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This report summarizes the effort performed in compliance with AID contract AID/ta-C-1278, "Research in Methane Generation." The purpose of the study was to provide experimental data necessary for the evaluation of methane generation from combined vegetable and animal waste. In the performance of this study, a rather complete literature review of the subject was undertaken, an experiment was conducted at the Taiwan National Livestock Research Institute to evaluate some of the unknown responses on a scale suitable for immediate application, a design approach was initiated, and further necessary analysis and research was identified. It was concluded that it is possible to utilize vegetable wastes to increase the methane production of relatively simple animal waste anaerobic digesters. It appears that significant reductions in capital cost, improved performance, and increased useful product can be obtained by utilization of a two-stage (acidogenic/methanogenic) continuous flow excrement anaerobic digester operating in conjunction with batch mode biomass (vegetable waste) leaches. Modular construction of the digester from elastomeric materials and suitable insulation is suggested. Further experimental research and prototype design is recommended prior to an extensive field trial program.

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FINAL REPORT

ON

RESEARCH IN METHANE GENERATION

Contract Monitor

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Washington, D. C.

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15 September 1976

ARDA

FINAL REPORT
ON
RESEARCH IN METHANE GENERATION

Approved:

Bruce Billings

Bruce H. Billings
Vice President

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This report summarizes the effort performed in compliance with AID contract AID/ta-C-1278, "Research in Methane Generation." The purpose of the study was to provide experimental data necessary for the evaluation of methane generation from combined vegetable and animal waste. In the performance of this study, a rather complete literature review of the subject was undertaken, an experiment was conducted at the Taiwan National Livestock Research Institute to evaluate some of the unknown responses on a scale suitable for immediate application, a design approach was initiated, and further necessary analysis and research was identified. It was concluded that it is possible to utilize vegetable wastes to increase the methane production of relatively simple animal waste anaerobic digesters. It appears that significant reductions in capital cost, improved performance, and increased useful product can be obtained by utilization of a two-stage (acidogenic/methanogenic) continuous flow excrement anaerobic digester operating in conjunction with batch mode biomass (vegetable waste) leaches. Modular construction of the digester from elastomeric materials and suitable insulation is suggested. Further experimental research and prototype design is recommended prior to an extensive field trial program.

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SECTION I

INTRODUCTION

The combustible characteristics of marsh gas have been recognized for centuries as documented observations from ancient Egypt, China and Rome attest. Count Allesdandro Volta is credited with the discovery in 1776 that marsh gas was produced by the anaerobic decay of vegetable matter. In 1806 William Henry proved that the combustible constituent of marsh gas was identical to the major constituent of coal gas. Shortly thereafter, Sir Humphrey Davy identified the same gas coming from farmyard manure. This constituent was subsequently named methane and shown to be a molecule composed of one carbon atom and four hydrogen atoms. In 1868 Pierre Béchamp suggested that methane was formed by microorganisms living anaerobically on simple carbon compounds. This was confirmed by Tappeiner in 1882-1884. Based on subsequent research, the first plant for producing methane from organic waste was built in 1900 at the "Homeless Lepers' Asylum," Matunga, India (now the Acworth Leprosy Hospital). At about the same time, the development of anaerobic digesters for sewage sanitation plants began. This latter technology has continued to develop so that an extensive, comprehensive, and contiguous field of knowledge now exists. Issuing from the same source, the related activities in biochemistry and industrial microbiology also provide supporting theory, processes, and data useful in the studies on anaerobic digestion of organic waste.

While both urban sanitation and industrial biochemistry are documented as a continually evolving technology, the development of small-scale anaerobic organic waste digesters for producing biogas and fertilizer has been highly fragmented, in time, in place, and in concept. Spasmodically, since the early 1900s, the interest in such technology has existed in Great Britain, Germany, France, Algeria, Austria, Russia, Italy, Kenya, Uganda, Rhodesia, South Africa, Japan, India, Taiwan, Korea, the Philippines, Pakistan, Thailand, Papua New Guinea, China, Canada and the United States. The reasons for the activity has varied, but includes fuel scarcity, fertilizer need, cost effectivess, sanitation, pollution control, ecological compatibility, and improvement in "standard of living." There exists no single document

summarizing this field. For more detailed information, refer to ESCAP (1975a, b, c), Sathianathan (1975), Fry (1974), and Fry and Merrill (19 3).

At present, the most significant activities in biogas technology are being pursued by JCRR, Taiwan; IARI, India; and the Association of Countries under ESCAP, UNESC.

The purpose of this study was to qualitatively evaluate the feasibility of increasing the production of biogas (carbon dioxide and methane) of animal waste anaerobic digesters by the use of vegetable waste augmentation. The guidelines for the study were:

1. Conduct a literature review to determine the current state-of-the-art in digestion of combined forms of waste.

2. In cooperation with Taiwan National University and Py Research Institute, develop an experimental design to qualitatively test the operating parameters and characteristics of methane generation utilizing combined vegetable and animal wastes.

3. Instrument existing Taiwanese methane generators and carry out the experimental design of Item 2 above.

4. Analyze the experimental data; develop design recommendations and prepare a report on all project activities and results.

Highlights of the literature review are documented in Section II. Based on this material, an experimental design philosophy was developed as outlined below.

It has been experimentally demonstrated that the addition of small quantities of certain vegetable wastes to the digester influent can increase the biogas production per unit animal waste influent; however, increased or inappropriate vegetable waste additions have consistently resulted in rendering the digester inoperative. Two possible methods for solving this difficulty are:

1. Suitable preprocessing of the vegetable waste, such as mechanical grinding or chemical processing in order to disintegrate the constraining ligneous structures.

2. Leaching of the vegetable waste in a semi-batch mode method so as to allow only the introduction of soluble vegetable materials into the digester.

The second approach was pursued as it offered both flexibility and simplicity. Furthermore, there exists a number of papers discussing the unsuccessful attempts to implement the first approach.

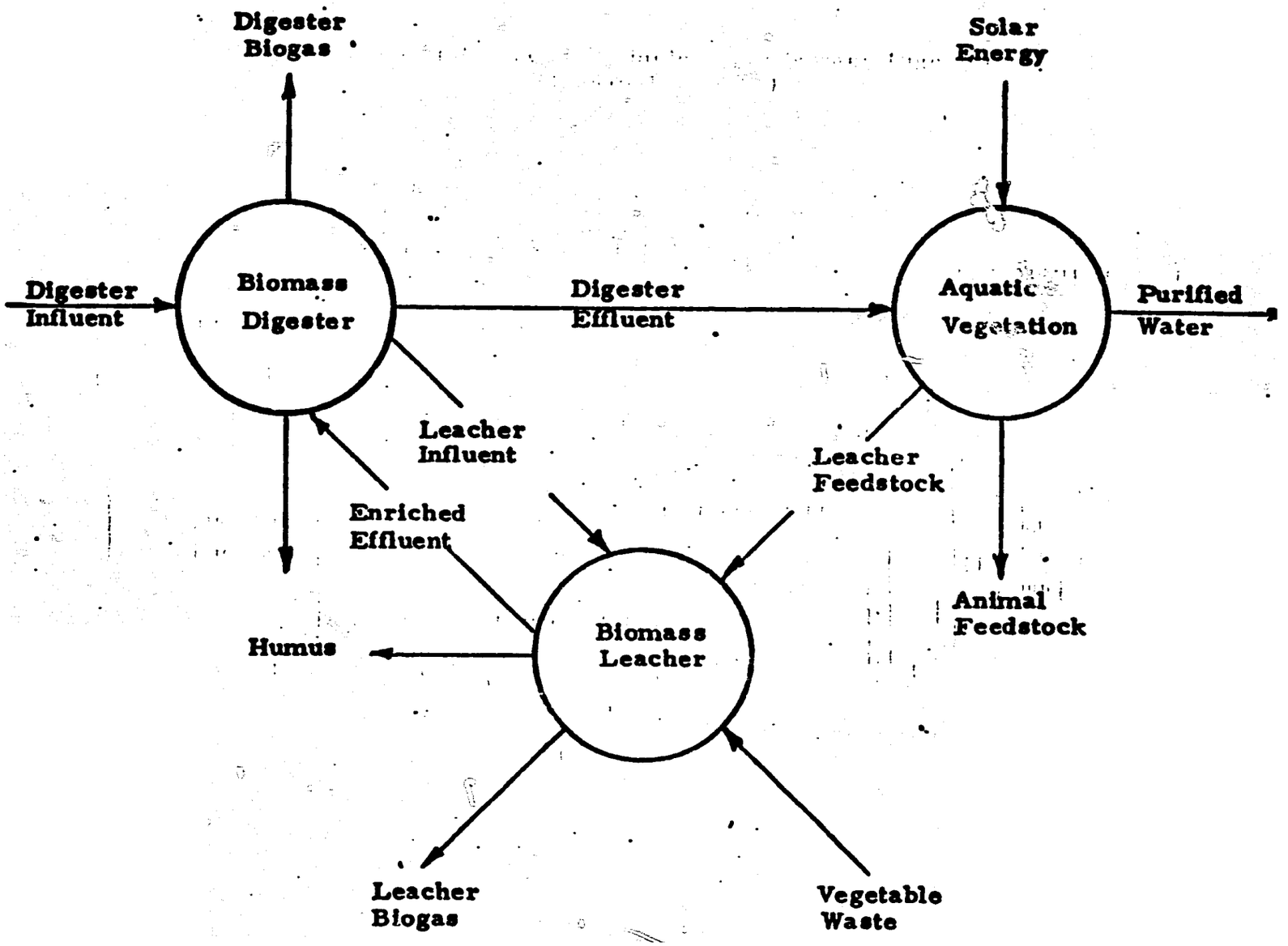
In addition to biogas production, anaerobic digesters also return the fertilization value of the influent in dissolved form in the liquid effluent and in humus form in the remaining spent ligneous solids. With some animal wastes, and depending on the digester design, a scum will form which must be periodically removed. This scum is readily usable as an enriched humus fertilizer. It is possible that for certain installations the liquid effluent cannot be immediately used to fertilize adjacent crops. In such instances it may prove advantageous to incorporate an additional element to the system that will effectively store the fertilizer in a useful form. The use of algae, water hyacinth, or water chestnut (caltrop) to purify the effluent is an example of one possible storage method. Nitrification/filtration composting of rice straw might prove to be an effective alternate.

A functional diagram summarizing the foregoing is depicted in Figure I-1. Examination of the details of the system as functionally depicted reveals several interesting features, some of which offer potential for optimization, others define operational constraints.

Anaerobic digestion can be considered on a macroscale as a three-step biological process utilizing heterogeneous groups of bacteria functioning in the absence of oxygen to degrade complex organic material into elemental molecular forms. The first step involves the hydrolysis of high molecular weight biopolymers, carbohydrates, fats, and proteins into lower molecular weight saccharides, fatty acids, and amino acids. The second step involves the production of volatile fatty acids (acetic, propionic, etc.), lower alcohols and aldehydes, carbon dioxide, hydrogen, ammonia, and hydrogen sulfide. The third step involves the generation of methane and carbon dioxide from the fatty acids, alcohols, and aldehydes; and the synthesis of methane from carbon dioxide and hydrogen.

The first two steps are the result of the metabolic processes of a group of bacteria which can be labeled as acidogenic. The third step is the result of the metabolic processes of a group of bacteria which can be labeled as methanogenic. The division of the anaerobic process into acidogenic and methanogenic has been demonstrated in a two-stage digester with each stage

Figure I-1. Functional Diagram - Methane Generation Studies



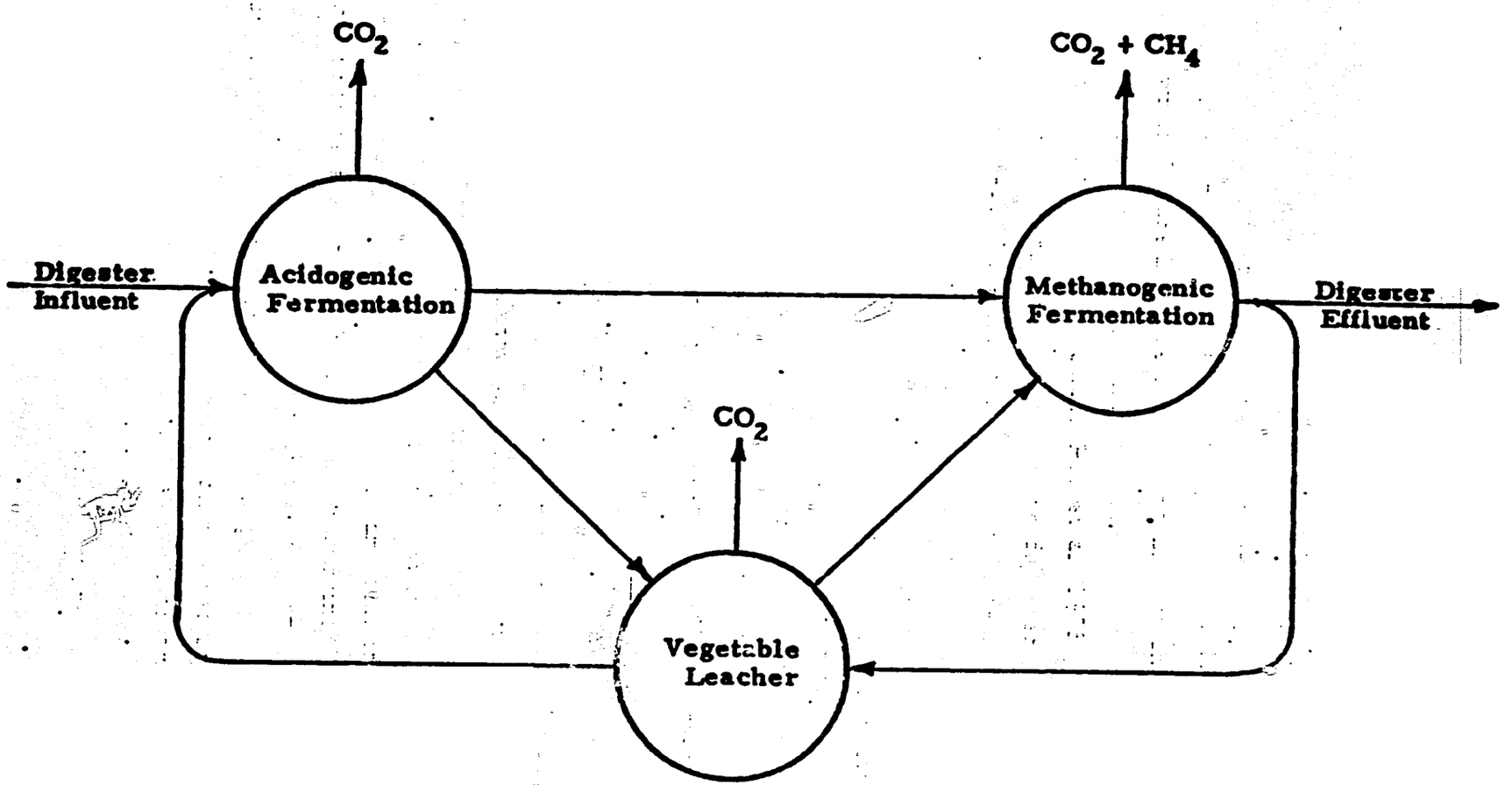
being operated at optimum environmental conditions (PH and temperature) for each of the bacterial groups.

These facts suggest that it would be advantageous to operate the biomass anaerobic digester as a two-stage unit (acidogenic, methanogenic), and the biomass leacher as an acidogenic digester. In this manner, the effluent from the two separate acidogenic segments could be used as a combined influent to a simple methanogenic digestion stage. Such an approach appears even more desirable when it is noted that the biogas evolved from the acidogenic fermentation process is primarily carbon dioxide whereas the biogas evolved from the methanogenic fermentation is rich in methane. A scheme of how this segment of the system could be configured is shown in Figure I-2. Note that several "feedback" paths are included. This feature can be utilized to control carbon/nitrogen ratio, solid/liquid ratio, hydraulic retention time, etc.

The concept of utilizing vegetable wastes implies that there are agricultural residues that are neither valued as food nor fiber. A list of candidate materials conceivably identifiable as waste is listed in Table I-1. Of the materials, rice straw is of particular interest due to its wide availability, and also due to its competitive value as an important material for rice paper or for mushroom culture compost substrate. For developing countries, the demand for rice straw as raw material for rice paper would tend to be limited. It is the potential use as a substrate for mushroom culture that warrants further consideration. Current practice is to mix rice straw with synthetic fertilizers, compost, and then grow mushrooms on this substrate combined with sterilized earth. In effect, this process provides protein assimilable by man from previously unassimilable forms. The anaerobic composting of rice straw by leaching with digester effluent might provide an alternate enriched substrate for mushroom culture. If such a concept proves valid, both fuel and food will result. The rice straw compost remaining after the harvest of the mushroom crop would be a vegetable waste available for acidogenic fermentation or suitable for use as humus.

Composting is defined for the purpose of this study as the aerobic decomposition of organic wastes to produce humus. This process has been utilized in agriculture for thousands of years. The first scientific investigation and documentation was provided by Howard (1940). Gotaas (1956) has prepared an excellent engineering text on the subject.

Figure I-2. Vegetation Augmented Anaerobic Digester



Rice Straw
Rice Husks
Bagasse
Sugar Cane Tops
Napier Grass
Water Hyacinth
Citronella Grass Waste
Banana Wastes
Sisal Wastes
Bamboo
Jute Wastes
Casaba/Sweet Potato Wastes
Sago Palm

Table I-1. Potential Vegetable Wastes

In the composting process, bacteria, fungi, molds, and other saprophytic organisms convert organic matter to carbon dioxide and water while producing significant heat. The remaining material consists primarily of stable carbohydrates, such as lignins, together with most of the original nitrogen and phosphorous nutrients. Such material is an excellent organic fertilizer.

Since the required feedstock and one of the resultant products are effectively identical for aerobic decomposition and for anaerobic fermentation, these processes should be considered as competitive alternatives. The advantages of composting are simple processing and effectively complete pathogen destruction. The major disadvantage is the loss of potential energy when compared with the methane produced by anaerobic fermentation. When appropriate provisions are made in the anaerobic processing to assure pathogen control, composting ceases to be the most economic waste recovery method.

The experimental phase of this study requires specially trained skilled personnel and suitable test facilities. Fortunately, the National Taiwan University and PLRI possess these necessary resources. On this basis, an experimental program was prepared as detailed in Section III. The results of the experiment are summarized in Section IV.

Based on the experimental results and the literature survey, further efforts are proposed in Section V. Section VI provides conclusions and recommendations incorporating material developed during the course of the study. For future reference, a rather complete bibliography has been included. Related material and specific details pertinent to this study are included in the Appendix.

SECTION II

LITERATURE REVIEW

To provide a basis for both the specific research conducted as part of this study and to aid in defining the total potential for biomass waste recovery in developing nations, an extensive literature review was undertaken. This section summarizes information abstracted from a selected set of the scientific literature in this field. The material tends to be limited to elements applicable to developing nations. A Bibliography, Section VII, is provided for those who wish to delve deeper. The publications of ESCAP (1975 a, b, c), Fry and Merrill (1973), Fry (1974), Poole (1974), and Sathianathan (1975) should be of particular interest.

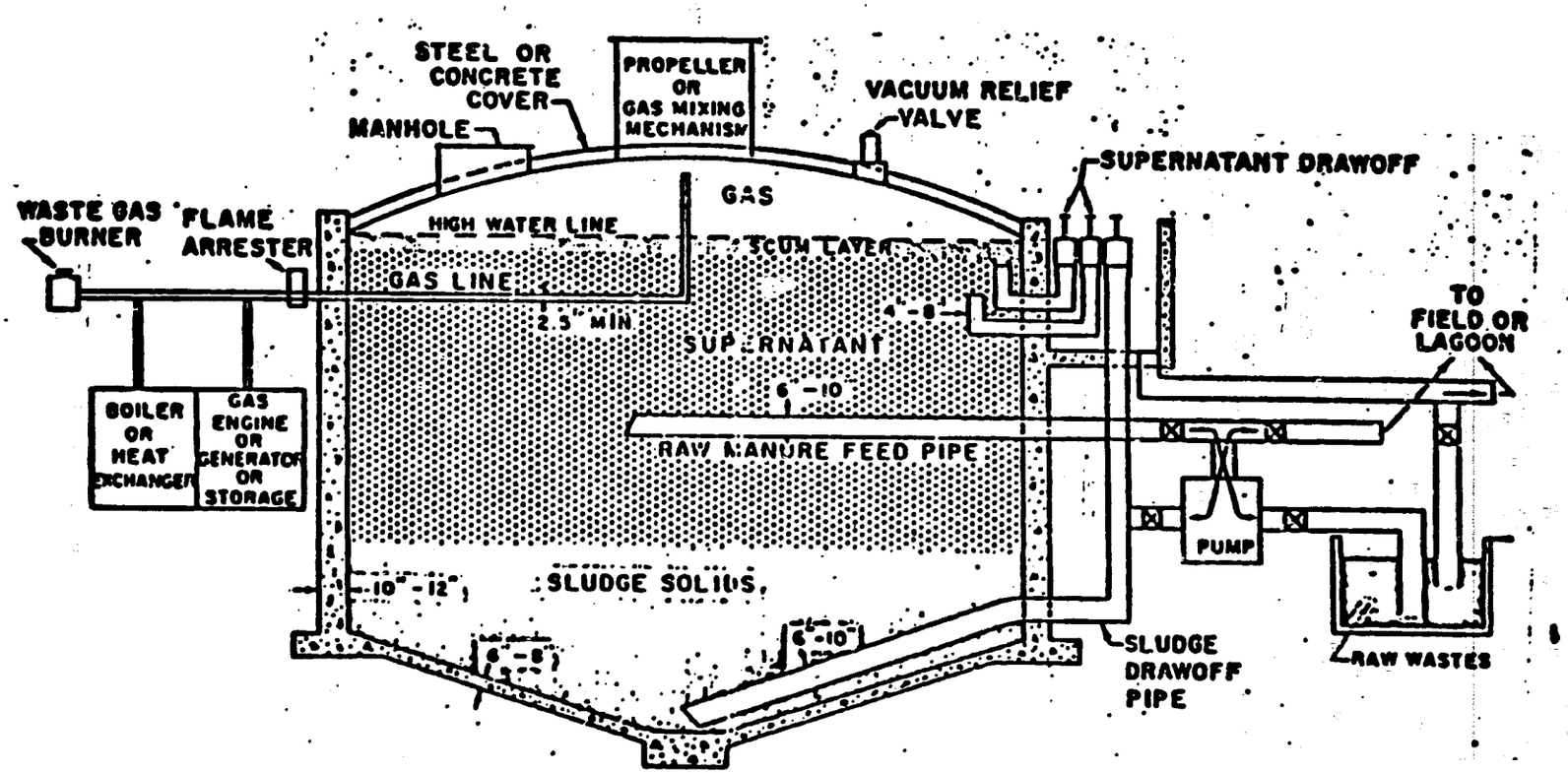
Anaerobic Digestion of Sewage Sludge

Pohland and Bloodgood (1963) reported on the performance of a laboratory scale anaerobic sludge digester operating at 36°C, 52°C, and 60°C under volatile solid loadings of from 0.5×10^{-3}, to 5×10^{-3} kilo/liter day. Optimum performance was reported at a temperature of 36°C and a volatile solids loading of 4×10^{-3} kilo/liter day, resulting in a gas production of 625 liters/kilo volatile solids exhibiting a 75% CH_4, 25% CO_2 composition. Higher temperatures consistently resulted in lower efficiencies as did other loading rates. This data is somewhat at variance with other studies, possibly because the bacterial cultures were not given sufficient time to acclimate to the other temperatures. It should be noted that no attempt was made to artificially control pH, so that at the poor operating conditions, a lower pH was always evident.

Anaerobic Digestion of Poultry Manure

Taiganides (1963) discusses the subject of anaerobic digestion of poultry manure and presents a number of sizing criteria for a single-stage digestion system. Figure II-1 depicts a typical digester considered suitable for operation in a machine/energy intensive agricultural environment. Table II-1 summarizes the design criteria recommended by Taiganides. No experimental data was provided to confirm the design

Figure II-1. Typical Single-Stage Sewage Digester
(Taiganides, 1963)



Poultry Manure Design Criteria

Manure production - 0.175 kilo/hen day (confined)
Total solids content - 25%
Organic solids - 0.035 kilo/hen day (confined)
Expected gas production - 0.012 M^3/hen day (25-day retention)
Composition - 60% to 80% CH_4; CO_2 remainder

Single Stage Digester Design Criteria

Operating temperature - 35°C
Detention time - 10 to 30 days
pH - 7 to 8
Digester loading and organic solids - 1 to 5 X 10^{-3} kilo/day liter digester
Total solids - 5% to 15% of influent

Table II-1. Anaerobic Digestion of Poultry Manure
(Taiganides, 1963)

philosophy. It would appear that a more economic solution would be to use a two-stage system of a simpler smaller configuration.

Anaerobic Digestion of Pig Manure

Kang (1975) has reviewed the development of the pig manure digester as it evolved in Taiwan. Although the technology had been highly developed by the Japanese on Taiwan during the early 1940s, it was effectively completely reinvented in the late 1950s. Today, more than 8000 units of the designs shown in Figure II-2 are functioning in Taiwan, and development of a more cost-effective elastometric bag design schematically shown in Figure II-3 is being explored. Chung Po, et al (1975), has published performance data on a typical small pig manure digester, a summary of which is given in Table II-2. Note that the variation in retention time was obtained by varying the amount of wash water, with the digester volume and the pig manure mass per day remaining constant. System response for various retention times varying the quantity of waste introduced per day into the digester would be required to completely map the operating characteristics. Based on other reported digester experiments, it would seem that an increase in percentage of solids could be tolerated with little or no degradation in performance. This would effectively reduce the required digester value per unit solid digested.

Anaerobic Digestion of Cattle Waste

Meenaghan, et al (1970), reported on the two-stage digestion of cattle wastes. Figure II-4 is a schematic of the system utilized in their experiment. Table II-3 summarizes the results of their experiment. It is apparent that anaerobic digestion did occur, that separation of the acidogenic and methanogenic processes was partially successful, and that this procedure could apparently provide a source of biogas while purifying (lowering the BOD) the polluted wastewater. It would appear that the experiment could have been more successful if the first stage (acidogenic) retention time had been less than the 5 days used, and the second stage (methanogenic) 5-day retention time had been greater. The substantiation of an anaerobic filter for the second stage digester would appear desirable. Methods for utilizing the enriched water resulting from this process were not discussed.

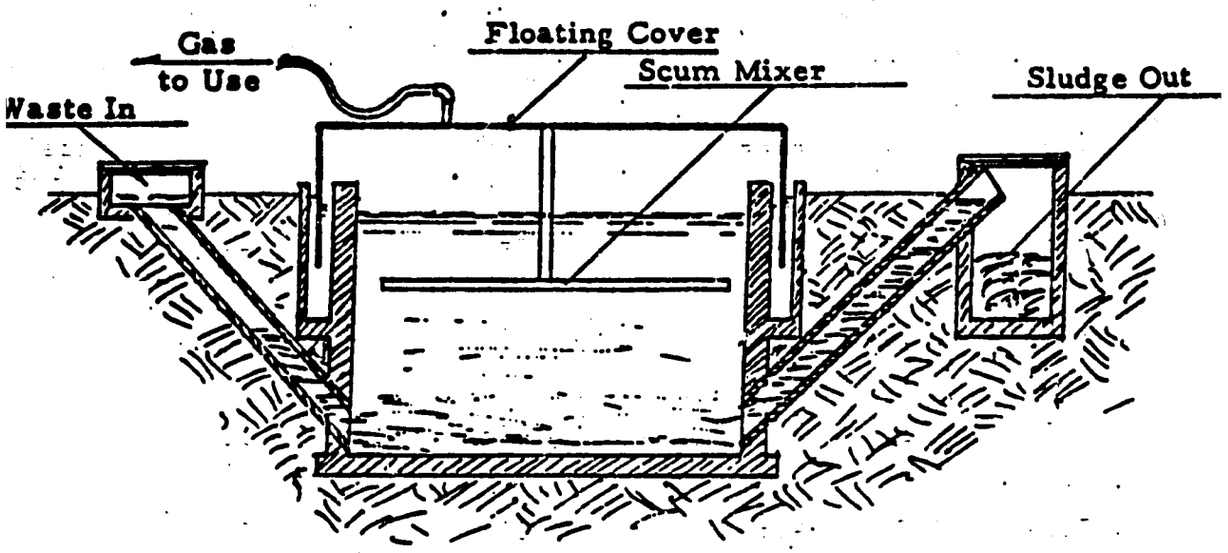


Figure II-2. Floating Top - Masonry Tank Design
(Kang, 1975)

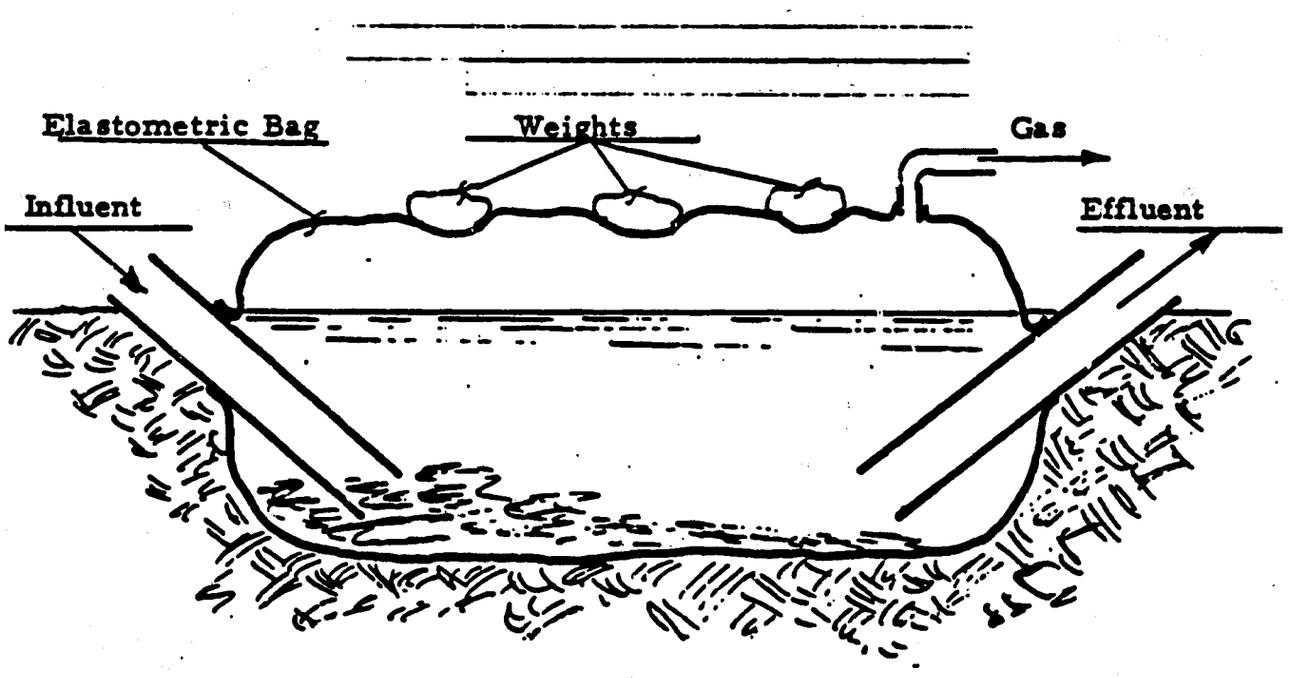


Figure II-3. Elastometric Bag Design
(Chung Po, et al, 1975)

Digester Volume	5530 liters
Waste Input:	
Total solids	5.125 kilo/day
Volatile solids	4.250 kilo/day
Effective "BOD"*	0.984 kilo/day
Effective "COD"**	3.080 kilo/day

Calculated Influent Characteristics vs. Reten

Retention time - days	6	8	12	16
Total solids - g/l	5.57	7.42	11.13	14.84
Volatile solids - g/l	4.61	6.14	9.21	12.29
COD, -mg/l	3345	4460	6690	8920
BOD, -mg/l	1070	1487	2140	2854

Measured Effluent Characteristics vs. Retention Time

Retention time - days	6	8	12	16
PH	7.2	7.2	7.3	7.4
Total solids - g/l	—	3.218	4.338	4.938
Volatile solids - g/l	—	2.032	2.622	2.638
COD - mg/l	1700	1900	2160	2160
BOD - mg/l	400	380	410	380

Biogas Production vs. Retention Time

Retention time - days	6	8	12	16
Total biogas produced - l/d***	1800	2200	2800	3100

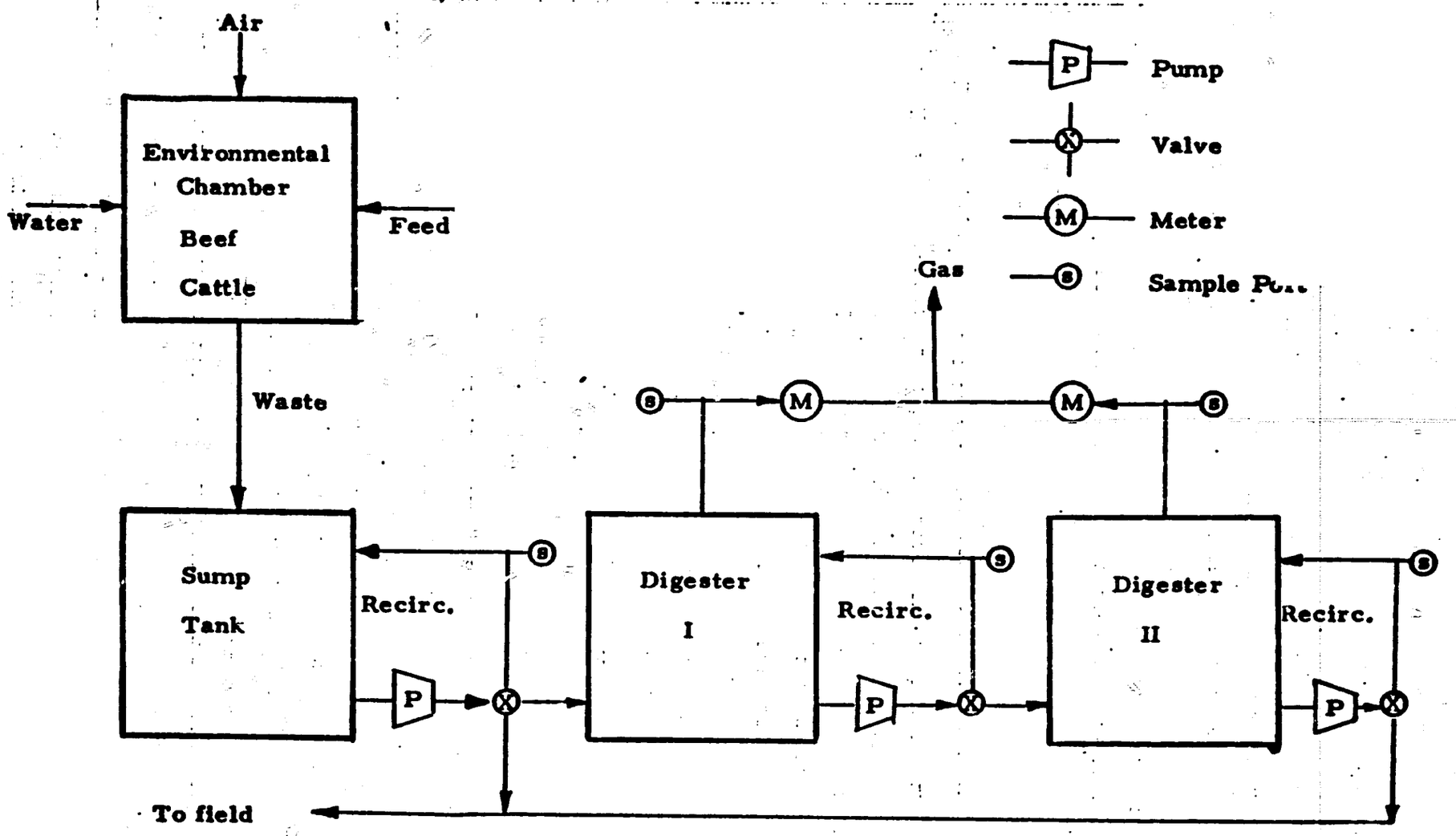
*BOD - Biological (Biochemical) Oxygen Demand

**COD - Chemical Oxygen Demand

***Composition not reported; however, by implication the CH_4 was apparently assumed to constitute 65%.

Table II-2. Anaerobic Digestion of Pig Wastes
Summary of Experiment/Results
(Chung Po, et al, 1975)

Figure II-4. Anaerobic Digestion of Cattle Waste Process Schematic
(Meenaghan, et al, 1970)



ENVIRONMENTAL CHAMBER

3 steers, 225 kilo initially, 350 kilo after 55 days
29 ± 1°C air temperature
50 ± 4% RH
5 min. air replacement time
Continuously lighted (200 watts)
165 liters/day water in/out
Feed: 90.81% Milo - dry rolled
7.50% Cottonseed meal
1.00% Calcium carbonate
.69% Vitamins, minerals, salt

SUMP TANK

165 liters/day liquid waste in/out
6900 mg/l BOD
13,000 mg/l COD
7.3 pH
16.2 C:N ratio
2100 mg/l alkalinity

DIGESTER 1

22.7 liters/day liquid waste in/out
5 day retention time
36°C
6900 mg/l BOD
6.3 pH
3750 mg/l alkalinity
0.273 m^3/day CH_4 production
0.242 m^3/day CO_2 production

DIGESTER 2

22.7 liters/day liquid waste in/out
5 day retention time
36°C
2900 mg/l BOD
7800 mg/l COD
7.1 pH
9.4 C:N ratio
4700 mg/liter alkalinity
0.243 m^3/day CH_4 production
0.093 m^3/day CO_2 production

Table II-3. Anaerobic Digestion of Cattle Wastes
Summary of Experiment/Results
(Meenaghan, et al, 1970)

Anaerobic Digestion of Cattle Manure and Vegetation

Laura and Idmani (1971) reported on the batch digestion of cow dung plus various other materials, primarily of vegetable origin. The results are summarized in Table II-4 in a form comparable to that reported by Boshoff (1967).

Desai and Biswas (1945) reported on studies with a small continuous flow digester utilizing primarily cow dung as the input material, although experiments with additions of vegetable matter were also performed. Table II-5 summarizes their experience. A positive correlation between ambient temperature and gas production was noted. Of principal concern to the research was the fertilizer value of the digested materials. The conclusions were that anaerobic digester fertilizer was superior to aerobically-fermented (composted) fertilizers.

Anaerobic Digestion of Vegetable Matter

Boshoff (1963, 1967) has described experiments on both batch and continuous digestion of vegetable matter. These experiments show that virtually any type of vegetable matter can be anaerobically digested. For batch digestion, both dung and vegetative residues of previous fermentations were utilized as starter materials, the former proving to be somewhat more effective. Fermentation of 35°C indicated both higher rates and higher total gas production per unit mass of matter when compared to fermentation at 22°C. Batch digestion can be approximately described by the mathematical relationship

$$V_t = V_T (1 - e^{-Kt})$$

where

t = time, days

V_t = accumulative gas

V_T = total gas producible

K = reaction constant, temperature dependent

80-Day Results

Material	Gas product. l/kilo dry	K day^{-1}	% decom-posed	Gas Comp.		
				%CO_2	%CH_4	% H
500 g fresh dung (15.57% dry matter)	208	.023	28.08	34.4	60.0	1.1
500 g fresh dung + 2 g cane sugar	207	.025	28.61	38.4	57.6	2.1
500 g fresh dung + 5 g ashes	190	.023	26.79	34.4	60.4	2.9
500 g fresh dung + 12 g fresh leguminous leaves	200	.024	28.88	32.0	61.6	4.0
500 g fresh dung + 6 g sarson oilcake	203	.021	28.45	30.4	67.4	---
500 g fresh dung + 5 g cellulose	208	.026	30.06	44.0	52.8	---
500 g fresh dung + 2 g casein	219	.026	31.12	32.0	64.0	2.4
500 g fresh dung + 5 g cane sugar + 5 g urea	260	.023	36.92	30.6	68.0	---
500 g fresh dung + 5 g cane sugar + 5 g $CaCO_3$	244	.026	33.01	28.0	70.0	---
500 g fresh dung + 100 mil urine	245	.023	33.83	32.0	67.0	---
500 g fresh dung + 2 g charcoal	160	.028	22.93	32.0	65.6	---
250 g fresh dung + 50 g dry leaves (non leguminous)	219	.020	32.52	28.0	68.0	0.6

Table II-4. Anaerobic Batch Digestion of Cow Dung/Additive (Laura and Idmani, 1971)

Material	Retention time-days	Gas Production liters/kilo(dry)	Composition		
			$\%CH_4$	$\%H_2$	%CO
Dry leaf powder	10	435	44.4	10.8	44.8
Sugar Cane Trash Powder	12	745	45.4	10.2	44.4
Maize Powder	11	810	45.9	10.3	43.8
Activated Sludge Powder	10	625	43.8	11.3	45.9
Straw Powder	7	935	46.4	9.9	44.7
Cow Dung	14	330	----	----	----

Table II-5. Gas Composition/Quality Anaerobic Fermentation (Desai and Biswas, 1945)

If an especially virile "starter" such as partially digested dung is utilized, the simple exponential form is somewhat in error during the early portions of the fermentation. Values reported by Boshoff for elephant grass fermentation are

$$K_{22^\circ C} = 0.0526 \text{ day}^{-1}$$

$$K_{35^\circ C} = 0.0600 \text{ day}^{-1}$$

He notes that K values for sewage sludge range from 0.12 to 0.30 day $^{-1}$. For batch digestion, the total gas producible ranged from 585 to 235 liters/kilo dry vegetation, the higher values being obtained using dung starter at 35°C, the lower values obtained using fermented vegetation residue at 22°C. Methane content was typically 60%. Total digestion times ranged from 40 to 60 days, which concurs with other recommended optimum durations. For continuous digestion, the gas production was typically 320 liters/kilo dry vegetation. Some comments of Dr. Boshoff are particularly interesting, and so are quoted exactly as published.

> "The production of methane gas on farms has become almost universally associated with farms where livestock is housed and where a supply of dung, either pure or in a mixture with grass in the form of bedding is readily available for fermentation. Installations in which the materials are fermented in batches have, because of their simplicity, also been generally adopted...
>
> "In the continuous fermentation carried out, the digesters were initially fed with dung, and as gas production commenced, small quantities of grass were fed daily to the dung until a steady daily rated gas production was obtained. Formal trials were carried out using the material obtained from such a digester, as starter material. As the digesters filled up with fibrous exhaust residues, appropriate quantities were periodically removed...
>
> "The batch method is the most common technique employed on farms for the production of methane gas by the anaerobic fermentation of vegetable matter. It is by no means the most efficient, the continuous method being considered more so, but the relative cheapness, and simplicity of the plant required for batch fermentation has generally led to being preferred...."
>
> Boshoff (1967)

Anaerobic Digestion of Cellulose

Pfeffer and Liebman (1974) reported on the performance of a 350-liter fermentator operating between 55°C and 60°C. The feed material was predominantly cellulose, being derived from urban refuse. The feed rate was approximately 2.5 kilo/day at a loading of approximately 60 gm/liter. The gas production was between 600 and 900 liter/day, or on a volatile solid basis, approximately 375 liters/kilo volatile solids added, or 685 liter/kilo volatile solids destroyed. Performance was somewhat erratic due to equipment malfunction.

Pfeffer (1974) reported on a parametric study of the response of a set of eight 24-liter laboratory digesters receiving 50 grams dry cellulose plus 6 grams dry raw sewage sludge. Hydraulic retention times from 4 to 30 days were examined. The temperature range investigated was from 35°C to 60°C. In order to provide proper nutrient levels in relation to available carbon, inorganic nitrogen and phosphorous salts were added. Sufficient sodium hydroxide was utilized to stabilize the pH at 6.7 to 6.8. Table II-6 summarizes the gas composition and production for the extreme temperatures. Increasing pH from 6.5 to 7.5 showed improved conversion efficiency (higher cellulose conversion), with the magnitude of improvement being temperature dependent.

Kispert, et al (1975), report on their studies leading to a proposal for a large-scale proof of concept program to evaluate anaerobic digestion of urban refuse. Experimental studies were conducted by the University of Massachusetts and MIT in support of the study. These studies, in general, supported the previous results reported by Golueke (1971-2, Pfeffer (1974). Of significant importance was the development of an on-line Adenosine Triphosphate Sensor (ATP) at the University of Massachusetts. ATP concentration can be directly correlated with biomass and microbial activity (Patterson, et al, 1970).

Lignin - Cellulose Digestion

The vegetable wastes, available for anaerobic digestion tend to be materials with low animal food content. These wastes are composed

Retention Time-days	35°C			60°C		
	%CH_4	%CO_2	SCF Gas / lbs v. s.	%CH_4	%CO_2	SCF Gas / lbs v. s.
4	69.8	30.2	2.02	58	42	6.17
6	64.3	35.7	2.91	57	43	6.75
8	58.6	41.4	3.36	57	43	6.16
10	57.2	47.8	3.84	57	43	6.64
15	53.8	46.2	4.23	56	44	6.61
20	53.4	46.6	4.28	55	45	6.90
30	53.8	46.2	4.39	55	45	7.20

Table II-6. Anaerobic Digestion of Cellulose Laboratory Digester Performed (Pfeffer, 1974)

primarily of lignin-cellulose fibers, wherein the ligneous structure tends to shield the cellulose materials from enzymatic hydrolysis. A number of studies have examined this subject, the papers of Cowling (1963) and Pew and Weyner (1962) typifying the results obtained. Mechanical fine grinding and/or hydroxide treatment to swell the material beyond its water-swollen dimensions are proven techniques for producing a substrate that will allow 90% removal of the cellulose by subsequent enzymatic digestion.

Comparative Yield Data

Poole (1974) has prepared an interesting review of thirteen published anaerobic digestion experiments. Table II-7 summarizes his comparisons.

Temperature Influence on Anaerobic Digestion

It has long been known that anaerobic digestion is influenced by the operational temperature. Golueke (1958) presented the results of an experimental evaluation of the effect of temperature on raw sewage sludge which suggested two distinct regions, mesophilic below 45°C, and thermophilic above 45°C. The results of this study are represented by Figure II-5 which plots the gas production versus temperature for the equivalent of a 30-day retention time. Pfeffer (1974) documented the results of a more extensive study which examined the influence of various parameters on anaerobic digestion of organic wastes, primarily cellulosic. Figure II-6 summarizes the data relating temperature and retention time to gas production per unit mass of volatile solids added to the reactor.

The data of Pfeffer, which was obtained under more stringent parameter control (pH, alkalinity) that that of Golueke, does also show distinct mesophilic and thermophilic regions.

In contemplation of this data, note that both acidogenic and methanogenic functions were concurrently represented in the test apparatus. Keenan (1974) has shown acidogenic and methanogenic microorganisms are influenced differently by temperature, the acidogenic being capable of functioning at high conversion efficiencies at moderate temperature of (15-20°C). It would seem plausible that the discrepancies between the results of Golueke and Pfeffer are related to the substrate-acidogenic microorganism interaction, and that the methanogenic response would tend

Material Digested	sewage	sewage	dry leaf	sugar cane	dry straw	chicken manure	steer manure
Reference	Maly & Fatrus (1971)	Maly & Fadrus (1971)	Singh (1971)	Singh (1971)	Singh (1971)	Imhoff; Bell (1973)	Bell (1973)
Digestion Technique	batch	batch	batch	batch	batch	batch	batch
Detention Time (days)	100	100	70+	70+	70+	50+	50+
Temperature (degrees C)	30	50	23-28	23-28	23-28	-	-
Reduction in Volatile Solids	49	50	-	-	-	-	-
Methane per kg vs Added (l/kg)	382	386	200	330	405	185	55
Methane per kg vs Destroyed (l/kg)	780	770	-	-	-	-	-
Ratio of CH_4 to CO_2	2.7	2.7	1.0	1.0	1.0	1.5	2.0
Net Conversion Efficiency kcal CH_4/kcal vs Added	0.60	0.60	-	-	-	0.64	-

Table II-7. General Yield Data for Varicus Materials

Material Digested	urban refuse	simulated refuse	fresh algae	fresh grass	fresh grass	fresh papyru
Reference	Pfeffer (1971)	Altmann (1973)	Golueke & Oswald (1960)	Boshoff (1967)	Boshoff (1963)	Boshof (1967)
Digestion Technique	batch	continuous	batch	batch	continuous	batch
Detention Time (days)	30	10	11-20	70	-	70
Temperature (degrees C)	35	37	45-50	32	32	32
Reduction in Volatile Solids (%)	45-57	66	62	-	-	-
Methane per kg vs Added	230	328	322	375	246	250
Methane per kg vs Destroyed (l/kg)	460	500	520	-	-	-
Ratio of CH_4 to CO_2	1.5	1.5	1.7	-	1.5	-
Net Conversion Efficiency kcal CH_4/kcal vs Added	0.52	0.56	0.53	-	0.45	-

Table II-7. General Yield Data for Various Materials (contd.)

Figure II-5. Effect of Temperature on Gas Production (After Golueke, 1958)

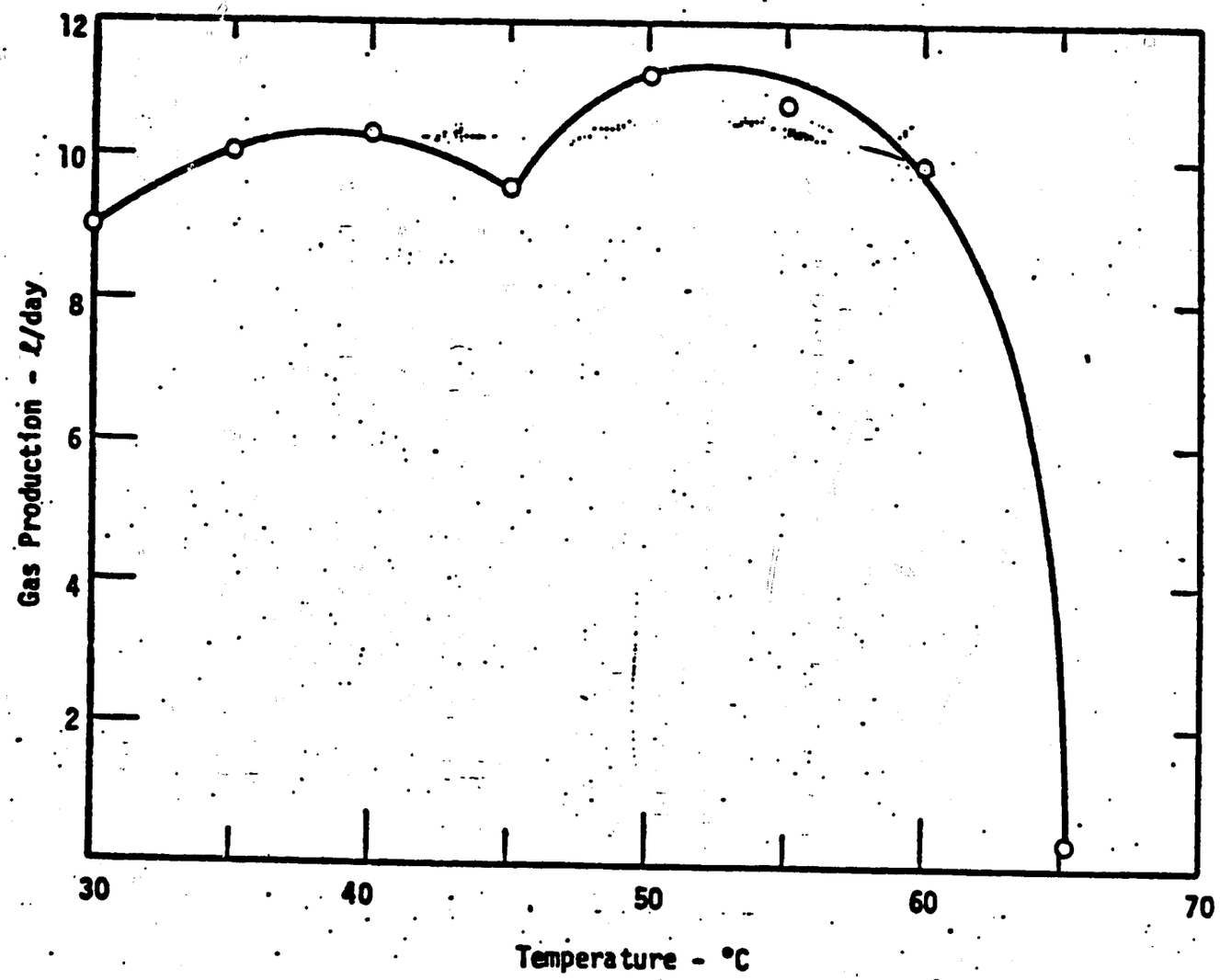
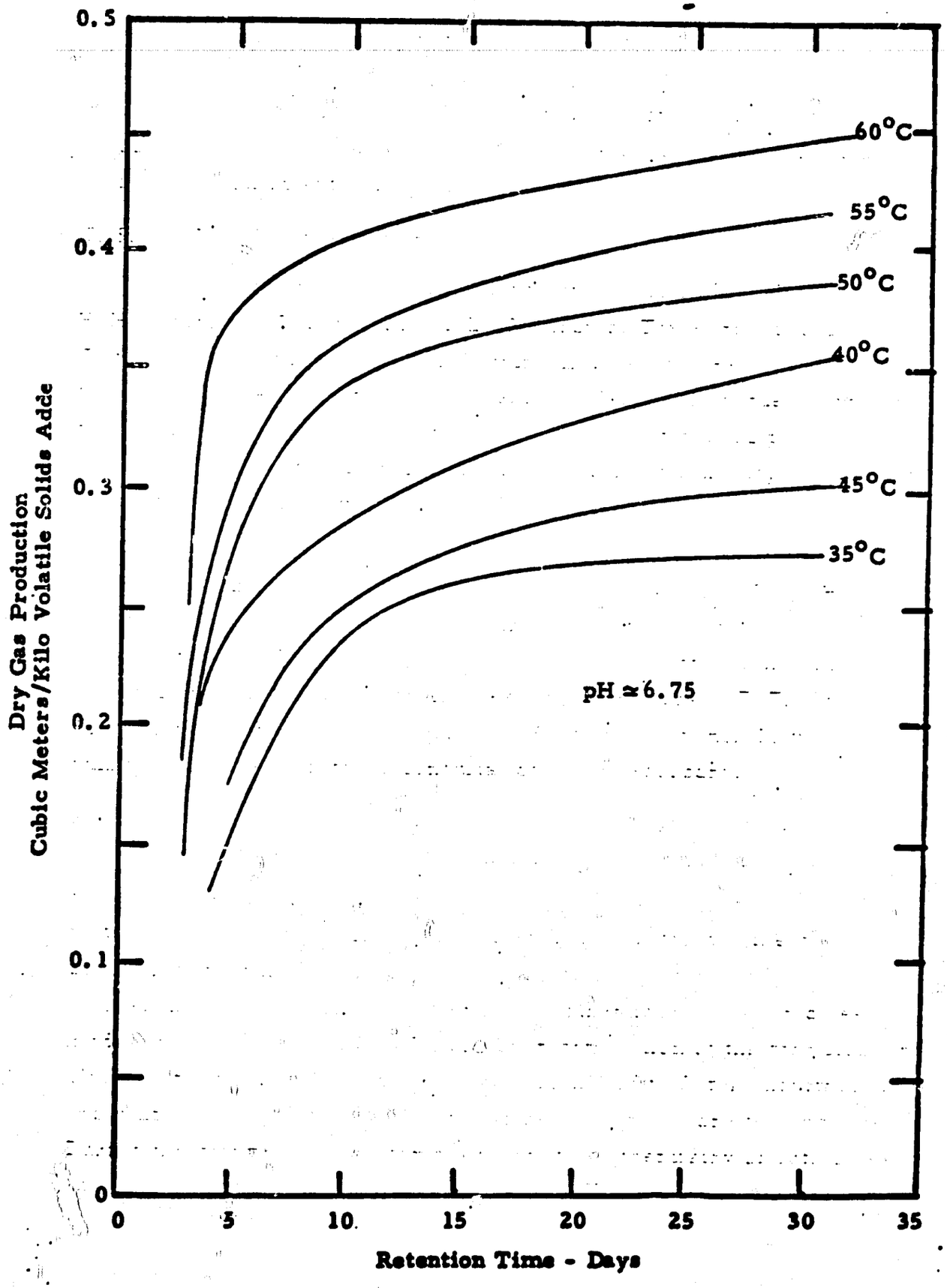


Figure [illegible]. Temperature - Retention Time Effects
Anaerobic Digestion
(Pfeffer, 1974)



to be a continuous function for the entire system. Research in this area would be useful as it would enhance the design optimization of split-stage anaerobic digestion systems.

Pressure Influence on Anaerobic Digestion

Based on inference from other biological research, any pressure-related anaerobic digestion phenomena would be a function of solubility, diffusion rate and partial pressure of the gases involved in the reaction. Two references to pressure phenomena were located. Symons and Buswell (1933) noted that fermentation under pressures of 680 atmosphere produced only volatile acids. Finney and Evans (1975) have reported increased methanogenic organism metabolism at 0.25 atmosphere, as evidenced by a minimum doubling time of 0.28 days in comparison to 1.8 days at 1.0 atmosphere. This effect could be useful in the design of industrial digesters; however, for small-scale agricultural waste digesters atmospheric pressure operation would appear desirable.

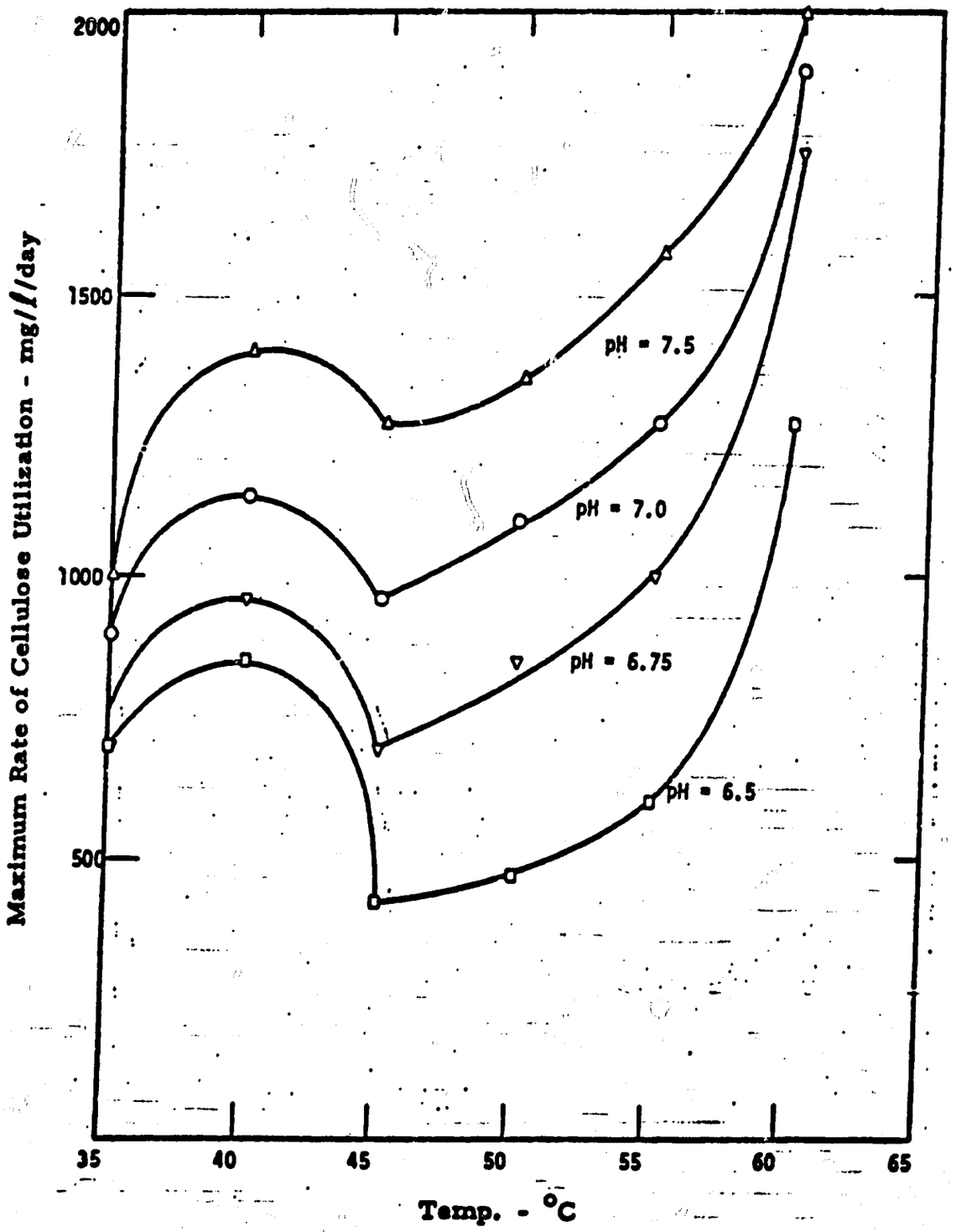
pH Influence on Anaerobic Digestion

The pH of the liquor in which the fermentation occurs has been observed to have a great effect on the process. Acidogenic fermentation, the first stage of anaerobic digestion, creates an acidic liquor with pH ranging from 5 to 6.5. Methanogenic fermentation, the second stage, tends to create a neutral or alkaline environment, with pH ranging from 7 to 8.5. In a single-stage digester, both processes occur and the resulting pH tends to be somewhere between the extreme values. Pfeffer (1974) has reported on the pH influence on the fermentation of cellulose in a single-tank digester. His results are shown in Figure II-7. Meenaghan, et al (1970) and Keenan (1974) have discussed pH influence on two-stage digestion, but neither performed the parametric variations required to firmly delineate the effect.

Carbon/Nitrogen (C/N) Ratio Effects

The effect of the carbon/nitrogen (C/N) ratio on anaerobic digestion is apparently understood by all researchers. Since the C/N ratio of the microorganism cells is approximately 30:1, the fermentation environment should reflect this ratio. Values of from 15:1 to 45:1 are apparently considered acceptable. Unfortunately, no literature was located addressing this specific item nor documenting experimental evidence defining the specific influence.

Figure II-7. Effect of pH on Anaerobic Digestion (Pfeffer, 1974)



Fuel/Food Production from Waste Digestion

Boersma, et al (1974), conducted research on a waste management system based on the utilization of power plant waste heat, animal waste digestion, and algae production from digester liquids. For optimum production of biogas, the anaerobic digester must be heated; power plants require fuel, some of which can be provided by biogas, and produce waste heat; algae can be grown on the enriched liquid effluent from an anaerobic digester, producing protein and cleaning the wastewater. The study proposes a system tying these functions together, based on results reported in the literature and some individual element experimentation. Actually, a system such as conceived by this study has been functioning successfully for several years at the Chang Hoa Animal Breeding Propagation Station in Taiwan.

Fuel/Feed Recovery from Animal Waste

Coe and Turk (1973) reported on a study for recycling cattle feedlot wastes to produce both feed and fuel. The basis of the investigation was the fermentation of the feedlot wastes to produce both biogas and a protein-rich feed supplement. The majority of the biogas would be required to energize the process, thus effectively all of the recycled products would be used by the feedlot, thereby eliminating consideration (and problems) of marketing and transportation. All water is recycled within the systems. The study concludes that the concept is economic (in the US) for feedlots with stock in excess of 5000 to 7000 head.

Feed Recovery from Animal Waste

Muller (1973) has prepared a general review of the recycling of animal waste including bedding or litter to feed supplement. It is his conclusion that "lactic fermentation has substantial advantages over other methods." While the experimental results are well documented, the economic selection between feed/fuel production has yet to be conclusively delineated.

Aquatic Vegetation: Waste Water Purification - Food/Fuel Source

Vietmeyer, et al (1976) have prepared a compendium on aquatic vegetation, emphasizing their potential use for food, energy, and pollution control in developing nations. Species of particular interest include various forms of algae (spiruliner platensis, spiruliner maxima), duck weed (Spirodela, Wolfia, Lemna) and water hyacinth (Erchhornia Crassipes). These forms of aquatic vegetation have been shown to be useful for both wastewater purification and the production of protein rich vegetation. The growth rate of such vegetation exceeds terrestrial alternatives. These potential advantages exist either for increased productivity for flooded agricultural land, a utilization of swamplands unsuitable for other crops. Table II-8 summarizes some properties of selected aquatic vegetation species.

Oswald (1961) described one potential method for producing animal feed (algae) from sewage wastewater. Golueke and Oswald (1963) suggested a modification wherein the algae would be digested to produce biogas. Oswald (1971) described the advantages of using algae for biological purification of sewage. Uziel, Oswald, and Golueke (1974) provided experimental verification of the fermentability of a number of algae species. Foree and McCarty (1969) also provided experimental and theoretical evaluations concerning the digestion of algae in anaerobic wastes, addressing potential problems associated with algae utilization in sewage purification lagoons.

Wolverton, McDonald, and Gordon (1975) have provided experimental verification of the anaerobic fermentation potential of water hyacinth for the production of biogas.

Crop	Growth Rate: Peak	Growth Rate: Average	Dry Mass Composition: Protein	Dry Mass Composition: Carbohydrate	Dry Mass Composition: Fat
Duck Weed (Wolffia Arrhiza)	500 $\frac{\text{Kg (dry)}}{\text{ha day}}$	10^4 $\frac{\text{Kg (dry)}}{\text{ha yr}}$	20%	44%	5%
Algae (Chlorella)	---	2.5×10^4 $\frac{\text{Kg (dry)}}{\text{ha yr}}$	42%	28%	7%
Water Hyacinth (Erchhornia Crassipes)	560 $\frac{\text{Kg (dry)}}{\text{ha day}}$	2.5×10^4 $\frac{\text{Kg (dry)}}{\text{ha yr}}$	--		

Note
- Duck Weed requires wind sheltered ponds
- Algae extremely difficult to harvest
- Aquatic vegetation as harvested contains 90-95% water

Table II-8. Aquatic Vegetation Properties
(Vietmeyer, et al, 1976)
(Oswald, 1961)

SECTION III

EXPERIMENTAL DESIGN

This section describes the experimental design as written during the period of 12-22 April 1976. Section IV describes the experiment that was actually performed and the results obtained.

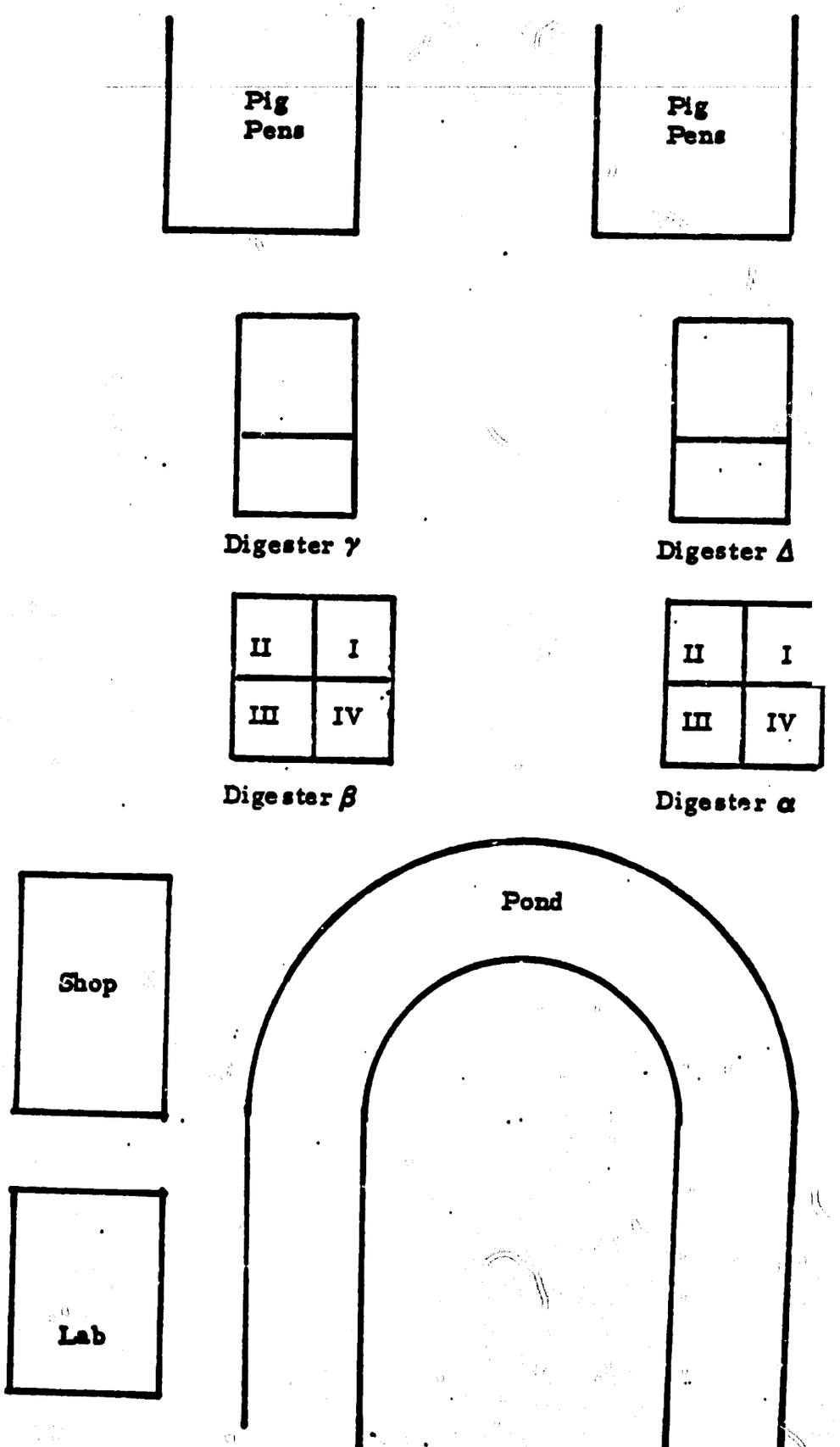
TASK I: Site/Team Selection

A site selection survey was undertaken on April 12, 1976 by Mr. H. H. Huang of JCRR and Dr. A. L. Johnson of The Aerospace Corporation. The digester test facility of the Provincial Livestock Research Institute, Hsinhua, has been selected as the test site due to its unique characteristics, possessing both necessary physical equipment and skilled personnel required to properly perform the study. Figure III-1 depicts the topological arrangement of the test facility.

To perform the study, Mr. H. H. Huang will be program manager, Dr. A. L. Johnson will provide technical direction, Mr. C. M. Hong, PLRI, assisted by Mr. M. T. Koh, will be in charge of the test facility, and Mr. S. L. Chen, PLRI, will provide the necessary analytical chemistry laboratory support. Additionally, Associate Professor T. T. Chou, Cheng Kung University, Tainan, and Professor H. H. Wang, National Taiwan University, will be available to provide consultation when necessary.

TASK II: Site Preparation

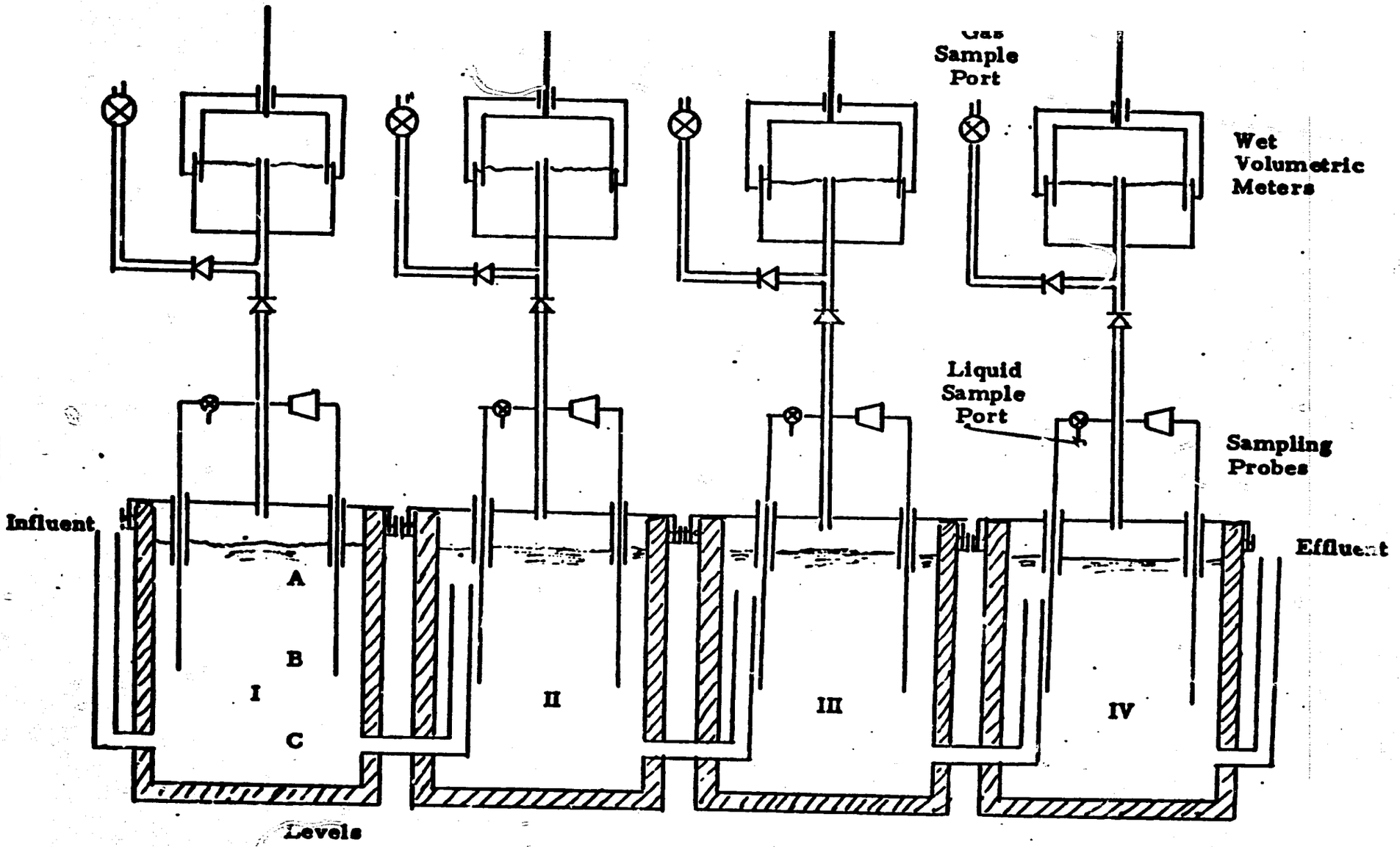
Of the four digesters of interest to the experiment, only digester α is currently in operation. To prepare the test site, it will be necessary to completely clean out the other three digesters and perform some modifications. In order to provide an experimental control, digester α will continue to operate as presently configured. Digester β, the other four-chamber digester, will be modified as shown in Figure III-2. Upon completion of the modification of digester β, it will be put into operation being fed with pig excrement from approximately the same number and size of swine as are feeding digester α. During the starting of digester β, the physical chemistry of both digesters α and β will be monitored as outlined in Task IV.



Digester Test Facility

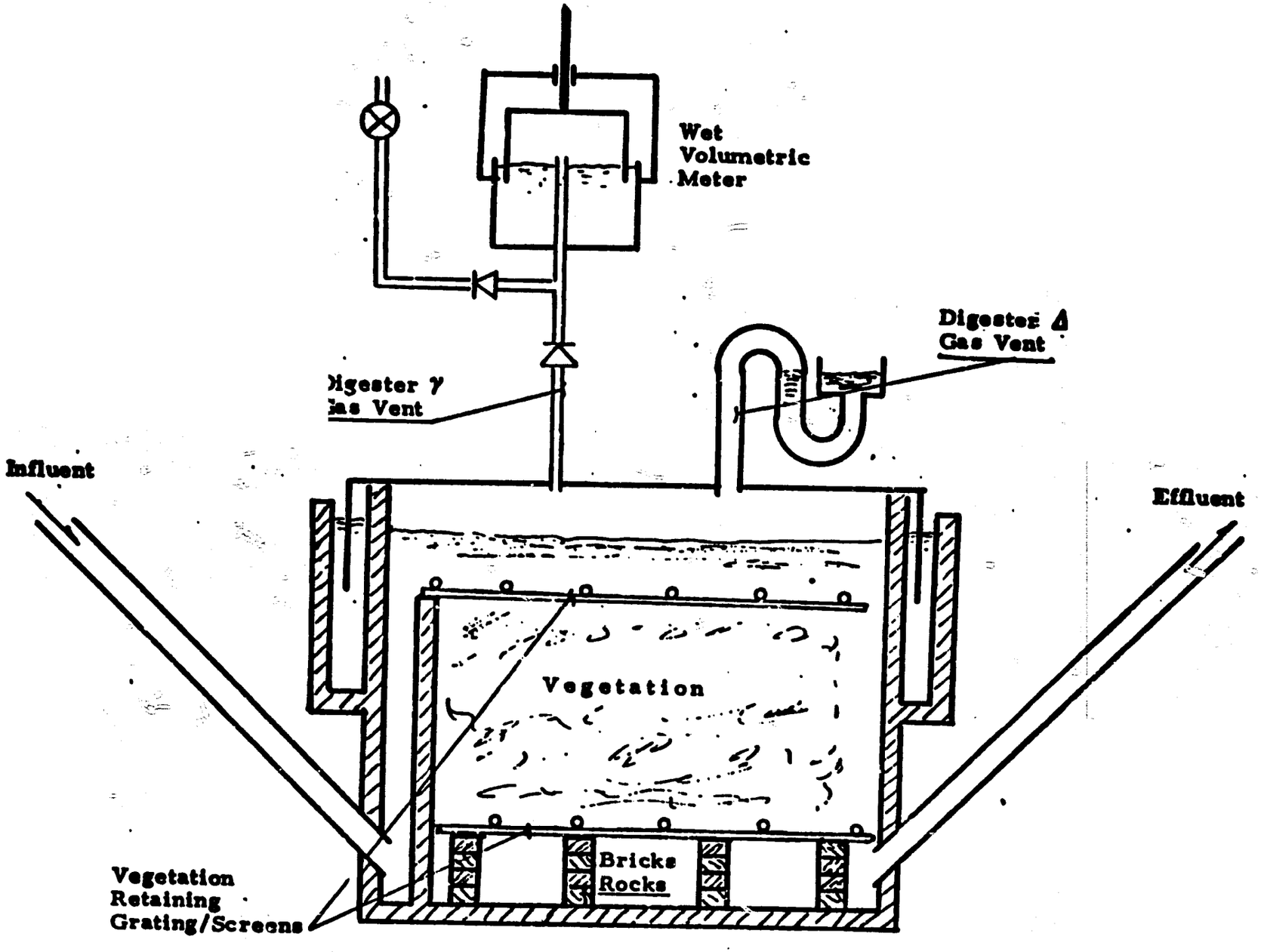
Provincial Live Stock Research Facility

Figure III-1



Fluid/Gas Schematic
Digester β

Figure III-2



Vegetable Waste Biomass Leacher

Figure III-3

Digesters γ and Δ, the single chamber digesters, will be modified to serve as vegetable waste biomass leachers as shown in Figure III-3. Digester γ is to provide acidogenically fermented supernatant to modified digester β and digester Δ is to serve as a test bed for examining the potential for composting rice straw to a mushroom culture substrate. Digester Δ will be loaded with rice straw and operated per Task V as soon as it is ready. The operation of digester γ will commence after digester β becomes stable.

Digester γ will be loaded with equal quantities of the vegetable waste sample, well mixed. It will be filled with the effluent from digester β as soon as digester β is stable. After 10 days, or as soon as significant gas production is observed, whichever occurs first, the operation will commence per Task VI.

TASK III: Vegetable Waste Procurement

Vegetable matter of the types and quantities listed in Table III-1 are to be procured and delivered to PLRI, Hsinhua. Delivery is to be coordinated with Mr. Hong. At PLRI, the vegetable matter is to be stored in separate piles under shelter suitable to protect the material from the wind and rain. The storage site is to be as close to the test site as possible. After delivery, each of the materials is to be tested under the supervision of Mr. Chen for the properties listed in Table III-2. Their data is to be recorded for use in the final report.

TASK IV: Physical Chemistry of Digesters α and β

Digester α

Liquid samples shall be obtained from the inlet to Chamber I and the outlets of Chambers I and IV by utilizing a bilge pump once per day. Sufficient excess fluid is to be discharged prior to sampling to assure a representative sample of the region of interest. Time of sampling is to be just prior to feeding of digester (cleaning of pig pens) or sufficiently after to allow digester to stabilize, whichever is more convenient; however, once selected, the relative time is to remain constant. The properties to be measured are listed in Table III-3. The quantity to be sampled is to be determined by the laboratory testing needs.

Test Vegetable Matter

Table III-1 - Vegetable Selection		
Type	Quantity Dry Weight*	Test
Rice Straw	200 kg	γ, Δ, P
Napier Grass	200 kg	γ, P
Citronella Pulp	10 kg	P
Sugar Cane Tops	200 kg	γ, P
Rice Husks (contained)	200 kg	γ, Δ, P
Water Hyacinth	200 kg	γ, P
Banana Waste Pulp	10 kg	P
Sago Palm	10 kg	P
Casaba/Sweet Potato Liquid Residue	30 kg	P

γ for use in γ digester

Δ for use in Δ digester

P for use in bench sample test

*except Casaba/Sweet Potato liquid residue

Table III-2 - Receiving Tests - Proximate Analysis
Dry Matter
Crude Protein
Crude Fat
Crude Fiber
Ash
HCl Insolubles
Nitrogen Free Extract
C/N Ratio

Table III-3

Physical-Chemical Properties

Digester α

Date Time By

Estimated 24-hr Influent - Liters
Estimated 24-hr Gas Production - Liters

Liquid Samples

Measurement	Location		
	Inlet 5	Outlet I	Outlet IV
Temperature °C PH C/N Ratio			
Gas Samples			
Volume % CO_2 Volume % CH_4			

At approximately the same time, the gas production for the past 24 hours is to be recorded, the gas accumulator is to be half-emptied, a gas sample is to be obtained, and the accumulator is to be emptied so that gas production for the next 24 hours may be measured. Gas sample properties are to be measured per Table III-3. Testing is to commence at starting of digester β.

Digester β

Liquid samples will be obtained from level B of Chambers I, II, III and IV once per day by utilization of the sampling probes. Sufficient fluid will be circulated at each depth to assure a representative sample of the region of interest. Time of sampling is to be just prior to feeding of digester (cleaning of pig pens) or sufficiently after to allow digester to stabilize, whichever is most convenient; however, once selected, the relative time is to remain constant. The properties to be measured are listed in Table III-4. The quantity to be sampled is to be determined by the laboratory testing needs.

At approximately the same time, the gas production for Chambers I, II and IV for the past 24 hours are to be recorded, each gas accumulator is to be partially emptied, a gas sample is to be obtained, and the accumulators are to be emptied so that gas production for the next 24 hours may be measured. Gas sample properties are to be measured per Table III-4. Sample quantity is to be determined by the laboratory needs.

TASK V: Rice Straw Anaerobic Composting

As soon as digester Δ is ready, it will be loaded with rice straw and filled with liquid from the digester pond. As soon as gas production commences, or after 10 days, whichever occurs first, effluent from digester α will be pumped into digester Δ at an average rate of 5 liters/hour. The effluent from digester Δ will flow into the pond. During such operation, a gas sample, if available, and a liquid effluent sample will be taken from digester Δ once per day and will be subjected to the same measurements as listed in Task IV. Upon the completion of the test, the duration of which is to be determined, the rice straw will be removed from the digester, its properties measured per procedures of Task III, and the results discussed with members of the PFA Mushroom Research Laboratory in order to evaluate the potential for growing mushrooms on the substrate.

Table III-4

Physical-Chemical Properties
Digester β

Date Time

Air Temperature
Estimated 24-hr Influent - Liters

	Measurement	Location			
		I	II	III	IV
Gas	24-hr Gas Production - Liters Volume % CO_2 Volume % CH_4				
	Depth	B	B	B	B
Liquid	Temperature ^{o}C PH C/N Ratio				

TASK VI: Waste Vegetation Augmented Biogas Production

After digester β has been stable for at least 10 days, supernatant from the top of Chamber I, and the effluent from Chamber IV, will be used as influent to digester γ. The effluent from digester γ will be returned as influent to Chambers I and II, the ratio to be heuristically determined. The operation of the system will continue until the effect of waste vegetation augmentation can be evaluated. The basis of evaluation will be the physical chemical measurements of Task IV.

TASK VII: Small Scale Vegetable Waste Digestion

Two sets of containers for each of the vegetable waste materials will be prepared per Figure III-4. Each container will be loaded with an appropriate amount of vegetation. One set will be filled with liquid from the outlet of Chamber I, digester α, the second set with liquid from the outlet of Chamber IV, digester α. At the end of the tenth day, or as soon as significant gas production commences, whichever occurs first, each container will receive one-fifth of its original liquid quantity from its original source. The effluent and gas, if any, will be tested per procedures of Task IV. Excess effluent will be returned to the influent source.

Small-Scale Vegetable Waste Digester

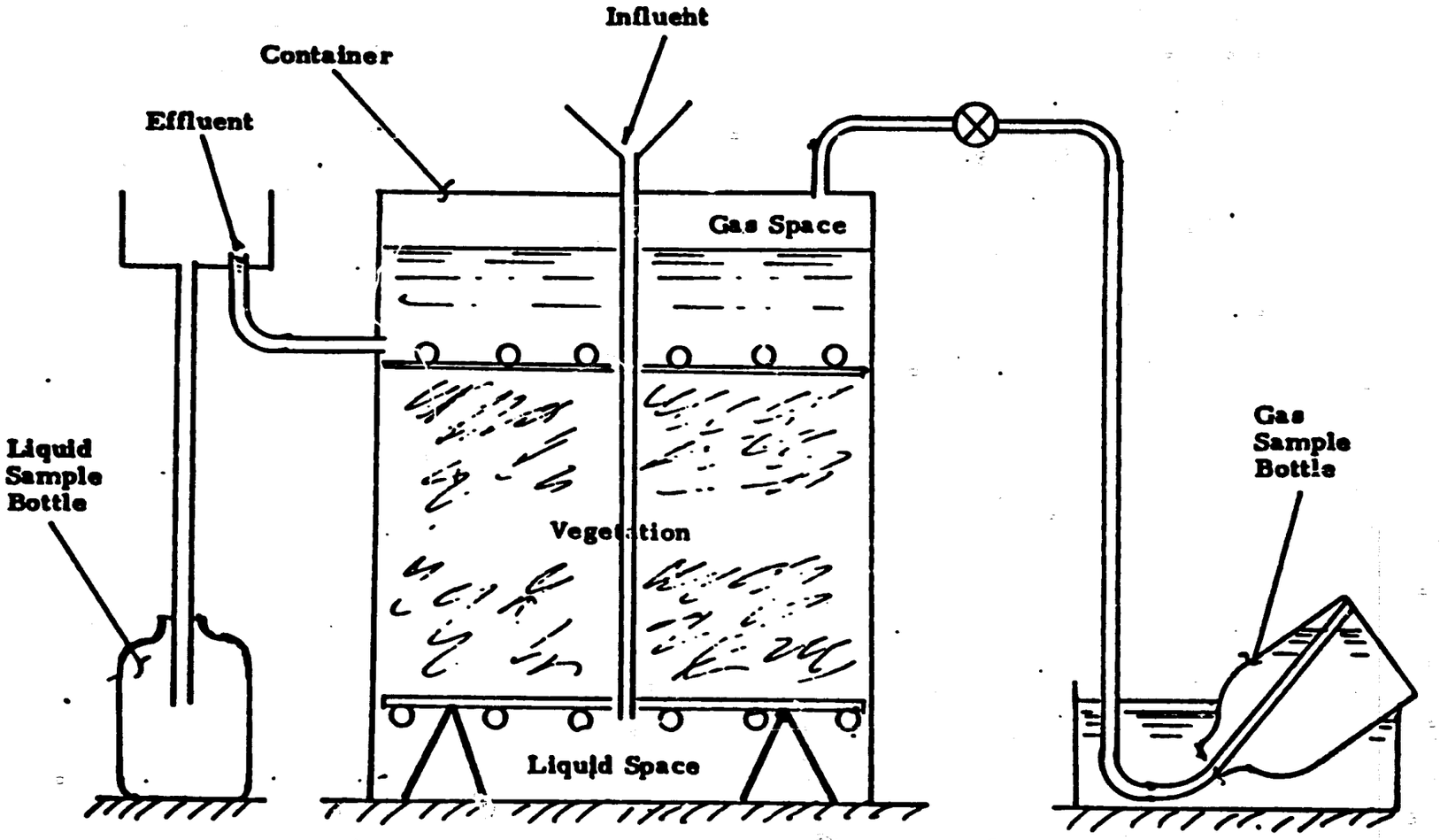


Figure III-4

SECTION IV

EXPERIMENTAL RESULTS

Task I: Site/Team Selection

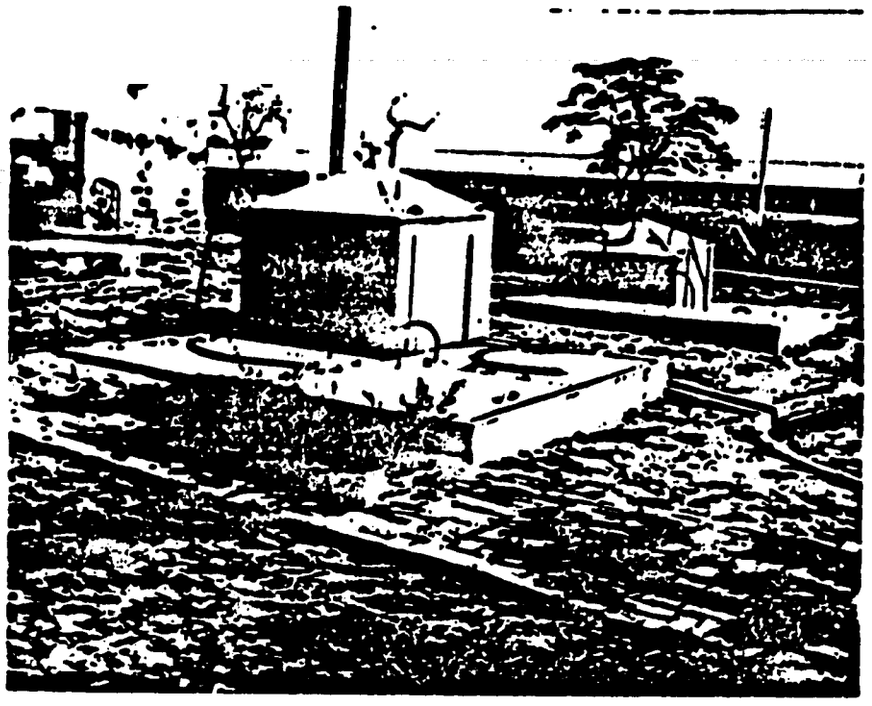
Task I was completed during the visit to Taiwan, from 8 April to 22 April, 1976, as discussed in Section III.

Task II: Site Preparation

The experimental test site was modified as outlined in Section III, the major work being completed by late May. Figures IV-1a, b show the site before preparation. Figures IV-2a, b show the site after preparation. Table IV-1 is the initial test schedule prepared during this same period.

The directions given in Task II, Section III require that the vegetabl waste leacher, digester γ, be prepared after digester β was stable. This caused an unforseen problem. Digester β stability was judged by comparison to the performance of digester α. Based on the schedule (Table IV-1) and past experience, digester β should have reached stable operation by mid-June; however, upon review of the progress in mid-July, digester β had not been judged stable, so digester γ had not been prepared. Careful examination of digester β showed that it was indeed stable, and that the difficulty was due to a gas leak in the cover of Chamber III, thus causing an extremely low measurement of gas production for this chamber. The leak was repaired. All other covers were carefully examined and found to be gas tight. The remaining problem of obtaining stable operation of digester γ in time to complete the experiment during the 14-31 July visit was resolved by utilizing a mixture of "fresh" vegetable waste and partially digested vegetable waste, the latter being obtained from the small scale vegetable waste digesters described in Task VII. Digester γ was thus functioning in five days rather than the fifteen that would normally be required. Figure IV-3a shows digester γ with vegetation loaded ; Figure IV-3b shows digester Chamber β III during cover repair.

Site Prior to Experiment



Digesters α and β with floating top on Chamber L. Pig sty digester Δ, in left background. Aeration ditch at right.

Figure IV-1a

Digester α, aeration ditch, aeration pond and shop.

Figure IV-1b

Site During Experiment

Digesters α and β with fixed cover, gas volume meters on each chamber. Pig sty, small vegetable digesters in left background. Aeration ditch at left.

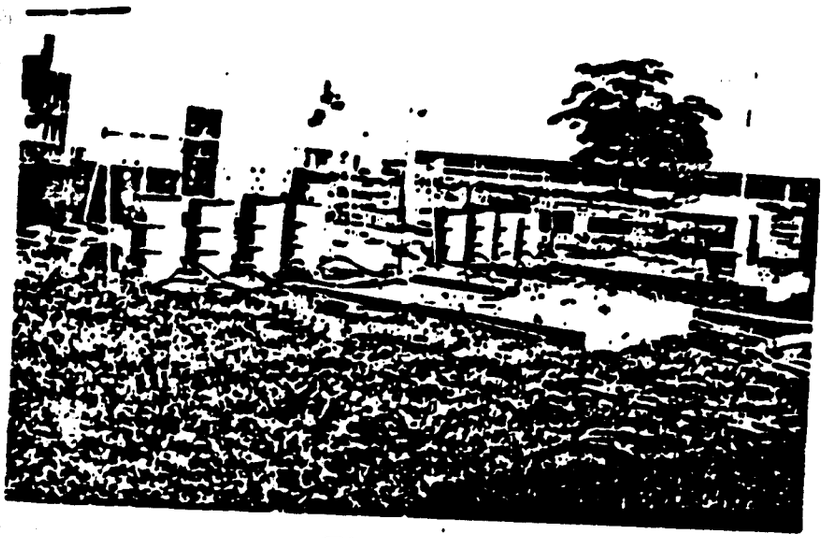


Figure IV-2a

Digesters α and β volume gas meters, aeration ditch, and shop.

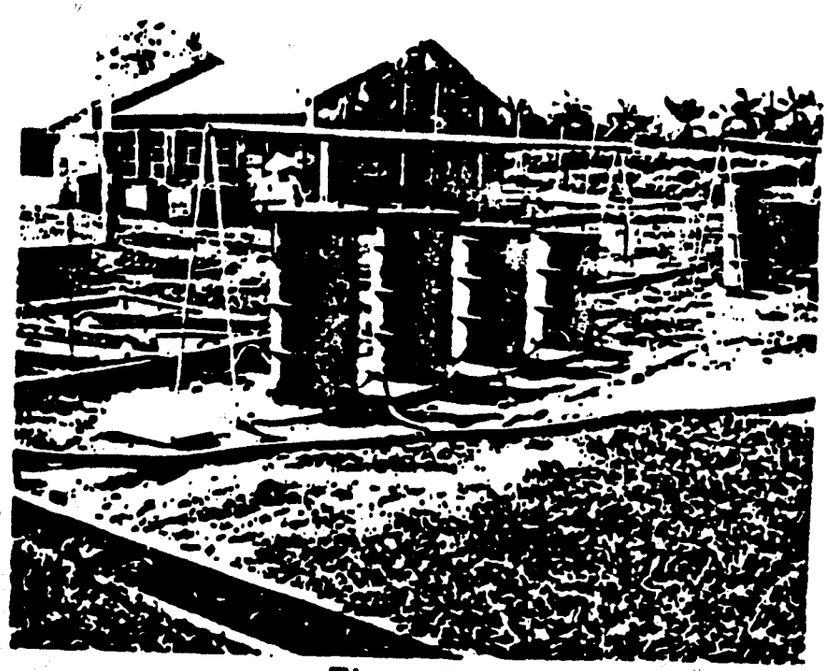


Figure IV-2b

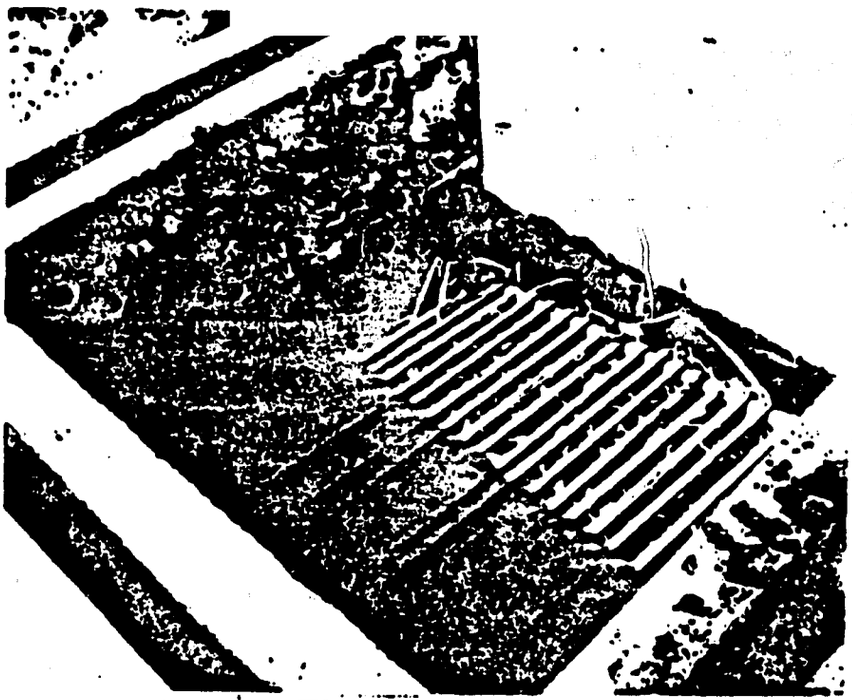
Work	Date	Time	Remarks
1. Pig waste be fed to Digester β	May 25		Task II
2. Taking liquid samples from inlet of Chamber I, the outlets of Chamber I and Chamber IV of Digester α	From June 9 to the end of test	8:30 a.m.	Task IV by use of bilge pumps
3. Taking gas samples and measuring gas production for the past 24 hours of Chambers I, II, III and IV of Digester α	From June 9 to the end of test	9:00 a.m.	Task IV
4. Taking liquid samples from Levels A, B and C of Chambers I, II, III and IV of Digester β	From June 9 to the end of test	8:40 a.m.	Task IV by use of sampling probes
5. Taking gas samples and measuring gas production for the past 24 hours of Chambers I, II, III and IV of Digester β	From June 9 to the end of test	9:15 a.m.	Task IV
6. Loading rice straw into Digester Δ and filling liquid from the pond	May 25		Task V
7. The effluent from Digester α will be fed into Digester Δ.	From June 4 to the end of test		Task V at an average rate of 4 liters/hours or by nature
8. Digester Δ, after the test is finished rice straw shall be removed from the digester and the rice straw sample shall be taken			Task V

Table IV-1. Biogas Test Schedule - TLRI (1976)

Work	Date	Time	Remarks
9. Loading equal quantities of rice straw, Napier grass, sugarcane top, rice husks and water hyacinth into Digester γ, then be filled with the effluent from Digester β	June 9		Task II and VII
10. Two sets of containers for each of the vegetable waste material, one set be filled with liquid from the outlet of Chamber I of Digester α, the second set with liquid from the outlet of Chamber IV of Digester α	June 4		Task VI
11. Taking liquids and gas samples from small-scale vegetable waste digestion	From June 14 to the end of test	10:00 a.m.	Task VI

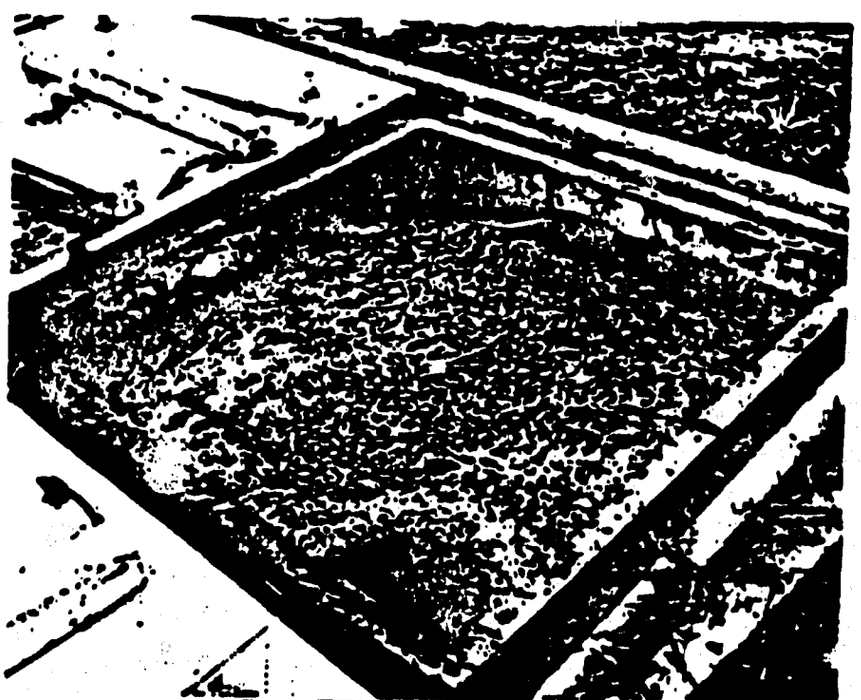
Table IV-1 (Continued) Biogas Test Schedule - TLRI (1976)

Vegetable Waste Digesters



Digester γ loaded with mixed vegetable waste prior to liquid fill/cover installation.

Figure IV-3a



Digester BIII while cover leak being repaired. Scum and flammable gas bubbles confirm digestion progressing.

Figure IV-3b

Task III: Vegetable Waste Procurement

Vegetable waste listed in Table III-1 were procured and tested as outlined in Table III-2. The results of the proximate analysis are summarized in Table IV-2.

Task IV: Physical Chemistry of Digesters α and β

At the mid-July review, it was disclosed that the quantitative evaluation of performance was not progressing as anticipated, primarily due to the lack of skilled personnel to operate some of the more sophisticated laboratory equipment. Between the time of the first (8-22 April) and second (14-31 July) visits, the technician trained to operate the gas chromatograph had taken another job; a replacement was not available. The laboratory had, therefore, reverted to the use of "wet" chemistry techniques for determining gas composition. This process proved to be very labor intensive, resulting in the accumulation of a large backlog of uncompleted chemical analysis. In order to resolve this dilemma, the number of test specimens required was reduced from that outlined in Section III so that the experiment could be completed.

While the resultant experiment is less extensive than outlined in Section III, the scope still remains broader than defined by the statement of work. All the qualitative aspects of the experiment were completed as were some quantitative measurements.

This experience demonstrated that simpler measurement procedures should be used for a complete quantitative evaluation. Difficulties in communication and scheduling between the laboratory analysis group and the experimental group also show that the separation of these functions is undesirable. These latter points are reflected in the suggested "follow-on" program outlined in Section VI.

Figure IV-4a & b show the process used to obtain liquid samples at various locations in various digestion chambers. The device utilized is referred to as a "thief". It is composed of a tube and a small diameter concentric rod. At the lower end of the rod is attached a rubber plug which can be pulled into place blocking the lower end of the tube. The

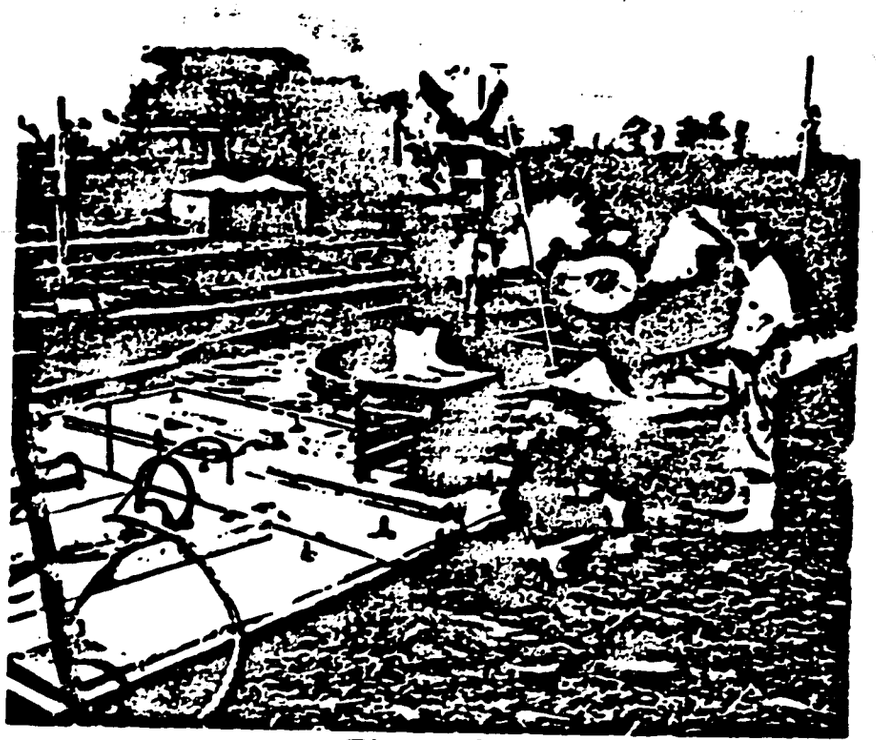
Material	% Water	% Crude Protein	% Crude Fat	% Crude Fibre	% Ash	HC Insolubles	Nitrogen Free Extract	Carbon Nitrogen (C/N) Ratio
Rice Straw	9.08	4.87	4.10	29.85	12.22	9.72	30.16	160
Rice Husks	8.82	2.21	2.12	42.35	13.22	12.68	18.60	160
Banana Waste Pulp	91.72	0.33	0.26	1.43	0.81	0.04	5.41	15
Sugar Cane Tops	72.21	2.07	1.32	9.12	1.99	0.32	12.97	12
Napier Grass	84.85	1.77	0.72	4.25	1.72	0.01	6.68	20
Citronella Pulp	40.27	5.82	3.41	16.84	5.13	3.13	25.40	18
Coconut Palm	80.49	0.80	0.89	5.56	0.72	0.02	11.52	40
Sweet Potato	31.13	0.33	0.42	2.18	0.33	0.04	15.57	15
Water Hyacinth	92.20	1.20	0.45	1.29	1.05	0.40	2.81	20

Table IV-2

Proximate Analysis

Waste Vegetation Receiving Tests

Liquid Sampling



Mr. Hong using liquid sample "thief".

Figure IV-4a

Dumping sample from "thief" into bucket.

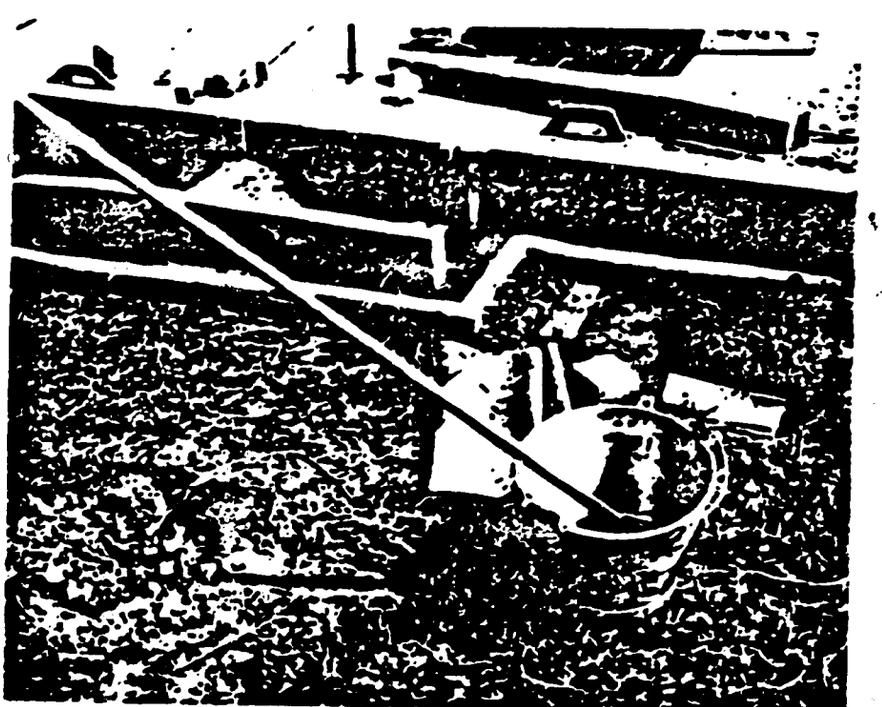


Figure IV-4b

tube is inserted through the test port to the desired depth, the rod handle is depressed, a sample flows into the tube, the rod handle is pulled, thereby reseating the plug, and the tube containing the liquid is withdrawn from the port.

While the chemical analysis of the digester liquid was greatly curtailed so that the effort could be completed, some data was obtained and is summarized in Table IV-3.

The gas production and composition results are reported under Task VI.

Task V: Rice Straw Anaerobic Composting

This task was not completed during the research period. No reportable quantitative measurements were made. Anaerobic digestion was evident on the twelfth day, the gas produced being primarily carbon dioxide. By the sixth week, the production rate was between 20 and 50 liters/day, the composition being about equal parts carbon dioxide and methane. The mixture was flammable. PLRI will complete the task and summarize the results at a later date.

Task VI: Waste Vegetation Augmented Biogas Production

This task represented one of the major elements of the experiment. The experiment was performed by establishing a pair of stable multichamber anaerobic animal excrement digesters (α and β) perturbating the stable operation by introducing leachate from vegetable leachers into one of the digesters (β) until a new stable condition was obtained, and then repeat this perturbation by switching the leachate into the other digester (α) and again observe the comparative response. The parameters monitored were gas production, gas composition, and digester biochemical state. The last item is reported as part of Test IV. Gas production was measured by using manually dumped floating dome volume meters. Appendix II describes the operation of these meters. Gas composition was primarily determined by wet chemistry techniques (Orsat analysis), although index of refraction instrumentation (Riker Mine Gas Monitor) and gas chromatograph determinations were also employed for comparison and verification.

Period	Quantity \ Chamber/location	I in	IV out	BIA	BIB	BIC	BIIB	BIIIB	BIVB	γ	Δ
I	pH	5.42	7.23	5.64	6.12	6.65	6.15	6.72	6.98	----	6.32
	BOD mg/liter	5900	430	----	----	----	----	----	----	----	450
	Volatile Solids mg/cc	23.0	0.80	3.10	1.80	2.40	1.70	1.20	0.80	----	2.30
	C/N Ratio	----	----	----	----	----	----	----	----	----	37.3
	CH_4/CO_2 %	23/69	56/35	----	38/54	----	42/46	48/44	53/42	----	----
II	pH	5.16	6.92	5.85	6.32	6.45	6.62	6.83	6.96	6.15	
	BOD-mg/liter	6750	415	----	----	----	----	----	----	750	560
	Volatile Solids mg/cc	28.30		9.50	0.60	2.40	3.20	2.10	0.60	2.80	3.80
	C/N Ratio	----	11.40	----	----	----	----	----	----	20.20	38.60
	CH_4/CO_2 %	18/73	64/22	----	43/51	----	46/52	54/41	62/35	----	----
III	pH	4.95	6.92	6.36	6.15	5.68	6.55	6.57	6.57	6.27	6.52
	BOD mg/liter	5500	380	----	----	----	----	----	----	1200	----
	Volatile Solids mg/cc	22.70	0.80	8.30	2.70	3.50	0.60	0.60	2.20	2.40	2.80
	C/N Ratio	15.10	6.30	18.20	25.30	21.30	15.50	12.20	14.30	26.40	35.30
	CH_4/CO_2 %	14/78	58/35	----	42/50	----	45/48	61/32	59/34	----	----
IV	pH	5.32	6.73	5.68	6.07	5.76	6.58	6.23	6.75	6.50	6.62
	BOD mg/liter	6850	480	----	----	----	----	----	----	1400	----
	Volatile Solids mg/cc	24.9	0.60	4.00	1.60	2.40	1.50	0.70	0.50	3.80	----
	C/N Ratio	14.4	7.80	12.50	10.70	17.90	20.30	12.85	7.60	23.20	----
	CH_4/CO_2 %	20/75	67/23	----	41/48	----	44/48	58/40	55/40	----	----

Table IV- 3. Typical Digester Biochemical Analysis

The experimental conditions are summarized in Table IV-4. The experimental results are summarized in Table IV-3 and Figure IV-5 It is evident from this data that vegetable waste leachate can be used to significantly augment the biogas production.

In the design of future experiments of this type, the use of continuously recording displacement meters is suggested. It was noted in this experiment that gas production appeared to go down during the early morning hours and on the week-ends. This phenomena proved to be a human factor rather than a biological factor. For gas composition, field instrumentation is recommended based on relative thermal conductivity or index of refraction. Occasional samples checked by the use of a gas chromatograph should suffice to keep the field recorded data in calibration.

Task VII: Small Scale Vegetable Waste Digestion

Nine pairs of batch mode vegetable waste digestion experiments were prepared per the procedure outlined in Task VII, Section III. The digesters were approximately 100 cm high, 30 cm deep and 15 cm wide. The experimental apparatus is shown in Figures IV-6a and 6b. Approximately 2 kilogram (wet) of vegetable waste was placed in each digester, the remaining volume was filled with water from the aeration ditch, the cover was sealed, and the digesters were left to ferment until gas production was noted. At this time, approximately 15 days after initiation, 4 liters/day of effluent from Chamber I of digester α was introduced into one set of digesters, and a similar quantity from α IV was introduced into the second set of digesters. After the gas production rate and effluent pH appeared to stabilize, a set of measurements were taken, the results of which are summarized in Tables IV-5 and 6. Gas production rate data was not taken.

From the data it is apparent that some form of digestion of all the vegetable wastes was occurring. The gas production rate of the rice straw and rice husks appeared to be considerably less than that of any of the other matter - other than the sweet potato waste, which was so low that the gas sampling/composition of this material is highly questionable. It would appear that the acidogenic digestion of the rice materials was so slow that the methanogenic organisms were capable of maintaining equilibrium.

Digester Parameters

Digester α

4 Sequential Chambers (I, II, III, IV)
Volume/Chamber ≃ 5500 liters
Separate Fixed Covers
Primary Influent (α I in)
- Excrement from 52 pigs
- Wt/pig ≃ 80 kilos
- Solid waste/pig ~ 2.4 kilo/day
- Liquid ≃ 2000 liters/day H_2O

Secondary Influent (α II in)
- None or
- αIV effluent - 500 liters/day or
- $\gamma + \Delta$ effluent

Digester β

4 Sequential Chambers (I, II, III, IV)
Volume/Chamber ≃ 5500 liters
Separate Fixed Covers
Primary Influent (β I in)
- Excrement from 52 pigs
- Wt/pig ≃ 80 kilos
- Solid waste/pig ~ 2.4 kilo/day
- Liquid ≃ 2000 liters/day H_2O

Secondary Influent (β II in)
- None or
- βIV effluent - 500 liters/day or
- $\gamma+\Delta$ effluent

Digester γ

Single 6000 liter chamber
Floating Top-Water Seal
Influent - 250 liters/day - αIV or βIV effluent
Initial Biomass loading - 250 kilo (wet) mixed vegetation

Digester Δ

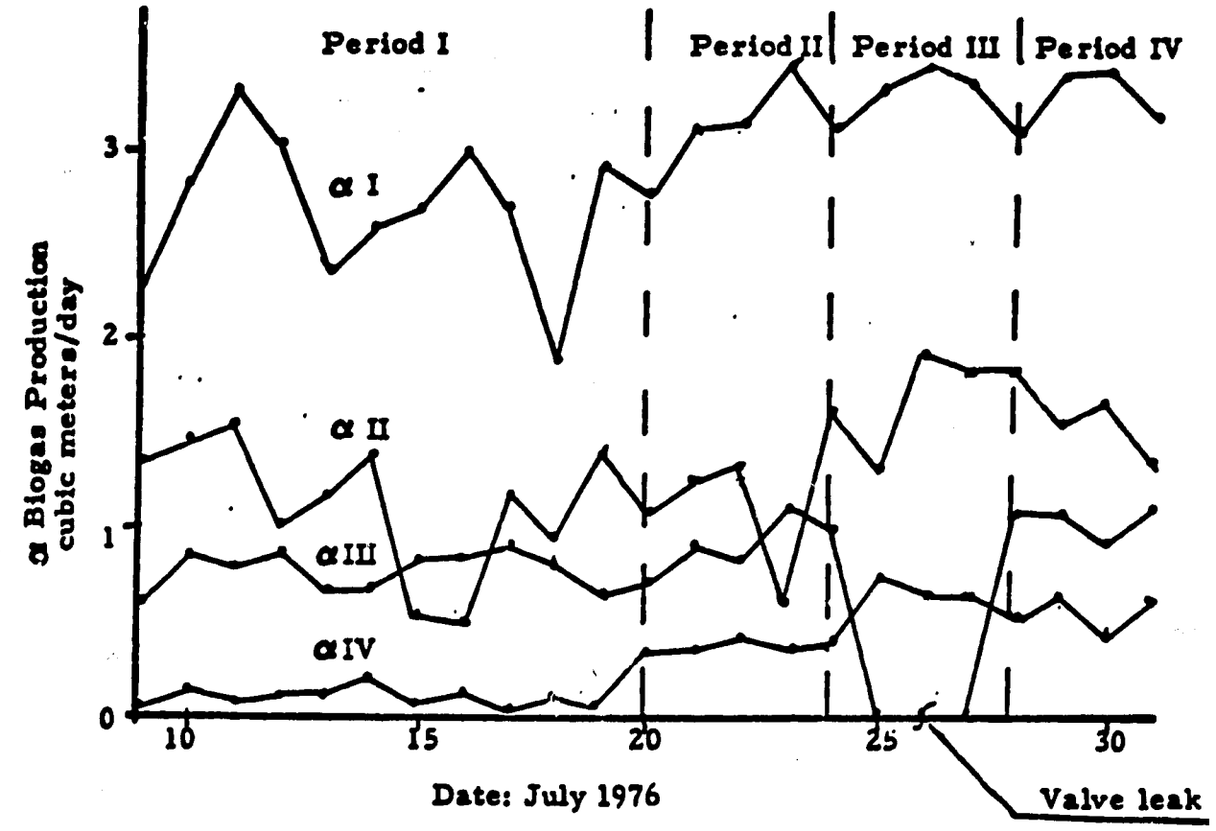
Single 6000 liter chamber
Floating Top-Water Seal
Influent - 250 liters/day - αIV or βIV effluent
Initial Biomass loading - 250 kilo (wet) rice straw

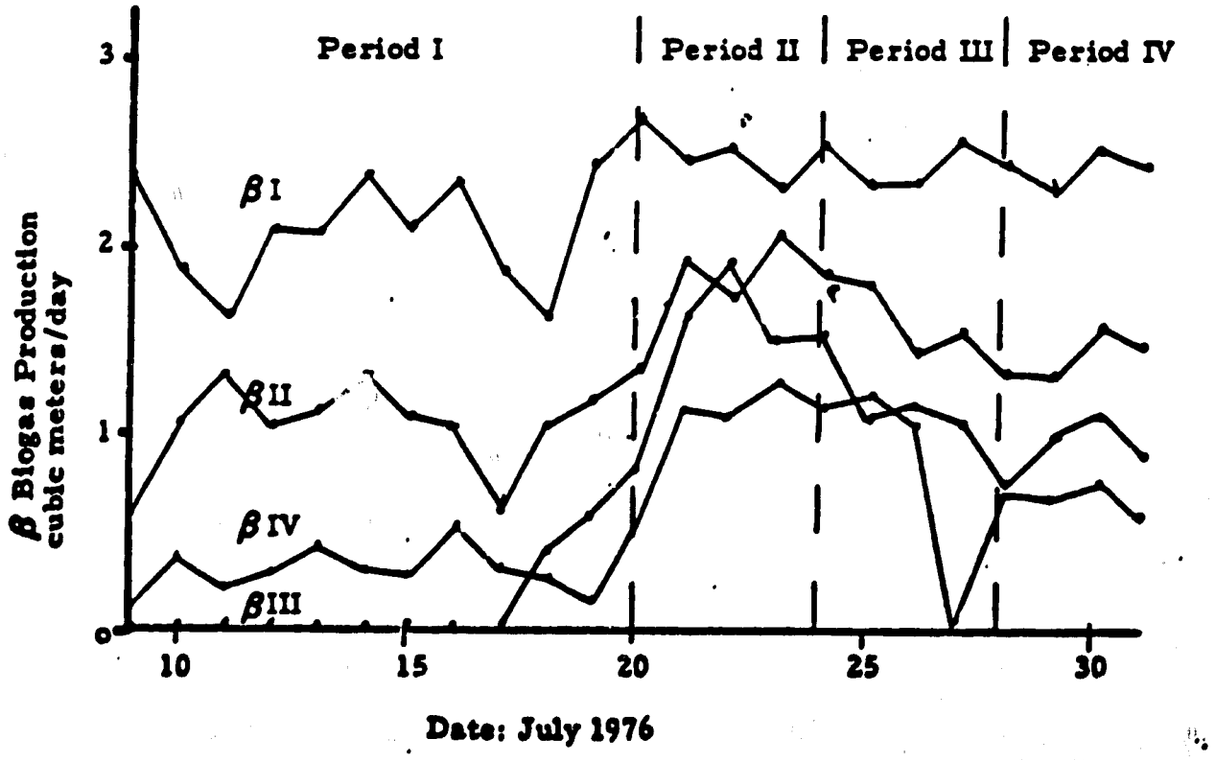
Influent Scheduling

Digester Element	Period I	Period II	Period III	Period IV
αI	Primary α	Primary α	Primary α	Primary α
αII	αI	αI + αIV	αI + γ + Δ	αI + αIV
αIII	αII	αII	αII	αII
αIV	αIII	αIII	αIII	αIII
βI	Primary β	Primary β	Primary β	Primary β
βII	βI	βI + γ + Δ	βI + βIV	βI + βIV
βIII	βII	II	βII	βII
βIV	βIII	III	βIII	βIII
γ	βIV	IV	αIV	βIV
Δ	αIV	IV	αIV	αIV

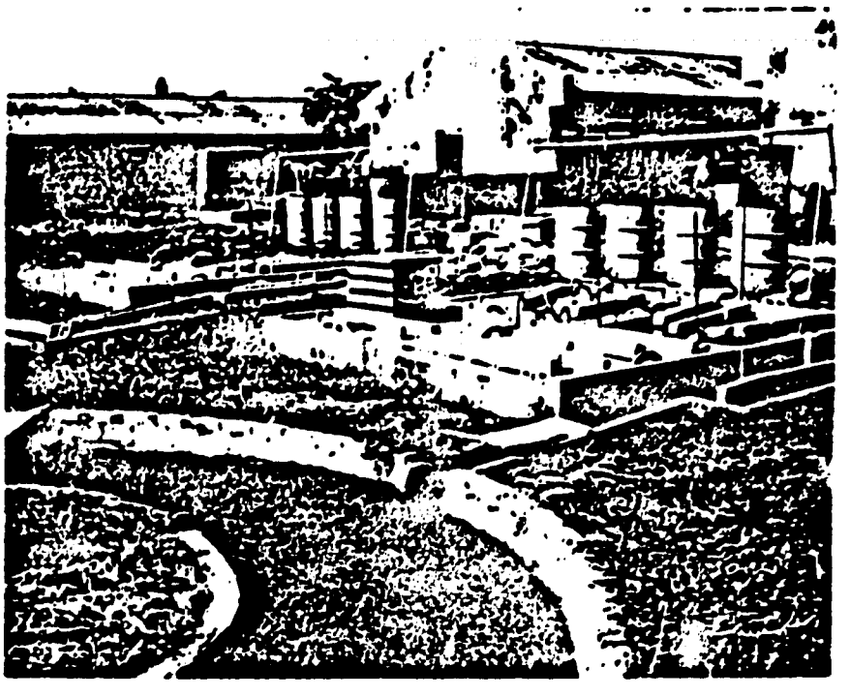
Table IV-4

Figure IV-5
Biogas Production Response





Site During Experiment



General view of experiment area.

Figure IV-6a

Small scale vegetable waste digesters.

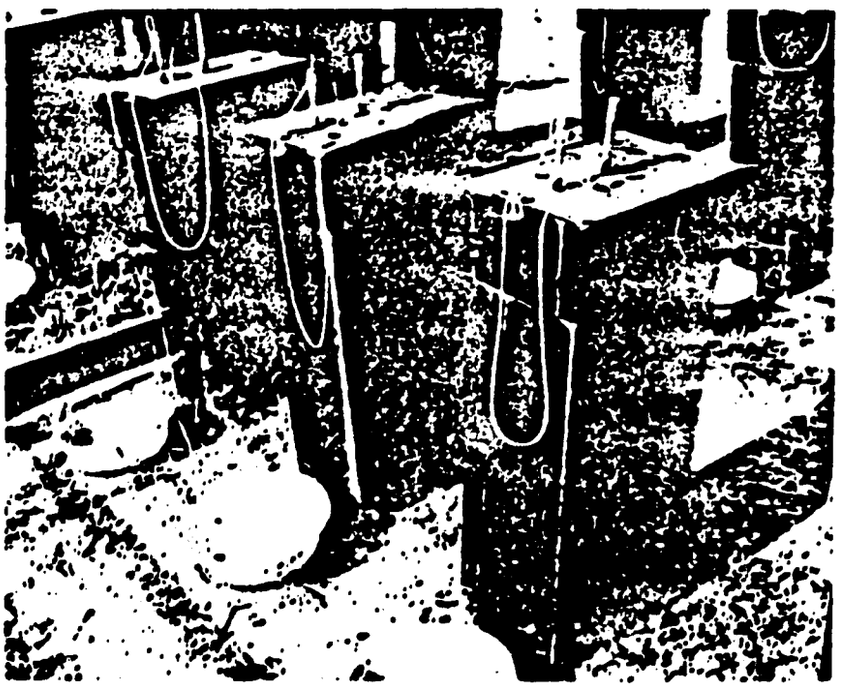


Figure IV-6b

Date		Rice Straw	Napier Grass	Citronella Pulp	Sugar Cane Tops	Rice Husks	Water Hyacinth	Banana Waste Pulp	Coconut Palm Waste	Sweet Potato Waste	Influent (I effluent)
28 June	pH	6.86	6.71	6.52	6.64	6.73	6.74	6.74	6.63	4.63	6.52
	BOD	1817	1750	3750	2625	----	----	----	----	3812	5850
	Volatile Solids	2.60	1.80	1.20	1.20	1.10	1.40	1.20	1.10	5.30	20.00
	CH_4/CO_2% Gas	----	----	35/62	----	25/72	43/46	42/52	15/80	5/93	XXX
1 July	pH	6.80	6.72	6.55	6.72	6.77	6.90	6.81	6.75	4.52	6.45
	BOD	----	----	129[illegible]	250	750	1000	250	2333	6175	5500
	Volatile Solids	----	----	----	----	----	----	----	----	----	21.9
	CH_4/CO_2 %	----	36/58	37/60	38/59	----	44/46	44/50	29/66	-/87	XXX
5 July	pH	6.88	6.71	6.65	6.83	7.00	6.70	6.84	6.84	4.44	6.50
	BOD	1000	133	----	1033	1600	266	5044	800	1300	5020
	Volatile Solids	1.99	1.10	1.10	1.10	1.00	1.60	1.10	0.90	0.90	22.6
	CH_4/CO_2 %	32/64	39/58	33/63	43/44	35/61	----	44/48	37/55	-/94	XXX
12 July	pH	7.14	7.05	6.58	6.79	6.80	7.03	6.98	6.79	4.62	6.54
	BOD	200	437	100	----	----	214	214	625	2600	5200
	Volatile Solids	1.50	1.10	----	1.30	----	1.20	----	1.30	6.20	23.00
	CH_4/CO_2 %	48/46	40/58	----	41/47	33/61	45/52	52/46	59/58	-/91	XXX
15 July	pH	7.22	6.76	6.65	6.77	6.74	6.83	6.81	6.78	4.62	6.48
	BOD	250	200	320	357	187	350	250	131	3700	5400
	Volatile Solids	1.40	0.40	0.80	0.80	1.20	1.20	0.40	1.00	5.20	22.9
	CH_4/CO_2 %	49/46	37/59	39/58	43/46	----	46/46	44/49	----	-/86	XXX

Table IV-5. Small Scale Vegetable Waste Digester Performance: αI Effluent - Digester Influent

Date	Measurement	Rice Straw	Napier Grass	Citronella Pulp	Sugar Cane Tops	Rice Husks	Water Hyacinth	Banana Waste Pulp	Coconut Palm	Sweet Potato Waste	Influent (IV effluent)
28 June	pH	6.52	5.89	5.57	6.63	6.71	6.71	6.71	5.66	3.46	6.73
	BOD	1505	2333	1500	1733	1015	1200	----	1650	----	430
	Volatile Solids	2.10	1.30	1.70	1.50	1.00	1.10	1.30	1.80	6.40	0.80
	CH_4/CO_2 %	23/59	8/89	5/89	18/75	----	----	33/59	6/89	-/92	XXX
1 July	pH	6.62	6.02	5.65	6.67	6.67	6.97	6.73	5.75	3.44	6.75
	BOD	100	466	1300	155	340	----	200	1100	----	460
	Volatile Solids	----	----	----	----	----	----	----	----	----	0.90
	CH_4/CO_2 %	36/53	20/73	4/92		----	----	38/58	12/81	----	XXX
5 July	pH	6.56	6.17	5.74	6.63	6.64	6.64	6.73	5.85	3.45	6.71
	BOD	400	470	1816	416	330	195	312	1440	3260	380
	Volatile Solids	1.30	2.00	----	1.80	----	0.50	0.90	1.20	----	1.70
	CH_4/CO_2 %	40/57	----	8/87	38/55	38/59	42/51	----	10/88	-/95	XXX
12 July	pH	6.84	6.22	5.82	6.59	6.78	6.70	6.76	6.02	3.60	6.74
	BOD	125	790	1275	1915	58	91	266	1050	2650	450
	Volatile Solids	1.10	1.30	1.60	1.10	0.60	----	0.90	1.00	7.70	0.80
	CH_4/CO_2 %		21/73	----	39/73	44/49	34/61	40/53	14/81	-/92	XXX
15 July	pH	6.62	6.34	5.91	6.60	6.75	6.85	6.76	6.18	3.34	6.72
	BOD	133	622	766	187	75	50	183	5.61	1375	425
	Volatile Solids	0.60	1.10	1.40	0.40	0.30	0.30	0.80	1.20	8.20	0.80
	CH_4/CO_2 %	43/48	30.62	----	46/44	42/52	46/48	42/55	----	-/94	XXX

Table VI -6. Small Scale Vegetable Waste Digester Performance: αVI Effluent - Digester Influent

With regard to the sweet potato wastes, the opposite conclusion is possible, that the acidogenic organisms could so readily attack the waste that a low pH resulted, thereby inhibiting further fermentation.

With regard to the influent variation, the leachate obtained from α IV effluent would appear to be the better choice since acidogenic digestion was desired. A reduced retention time would seem advantageous in order to maintain a more acidogenically biased process.

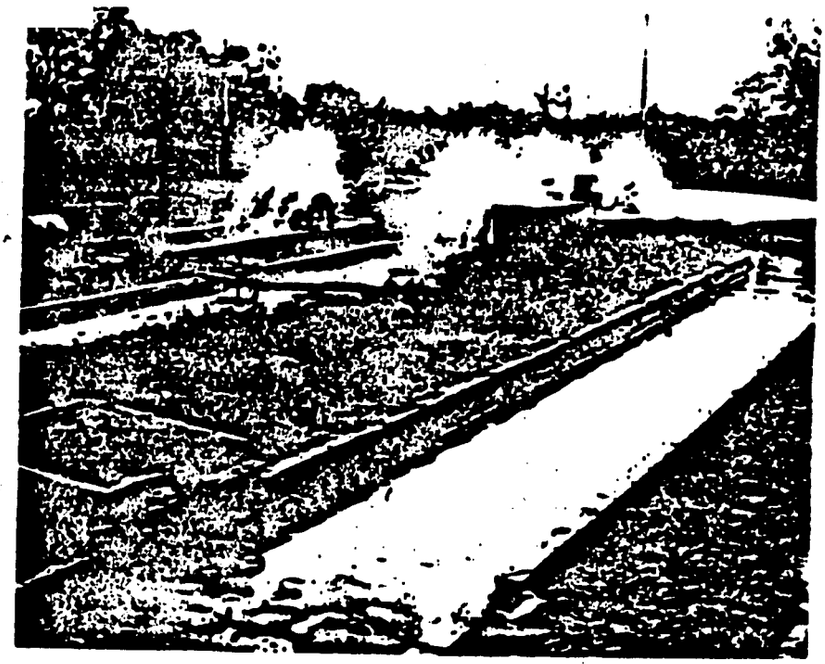
A more thorough experiment would appear desirable, limiting the wastes to rice straw, napier grass, water hyacinth, and sweet potato waste.

The effect of varying temperature and leachate retention time should be examined.

Task VIII: Aquatic Vegetation, Waste Water Purification/Biomass Production

This task was not included in the set described in Section III, but is included as it was performed as an element of the total experiment. As normally operated, the animal excrement anaerobic digesters discharge waste water with a BOD of about 400 mg/liter. As this is too high to dump in the local drainage ditch, an aeration ditch and pond are normally used to lower the BOD to about 250 mg/liters. This waste water is still an excellent nutrient supply since the nitrogen and phosphorus compounds have not been removed. As it is not practical to use the waste water from the experimental site as liquid fertilizer, the idea of using aquatic vegetation was attempted. A few water hyacinth plants were placed in the aeration pond in early June. Within three weeks, the entire surface of the 20 meter diameter pond was covered with plants. The BOD of the waste water leaving the pond was approximately 100 mg/liter. A number of the plants were harvested and used as pig feed. The animals consumed the vegetation without any coercion. More plants were harvested, without any visible effect on the pond leaf cover, and used as feed stock for digester γ. Figure VI-7a shows the aeration pond prior to introduction of water hyacinths, Figure IV-7b shows the pond 6 weeks after water hyacinths introduction.

Aquatic Vegetation



Aeration ditch and pond prior to introduction of water hyacinth.

Figure IV-7a

Aeration ditch and pond 6 weeks after introduction of water hyacinths.

Figure IV-7b

The researchers at PLRI plan to explore the economics of this process for application to large scale pig farms. Presently the liquid wastes from these farms are piped to the sea. It may prove more economical to anaerobically digest the waste water, purify with vegetation such as duck weed or water hyacinth, and recycle the purified water for use on the pig farm. The vegetation would provide supplemental feed.

SECTION V

DISCUSSION

The study has shown that it is possible to increase the biogas production of a continuous flow anaerobic digester by use of a biomass leacher. To pursue this development, it would be useful to provide a theory that could be used to establish a set of design considerations.

Microbiological Aspects of Anaerobic Digestion

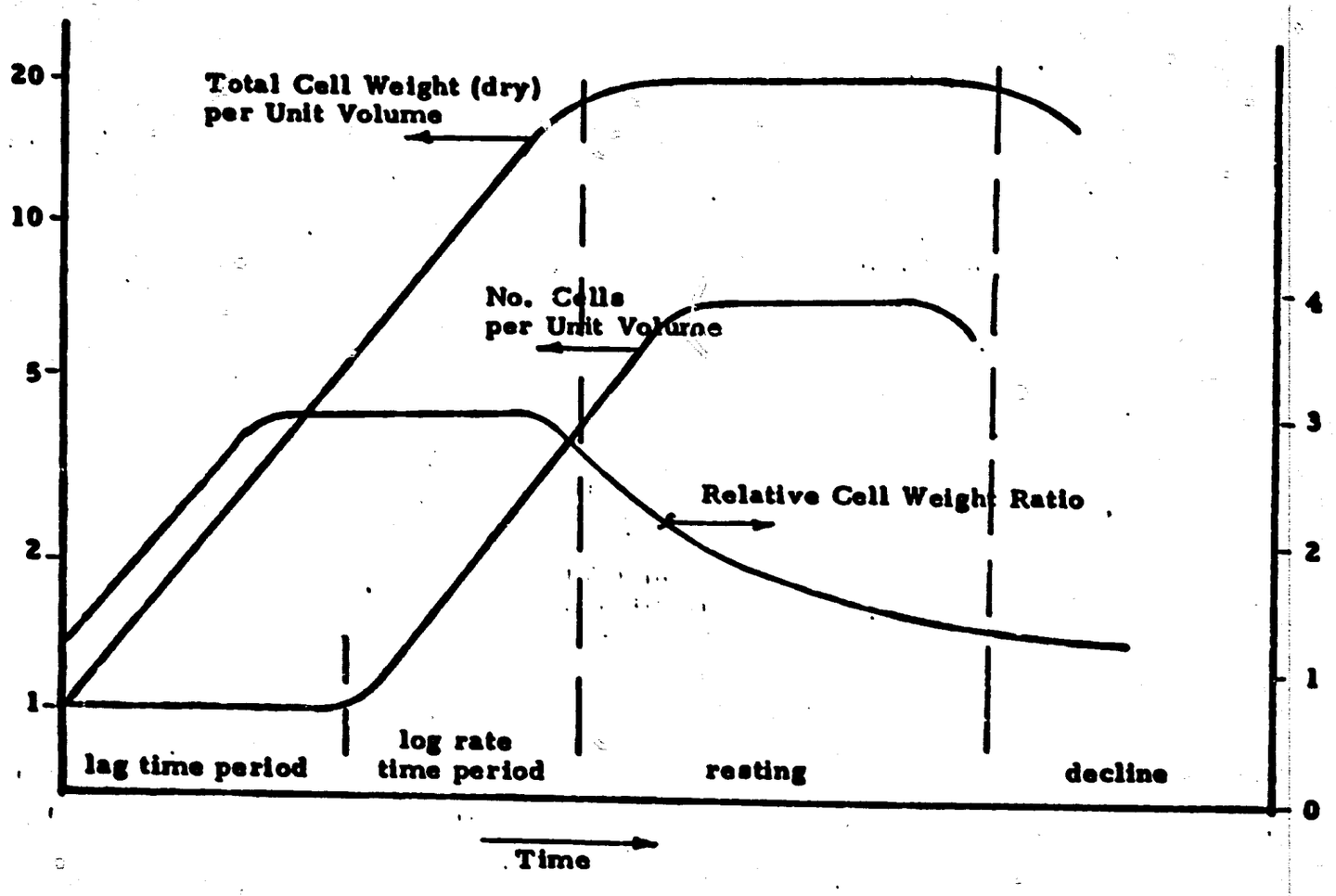
A comprehensive theory on microbiological phenomena has been developed, much of which is adaptable to the subject of anaerobic digestion of organic waste. The major limitation is that the theory tends to be based on the behavior of pure culture microorganisms whereas biological waste treatment involves consecutive exposure to synergistic bacterial heterocultures.

Observations of monoculture bacterial batch mode growth after introduction into fresh culture medium show that the microbiological population passes through the following phases (Aiba, et al, 1965):

1. Average cell mass increase without division.
2. Cell population increase at constant growth rate (average cell mass remains constant).
3. Average cell mass decrease while maintaining population growth rate.
4. Cell population growth rate decreases to zero.
5. Cell population decreases.

Step one occurs as the cells mature in the fresh culture medium. Step two represents the division of mature cells in a medium with adequate nutrients. Step three occurs as the culture medium becomes depleted in one or more necessary nutrients, or as inhibitory metabolic products are produced by the organisms. Step four occurs when the culture medium has become so depleted in a vital nutrient, or when so inhibited by a toxic metabolic product that the cell production rate equals the cell distribution rate. Step five will eventually occur as the effectively dormant cells age and die more rapidly than new cells are produced. The phenomena described above are graphically depicted in Figure V-1. Also identified are four alternate phase definitions.

Figure V-1. Schematic Representation of Bacterial Response in Batch Culture (Aiba, et al, 1965)



Mathematically, it is possible to express the relationship governing microorganism growth rate by the following empirical differential expression (McCarty, 1966, 1970).

$$\frac{dm}{dt} = a\frac{de}{dt} - bm \qquad (1)$$

where

m = microorganism mass/unit volume - $[M/L^3]$

a = growth rate yield coefficient - $\frac{\text{Cell Mass Produced}}{\text{Nutrient Mass Consumed}}$

$\frac{de}{dt}$ = nutrient consumption rate/unit time - volume $[M/TL^3]$

b = microorganism decay coefficient - $[1/T]$ (reciprocal of average cell life).

t = time - $[T]$

The nutrient consumption rate/unit volume under conditions of limiting nutrient supply can be mathematically expressed as

$$\frac{de}{dt} = \frac{kms}{c + s} \qquad (2)$$

where

k = maximum rate of nutrient consumption/unit mass - volume $[I/TL^3]$

c = nutrient concentration at which $\frac{de}{dt} = \frac{mk}{2}$ - $[M/L^3]$

s = existing nutrient concentration - $[M/L^3]$

Combining equations (1) and (2), the result can be expressed as

$$\frac{1}{m}\frac{dm}{dt} = \frac{aks}{c + s} - b \qquad (3)$$

Equation (3) can be utilized to mathematically define the microorganism mass curve shown in Figure V-1; however, it is apparent that for a batch mode culture growth, the existing nutrient supply, s, is a function of the original nutrient supply and total nutrient consumed from initiation of experiment to the time of observation.

Rather than use batch mode, a continuous flow system can be considered. In such a system, liquid flows into and out of the culture chamber at a fixed rate, carrying nutrient in and washing some microorganisms and remaining nutrient out. For such a system the governing equation analogous to equation (3) is

$$\frac{1}{m}\frac{dm}{dt} = \frac{aks}{c+s} - b - fq \qquad (4)$$

where

f = ratio of suspended microorganism/unit volume to total microorganism/unit volume

q = liquid flow rate per unit volume - [1/T]

Such a system will continue at equilibrium when the net rate of cell production within the culture chamber equals the rate of cell removal in the effluent. Note that f has two limiting values, 0 when the microorganisms are growing exclusively on a substrate, and 1 when the microorganisms are growing exclusively in a liquid suspension.

In order to apply the foregoing, it will be useful to examine the behavior of anaerobic digesters. Anaerobic digestion can be considered on a macroscale to be a three-step biological process utilizing heterogeneous groups of bacteria functioning in the absence of oxygen to degrade complex organic material into simpler molecular forms. The first step, sometimes identified as acid fermentation, involves the hydrolysis of high molecular weight biopolymers, carbohydrates, fats, and proteins into lower molecular weight saccharides, glycerol, fatty acids, peptides, and amino acids. In essence, this step involves the use of extracellular enzymes to convert solid material into soluble form. The second step, sometimes referred to as acid regression, is the formation of volatile fatty acids (acetic, propionic, etc.), lower alcohols and aldehydes, carbon dioxide, hydrogen, ammonia, and hydrogen sulfide. This step is intercellular; however, it also produces the enzymes required for the first step. The third step, occasionally identified as alkaline fermentation, is the generation of methane and carbon dioxide from the fatty acids, alcohols and aldehydes; and the synthesis of methane from carbon dioxide and hydrogen.

The first two steps are the result of the metabolic processes of a group of microorganisms which have been labeled "acidogenic" or "non-methanogenic." The third step is the manifestation of the metabolic processes of a group of microorganisms which have been labeled "methanogenic." These steps can be graphically depicted as shown in Figure V-2. Toerien and Hattingh (1969) have reviewed the microbiology of this total process. A conclusion which can be derived from such a review is that processes function with various heterogenetic mixtures of microorganisms, each mixture apparently adapting to the material to be digested and the environment in which it is to be digested. It would not appear to be advantageous to attempt to develop monocultures for such processes, given the variables in substrate to be digested, the varying environment, and the limited optimum response of each particular monoculture.

The concept of this total process can be aided by considering a response graph such as shown in Figure V-3 depicting the batch fermentation of organic waste. A similar response graph for the semi-continuous flow fermentation of organic waste is shown in Figure V-4. For semi-continuous flow a portion of the liquid was withdrawn daily and an equivalent volume of waste was added and mixed with the material remaining in the digester. The results depicted in Figures V-3 and V-4 imply that while two distinct bacterial processes are involved, they can coexist. Conversely, the division of the continuous flow processes into distinct acidogenic and methanogenic stages has been demonstrated in a two-vessel digester, with each step being operated under appropriate environmental conditions (pH and temperature) for each of the groups of microorganisms (Keenan 1974).

The emperical equations used to describe monoculture microorganism activity have been applied to the study of anaerobic digesters (McCarty, 1966, 1967; Lawrence and McCarty, 1967, 1970). When these equations are applied to describe continuous flow, single stage, mixed culture digesters, the results are useful in evaluating alternate recycle configurations; however, little can be concluded regarding the influence of the microbiological colonies as they are completely intermixed. The application of these quasi theoretical procedures to the two-stage digester (separate acidogenic and methanogenic chambers) does provide further insight. In this case, the equations are applied individually to each of the stages. Coupling between the stages occurs

Figure V-2. Anaerobic Digestion Process

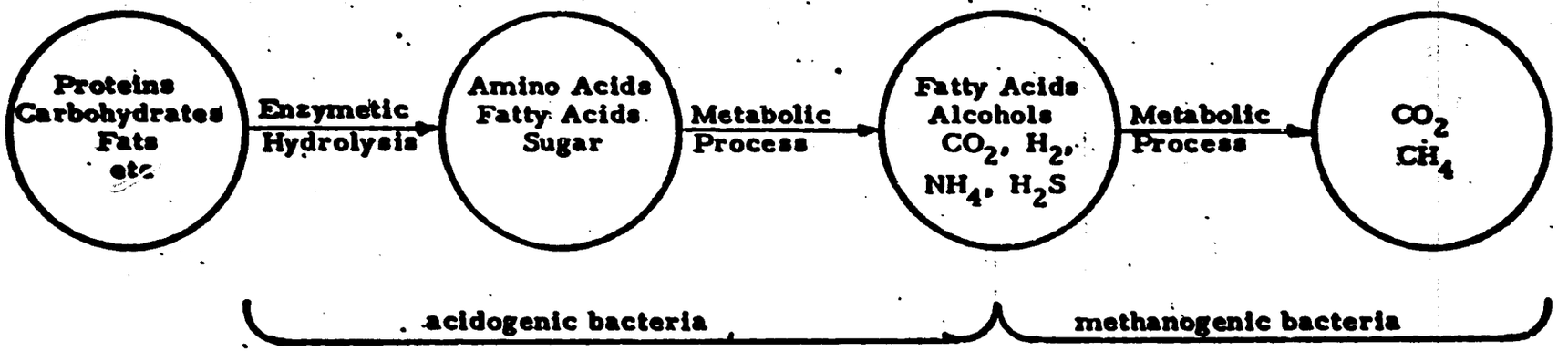


Figure V-3. Batch Mode Digestion Chemical Response
(Eckenfelder and O'Conner, 1961)

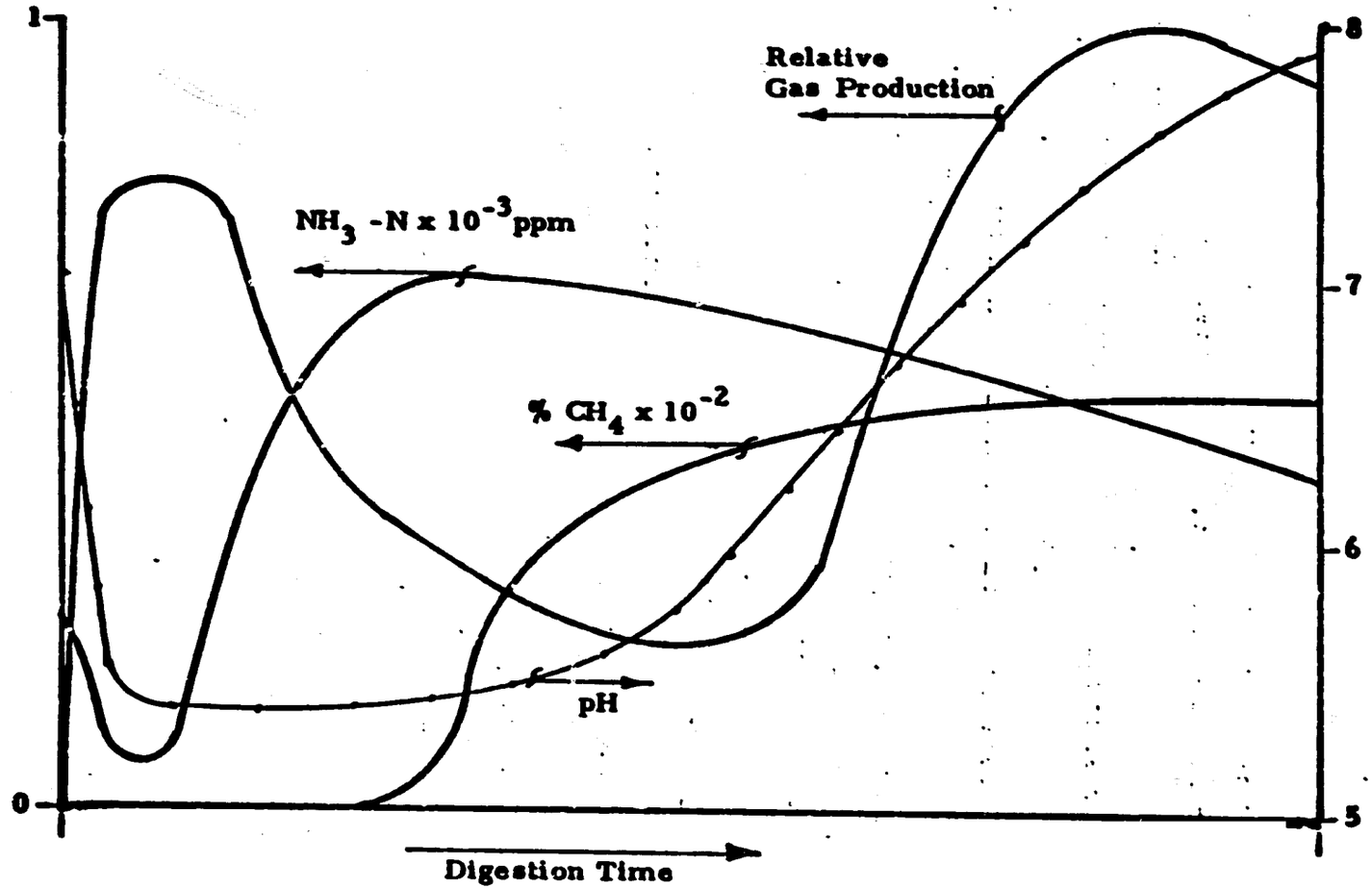
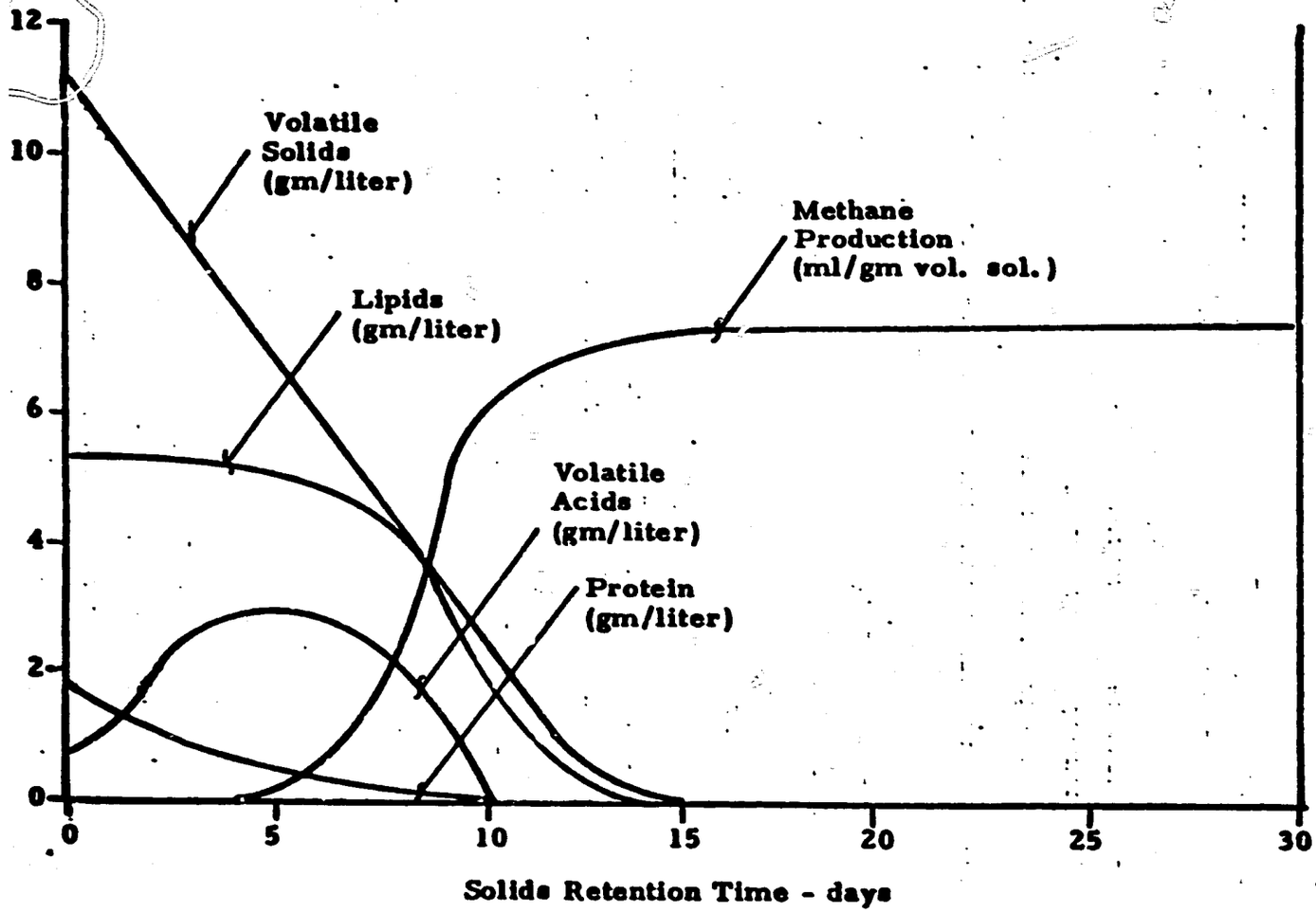


Figure V-4. Continuous Mode Digestion Effluent Characteristics (McCarty, 1966)



since the effluent from the first stage is the influent for the second stage. For practical operation, it can be assumed that the system will function in a steady state mode. Thus the microorganism mass within each vessel will be effectively constant, which is equivalent to the mathematical statement

$$\frac{dm}{dt} = 0$$

The resulting mathematical expression for steady state operation of a continuous flow digester can be derived from equation (4) as

$$fq = \frac{aks}{c+s} - b \qquad (5)$$

The reciprocal of fq is equal to the average microorganism retention time (MRT) in the stage being considered. For most configurations, MRT is numerically equal to the solids retention time (SRT) that is commonly used in anaerobic digester engineering. Equation (2) is the other mathematical relationship of interest for this discussion.

The microorganism mass in each chamber is composed of a heterogeneous mixture, thus the rate "constants" are based on an ill-defined mixture and therefore must be considered as only order of magnitude values due to the variability of the culture. For consistency of the analogy, the nutrient concentration, s, will now be considered to be "waste" concentration, which is again an approximate quantity. A typical measurement of waste concentration is biological oxygen demand (BOD). The waste concentration, s, is the average concentration in the vessel and therefore is also the waste concentration of the effluent. For consistency, this definition of s will change $\frac{de}{df}$ to a measure of the waste consumption/unit volume. With these revised definitions, it is possible to evaluate the influence of each of the terms and thereby indicate the trends desirable for a two-stage anaerobic digester.

As cost is directly related to size, it is important to utilize as small a digester volume per unit waste processed as is practical. This can be accomplished by designing for a high liquid flow rate per unit volume (q). Rewriting equation (5) to explicitly show the dependence of q on the other parameters of the system, the expression becomes

$$q = \frac{1}{f}\left(\frac{aks}{c+s} - b\right) \qquad (6)$$

The liquid flow rate per unit volume is large if f is small, which can be accomplished by using an immobile microorganism substrate such as provided by the anaerobic filter (Young and McCarty, 1969). It is not possible to manipulate a, the growth rate yield coefficient. The parameters k and c are interrelated, being functions of the microorganism metabolic process. The ratio of k/c can be maximized by controlling temperature, pH, carbon/nitrogen ratio and removing inhibiting constituents. Finney and Evans (1975) suggest that the methanogenic process can be aided by lowering the biogas partial pressure. The waste concentration, s, should be large if the only requirement is to increase q; however, s should be small if an efficient conversion system is desired. The microorganism decay coefficient, b, is also a function of the same parameters as governing k and c, thus somewhat constraining the selection of temperature, pH, and pressure.

Just as a large q is desired, a large volume of nutrient consumption per unit volume $\left(\frac{de}{df}\right)$ is also desirable to assure a high efficiency of conversion per unit volume. From the previous discussion plus consideration of equation (2), it is apparent that a large value of microorganism mass/unit volume, m, is thus desirable. The value of m can be increased by increasing the average microorganism retention time by simply increasing digester volume; however, such a solution results in higher digester costs. A more cost effective solution would again seem to be the adoption of the anaerobic filter.

Design Considerations

The acidogenic stage involves the extracellular enzymatic degradation of solid material, thus the existence of nondigestible (refractory) solids in the first stage of a continuous flow two-stage digester would be expected. Two distinct solid phases do, in fact, occur; sludge solids which accumulate on the bottom of the digester, and "mat" solids which form in the scum layer at the top of the digester. The sludge solids are readily removed by draining some fluid from the bottom. The mat which builds up on the top requires mechanical agitation to minimize adverse effects with eventual physical removal usually proving necessary. This problem is minimal if the waste is human, poultry, or swine excrement; serious if the waste is ruminant excrement; and impossible if the waste is unprocessed vegetable matter containing lignin, cellulose or similar fibrous materials which are difficult

to degrade. M. Wolff reviewed the general problem of anaerobic digestion of cellulosic materials which he documented in an internal Aerospace Corporation memo in August 1974. A copy of the pertinent text is included as Appendix I. The conclusion of this previous in-house study was that lignocellulosic materials could be digested given appropriate pre-treatment and proper anaerobic environment. An approach not discussed was the use of batch mode procedures to anaerobically digest lignocellulosic materials. This method was examined as a part of this study and found to be successful.

To stabilize the acidogenic stage of the digester, it is helpful to design for a hydraulic retention time of 24 hours or less (Keenan, 1974) and to recycle 50% to 80% of the sludge solids (Pfeffer and Liebman, 1975). There does not appear to be any advantage to operate the acidogenic stage at elevated temperatures. It is important, however, to maintain a relatively steady temperature, thus some form of insulation is desirable. Since the removal of the scum-formed mat will be eventually required, access to the acidogenic digestion stage vessel will be required.

The effluent from the acidogenic stage will be influent to the methanogenic stage. As the metabolic processes of the methanogenic microorganisms are entirely intercellular thus involving only matter in solution, there is no reason for solid material to be introduced into this stage of the process. Thus it would be possible to utilize an anaerobic filter consisting of a vessel packed with an inert material to provide an extensive surface area and restricted fluid passage within the chamber. Further, since the methanogenic processes are enhanced by operation at elevated temperatures (up to 60°C), both heating and insulation should be utilized. As there is no reason to have access to this stage, it would be advisable to bury this stage below the local frost line so as to aid in thermal insulation and temperature stabilization. Hydraulic retention time for the methanogenic anaerobic filter will depend on the surface area/unit volume of the core, the allowable waste concentration of the effluent, and the specific composition of the influent, together with the environmental conditions maintained within the unit. Hydraulic retention times of less than 24 hours should be achievable.

The effluent from the methanogenic stage will be enriched in nutrients but should have a low BOD. Part of the effluent can be used as a leachant

for batch mode waste vegetation digesters (biomass leaches) with the resulting enriched (increased BOD) liquid being used as influent for the methanogenic stage. The vegetation digesters will be operated in a manner intended to maintain acidogenic conditions. Low hydraulic retention times, moderate temperature (15°C) and frequent introduction of fresh vegetable matter (30-60 days) should suffice to maintain these conditions.

The remaining methanogenic stage effluent can be used to nurture aquatic vegetation (duckweed, water hyacinth, etc.), thereby producing either animal or digester feedstock while purifying the discharged water. Alternately, the enriched effluent can be used directly as a fertilizer for a more conventional food crop.

The mat periodically removed from the acidogenic digester, together with the decayed matter removed from the batch mode vegetation digesters, can be used as a humus, thereby returning nutrients to the soil. The design of this segment of the system depends on the particular climatic and agricultural characteristics of the intended region of use, the type of excrement available for the continuous flow segment, the type of waste vegetation available, and the relative value of the possible product.

Gas produced by the methanogenic stage will be rich in CH_4. Storage of this gas in separate bladders is suggested. The 98% CO_2 gas from the acidogenic stages can be vented to the atmosphere or utilized to enhance crop growth if hydroponic or greenhouse agricultural techniques are practiced. It may prove desirable to operate the biomass leacher in a mixed mode (acidogenic and methanogenic), thereby producing a combustible biogas. If so, such gas should be either stored or utilized to maintain the temperature of the process, particularly the methanogenic tank.

The use of elastomeric bladders for every chamber of the system appears to be cost effective in comparison to alternate construction methods

To evaluate the theory and the design evolved therefrom, further studies are proposed in the next section. From the results of these proposed studies, it would be possible to complete the design outlined above so that its true cost effectiveness could be evaluated.

SECTION VI

CONCLUSIONS

This study resulted in the following observations:

1. Pig excrement plus pigsty cleaning water served as the primary influent for a multistage anaerobic digester. Acidogenic and methanogenic separation was observed.

2. Gas production from the first stage tended to be high in CO_2 whereas latter stages tended to be high in CH_4.

3. The effluent from the digester could be "polished" by use of a water hyacinth pond.

4. A batch mode vegetation leacher was operated utilizing digester effluent as influent and discharging enriched (higher BOD) leachate into the methanogenic stage. The biomass leacher tended to operate as an acidogenic digester if the hydraulic retention time was kept short.

5. The leachate introduction into the methanogenic stages results in increased methane production of from 20-40% over that produced by the digesters without leachate or effluent recycle. Effluent recycle alone shows a 5-10% increase in methane production, the cause apparently attributable to mixing. These values are applicable only to the conditions under which this particular experiment was run. In evaluating the improvement due consideration should be given to the fact that the operating conditions were dictated by the experimental facility and were not, therefore, necessarily optimum.

6. Small-scale biomass leacher experiments showed that any vegetable matter could be utilized to produce a high BOD leachate from vegetation and enriched (high N, P) digester effluent.

SECTION VII

RECOMMENDATIONS

The experiment has shown that increased methane production can be obtained by utilization of a vegetable leacher. The experiment was primarily directed towards obtaining qualitative results although some quantitative data were obtained. To determine the actual improvement that could be obtained by the technique utilized in this experiment it will be necessary to perform a more detailed experiment directed towards quantitative results. The proposed follow-on experiment would be composed of the following elements:

1. Two pig herds, each containing approximately 50 adolescent pigs, to be used as the excrement source (same as original experiment).

2. Two dual-stage continuous flow digesters would be used. The first stage would be sized so that the solids retention time was between 12 and 24 hours (acidogenic), the second stage so that the microorganism retention time was at least 100 hours (methanogenic). Instrumentation would be installed for obtaining 24-hour integrated average liquid flow rates; inlet, interstage, and outlet oxygen demand (BOD, COD, TOC, or alternate); temperature and pH in each chamber; and gas production/composition (CO_2, CH_4) per stage. Provisions for both liquid and gas sampling to obtain more detailed chemical analysis would be included. Such detailed analysis would be made weekly.

3. Two biomass leachers, ducted to be operated either singularly or in parallel would be utilized. One unit would be filled with rice straw, the other with water hyacinth. Leachate would be pumped from a sump located between the digester discharge and the aquatic vegetation (water hyacinth) purification pond. Leacher effluent would be introduced into the methanogenic stage of one of the digesters. The liquid flow rate would be established so as to maintain acidogenic conditions within the leacher. The methanogenic stage of the control digester would receive an equal amount of liquid from the sump so that retention time effects would be equal between the control and the test digester. Instrumentation and measurements would be effectively the same as described for the digesters (2).

4. An aquatic vegetation purification pond utilizing water hyacinth would be used to polish the digester effluent. Inlet and discharge water quality would be determined as well as biomass growth rate so as to establish the effectiveness of the pond as an element of the total energy recovery system.

The initial phase of the experiment would be devoted to establishing a stable system. The digesters would be operated utilizing pig excrement only until stability was obtained. During this period, the purification pond would be periodically harvested in order to obtain a supply of water hyacinth for one of the biomass leachers as well as to determine the appropriate harvesting rate required for the pond. Rice straw would be placed in the other biomass leacher.

After stability was obtained, the biomass leachers would be closed and then slowly filled with digester effluent over a period of 7 to 10 days. When full, the leaches would be allowed to discharge into the test digester as described above. This mode would continue until a new stable condition had been observed for 7 days. The control and test digester would then be switched and the above process repeated.

Having demonstrated base-line transient operation, pertubations about this condition would be explored by varying the digester retention time and the relative leachate feedback quantity through the biomass digesters.

Quantitative system response would be documented and compared with theory and comparable experimental data obtained from the literature review.

A final report plus a set of papers would be prepared for publication.

Long Range Goals

Based on the certainty of increasing prices for animal feed--primarily as a result of the increasing cost of fuel--together with the necessity for pollution control of agricultural wastes, the concept of utilizing such wastes for feed/fuel substitutes appears very attractive. While urban and industrial

waste treatment facilities have been well developed throughout the world, analogous systems for agricultural wastes are relatively unknown. This is partially the result of the environmental acceptability of low density waste recycling, which is commonly practiced with the less intensive agricultural crops/animal husbandry techniques. When intensive cultivation is practiced for increased crop and/or dense populations of animals are grown in a confined space, the energy utilization per unit of food value produced must necessarily increase, as will the pollution potential from the animal wastes. Consideration of this problem suggests that conservation, recycling, and energy production should be practiced to alleviate these problems. It appears, in fact, that such practices are not only desirable, they are also necessary if the world standard of living and quality of life are to progress.

A review of the literature, and a survey of existing experimental facilities shows that a number of alternative recycling paths are possible, the two predominant ones being animal waste recycling for feed supplement and anaerobic waste digestion for methane production with fertilizer production and water purification/feed production. Figure VII-1 presents a schematic of the total concept. Segments of the total system have been researched in great detail. It is proposed that integrated experimental test effort/demonstration facility development be undertaken in various developing nations to provide the information and physical example for the introduction of these practices into their agricultural sector. A suggested formation plan follows:

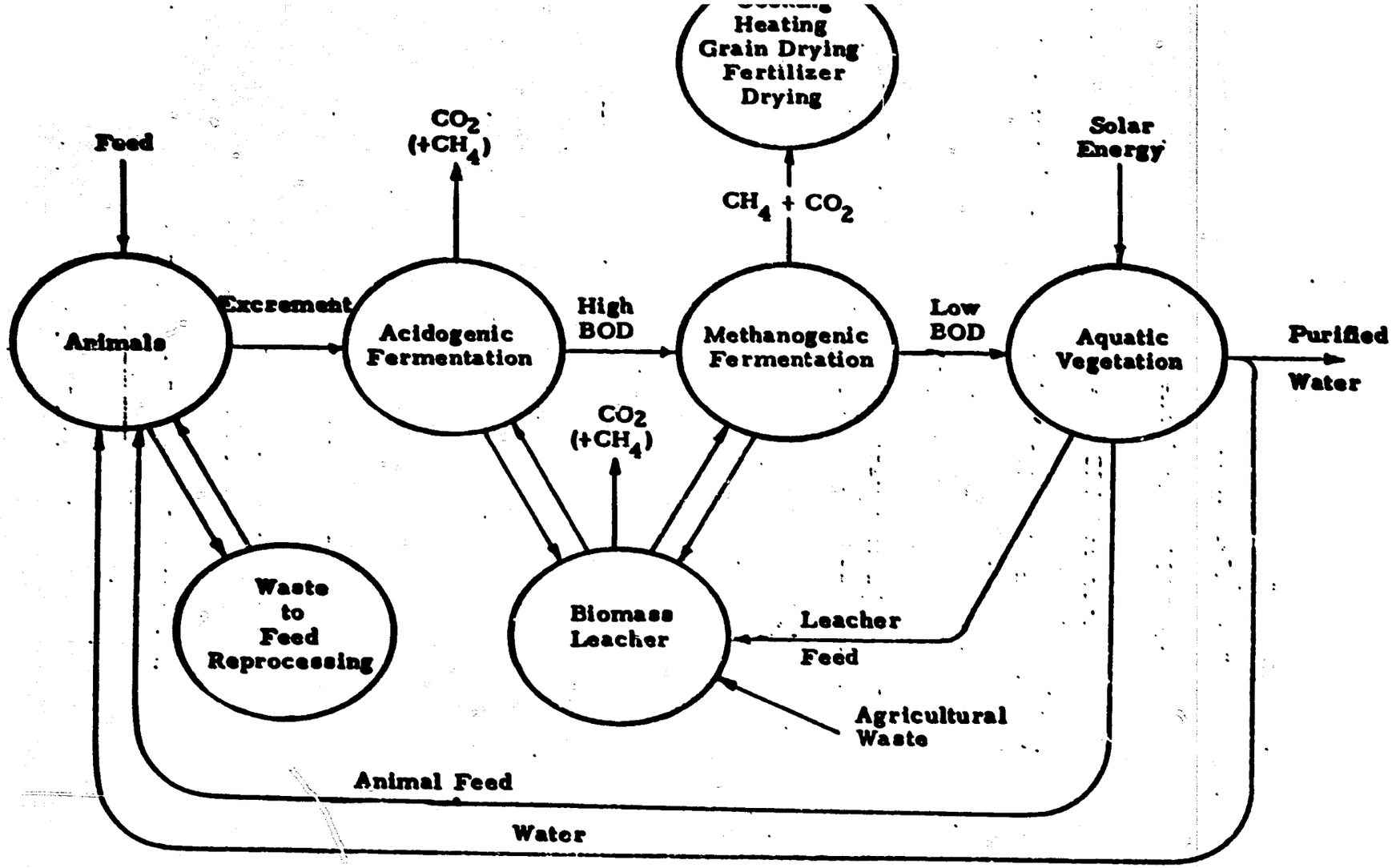
I. <u>Digester Development</u>

Several aspects of digester development should be explored:

a. <u>Separation of acidogenic/methanogenic processes</u>: As a rule of thumb, the retention time for the acidogenic unit should be between 12 and 24 hours, whereas that of the methanogenic unit should be between 100 and 200 hours.

b. <u>Anaerobic Methanogenic Filter</u>: It appears that the retention time of an anaerobic methanogenic filter will approach that of the acidogenic container. The concept of a methanogenic filter (using rocks in the chamber to add surface area) should be examined.

Figure VII-1. Integrated Agricultural Waste Recovery/ Food/Energy Production Schematic



c. Solids Concentration: The retention time can be increased if the solid concentration is increased, for a given size digester. Data indicates that up to 10% solids can be introduced into a 24-hour acidogenic chamber with little effect on the chemistry of the output. This effect should be explored.

d. Retention Time: The literature indications that retention time (in laboratory size units) has a strong influence on the efficiency of conversion. This area should be explored further with field-sized units.

II. Efficient Purification/Feed Productivity

The use of ponds using Water-Hyacinth, Duck Weed, Algae and Water Chestnut should be evaluated for efficient purification/feed production. The vegetable growth could be used as either animal feed or vegetation input.

III. Vegetation Leacher

The concept has been proven but some parametric performance data is required, including batch operation time, fluid retention time, etc.

IV. Fertilizer Drying

The biogas from the digesters can be utilized to dry fertilizer, for either storage or as a sterilization process, prior to using as a feed supplement.

V. Grain Drying

The biogas from the digesters can be utilized for grain drying. Such use should be explored.

VI. Animal Waste as a Feed Supplement

The literature shows that animal waste can be utilized as a feed supplement if it is either fermented (silaged) or heat sterilized. Since this use is in partial conflict with its use as a source for biogas, a combined research is suggested.

VII. Various Waste Evaluation

Most digester work to date in Taiwan has concentrated on pig dung. Examination of poultry and cattle waste as a source of energy/feed supplement should be concurrently undertaken. Sequential patterns should be explored.

VIII. Digester Bag Development

The development of digester bags should be continued. The concept of a four-bag system appears sufficiently attractive to pursue as an initial concept (acidogenic, methanogenic, vegetable waste leacher, gas accumulation). Sizing of these units, preferably of equal size, should be explored.

IX. Review of Other Research

The efforts of other researchers in these fields should be continuously reviewed.

X. Integrated Operation

The integrated operation of grain drying, fertilizer drying, animal waste feed supplement, digester operation for biogas/fertilizer production, water pollution control/feed production from aquatic plants, and waste vegetation anaerobic digester should be demonstrated.

SECTION VIII

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APPENDIX I

THE USE OF CELLULOSIC MATERIALS IN ANEROBIC DIGESTORS FOR METHANE PRODUCTION

This is a review of literature and a discussion of the use of farm wastes such as grain stalks and cattle manure to produce methane gas, nitrogen fertilizer, and as a by-product, humus for the soil.

PROBLEMS

Attempts to feed anerobic digestors directly with cellulosic waste are generally frustrating. Chung Po (Taiwan) reported, "It just clogged the digestor". Grass did the same at the University of Pennsylvania. Wood chips and sawdust at the University of California, Berkeley, were hardly affected. Nevertheless, pure cellulose samples digest readily, so in principle, it is possible.

Recent research has been mainly concerned with urban waste disposal, ecological problems, and the world protein shortage, so that little attention has been paid to cellulose, except newsprint and cattle manure.

VARIED OPINIONS FOUND

The professional opinion concerning practicality of digesting the manure of ruminants is "varied". An eminent authority, C. G. Golueke, has stated (Bioconversion Conference, Amherst, 1973) it is obvious that the remains of an anerobic digestion in the stomach of a ruminant will not efficiently undergo a second digestion. On the other hand, United Aircraft Research Labs report a methane yield of 3800 Btu/lb or 4 cubic feet/lb from cattle manure. Further, the reported existence of 20,000 methane digestors using cattle dung in India is an impressive endorsement. Meenaghan, et al, (1970) obtained 58% digestion of cattle manure in 10 days at 97°C.

DIGESTION OF CELLULOSE WASTE

Obviously, cellulose is available in many forms: manure, wood, grain stalks, leaves, paper, etc. All of these have been successfully digested in a laboratory somewhere. The differences of technique and results obtained depended on the physical structure.

Klein and Chan at the University of California (Berkeley, 1968) in the laboratory performed digestion of kraft paper, green garbage, and pine wood with these results:

MATERIAL	CELLULOSE (%)	RETENTION (DAYS)	DIGESTION %	CH_4 %	YIELD ft^3/lb
Brown paper	99.8	12	80	65	13
Wood powder (with sludge)	80	15	5	70	?
Green garbage	?	12	50	65	14

Temperature was probably 25-27°C. Minor nutrients were generally not added but when they were (to increase N:C ratio to 1:30 from 1:70), gas production increased about 30%. The coarse wood powder from a 1/8 inch screening did not digest well.

Desai and Biswas (1945) in India digested cow dung in field tanks and obtained year-round gas yields of 1.35 ft^3/lb, but summer yield was 4.0 ft^3/lb. Doubling the retention time increased yield to 5.25 in summer. In the lab they reported 85% digestion of powdered rice straw and leaves when NH_4SO_4 was added.

VARIETY OF SUBSTRATES ARE DIGESTIBLE

Apparently bacteria are able to metabolize a great variety of organic materials. Symons and Buswell (1933) tested 45 pure substances, including oxalic acid, formic acid, starch, xylose, acetone, sugars, and trimethylene glycol, and recovered 80-100% of the carbon as gas, except for 46% using the last substance. They feel that careful avoidance of oxygen and attention to nitrogen feeding were important to complete fermentation.

EFFECT OF STRUCTURE ON DIGESTION OF CELLULOSICS

One of the most illuminating results showing how indigestible raw plant material can be, was obtained by Mandels, et al (1974), who used isolated cellulose enzyme to convert cellulose to glucose at 50°C. Some samples were ball-milled and some not. Results are below:

MATERIAL	% SACCHARIFICATION (48 hours) unmilled	milled
Cotton	10	55
Bagasse	6	48
Boston Globe newspaper	27	70
Rice hulls	low	high

Ball-milling gave much superior results compared to mulching, hammer-milling, shredding, granulating, boiling, NaOH soaking, and other means. The enzyme was derived from the fungus Trichoderma Viride and can be recycled after filtering.

Pew and Weyna (1962) concluded that difficulties with digestion of spruce wood was due to three-dimensional chains of lignin surrounding the carbohydrate chains. They found that even the lignin became soluble in NaOH after 5 hours of "vibratory milling", but that 10 minutes was enough to permit two-thirds of the cellulose to be removed with enzymes. Cotton and aspen wood were similar. The evidence suggested that lignin protects carbohydrates by a cage-like network around them so that the large enzyme molecules cannot enter.

THE IMPORTANCE OF NUTRITION IN BACTERIAL DIGESTION TO PRODUCE METHANE

Most procedures, methods, and apparatus used for methane production in the U. S. have assumed the role of sewage disposal. In view of the pot-pourri of substances entering sewage digestors, little attention has been given to control or supplementary feeding of minor nutrients to the bacterial population. Illogically, this attitude has affected research on conversion of solar energy using fermentation of single species of plants such as chlorella and water hyacinth; nutrient needs were ignored, even though they could have been determined.

Whenever a known, constant diet of organic matter is to be fed to a digestor, it is obvious that the nutrient needs of the bacteria can be attended to at very little expense of time or money. When the fermentation is to be associated with an agricultural enterprise, common fertilizers such as ammonia, phosphorus, and potassium, can be routinely supplied at costs of pennies per pound.

Because of the nutrition factor, much of the research on methane production for energy purposes must be redone and conclusions reached in the past must be used cautiously. For example, in work done at the University of Pennsylvania (1973), digestors were operated on manure,

dog food, waste, 100% grass, and seaweed. No nutrients were added; alkalinity was adjusted using $CaCO_3$ rather than NH_4OH. The stability of digestions was erratic and it was apparent that stability depended on feed containing nitrogen (dog food). The digestor operated on grass gave an excellent methane yield for a month, but slowly died.

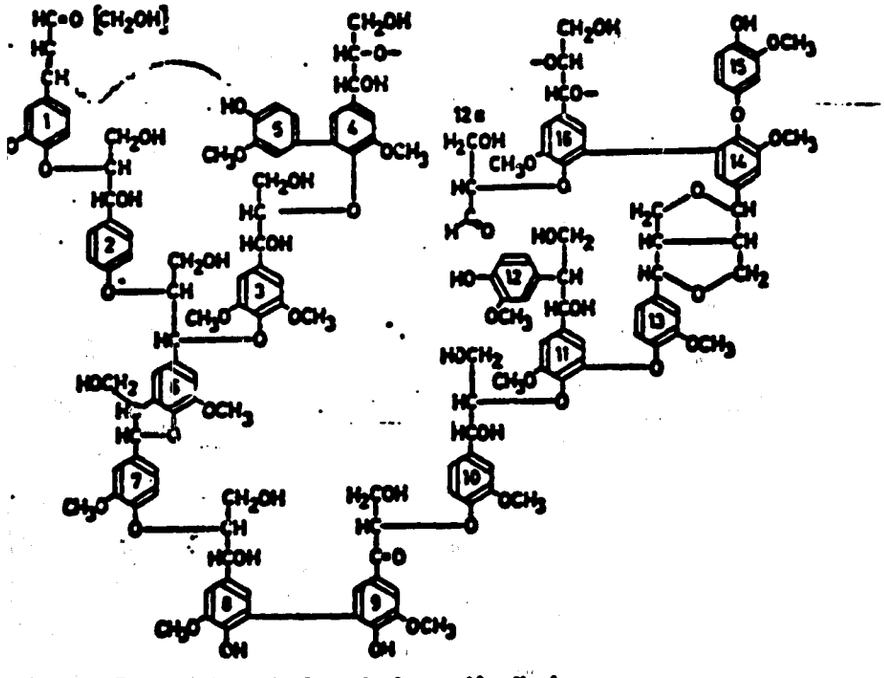
On the other hand, Pfeffer (1970) at the University of Illinois successfully digested newspaper waste. He added nitrogen and phosphorus nutrients after analysis of the feed. Real municipal waste digested satisfactorily.

Dubos (1928) decomposed cellulose both with and without the addition of NH_4SO_4 and found 55% and 96% digestion, respectively.

In short, there is solid evidence that yield improvements do result from proper nutrition and there is hope for further improvement when more is understood about the nutritional needs of bacteria.

DIGESTION OF LIGNIN

The utilization of lignin by bacteria must be chemically much different than cellulose in view of its composition shown below:



Recent schematic formula for conifer lignin

To decompose lignin, bacteria must break up a variety of linkages which are quite different than the repeating linkages of polysacharrides. Apparently (Kirk, 1971) decomposition requires using at least three different enzymes.

Cowling (1961) showed that white-rot fungi polyporus versicolor can destroy over 97% of lignin in sweetgum wood.

Acharya (1935) observed loss of 35% of the lignin in rice straw.

Cartwright and Holdom (1973) found an Arthrobacter species of bacteria which apparently adapted itself to the use of lignin as a sole carbon source after 10 months. In 14 days at 25°C, 10% of lignin was consumed. They report:

"Only one organism, a coryneform bacterium, was obtained which survived repeated sub-culture on the same medium. When first isolated, the organism grew sparsely but, after maintenance on lignin medium in screw-cap bottles for 10 months with infrequent subculture, transfer to plates gave much greater growth than when the organism was first isolated. The desnity and rapidity of such growth was sufficient to indicate the utilization of lignin as sole carbon source and a requirement for a long adaptation period to the substrate."

Plant pathologists (Kirk and Highly, 1973) at the U.S. Forest Products lab found that lignin was decomposed by white-rot fungi polyporus versicolor and Ganoderma applanatum, in amounts of 52 to 86% after 90 days at 27°C. Brown-rot fungi was not able to decompose lignin.

Taylor, et al (1970), found and isolated a bacterium which utilized aromatic benzene compounds as sole carbon sources. The bacterium, named pseudomonas, grew rapidly provided nitrate was present. The benzene ring is not inviolate.

Many experiments have been done with chemically isolated lignin that seemingly indicate the inability of bacteria to attack it. Boruff and Buswell (1934) found that isolated corncob lignin was bacteriostatic to inoculum grown on glucose. On the other hand, using natural chopped cornstalks and detailed quantitative analysis, before and after, they found that 57% of the cellulose and 42% of the lignin was gasified after 136 days at 25-30°C.

TABLE I

TOTAL WEIGHTS OF MATERIALS ADDED TO AND REMOVED FROM CORNSTALK FERMENTATIONS AT 25-30°C

	Cornstalks added, g.	Total added, g.[a]	Residue removed: After 136 days: Cornstalks	Residue removed: After 136 days: Total[b]	Residue removed: After 600 days: Cornstalks	Residue removed: After 600 days: Total[b]	Fermented: In 136 days: Total	Fermented: In 136 days: %	Fermented: In 600 days: Total	Fermented: In 600 days: %
Total solids	60.0	69.0	20.11	30.0	21.4	30.5	30.0	44	38.5	56
Total volatile matter	57.6	63.2	25.07	33.4	18.7	23.7	29.8	47	39.5	63
Ash	2.40	5.8	0.44	5.6	2.7	6.8	0.2	3	1.0	17
Water soluble[c]	3.65	12.6	.74	9.7	1.8	10.9	2.9	23	1.7	14
Ether soluble	1.39	1.4	.17		0.2					
Ethyl alcohol-benzene soluble	3.92	3.9	1.74		.0					
Pentosans, total	12.60	12.7	5.93	5.9	3.7	3.7	6.8	54	9.0	71
Cellulose C. & B.	22.32	22.3	9.61	9.6	3.4	3.4	12.7	57	18.9	85
Lignin	15.06	15.1	8.75	8.8	7.1	7.1	6.3	42	8.0	54
Protein	1.43	3.9	1.22		2.7					

[a] Includes materials in inoculum liquor. [b] Includes materials in filtered mother and wash liquors. [c] Not corrected for ash. [d] Analysis made according to Bray, *Paper Trade J.*, 87, 59 (1928).

The results above can hardly be disputed in view of the quantitative accounting (± 1%) for the carbon content which the authors maintained. They concluded that chemical isolation of lignin creates bacteriostatic compounds not found in nature.

EFFECT OF PRESSURE

In all literature examined, only one reference to pressure was noted. Symons and Buswell (1933) reported that 10,000 lb/in^2 caused the fermentation to produce volatile acids only, with almost no gas.

CONCLUSIONS

The preponderance of experimental evidence supports a view that all cellulosic materials are susceptible to anerobic digestion by bacteria. Even the lignin component of organics is probably digestible. In order to promote rapid and efficient digestion, it is necessary to:

1. Provide means, such as ball-milling, to partially break up the crystalline structure of cellulose, as in cotton, and to crush the complex ligno-cellulose structure, as in wood.
2. Provide proper nutrients for bacteria including nitrogen, phosphorus, and other substances which are necessary for their growth and the manufacture of enzymes.

There also exists evidence that bacteria or "bacterial societies" can adapt or mutate in a period of a few months, enabling them to make use of previously unutilizable substrates. If this is true, then cultures must be grown and maintained for specific purposes rather than simply assuming they exist in every gutter and swamp as in the past. This may be quite important at high temperatures 50-60°C. A promising direction of progress lies in correlating and understanding the life-processes of bacteria in relation to the engineering processes we desire to obtain. Some ligno-cellulosics appear more digestible than others. The easier ones are pithy and soft like grain stalks, leaves, and corncobs, whereas the more difficult are hard woods.

Milo Wolff
August 12, 1974

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APPENDIX II

GAS METER EQUATIONS

The gas meter utilized in these experiments is based on an inverted floating container constrained within a water filled open drum as depicted in Figure AII-1. With valve 1 open and valve 2 closed, the gas from the digester flows into the floating dome causing a vertical displacement. Periodically, the inlet valve is closed, the measurement Ho is recorded, and the outlet valve opened, thereby exhausting the gas in the dome. When the dome has settled to its lowest point, valve 2 is closed, valve 1 is opened, and the measurement continued. Due to the mass of the containment dome, the variable displacement of the cylindrical skirt in the water seal, and the non-linear operation resulting from the cyclic operational mode, the corrected gas production is not a simple linear function of the height Ho.

It is apparent that the gas measurement must equal the gas container under the dome at time of dump less the "dead volume" at end of dump. The gas contained under the dome at the height Ho can be determined from equilibrium equations as:

<u>Σ Vertical Forces</u>

$$W + \frac{\pi Do^2}{4} Po = \frac{\rho Di^2}{4} Pi + Dt[\ (L-Ho)+Po] \qquad (1)$$

where: W = weight of dome

Do = outside diameter of dome

Di = inside diameter of dome $D = \frac{Do+Di}{2}$

Po = external pressure

Pi = internal pressure

t = wall thickness

ρ = density of water

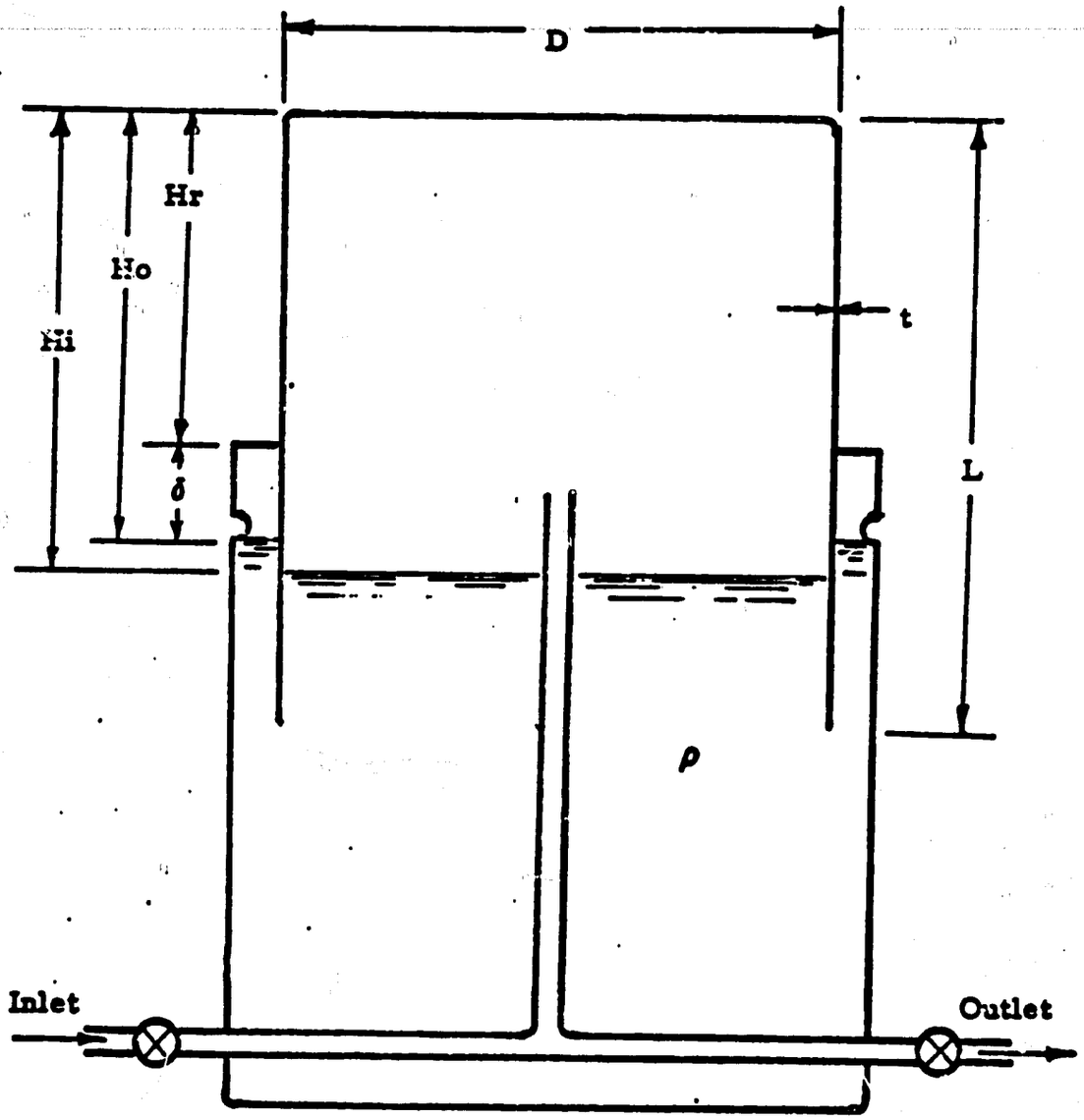
L = skirt height of dome

Ho = external dome height above water

Hi = internal dome height above water

Figure AII-1

Gas Meter



Equilibrium of Pressures

$$Pi + (L - Hi)\rho = Po + (L - Ho)\rho \tag{2}$$

For thin walls, using a nominal diameter D, equation 1 can be rewritten as:

$$Pi = \frac{4W}{\pi D^2} + Po - \frac{4t\rho\,(L - Ho)}{D} \tag{3}$$

Equation 2 can be rewritten as:

$$Hi = Ho + \frac{(Pi - Po)}{\rho} \tag{4}$$

By combining equations 3 and 4:

$$Hi = \frac{4W}{\pi D^2 \rho} + Ho\left(1 + \frac{4t}{D}\right) - \frac{4tL}{D} \tag{5}$$

The volume of gas under the dome is:

$$Vi = \frac{\pi D^2}{4} H_i \tag{6a}$$

Hence by use of equation (5):

$$Vi = \frac{W}{\rho} - \pi\, DtL + \frac{\pi D^2}{4}\; Ho\left(1 + \frac{4t}{D}\right) \tag{6b}$$

The value should be corrected to the equivalent volume of pressure Po as:

$$Vo = Vi\;\frac{Pi}{Po}$$

But the pressure ratio from equation 3 is:

$$\frac{Pi}{Po} = 1 + \frac{4W}{Po\,\pi D^2} - \frac{4t\rho\,(L-Ho)}{D\;Po}$$

Hence:

$$Vo = \left[\left(\frac{W}{\rho} - \pi D\,t\,L + \frac{\pi D^2}{4} Ho\left(1 + \frac{4t}{D}\right)\right)\left(1 + \frac{4W}{Po\,\pi D^2} - \frac{4t\,\rho\,(L - Ho)}{Po\;D}\right)\right]$$

The volume per cycle is Vo minus the quantity of gas remaining between the surface of the water and the roof of the dome when the skirt has contacted the bottom and the internal pressure equals the external pressure. The dome was constructed so that the top would be flush with the rim of the water tank with the dome unpressurized. To be assured that no water would enter the gas system, holes were drilled in the water tank a distance δ below the rim. Thus a dead volume $\frac{\pi D^2}{4}\delta$ exists at each cycle and must therefore be subtracted from Vo to determine the volume produced per cycle. Further, the height read is not Ho, but for convenience, rather $Hr \simeq Ho - \delta$. Substituting these effects together with the following physical dimensions of the system

W	=	7 kilogram
p	=	1 gm/cc
d	=	54 cm
t	=	0.05 cm
L	=	80 cm
δ	=	10 cm
Po	=	1.034 kilo/cm^2

the following numerical result is obtained:

$$Vc = [29308.42 + 2998.70Hr]\,[1.0027 + 0.00000358Hr] - 22902.21 \text{ cm}^3$$

Neglecting the second Hr term, converting to cubic meters, and generalizing for n cycles, the total gas production becomes:

$$V_{total} = 0.0064235n + 0.0023049 \sum_{i=1}^{n} Hr \quad M^3$$

APPENDIX III

WASTEWATER/SEWAGE POLLUTION MEASUREMENT

Biochemical (Biological) Oxygen Demand BOD

BOD determination is used to quantify the organic content of polluted water. The procedure is based on the determination of the amount of dissolved oxygen consumed by a "seeded" mixed bacterial culture in a sample of the polluted water. A number of laboratory methods have been developed, the most common being the 5-day, 20°C test, the Warburg respirometer test, and the electrolysis cell test. The use of a 5-day incubation period at 20°C is quite arbitrary, being apparently originally developed in Great Britain where 5 days represent the maximum time required for tributary water to reach the sea. Other functions and temperatures can be used and correlated to the 5-day 20°C test. In these tests, the sample is diluted with a known quantity of a specially prepared water solution which contains adequate nutrients and oxygen for the incubation period. After incubation at a fixed temperature, the results are defined by

$$BOD = [(DO_1 - DO_2)\frac{V_b}{V_s}] - (DO_1 - DO_3), \text{ (mg/liter)}$$

where

DO_1 = Dissolved oxygen in dilution water only sample at the end of the incubation period (mg/liter)

DO_2 = Dissolved oxygen in diluted sample at the end of the incubation period (mg/liter)

DO_3 = Dissolved oxygen originally present in undiluted sample (mg/liter)

V_b = Volume of the test flask (dilution waste and sample)

V_s = Volume of sample - undiluted

The kinetics of the BOD process can be represented by

$$\frac{d(BOD)}{dt} = -K_T(BOD)$$

where

t = time from start of test

T = temperature of process

BOD = Biochemical Oxygen Demand at time t

K_T = reaction "constant"

$= K_{20°C} \times K_o^{(T-20°C)}$

where

$K_o \simeq 1.056 \ (20°C \leq T \leq 30°C)$

The Warburg respirometer procedure is based on measuring the volume of oxygen consumed from the space over a measured quantity of a bacterial cultured seeded sample by use of a manometer. The carbon dioxide produced is removed by a separate container of KOH located within the flask containing the sample and the gaseous oxygen.

The electrolysis cell process is similar to the Warburg; however, the oxygen pressure over the sample is maintained by an electrolysis cell, measurement of the oxygen consumed being determined from the ampere hours of operation of the electrolysis cell required to maintain the oxygen pressure. The carbon dioxide produced is removed by KOH.

The limitations of the BOD measurement include the following:

1. The necessity of using a concentrated, active, acclimated bacterial culture seed.

2. The necessity of the pretreatment to eliminate toxic materials.

3. The arbitrary time/temperature constraints.

Because of these limitations, several alternate processes are used to quantify the content of organic matter in wastewater and sewage. These alternate procedures are all less time consuming, can generally be correlated with BOD, but have not as yet been accepted by governmental regulatory agencies charged with monitoring water purity.

Chemical Oxygen Demand (COD)

The chemical oxygen demand is a measurement of the equivalent oxygen demand of the organic matter that can be oxidized by a strong chemical oxidizing agent in an acidic medium. Potassium dichromate is the oxidizing agent generally used. The principle reaction can be expressed in an unbalanced form as

$$\text{Organic Matter } (C_xH_yO_z) + Cr_2O_7^{--} + H^+ \xrightarrow[\text{catalyst}]{\text{Heat}} Cr^{+++} + CO_2 + H_2O$$

For a given type of waste, excellent correlation can be obtained between COD and BOD. Since COD can be determined in a few hours whereas BOD requires a few days, COD measurements have proven useful for control and operation of wastewater/sewage treatment plants.

Total Organic Carbon (TOC)

The total organic carbon test has been developed as an extremely rapid, simple alternate to BOD/COD. In this test, the sample is acidified, aerated, and then a measured quantity is injected into a high temperature furnace. The organic material is oxidized to carbon dioxide and water. The quantity of carbon dioxide produced is measured by use of a gas chrometograph.

Total Oxygen Demand (TOD)

The total oxygen demand test is an alternative to the TOC, the measurement being the consumption of oxygen from the air in a platinum-catalyzed combustion chamber into which a measured quantity of the sample has been introduced.

Theoretical Methane Production

A prediction of the quantity of methane that can be produced by a given anaerobic digestion installation is important in determining the cost effectiveness of the system. Bushwell and Mueller (1952) suggested the following formula:

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right) CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right) CH_4$$

Toerien and Hattingh (1969) in reviewing extensive research on anaerobic digestion show that the total process involving the combined acidogenic and methanogenic processes is much more complex than implied by the prediction equation. McCarty (1964) has proposed an alternate procedure based on the fact that waste stabilization by anaerobic fermentation is directly related to methane production. Consider the following equation

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Mass balance will show that for every kilo of oxygen consumed, 0.350 cubic meters of methane at standard temperature (20°C) and pressure (1 atmosphere) are required. Considering this fact in an inverted manner, if the average biological oxygen demand (BOD) and flow rate of the influent is known, the maximum possible methane (CH_4) production can be determined. Further, given the BOD of the effluent, it is possible to predict the total CH_4 produced since the mass balance equation can be interpreted as 0.350 cubic meters of CH_4 (STP) produced per kilo of BOD stabilized. This fact is useful both for predicting systems performance and for evaluating experimental results.