrate)
F = volumetric rate of substrate utilization by microorganisms (mass substrate/ volume-time)
X = cell mass concentration (mass micro-organisms/volume).

Different models of μ have been proposed. These are: (1) Monod (Ripley & Boyle, 1983; Mosey, 1983), (2) inhibition (Andrews, 1969; Hill and Barth, 1977; Hill, Tollner and Holmberg, 1983), (3) Contois (Ripley and Boyle, 1983), (4) Chen and Hashimoto (1978), and (5) first-order (Pfeffer, 1974). Chen and Hashimoto's model is:

$$\mu = (\mu_m S/So)/(K + \{1 - K\}\{S/So\}) \qquad (2)$$

where:

μ_m = maximum specific microbial growth rate (time^{-1})
S = effluent volatile solids (VS) concentration (mass/volume)
So = influent VS concentration (mass/volume)
K = substrate inhibition coefficient (dimensionless)

Fermentation kinetics are based on microbial and substrate mass balance (Hashimoto et al.. 1980; Hill, 1985). Combining these mass balances for a well-mixed continuous system yields:

$$V\,dX/dt = QXo - QX + (\mu - Kd)XV \qquad (3)$$

where:

V = effective digester volume
dX/dt = volumetric rate of cell mass accumulation (mass/volume-time)
Q = volumetric flow rate (volume/time)
Xo = influent cell mass concentration (mass/volume)
Kd = cell death coefficient (time^{-1})

For Chen and Hashimoto's model assuming $Kd = 0$ (normally negligible) and using the proportionality between So and total methane yield (B):

$$S/So \, \alpha (Bo - B)/Bo$$

where Bo is the ultimate methane yield (li $CH_4{}^2$/gm VS added) and B is the total methane yield (li CH_4/gm VS added). Equation (3) reduces to:

$$B = Bo\,(1 - K\,\{\mu_m\,HRT - 1 + K\}) \qquad (4)$$

where HRT is the hydraulic retention time.

Bo, μ_m and K are the three fundamental steady-state kinetic parameters for continuous well-mixed anaerobic digestion systems. μ_m increases linearly with temperature until 60°C in accordance with the following equation:

$$\mu_m = 0.013\,T - 0.129 \qquad (5)$$

then drops sharply at 65°C (Hashimoto, Varel and Chen, 1981; Chen, 1983).

Bo is a function of species, ration, manure age, waste collection method and storage, as well as the amount of foreign material in waste (Chen, 1983); Hashimoto, Varel and Chen, 1981). It may be evaluated from long-term batch digestion or by linear regression of HRT^{-1} and B, for HRT > 10 days (Chen and Hashimoto, 1978).

K is a measurement of overall digester performance. A low K indicates a more efficient digestion. For livestock wastes, K is essentially dependent on So, increasing gradually at small So but exponentially at higher So. Substrate-induced process inhibition, due to high levels of free-ammonia and volatile fatty acids, often starts at the point where K rises (Chen, 1981, 1983; Chen and Hashimoto, 1978).

K is relatively independent of temperature and HRT in the mesophilic range but not in the thermophilic range (Chen et al., 1984). For swine waste, the following empirical equations have been derived by Hashimoto (1984):

Feed without antibiotics:

$$K = 0.6 + 0.0206 \exp(0.051\,So) \qquad (6)$$

Feed with antibiotics:

$$K = 0.5 + 0.0043 \exp (0.091 So) \tag{7}$$

MATERIALS AND METHODS

Substrates

Surface-scraped swine waste, partially drained of urine and collected from experimental sows at the Bureau of Animal Industry (BAI) in Alabang, Muntinlupa, Rizal, was used as substrate. This was slurrified by repeated blending (Monospeed Hanabishi blender) and screening (+10 mesh) of a predetermined mixture of tap water and waste. Solid-liquid fractions were separated after the slurry had settled overnight at 0-4°C.

The properties of both fractions are shown in Table 1 for batch digestion (including control and unseparated blended substrates) and Table 2 for semicontinuous high-rate digestion. An improved slurry preparation procedure in high-rate digestion resulted to insignificant differences between the dry-basis gravimetric compositions of separated fractions at $\alpha = 0.05$. Either fraction consisted of 70.55% VS, 27.37 % Ash, and 40.36% Total Carbon (TC). The main difference, therefore, between solid and liquid fractions was in terms of solid concentration.

Start-Up

The digesters were first purged with CO_2 gas, filled with $NaHCO_3$ buffer solution, and inoculated with synthetic inoculum (ITDI) or active sludge from operating swine waste digesters. Adaptation or acclimation for 2 days to one week followed before organic loading began.

Batch Digestion

One-liter filtration flasks served as batch digesters. Digester temperature was maintained constant by submerging to neck level the flasks in a 35 °C water bath. Temperature control, however, was not strict due to intermittent power failures. Mixing was done manually by shaking of flasks thrice daily.

The batch digesters were step-loaded until the desired total organic load of 30 gm VS was attained. Net organic load at the start of the strictly-batch phase, however, was much lower due to partial methanation of the substrate as well as VS washout in the effluent displaced during loading.

Table 1. Substrate Properties in Batch Anaerobic Digestion of Swine Waste

PARAMETER	CONTROL	UN-SEPARATED BLENDED	SOLID FRACTION	LIQUID FRACTION
Total Solids, %[1]	5.73	5.13	6.42	1.81
Volatile Solid, %[2]	78.77	75.42	72.52	70.26
pH	7.34	7.30	7.35	7.63
Alkalinity, g/li as $CaCO_3$	1.94	2.83	5.75	2.21
Volatile Fatty Acids, g/li as HAc	1.00	1.34	0.88	0.97
NH_3-N, g/li as N	0.14	0.12	0.13	0.10

[1] Wet basis.
[2] Dry basis.
[3] To pH 3.7.

Table 2. Substrate Properties in Semicontinuous High-Rate Digestion of Swine Waste

PARAMETER	SOLID FRACTION	LIQUID FRACTION
Total Solids, %[1]	1.00- 5.07	5.51-18.23
Volatile Solids, %[2]	66.38-75.31	68.49-74.02
Ash, %[2]	22.19-29.61	26.17-30.08
Total Carbon, %[2]	39.10-43.23	38.84-41.02
pH	6.5[4]-7.6	6.8-7.5
Alkalinity, g/li as $CaCO_3$[3]	0.85-5.80	1.01-2.93
Volatile Fatty Acids, g/li as HAc	0.16-2.48	0.27-1.01
NH_3-N, g/li as N	0.03-0.18	0.03-0.13

[1] Wet basis.
[2] Dry basis.
[3] To pH 3.7.
[4] Adjusted to pH 7.2.

Biogas produced was collected by the brine displacement method. The process was terminated after five (5) successive days of nil gas production. Operating conditions are shown in Table 3.

High-Rate Digestion

Two dissimilar column reactors, the Baffled Upflow Anaerobic Reactor (BUAR) for the solid fraction (Figure 1) and the Anaerobic Packed-Bed Filter Reactor (APBF) for the liquid fraction (Figure 2), were designed and fabricated.

A common feature of these reactors was biomass retention. The BUAR used a system of baffles to settle flocs and create new active sites while the APBF utilized a coco-shell charcoal packing to entrap and immobilize active biomass. Channelling of fresh slurry, however, was a serious problem in the APBF.

Both reactors were half-submerged in a water bath, exposing in the process their upper ends to ambient conditions and creating a thermal gradient within. This induced convective mixing of reactor contents. This mixing mode had been used and reported before by Comerford & Picken (1985). Further agitation was provided by the rising gas bubbles, and, on the whole, mixing was fairly adequate.

A shift to a new process environment was completed in a single step instead of proceeding gradually but the reactors were allowed to acclimate for several days thereafter until steady-state was reached. The criterion used to define steady-state was a COV (coefficient of variation) ≤ 10 % for the 5-day (successive) daily methane production rate (G_m). This criterion was a modification from Hill et al. (1985, 1986, 1988).

Table 3. Operating Conditions in Batch Digestion

PARAMETER	CONTROL	UN-SEPARATED BLENDED	SOLID FRACTION	LIQUID FRACTION
Effective volume, li	1.20	1.16	1.14	1.22
Inoculum/Substrate ratio	0.61	0.95	0.54	0.76
Net organic load, gm VS[1]	22.07	22.35	24.27	14.54
Retention time, days	62	85	84	50
Strictly-batch mode	43	63	63	27

[1] The organic load at the start of the strictly-batch phase. This is much less than the desired load of 30 gm VS per digester due to the displacement of effluent during loading.

K

The substrate inhibition coefficient K was evaluated using Equation (4). Considering the small effective reactor volumes (2.0 li for the BUAR and 1.3 li for the APBF), the semicontinuous operation and the natural convective mixing mode were assumed to approximate the assumptions of a continuous well-mixed system for which Chen & Hashimoto's equation had been premised. Rearranging Equation (4):

$$K = (Bo/B - 1)\,(\mu_m\,HRT - 1) \qquad (8)$$

where μ_m was calculated using Equation (5). Data used were obtained under various combinations of OLR, HRT and temperature. This was justified since K is independent of HRT and temperature in the mesophilic range (Chen et al., 1984; Hashimoto et al., 1980). Calculated K's for both fractions (Table 6) were then plotted against So.

The exponential relationship between K and So had often been expressed in the form $K = \alpha + \beta \exp(\phi So)$ where α, β and ϕ are constants (Hashimoto, 1984). Determination of these constants from experimental data, using its linearized form $\text{Ln}(K-\alpha) = \text{Ln}\,\beta + \phi So$ (Dowdy & Wearden, 1983), involved the following steps: (1) an α was assumed (estimate the point where the curve intersects the K-axis, (2) Ln (K-α) vs. So was plotted (the plot should be linear, hence, all points which significantly strayed away from the line were rejected, see Figures 7 and 8), and (3) by linear regression, r^2 of the linearized form was evaluated. The solution was that which gave the highest r^2, and this corresponded to an α equal to 0.429 for the solid fraction and 0.798 for the liquid fraction. β was evaluated by taking the antiln of the regression constant while ϕ was equated to the slope of the regression line. The derived equations are:

Solid Fraction:

$$K = 0.429 + 0.00177 \exp(0.1867\,So),\ r^2 = 0.997$$

Liquid Fraction:

$$K = 0.798 + 9.43\times10^{-8} \exp(1.8079\,So),\ r^2 = 0.863$$

These are shown as solid lines in Figures 9 and 10.

The graphs indicate that for values of So less than 30 and 8 gm VS/li for the solid fraction and liquid fraction, respectively, the process was efficient and uninhibited but beyond these process inhibition might start. Process inhibition could be caused by one or more of the following (Hashimoto et al., 1980): (1) overloading (the microorganisms cannot cope up with substrate additions to the system), (2) inhibitory substances (e.g., VFA, free-ammonia, heavy metal cations) exceed their threshold levels, and (3) mass transfer of substrate and/or products is reduced due to the high solids concentration.

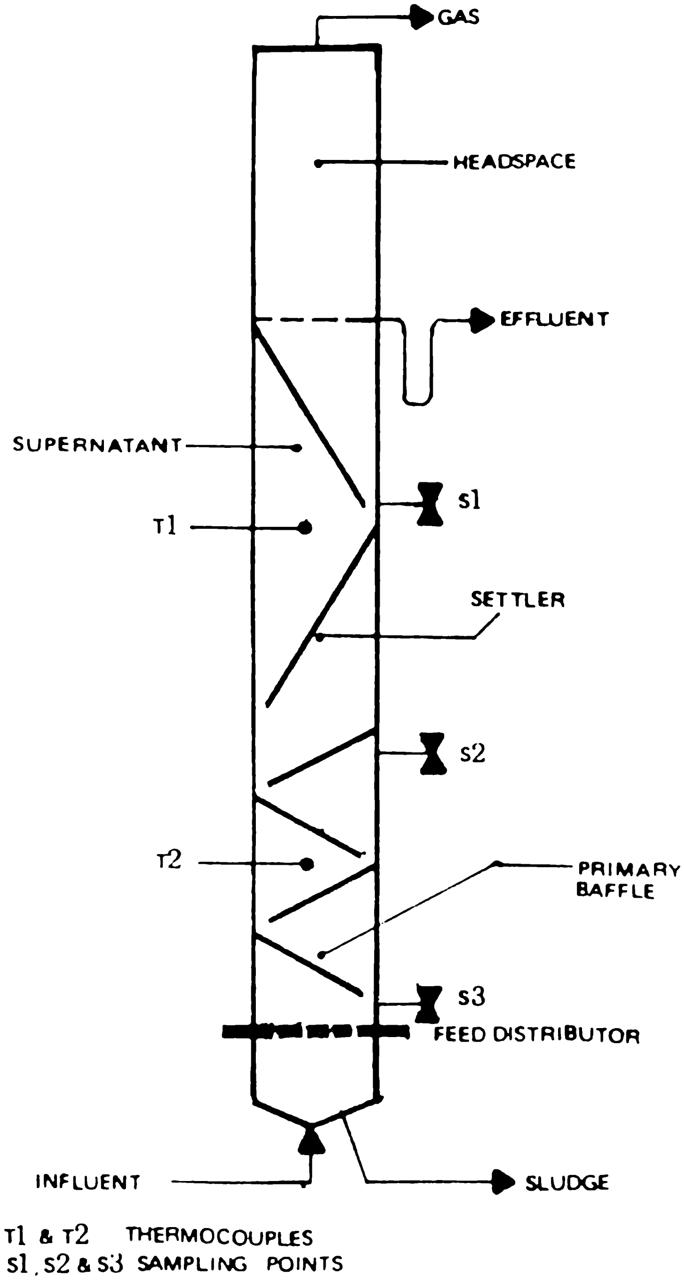

Figure 1. Schematic of the Baffled Upflow Anaerobic Reactor (BUAR)for the Solid Fraction of Blended Swine Waste.

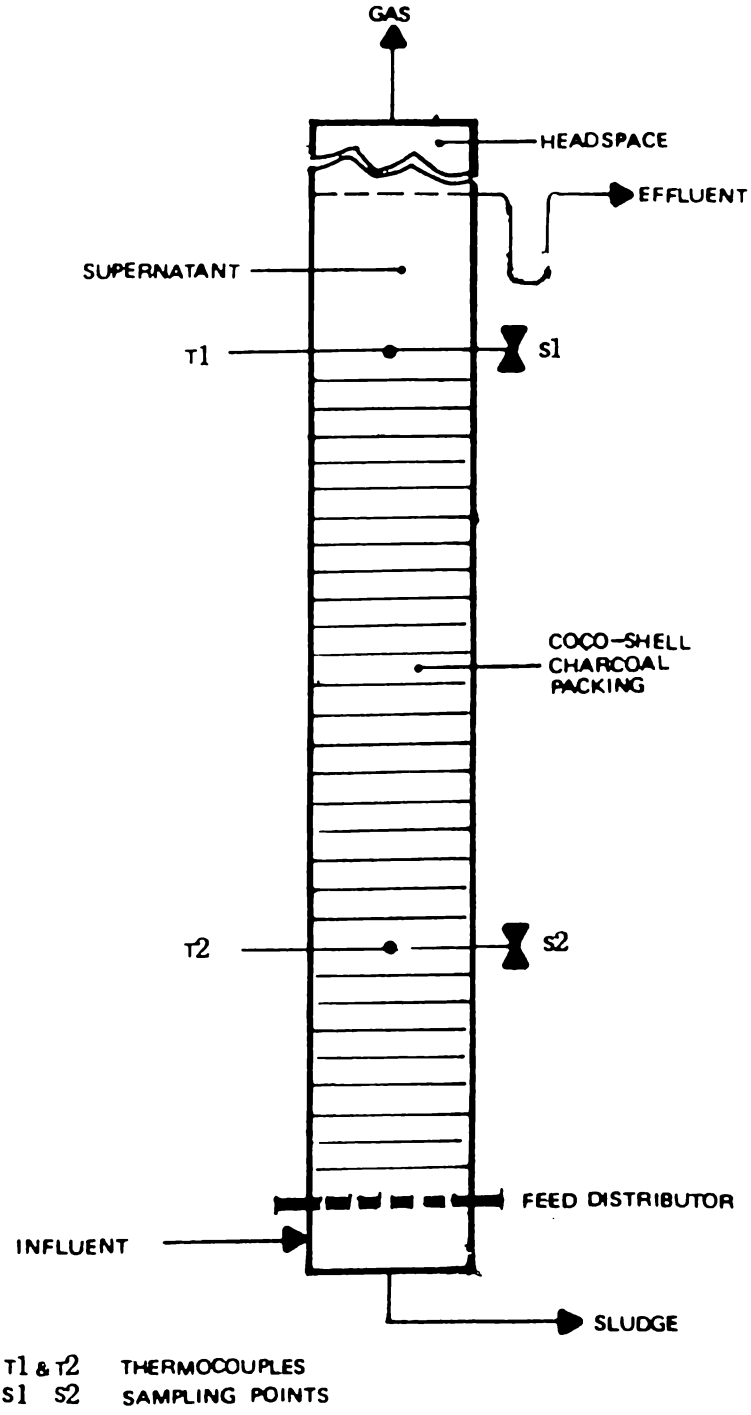

Figure 2. Schematic of the Anaerobic Packed-Bed Filter Reactor (APBF) for the Liquid Fraction of Blended Swine Waste.

The high-rate reactors were loaded daily, hence, semicontinuously. Different operating combinations of organic loading rate (OLR), HRT and temperature (T) were used as shown in Table 4.

Analytical Methods

Fresh swine waste, slurries, effluents and sludges were analyzed for gravimetric composition, pH, alkalinity, volatile fatty acid (VFA) and free ammonia-nitrogen using standard methods (APHA, 1981). Methane content was determined by gas chromatography (Shimadzu Model GC-6A).

Table 4. Operating Conditions in High-Rate Digestion

(a) Solid Fraction

Trial	So Gm VS/li	OLR Gm VS/li-day	HRT Days	T Deg C
1	6.52	0.44	15	35
2	22.47	1.49	15	35
3	34.89	2.32	15	36
4	28.02	2.32	12	35
5	14.58	2.32	6.3	35
6	22.37	2.04	11	33.5.
7	22.37	2.04	11	36.5
8	27.52	2.50	11	39.5

(b) Liquid Fraction

Trial	So Gm VS/li	OLR Gm VS/li-day	HRT Days	T Deg C
1	6.00	0.60	10	36
2	9.20	0.92	10	35
3	12.92	1.29	10	36
4	8.44	1.30	6.5	35
5	3.85	1.29	3	35
6	8.19	1.17	7	35.5
7	8.19	1.17	7	39
8	9.11	1.30	7	42

RESULTS AND DISCUSSION

Bo

The ultimate methane yield of solid and liquid fractions of swine waste were determined by extrapolation of data for batch-digestion rather than high-rate digestion since relatively short HRT's (maximum of 15 days for the solid fraction and 10 days for the liquid fraction) were used in the latter.

The total methane yields (B) at STP were calculated on those days (θ) when gas analyses were available (Table 5) and these were plotted against θ^{-1} as shown in Figures 3, 4, 5 and 6 for control, unseparated blended, solid fraction and liquid fraction, respectively. Next, Bo was determined by linear regression (Bo = B as $\theta \rightarrow \infty$).

Results showed that the liquid fraction had the highest Bo (0.489 li CH_4/gm VS added) while the control substrate had the least (0.358). Bo of the unseparated blended waste and solid fraction were 0.478 li CH_4/gm VS added and 0.373 li CH_4/gm VS added, respectively. r was very high for all substrates.

Since Bo is a measure of the ultimate biodegradability of the substrate, it seems that the higher concentration of refractory (nondegradable) particles in the solid fraction accounted for its lower Bo in contrast to the liquid fraction which consisted mostly of reduced or soluble organics and easily degradable suspended solids and finer sediments.

The high Bo of the unseparated blended waste could be explained similarly. Essentially, it consisted of all VS that was divided between the two fractions and had, therefore, a lower proportion of the refractory fractions than the solid separate.

Since the control substrate had a composition almost similar with the unseparated blended substrate, their Bo's should be theoretically the same. The result, therefore, suggests that methane conversion of the control substrate proceeded at a slower rate than did the blended substrate since comminution of the latter exposed a greater surface area and significantly enhanced contact between microorganisms and substrate. The lower B thus obtained for control naturally extrapolated into a smaller Bo since the digestion period was relatively short (62 days). This particular error could have been rectified had digestion proceeded to a much longer period than those in blended and separated wastes.

Experimental results compare well with the range 0.44-0.52 li CH_4/gm VS added for corn-based high-energy feed reported by Iannotti et al., 1979; Kroeker et al., 1979; Stevens & Schulte, 1979; Fischer et al., 1975; and Hashimoto, 1983.

Table 5. Raw Data for the Determination of Bo

Day	Per Cent CH_4	B, Li CH_4/Gm VS Added
	CONTROL	
31	68.13	0.1144
36	64.18	0.1309
37	66.12	0.1395
38	62.60	0.1371
47	73.19	0.2071
50	63.11	0.1849
52	72.40	0.2143
	UNSEPARATED BLENDED	
31	69.84	0.1550
32	66.60	0.1558
36	66.34	0.1851
37	64.30	0.1871
38	61.92	0.1851
49	71.77	0.2476
52	88.04	0.3046
	SOLID FRACTION	
30	54.19	0.0948
35	57.40	0.1378
37	55.57	0.1434
48	67.52	0.1998
	LIQUID FRACTION	
30	55.07	0.1536
31	50.64	0.1494
35	54.00	0.1885
36	64.11	0.2282
37	53.97	0.1981

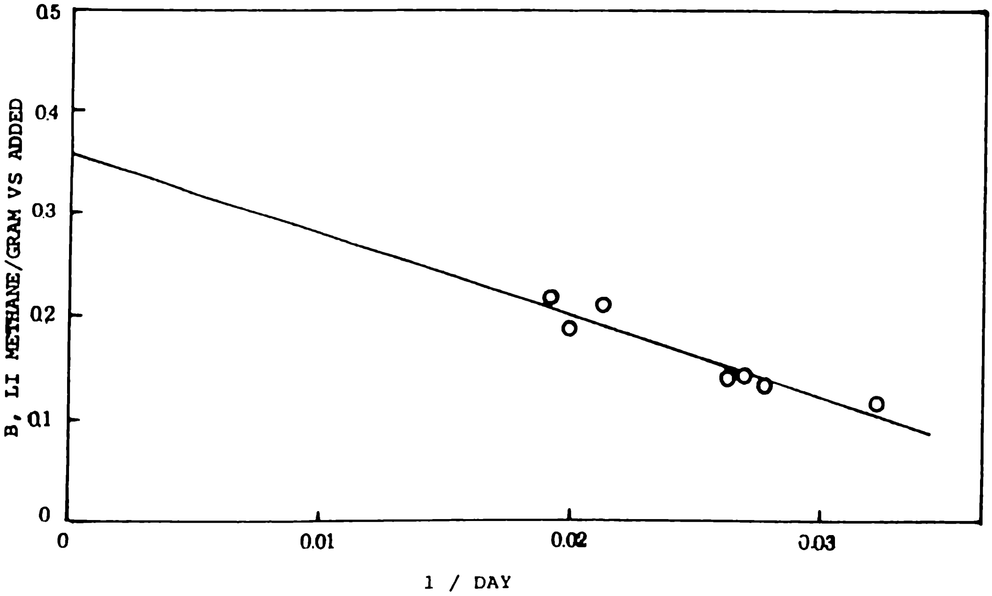

Figure 3. Bo of Control Substrate
(Bo - 0.358 Li Methane/Gram vs, r = 0.948)

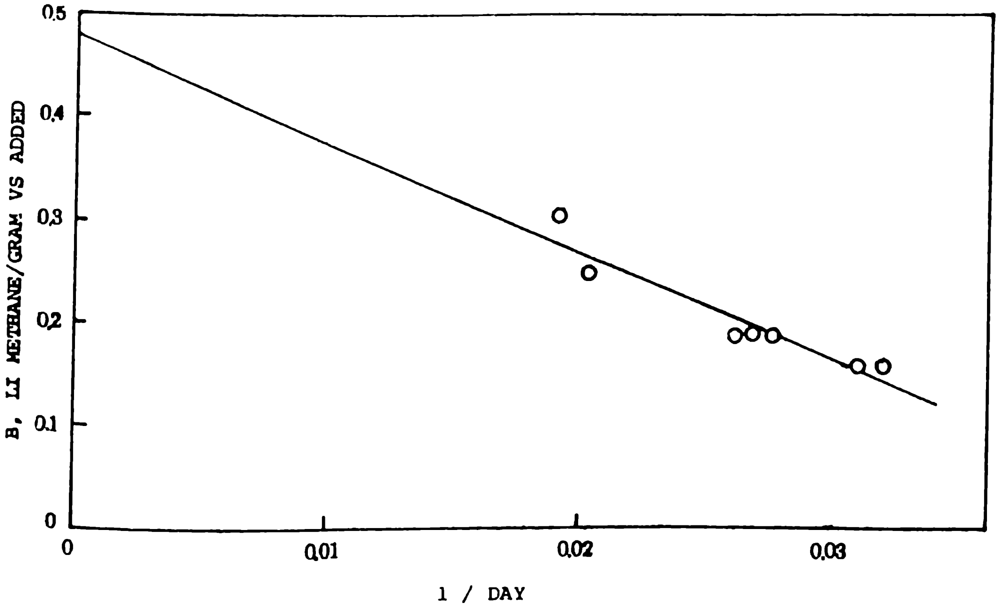

Figure 4. Bo of Unseparated Blended Swine Waste
(Bo = 0.478 Li Methane/Gram vs, r = 0.952

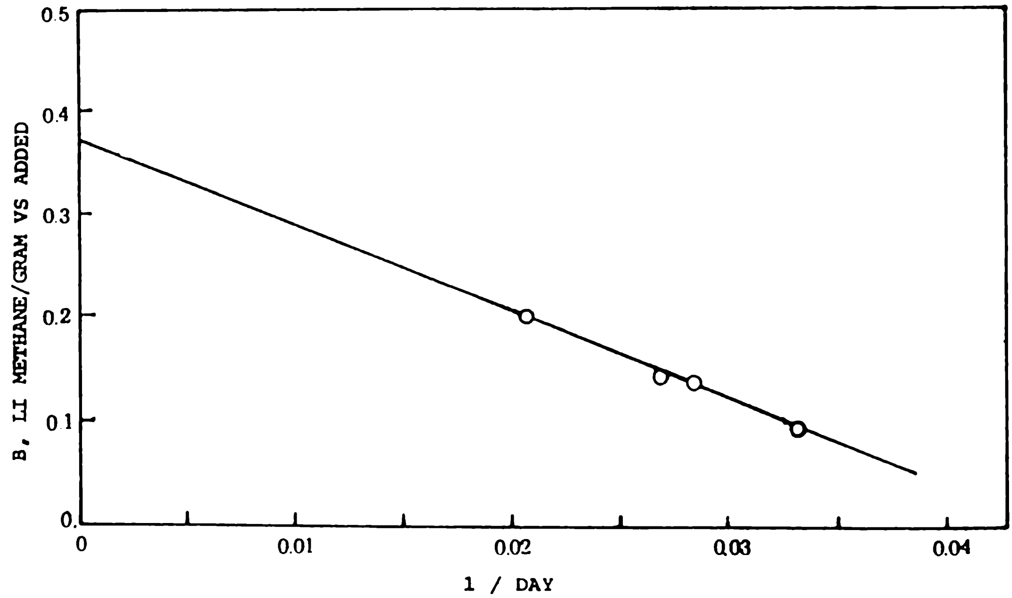

Figure 5. Bo of the Solid Fraction
(Bo = 0.373 Li Methane/Gram vs, r = 0.998)

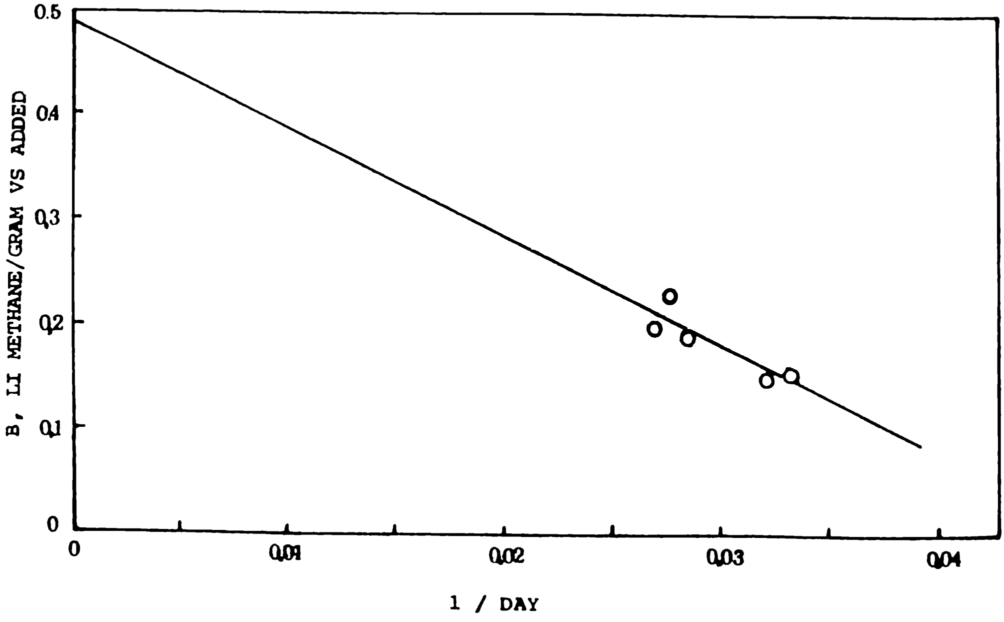

Figure 6. Bo of the Liquid Fraction
(Bo = 0.489 Li Methane/Gram vs, r = 0.883)

Although there is not much information that could be obtained from comparing experimental K values with established data since different experimental methods, procedures and substrates were used, thus causing difficulty in determining whether differences in K were due to apparent causes or other experimental differences (Hashimoto, 1984), it is nevertheless observed that the gap in threshold So concentrations between experimental results and the 50-60 gm VS/li range reported by Chen (1981) and Hashimoto (1984) is quite significant.

It is difficult to explain this gap in terms of differences in substrates, which would not be very considerable even for different swine waste slurry preparations. Rather, differences in experimental procedures and reactor configuration could have contributed to the result.

Table 6. Calculated K

So gm VS/li	HRT Days	T Deg C	B Li CH_4/gm VS	μ_m Day^{-1}	K
(a) Solid Fraction Bo = 0.373					
6.592*	15.0	35.0	0.301	0.326	0.927
14.581	6.3	35.0	0.260	0.326	0.457
22.372*	11.0	33.5	0.331	0.307	0.299
22.372	11.0	36.5	0.312	0.346	0.545
22.473*	15.0	35.0	0.229	0.326	2.442
27.521*	11.0	39.5	0.147	0.384	4.957
28.016	12.0	35.0	0.299	0.326	0.718
34.888	15.0	36.0	0.262	0.339	1.727
(b) Liquid Fraction Bo = 0.489					
6.001	10.0	36.0	0.366	0.339	2.876
9.205	10.0	36.0	0.222	0.339	2.876
12.921*	10.0	36.0	0.238	0.339	2.522
8.445	6.5	35.0	0.273	0.326	0.886
3.846*	3.0	35.0	0.207	0.326	-0.030
8.194*	7.0	35.5	0.277	0.333	1.017
8.294	7.0	39.0	0.247	0.378	1.613
9.107	7.0	42.3	0.208	0.421	2.630

*Rejected data.

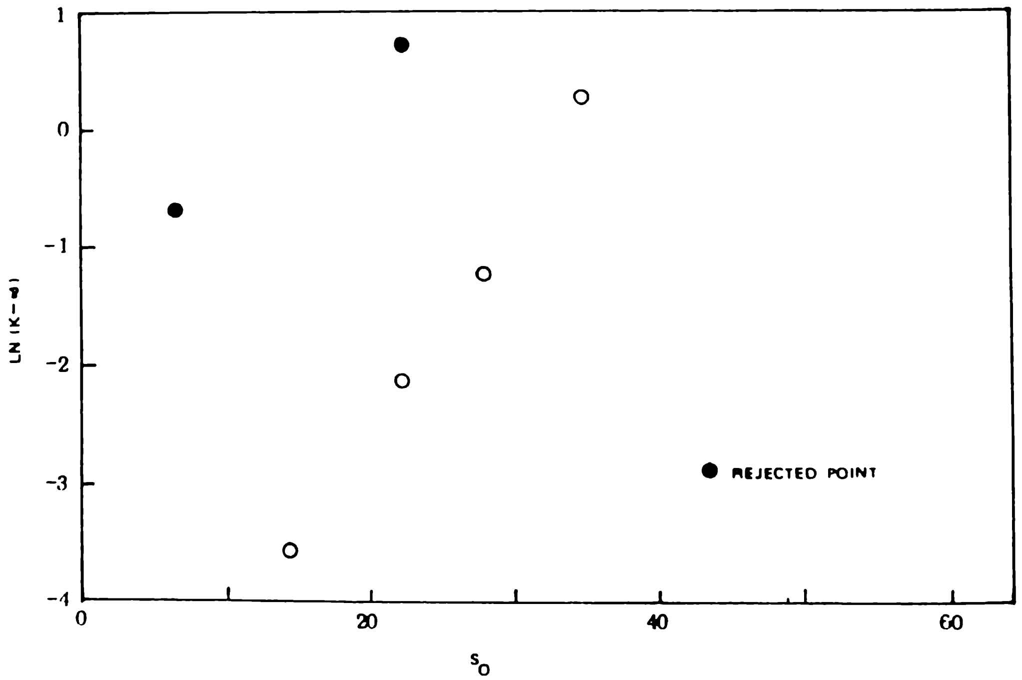

Figure 7. Plot of Ln (K - α) vs. So (Solid Fraction)
$\alpha = 0.429$

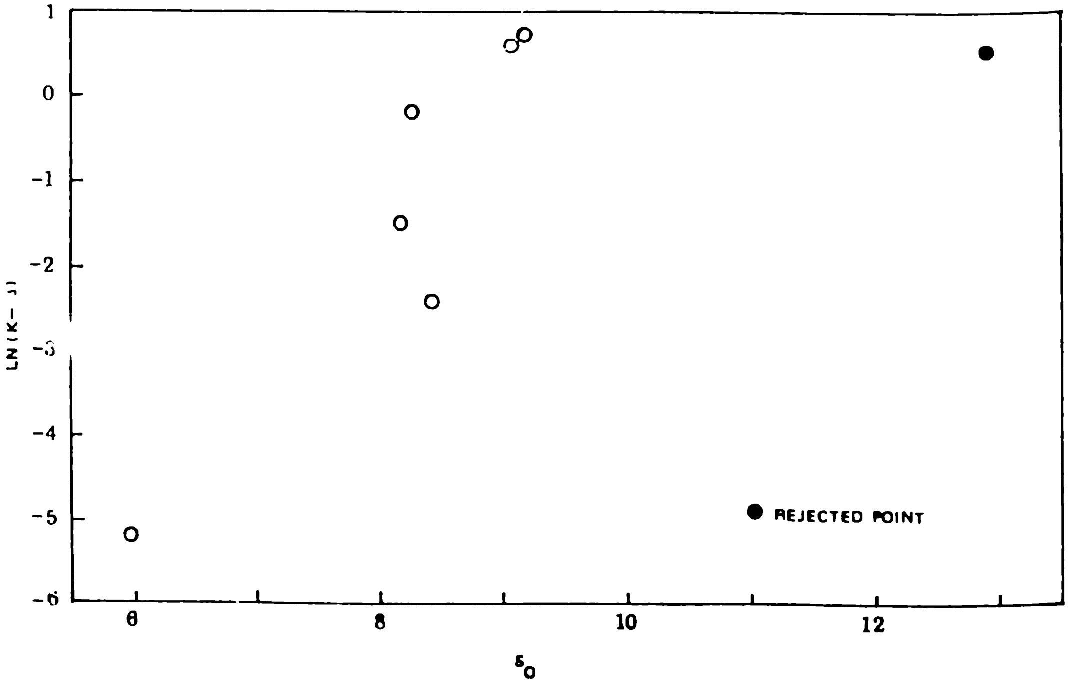

Figure 8. Plot of Ln (K - α) vs. So (Liquid Fraction)
$\alpha = 0.798$

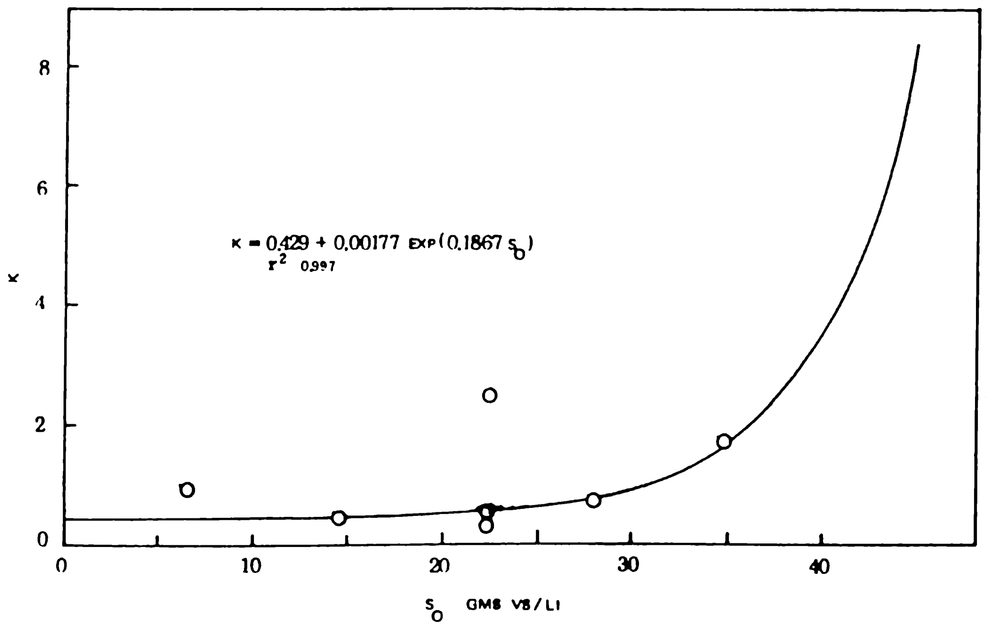

Figure 9. K Curve for the Solid Fraction
$K = 0.429 + 0.00177 \exp(0.1867\,So)$, $r^2 = 0.997$

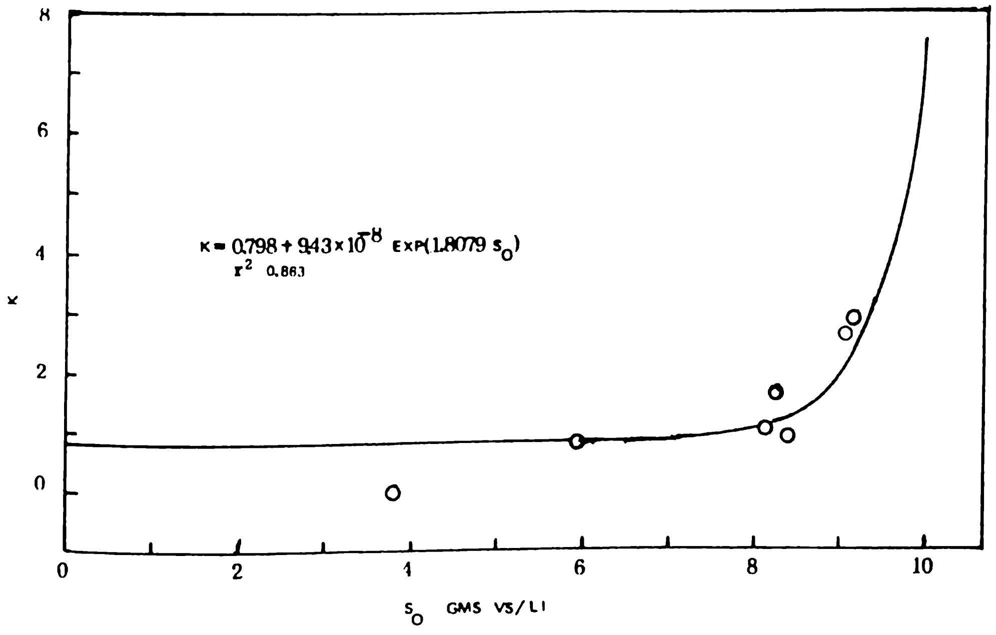

Figure 10. K Curve for the Liquid Fraction
$K = 0.798 + 9.43 \times 10^{-8} \exp(1.8079\,So)$, $r^2 = 0.863$

For example, spent sludge was not drained regularly (e.g., every loading). The solids build-up at the bottom of the reactor might have restricted the mass diffusion of fresh substrate despite the agitation provided by natural convection and gas evolution as well as the overload limit of the reactors. The small diameter-to-effective height (D/H) ratio of the columns (3.7/46.5 or 0.16 for the BUAR; 3.7/49.1 or 0.15 for the APBF) produced a thicker sludge bed compared to a bigger D/H ratio at the same feeding rate, thereby limiting the holding capacity of the reactors.

CONCLUSION

The ultimate methane yield (Bo) of solid and liquid fractions of swine waste obtained from this experiment were comparable with established data for swine waste. Although Bo is entirely dependent on substrate type, experimental procedures could significantly affect the calculation of Bo through the extrapolation of data from batch digestion.

Empirical equations relating the substrate inhibition coefficient (K) to influent substrate concentration (So) were derived for solid and liquid fractions of swine waste. Threshold So concentrations (where process inhibition might start) obtained were lower than established data because of high solids build-up and probable defects in reactor configurations which limited the diffusion of substrates and the overload limit of the reactors.

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