GRI-82/0084

MARINE BIOMASS PROGRAM: ANAEROBIC DIGESTION SYSTEMS DEVELOPMENT AND STABILITY STUDY

FINAL REPORT
(February 1-December 31, 1982)

Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, Illinois 60631

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IGT Project No. 30558

for

GAS RESEARCH INSTITUTE

Contract No. 5082-225-0607

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Biomass Research

June 1983

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. GRI-82/0084	2.	3. Recipient's Accession No.

4. Title and Subtitle
MARINE BIOMASS PROGRAM: ANAEROBIC DIGESTION SYSTEMS DEVELOPMENT AND STABILITY STUDY

5. Report Date
Published — July 1983

6.

7. Author(s)
Fannin, K.F., Srivastava, V.J., Mensinger, J.D., Chynoweth, D.P.

8. Performing Organization Rept. No.
30558

9. Performing Organization Name and Address
Institute of Gas Technology
3424 South State Street
Chicago, Illinois 60616

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C)
(G)

12. Sponsoring Organization Name and Address
Gas Research Institute
8600 West Bryn Mawr Avenue
Chiago, Illinois 60631

13. Type of Report & Period Covered
Final Report
Feb. 1 - Dec. 31, 1983

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

Marine biomass represents a significant potential worldwide energy resource that can be converted to methane by anaerobic digestion. Through efficient biomass production, harvesting, and conversion techniques, competitive methane gas costs are achievable. The objective of this research project is to develop and define an anaerobic digestion process for producing methane from giant brown kelp (Macrocystis pyrifera).

The performance of kelp in these digestion studies, in terms of loading rates, methane yields, methane production rates, and process stability is the best ever reported for particulate forms of biomass. Methane yields as high as 0.42 SCM/kg (6.8 SCF/lb) VS added were demonstrated. Upflow solids reactors (USR's) that passively retained solids longer than the liquid portion of the feed, demonstrated better overall performance than stirred tank reactors (STR's) operated at similar loading rates of up to 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day). The application of attached film reactors as part of two-phase systems was demonstrated.

Kelp continues to show superior performance as a feedstock for gas production when compared with other particulate biomass feedstocks. Further work on upflow solids reactors and two-phase reactor systems is expected to improve gas cost estimates over those made using other state-of-the-art reactors.

17. Document Analysis a. Descriptors

Marine Biomass; Methane; Anaerobic Digestion; Biomass Composition

b. Identifiers/Open-Ended Terms

Kelp; Macrocystis pyrifera; Biological gasification; Reactor designs; Loading rate; Methane yield; Organic and inorganic composition

c. COSATI Field/Group 21/21D

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Release Unlimited	Unclassified	149
	20. Security Class (This Page) Unclassified	22. Price

RESEARCH SUMMARY

Title: Marine Biomass Program: Anaerobic Digestion Systems Development and Stability Study

Contractor: Institute of Gas Technology
GRI Contract No. 5082-225-0607

Principal Investigators: K. F. Fannin and D. P. Chynoweth

Report Period: February 1-December 31, 1982
Final Report

Objective: This research is part of an overall program designed to determine the technical and economic feasibility of large-scale commercial production and harvesting of giant brown kelp (Macrocystis pyrifera) in the open ocean and its conversion to methane and valuable by-products. The objective of this research project is to develop and define an anaerobic digestion process for producing methane from kelp and evaluate microbiological and chemical factors affecting process stability.

Technical Perspective: Marine biomass offers a potentially vast renewable energy resource for countries throughout the world with substantial coastal regions. In the United States, for example, the area available for growth of marine plants in coastal waters, including Alaska and Hawaii, has been estimated to be about 2.3 million km^2 (908,000 square miles) or about 58×10^7 acres. If one assumes a growth yield of 5 kg/m^2 (20 dry tons per acre) per year and a heating value of 10 MJ/kg (9×10^6 Btu/ton), that area could produce a biomass gross energy equivalent of about 100 quads/year.

The success of a large-scale energy-from-marine biomass system will, however, be determined by the technical and economic feasibility of ocean farming and stable biological gasification processes for conversion to methane and other valuable products. To develop and determine the feasibility of these processes, GRI is conducting a comprehensive research program.

Results: The performance of kelp in these digestion studies, in terms of loading rates, methane yields, methane production rates, and process stability, is the best ever reported for particulate forms of biomass. Solids retention time (SRT) was shown to have a marked effect on the methane yield during the anaerobic digestion of kelp when below about 30 days. Methane yields as high as 0.42 SCM/kg (6.8 SCF/lb) VS added were, however, demonstrated at hydraulic retention times (HRT's) and SRT's of about 200 days in a mesophilic stirred tank reactor. This methane yield was about 81% of the

stoichiometric theoretical yield attainable with the kelp lot studied. Longer SRT's but shorter HRT's were achieved at specified loading rates and reactor sizes in upflow solids reactors (USR's) than in stirred tank reactors (STR's). USR's passively retained solids longer than the liquid portion of the feed.

USR's were studied to determine the effect of increasing kelp loading rates on methane yields. Using USR's organic loading rates of as high as 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day) and methane production rates of more than 3.3 vol/vol-day were achieved. The performance of these reactors was extremely stable and good materials balances demonstrated good recovery of the organic feed solids in the liquid effluent and gas.

A fluidized bed reactor (FBR) was operated as a second-stage digester on the effluent from a USR receiving kelp at a loading rate of 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day). The effective loading rate in the FBR was 4.5 kg VS/m^3-day (0.28 lb VS/ft^3-day) and the methane yield from the combined USR-FBR system was about 0.37 SCM/kg VS added (6.0 SCF/lb VS added). Previous data suggest that the size of the FBR can be further decreased to optimize the system and to increase the methane production rate.

At loading rates of up to 6.4 kg/m^3-day (0.40 lb VS/ft^3-day), increasing the frequency of an STR digester from once to 25 times a day had no substantial effect on digester performance. Kelp digestion in STR's followed Monod kinetics up to a retention time of about 25 days. At longer SRT's the biodegradable substrate concentration may have been below the minimum level needed for non-limited organism growth.

The ammonia nitrogen concentration in kelp digester effluent increased with SRT. These concentrations ranged from 110 to 220 mg/L at an SRT of 7 days to 800 to 910 mg/L at an SRT of 200 days. These data suggest that the cell synthesis requirements for digesters decrease or that higher amounts of ammonia are released at longer SRT's and indicate that the effluent from such digesters may have a higher fertilizer value.

An SRT acid-phase digester was maintained and studied at a loading rate of 9.6 kg VS/,^{3}-day (0.60 lb VS/ft^3-day) with daily pH adjustment to 7.0. Volatile acids concentrations were maintained between 22,000 and 28,000 mg/L as acetic over several HRT's. Furthermore, additional studies demonstrated that the volatile acids production ability of bacteria could be maintained even in the presence of volatile acids concentrations as high as 50,000 to 60,000 mg/L as acetic in an adapted culture.

The fraction of the theoretical methane yield achieved experimentally with kelp was found to increase logarithmically with the mannitol content. The organic composition of kelp

can vary substantially, depending on the conditions of growth and harvest. Mannitol and algin are two important organic components whose concentrations in kelp are somewhat inversely related. There was a correlation between the percent of the theoretical methane yield achieved experimentally and the mannitol content of kelp at 35°C and 15 to 18-day SRT's.

Since the theoretical methane yield of algin is substantially lower than that of mannitol, kelp lots that have higher concentrations of algin relative to mannitol can be expected to have lower methane yields. These observations emphasize the importance of controlling the growth of kelp to be used for methane production in order to maximize the mannitol and minimize the algin content. The optimum algin to mannitol ratio may, however, be determined by establishing the optimum systems costs that can be achieved using the value of both the energy and by-products from the process.

Kelp is a very promising species for large-scale methane production from renewable biomass. Although considerable progress has been demonstrated in the anaerobic digestion of kelp, further research is needed in several important areas. The design of the upflow solids reactor and a second-stage reactor needs further evaluation and optimization. These studies should include large-scale demonstration reactors to enable the evaluation of materials handling, process control, and effluent utilization options. Further work is needed on the effect of feed composition and inocula development on anaerobic digestion. In addition, different operating conditions, including two-phase digestion, may affect process performance and stability and methods for process control need further study.

Technical Approach

Studies were directed toward evaluating the performance of single- and two-stage anaerobic digestion systems at high loading rates and studying factors affecting digester destabilization. Mesophilic anaerobic digestion studies were performed with giant brown kelp (Macrocystis pyrifera) in upflow solids reactors, stirred tank reactors, and in other digester designs, such as fluidized bed and upflow sludge blanket reactors as second-stage digesters, that have potential application in two-stage digester systems. The effects of several operating parameters, including solids retention time, were evaluated.

High concentrations of soluble fermentation products were promoted to evaluate their toxicity to microorganisms and to promote microbial populations with higher tolerance to these products. The potential for digester destabilization through oxygen toxicity was studied. The relationship between SRT and nitrogen required during anaerobic digestion was evaluated.

Project Implications

Kelp has continued to show superior performance as a feedstock for gas production compared with other particulate biomass feedstocks. Producing cost competitive methane from marine biomass will require innovative reactors. Development of the upflow solids reactor and two-phase reactor systems provides high methane production rates while retaining greater gas yields. Bench scale experiments performed by the Institute of Gas Technology will continue to focus on increased process stability, kelp composition effect on gas yields, and further development of two-phase systems. While precise economics are difficult to develop on bench scale reactors, these upflow reactors and two-phase reactor systems suggest improved cost performance over state-of-the-art reactors currently evaluated in methane from kelp system studies.

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INTRODUCTION

Background

Biomass may be defined as vegetation from land and water and the residues and wastes created by utilizing this vegetation. Biomass, which contains about 10 to 18 GJ of energy per dry ton (about 4500 to 8000 Btu/lb), represents a significant world wide energy resource. By some accounts, worldwide biomass production is almost 10 times the 1980 world wide energy consumption.[1] Depending on production and conversion efficiencies, biomass can be technically and economically competitive with conventional nonrenewable energy sources as a significant energy resource. Development of renewable biomass resources requires concurrent research on growth, harvesting and collection, and conversion techniques.

Marine biomass offers a potentially vast renewable energy resource for countries throughout the world with substantial coastal regions. In the United States, for example, the area available for growth of marine plants has been estimated to be about 2.3 million km^2 (908,000 square miles or 58.1×10^7 acres).[2] If one assumes a growth yield of 5 kg/m^2 (20 dry tons per acre) per year and a heating value of about 10 MJ/kg (9×10^6 Btu/dry ton), that area could produce a biomass gross energy equivalent of about 100 exajoules (quads). However, the success of a large-scale energy-from-marine biomass system will be determined by the technical and economic feasibility of ocean farming and biological gasification processes for conversion to methane and other valuable products.

The most effective method for converting biomass to usable energy forms depends to a large extent upon the physical and chemical composition of the material. Widely used processes for recovering usable energy from biomass include direct combustion, anaerobic digestion, fermentation, thermal liquefaction, and thermal gasification. Because marine biomass contains almost 90% moisture, anaerobic digestion is particularly suited to this biomass form for producing methane.

Methane production by anaerobic digestion is a process occurring widely in nature in such environments as ocean and lake sediments, marshes and wooded areas, and in the digestive tracts of animals. This process involves the biological conversion of the organic components of biomass into simple

products such as acetate, CO_2, and H_2 by a mixed population of nonmethanogenic bacteria. These products are then utilized by a mixed population of methanogenic bacteria for the production of CH_4, CO_2, and H_2O. The nonmethanogenic bacteria are a relatively hearty and fast-growing group of organisms, whereas the methanogens are fastidious and slow-growing. Because at least two very distinct groups of organisms are involved in anaerobic digestion, some investigators have proposed separating these organisms into two phases, each promoting the predominant activity of one group of organisms. Whether methane production is performed with these phases combined or separate, the process is strictly anaerobic and must be performed in the absence of air.

Controlled anaerobic digestion for the purpose of methane production and recovery is performed in specially constructed digesters or reactors. A major objective of anaerobic digestion of kelp is to produce methane gas at a low cost. Low costs require high methane yields and high methane production rates, which can be achieved through long solds retention times (SRT's), high organic loading rates, and short hydraulic retention times (HRT's). Long SRT's can be attained by reducing the loading rate or by retaining the solids but removed the liquid. This latter procedure permits both long SRT's and short HRT's.

Program Objective

This research is part of the Energy From Marine Biomass program sponsored by GRI. The objective of the overall program is to determine the technical and economic feasibility of the large-scale commercial production and harvesting of kelp (Macrocystis pyrifera) in the open ocean and its conversion to methane and valuable by-products.

Previous Work

Work Performed

The detailed results of previous work appear in eight annual and final reports[3-10] and are summarized in several publications.[11-18] These studies were conducted on a specific species, Macrocystis pyrifera, that was selected on the basis of available data on the growth and gasification of kelp. The initial studies, conducted with IGT in-house support, were directed toward characterizing kelp, developing mesophilic and thermophilic kelp digesting

cultures, evaluating pretreated feeds and anaerobic digestion at different temperatures, determining the effect of kelp storage at 4°C, evaluating the effect of particle size on anaerobic digestion, and developing an active kelp digesting inoculum. Previous studies also evaluated the anaerobic digestion performance of kelp in relation to the composition of several kelp lots; identified factors that affect methane yields, rates, and digester stability (for example, nitrogen and mannitol); evaluated various methods of kelp feed preparation and treatment on digester performance (for example, freshwater dilution, seawater dilution, no dilution, and desalting); and evaluated the effect of operating conditions on methane yields, rates, and digester stability (for example, temperature, organic loading rate, retention time, start-up culture inoculum and feeding frequency).

We also studied advanced digestion operations such as separation of microbial phases, advanced digester configurations, and specialized inocula. The goals of these studies were higher efficiencies, improved kinetics, and reduction in costs of reactor construction and operation. These studies demonstrated that high methane yields and production rates can be achieved by using a highly biodegradable kelp lot in innovative digester designs that promote high solids retention times.

Higher methane yields and production rates than previously observed in this program were recently obtained. These high yields and rates are primarily a result of using a single highly biodegradable kelp lot and unconventional digester designs that promote long solids retention times. A mesophilic conventional stirred task reactor (STR) receiving diluted kelp at a loading rate of 1.6 kg kg VS/m^3-day (0.10 lb VS/ft^3-day) and 15-day retention time exhibited a methane yield of about 0.32 SCM/kg (5.2 SCF/lb) VS added. This yield increased to about 0.35 SCM/kg (5.6 SCF/lb) VS added when undiluted kelp was studied at the same loading rate but with a higher retention time of about 50 days. Two other digester designs, upflow solids reactor (USR) and baffle flow reactor (BFR), showed still higher methane yields of about 0.37 SCM/kg (6.0 SCF/lb) VS added using undiluted kelp when also operated at a loading rate of 1.6 kg VS/m^3-day (0.10 lb VS/ft^3-day). Both of these digesters promoted longer solids retention time than hydraulic retention times. Another STR, operated at a loading rate of 3.2 kg VS/m^3-day (0.20 lb VS/ft^3-day) with frequent feeding, 40 times a day, demonstrated a lower

volatile acids concentration and a higher methane yield than did a digester receiving a once-a-day feeding. A loading rate as high as 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day) with a methane yield of 0.28 SCM/kg (4.5 SCF/lb) VS added was achieved in an STR.

Studies on acid-phase digestion demonstrated that an STR could be operated on a long-term basis at volatile acids concentrations exceeding 20,000 mg/L as acetic. The effluent from this digester was used as a feed source for methane-phase digesters. One digester, a packed bed reactor (PBR), when operated at a 10-day HRT, showed a methane production rate of 1.6 vol/vol culture-day which was about 33% higher than that observed in an STR operated under similar conditions.

The potential impact of digester scale-up and stability problems on program feasibility has not yet, however, been addressed. For example, effective anaerobic digestion has only been demonstrated at the laboratory-scale and with certain kelp lots. Scale-up feasibility should be determined in both the bioconversion and kelp growth areas. Unstable digestion, as has been demonstrated in several kelp lots, could seriously undermine program feasibility.

Additional basic and applied research is needed on the anaerobic digestion process. These basic studies should be designed to determine the conditions necessary to optimize the microbiological parameters that promote the stable high-rate performance of metabolic activities. Other studies should be performed on a) bioconversions process definition and optimization to demonstrate a positive energy balance, b) effect of kelp composition on digester stability, c) effect of reactor design on digester stability, d) methods for recovery of destabilized digesters, e) effects of kelp storage at room temperature and its effects on conversion, f) digester effluent composition and disposal and/or utilization alternatives.

Major Technical Problems Encountered

The performance of digesters operated on different kelp lots was found to be quite variable. This led to suspension of several planned experiments, designed for kinetics data acquisition and advanced digestion, until the cause of this variability could be determined. After examining several parameters, it was determined that nitrogen was a limiting nutrient in certain kelp

lots. Also, mannitol content in non-nitrogen-limited kelp appeared to substantially affect digester performance.

Previous Major Accomplishments and Significant Findings

Stable digestion was achieved with undiluted kelp having a salt content of 5%. Application of techniques to reduce the salt content or to employ dilution procedures prior to kelp digestion was found unnecessary. These findings have a significant impact on energy requirements and capital costs.

Particle size reduction below that achieved with a hammermill equipped with a 0.5 mm (0.02 in.) head did not significantly improve the biological conversion of kelp. This finding reduces the preprocessing energy requirements, which can be costly.

Several inocula derived from anaerobic marine environments did not show improved performance over an inoculum derived from digesters receiving sewage sludge and municipal wastes.

The nutrient content of kelp was found to be variable and to have a significant effect on kelp fermentation. The critical maximum C/N ratio of about 14 was found to be needed for stable digestion at 15 to 18-day hydraulic and solids retention times. More recent data, presented below indicate that the nutrient requirements of digestion are lower at longer SRT's. Since kelp nutrient content is affected by the nutrient content of the surrounding waters, some control over nitrogen content can be realized by controlling growth conditions.

Kelp mannitol content was shown to be quite variable and to have a significant effect on methane yields at 15 to 18-day hydraulic and solids retention times.

Preliminary data with an upflow solids reactor and a baffle flow reactor suggested that methane yields and culture stability were superior in these reactors compared to those with a stirred tank reactor operated under similar conditions.

Studies to determine the effect of feeding frequency on digester performance did not show any significant difference between a frequently-fed and a once-a-day fed digester at a 3.2 kg VS/m^3-day (0.20 lb VS/ft^3-day) loading rate.

An acid-phase STR digester was operated on a long-term basis at volatile acids concentrations exceeding 20,000 mg/L as acetic. Also, two methane-phase digesters, one PBR and one STR, were operated on the effluent of an acid-phase digester. Results at a 10-day HRT showed a 33% higher methane production rate in a PBR than in an STR.

Conclusions

Kelp is a highly suitable substrate for methane production by anaerobic digestion. The growth conditions of the kelp may, however, affect its composition which will, in turn, affect its performance in anaerobic digestion. Previous studies concentrated on obtaining baseline data on several kelp lots and on determining factors that limit methane yields. Preliminary studies conducted with an upflow solids reactor and a baffle flow reactor showed superior performance over conventional STR's. Further studies utilizing these innovative digestion technologies are needed. Additional factors limiting methane production rates, process stability, and process kinetics should be identified.

RESEARCH PLAN FOR THIS YEAR

Objectives

The research objectives for this program were to develop and define an anaerobic digestion process for producing methane from kelp and to evaluate microbiological and chemical factors affecting process stability. Studies in progress were specifically directed toward identifying the chemical and microbiological factors that affect methane yields, methane production rates, and process stability; evaluating and selecting a specific reactor design to be used in the process; and determining the operating conditions needed to provide optimum process stability while promoting high methane yields and production rates. The approach was to improve methane yields, methane production rates, and process stability to provide a basis for developing an economically feasible large-scale digestion system with a positive net energy balance.

Approach

Task 1. Anaerobic Digestion Process Development and Techniques Study

Based on the results obtained and the progress made during the previous contract period, the design and process development studies of anaerobic digestion systems were continued to evaluate higher organic loading rates without sacrificing methane yields. This study was focused on identifying a process that promotes longer solids retention times (SRT's) than hydraulic retention times (HRT's) and that could be operated as either a combined- or a two-phase system. Our previous studies demonstrated that the two most promising designs for further study were the upflow solids reactor (USR) and the baffle flow reactor (BFR). Because we had more experience with the USR in both combined- and two-phase digestion, this digester design was studied. Emphasis was placed on maximizing loading rates without sacrificing methane yields.

As the loading rate was increased, the amount of unreacted organics, including solids, discharged in the digester effluent increased. To recover the potential methane from the effluent and to enhance process stability, second-stage digesters were studied. One such stage, consisting of a packed bed reactor (PBR) configuration, had been previously studied in our laboratories at relatively low loading rates with high methane yields and good

process stability. The performance of this digester was expected to remain good at higher loading rates, provided solids washout from the USR first stage remained sufficiently low to minimize clogging of the support medium. When solids carryover from the first- to the second-stage digester at high loading rates resulted in clogging, the PBR was replaced by a fluidized bed reactor (FBR). As high loading rates were achieved in another USR, a second-stage upflow sludge blanket reactor (USBR) was added to that digester.

The data from these studies will be used as a basis for the design of a larger-scale experimental test unit (ETU) during a subsequent project period. The primary function of this unit would be to validate digester operation and performance data obtained in the bench-scale tests and to evaluate larger-scale equipment for chopping, slurry preparation, mixing behavior in the digester, pre/posttreatment, and dewatering. This unit would also provide sufficient effluent for evaluation of its potential animal feed and fertilizer value. The final process scheme selected as a result of these studies would be operated as an integrated ETU. Integrated operation would permit optimization of the final conceptual process design and provides a data base for a detailed systems analysis.

Stirred tank reactor (STR) kinetic studies were previously initiated to establish a data base for developing process kinetic models essential to the design and operational modes for larger-scale systems and to provide a uniform basis for comparison with performance characteristics of other feedstocks. Consequently, to provide program continuity and to maximize the benefit of previous research expenditures, studies to determine the effect of feeding frequency on the performance of the digestion process and to evaluate process kinetics in an STR were continued. A digester attached to an autofeeder was to be used to evaluate the effect of feeding frequency on methane production rates, methane yields, and digester stability by comparing its performance to that of a digester fed on a once-a-day basis at increasingly high loading rates. During this contract period, the process kinetics were evaluated.

Task 2. Anaerobic Digestion Process Stability Study

The objective of this task was to evaluate factors that affect process stability and to recommend approaches for optimizing digester start-up and recovery procedures.

Our previous studies demonstrated that volatile acids produced during digestion can inhibit the microorganism population, with resulting digester instability and potential failure. Therefore, the effect of volatile acids and other fermentation products on anaerobic digestion process stability were evaluated.

The feasibility of developing a fermentation-product-tolerant microbial population was demonstrated in our previous studies on acid-phase digestion. As the acid-forming bacterial culture was operated with volatile acids concentrations that were very close to toxic levels, the organisms appeared to become more tolerant. The volatile acids toxicity threshold appeared to increase from approximately 14,000 mg/L to about 30,000 mg/L.

Initially, the major fermentation product concentrations were determined using gas chromatography. Studies were initiated to gradually acclimatize these cultures to higher concentrations of these fermentation products. Continuation of this work in further studies may enable the development of fermentation-product-tolerant bacteria with potential application to improving anaerobic digestion process stability.

Our previous data have clearly documented that kelp compositional variability, for example, markedly affects both methane yields and digester stability. Nitrogen in forms readily utilized by bacteria is more important to process stability than the total amount of nitrogen in the system. Provided nitrogen is available in readily metabolizable forms, the total nitrogen content requirement for stable digestion may be less than that observed in our previous studies. Depending upon the cost of the nitrogen forms required, a lower total nitrogen requirement in certain nitrogen-limited kelp lots may improve the net energy balance and lower the cost of stable digester operation.

These nitrogen forms and their effect on anaerobic digestion were investigated in this study. The amino acids composition of the USR system feed and effluent were determined. This analysis determined the specific amino acids found to be utilized most substantially. Further studies to evaluate the performance of anaerobic inocula with added amino acids, ammonia, and no added nitrogen are needed for predicting performance of specific kelp lots in anaerobic digestion on the basis of chemical analyses.

Since the digestion process is anaerobic, the introduction of oxygen may cause digester instability and potential failure. The oxygen tolerance of the kelp anaerobic digestion process was determined by observing performance of agitated kelp to digesters. Based on these data, methods for reducing digester instability due to oxygen toxicity were recommended.

WORK PERFORMED DURING THIS YEAR

Materials and Methods

Digester Design

Anaerobic digestion studies were focused on reactor designs that promote retention of the kelp solids and associated microorganisms for a longer period than the kelp liquid. One reactor design, the USR, passively promoted long SRT's and microorganisms retention times through settling.[3] The USR was selected as a first-stage reactor for study at increasingly high kelp loading rates. It was anticipated that, at high kelp loading rates, an increased concentration of unreacted kelp would wash out of this first-stage USR. Consequently, different reactor configurations were evaluated as potential second-stage reactors. This included the packed-bed (PBR), fluidized bed (FBR), and upflow sludge blanket (USBR) reactors. Stirred tank reactors (STR) were also studied as either baseline digesters or used in evaluating the relative performance of the USR as one- or two-stage systems and for evaluating the effects of feeding frequency on digester performance. Additional stirred and non-stirred reactors were maintained as sources of digester inocula and for special experiments.

Upflow Solids Reactors

The USR was designed to promote the retention of microorganisms and unreacted solids through passive settling. In this configuration, the upward movement of the kelp feed through microorganisms attached to unreacted solids that were denser than water promoted increased SRT's and microorganism retention times at lower HRT's.

The USR is conceptually illustrated in Figure 1. These digesters were fed from a bottom port and the effluent was removed from a port located near the top of the reactor. Several peripheral rings were installed in the reactor to prevent feed short-circuiting. Studies were performed at 35°C in thermostatically controlled environmental chambers. The methane rate in these reactors can be increased by increasing the feed loading rate while maintaining the methane yield by promoting long SRT's but short HRT's. By removing the liquid from the digester at a faster rate than the solids, longer SRT's can be achieved without increasing the reactor size, thus reducing capital costs. These reactors are suited for poorly degradable feeds with low to high solids contents.

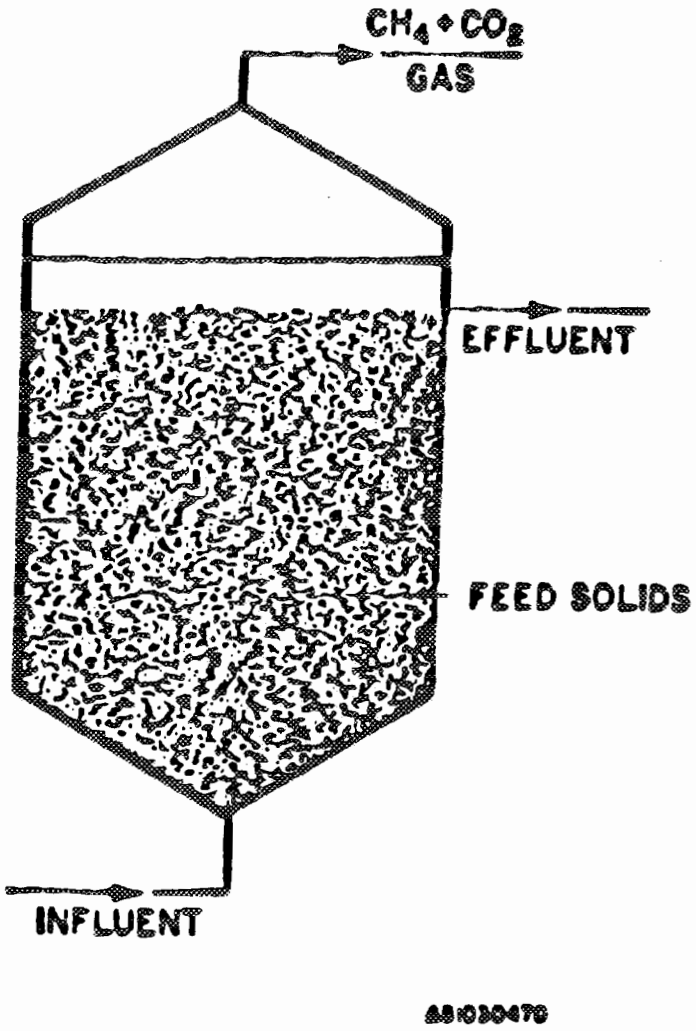

Figure 1. UPFLOW SOLIDS REACTOR

Second-Stage Reactors

Packed-Bed Reactor (PBR). Attached film reactors, such as the PBR, retain the microorganisms in the reactor while permitting the solids and the liquid portion of the biomass feed to pass through the system. This reactor contains a solid medium upon which bacteria attach, thus preventing their washout at relatively short HRT's. Consequently, these reactors are best suited for highly biodegradable feeds containing relatively low concentrations of particulate-associated solids that require short SRT's for effective conversion. The PBR, illustrated in Figure 2, consists of a filter bed filled with inert support media such as gravel, rocks, charcoal, or plastic. One limitation of the PBR is that feeds containing high concentrations of suspended solids can clog the packing medium.

The PBR used in these studies consisted of a filter bed filled with an inert support medium comprised of randomly packed porcelain raschig rings. This 4-L reactor was attached to the effluent of a USR and was fed through a bottom port using a peristaltic pump. This reactor was also maintained in a temperature-controlled environmental chamber at 35°C.

Fluidized-Bed Reactor (FBR). The FBR was another attached film reactor that also contained an inert support medium for microorganism attachment. This reactor, illustrated in Figure 3, contained a support medium of sand, which was sufficiently small and light to permit hydraulic fluidization and passage of suspended material through the reactor without clogging at total suspended solids (TSS) concentrations of less than 4%.[3] When such clogging occurred in the PBR, an FBR was substituted for that reactor. This 4-L cylindrical digester was operated as the second stage of a USR and was maintained in a 35°C temperature-controlled chamber.

Upflow Sludge Blanket Reactor (USBR). The USBR was used as a second-stage digester for a first-stage USR. The USBR, illustrated in Figure 4, employs the upward movement of soluble organic feed through a sludge blanket consisting of microorganisms and unreacted solids.[12] The liquid moves through the solids, thus promoting a longer SRT than HRT. The USR is employed with feeds containing higher amounts of particulate-associated solids. The major differences between USBR and USR digesters are that the USBR sludge solids are expanded and that a separator is needed to retain this sludge while separating the gas and liquid from the effluent. Use of a separator has not been

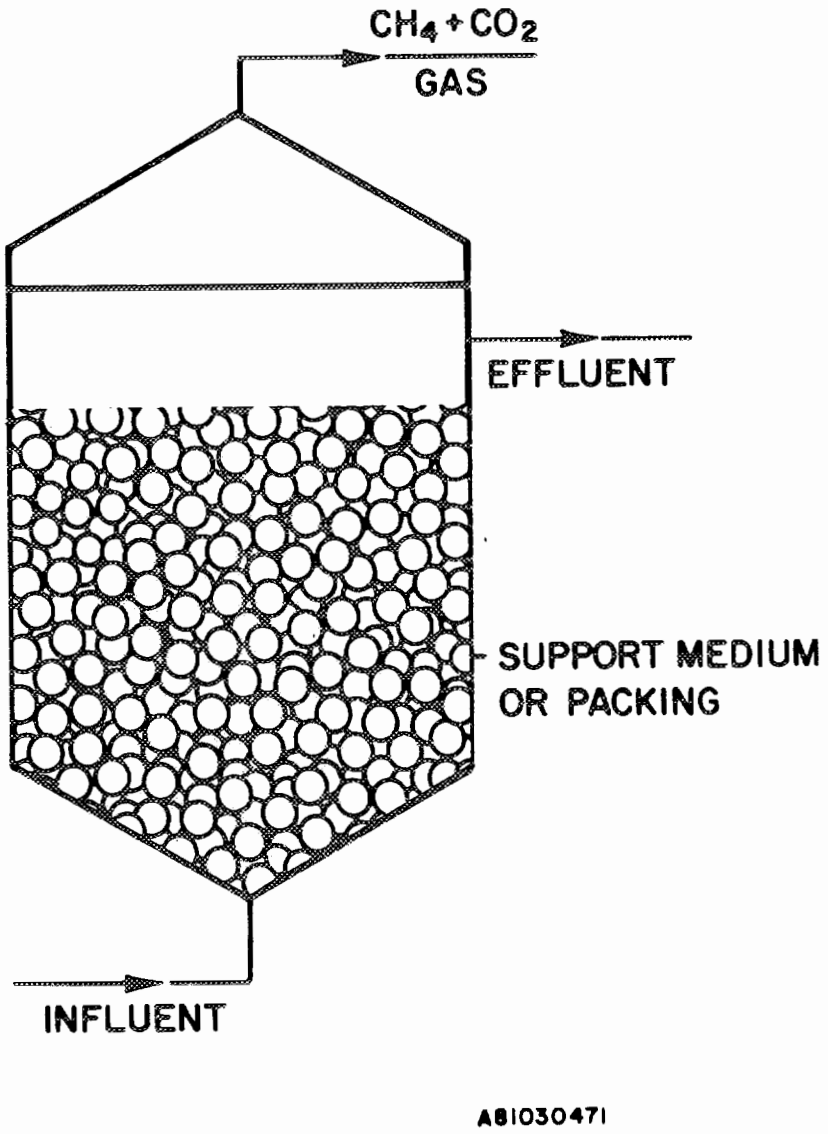

Figure 2. PACKED BED REACTOR

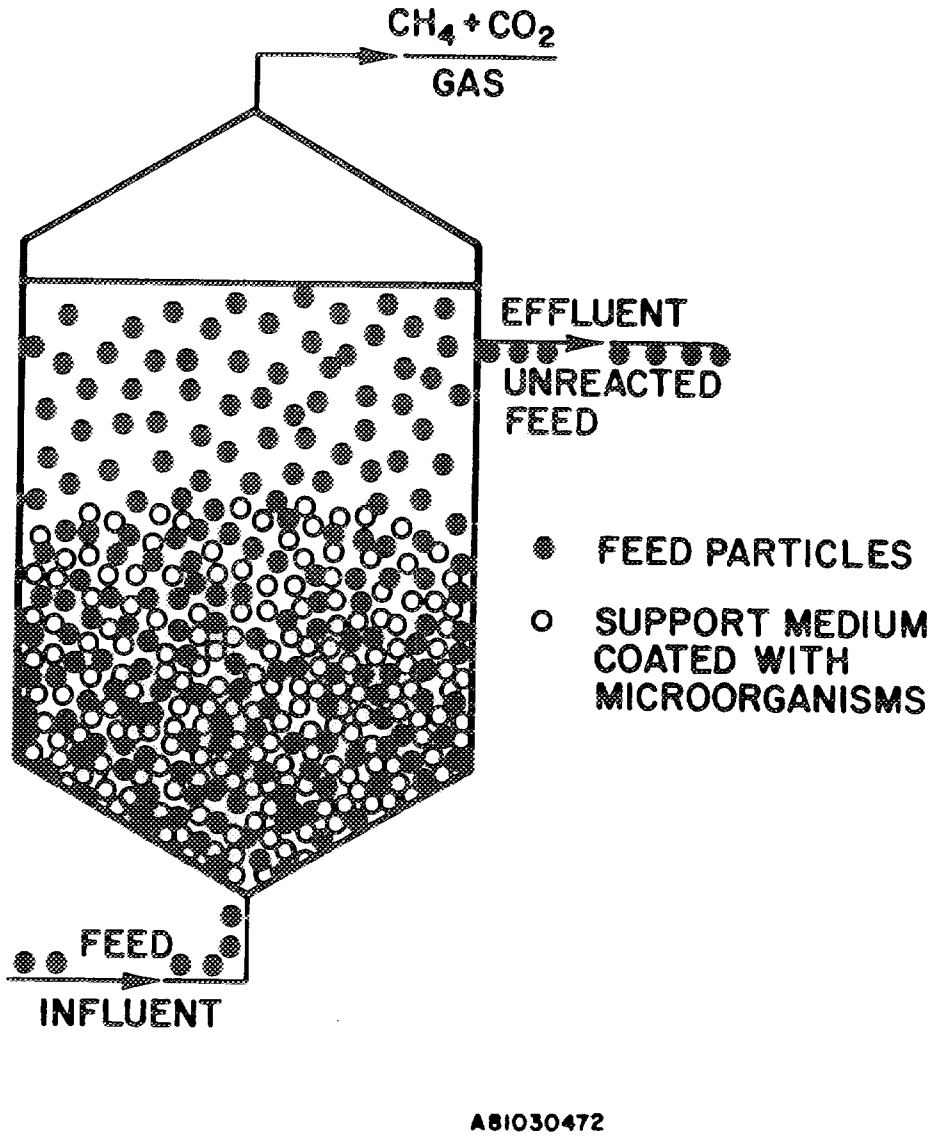

Figure 3. FLUIDIZED BED REACTOR

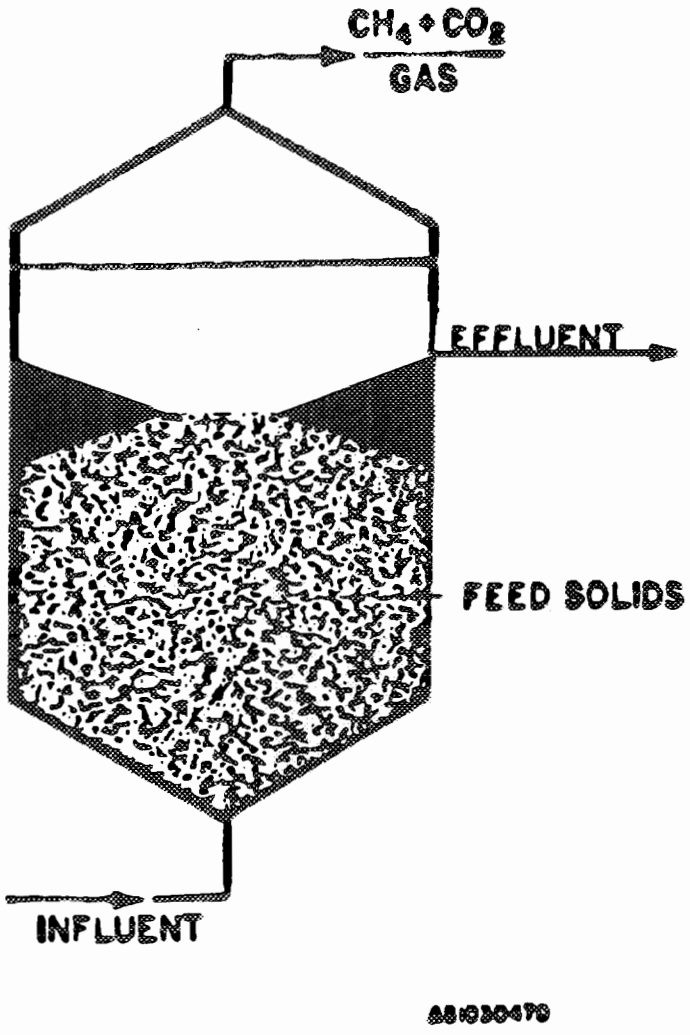

Figure 4. UPFLOW SLUDGE BLANKET REACTOR

necessary with a kelp USR since the more dense biomass solids are not expanded and help to achieve this separation.

The 6-L trapezoidal digester used in this study was not mixed mechanically, had a set of baffles to promote gas/solids separation, and was maintained at 35°C in a thermostatically controlled environmental chamber.

Stirred Tank Reactor (STR). STR's, such as the one illustrated in Figure 5, are used widely and are considered conventional for sewage sludge digestion. Reactors of this type were used in the kelp research program to establish baseline conditions for kelp digestion and to evaluate the effects of kelp compositional variability and changes in digester operating conditions on anaerobic digestion performance and stability. Their use with poorly degradable feeds, however, may be limited since such feeds require relatively long SRT's and microorganism retention times for effective degradation and high methane yields. In stirred tank reactors, long SRT's and microorganism retention times also require long HRT's and result in larger reactor sizes and higher capital costs. STR digesters can, however, be modified to include solids settling and recycle back to the digester. Conventional STR digester designs without solids recycle were used to provide baseline digestion data under selected operating conditions and to provide a basis for evaluating the performance of unconventional digester designs.

Two types of STR's were used in these studies. The first type was constructed of either Plexiglas or Corning glass, had a culture volume of 1.5 L, was shaken continuously at approximately 130 rpm by a New Brunswick gyratory shaker, and was incubated in a thermostatically controlled environmental chamber. The other STR digester type consisted of Plexiglas cylindrical tanks, had a culture volume of 5 or 7 L, was maintained at a constant temperature by heating tape connected to a temperature controller, and was mechanically mixed by propellers connected to a motor-driven shaft.

Digester Operation

Start-Up

Digesters were inoculated with a culture originally derived from a mixture of effluents from an IGT pilot-scale digester that was receiving municipal solid waste/sewage sludge and from a municipal high-rate digester that had been gradually converted, since July 1975, from a feed of municipal

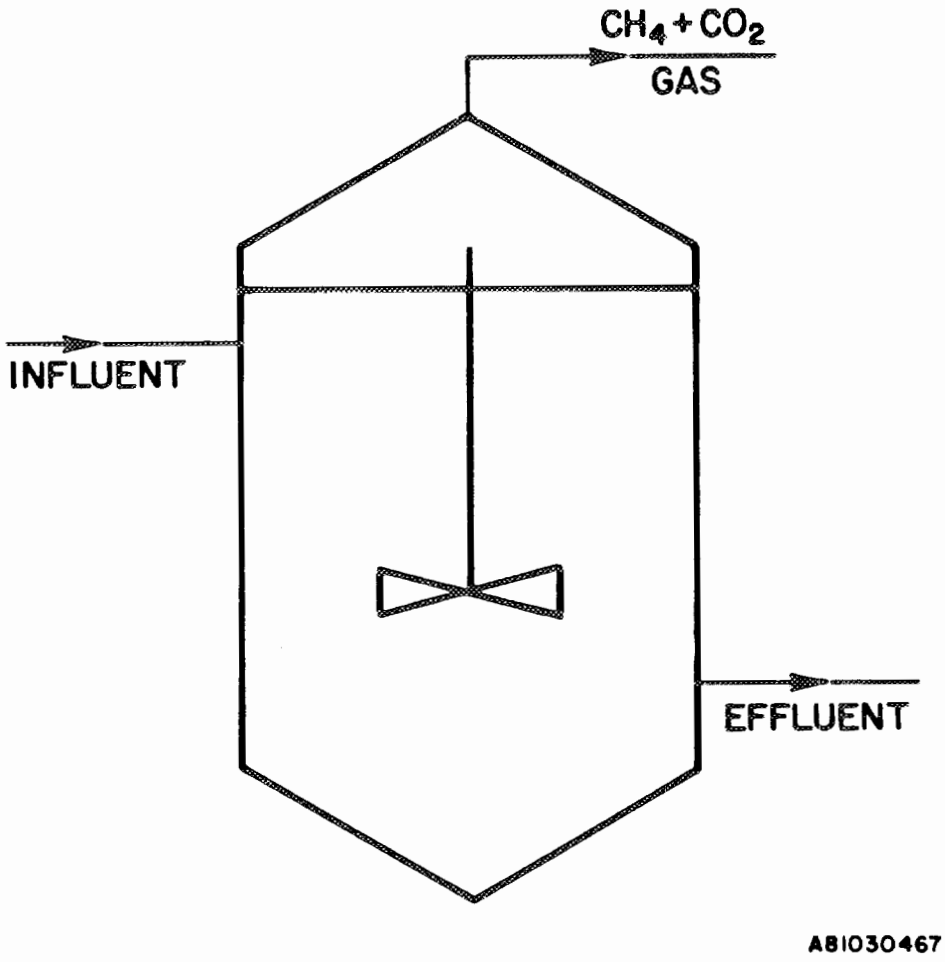

Figure 5. STIRRED TANK REACTOR

solid waste/sewage sludge to raw kelp under a variety of operating conditions. Before inoculation, each digester was pressure tested for leaks at 21 kPa (3 psig) for about 10 to 24 hours. When no leaks were detected, air was voided from the system by an oxygen-free water displacement pump. The temperature was adjusted to the experimental level using water in the digester, and the gas-collecting system was filled with an acid-salt solution and checked for gas leaks. The head-space in the digester was filled with helium and, under continuous helium out-gassing, the inoculum was transferred to the digester. The digester head-space was thoroughly out-gassed with helium to ensure the displacement of air from the system. Processed kelp was fed into the feed port and an equal volume of culture was wasted from the effluent port. Digester loading rates were gradually increased to minimize fermentation imbalance during start-up.

Feeding

With the exception of the digesters operated on autofeeders, all digesters were fed on a once-a-day basis. Before feeding, gas production was measured at atmospheric pressure, and room temperature and barometric pressure were recorded. The effluent volume at a specified loading rate was withdrawn, and the temperature and pH of this effluent were measured and recorded. A feed volume equal to that withdrawn was added to the digester. If required, the pH was adjusted to 7.0 to 7.2 with a solution of 5N NaOH and 2.5N $NaHCO_3$ or with 8N HCl.

Sampling and Monitoring

Digester performance was evaluated regularly by monitoring digester gas production, pH, volatile acids, and gas analysis (Table 1). Gas production and pH were determined daily. Gases were analyzed at least once a week to evaluate digester performance. Digester effluents were sampled for volatile acids on a weekly basis, and for total and volatile solids, total suspended solids, soluble and total carbon, as required, during stable performance. These samples were analyzed immediately or were preserved as described in Standard Methods[19] (in capped polyethylene or polypropylene bottles placed in a freezer). Selected preserved samples were analyzed as rapidly as possible to delineate trends in the digestion process and to clarify unusual digester performance.

Table 1. ANALYTICAL SCHEDULE FOR DIGESTER OPERATION

Analysis	Frequency
Gas Production Measurement	Daily
Digester Temperature	Daily
Digester Effluent pH	Daily
Volatile Acids	Weekly
Gas Composition	Weekly

Raw feeds and digester feed slurries were analyzed for total and volatile solids, heating value, elements, organics, and anaerobic giogasification potential, as required, for feed characterization and mass balance calculations.

Analytical Procedures and Performance Calculations

The analytical procedures and performance calculations are described in Appendix A. The analytical procedures include those for digester gas composition, volatile acids, hydrogen sulfide, alkalinity, conductivity, soluble carbon, moisture, volatile solids, ash, heating value, carbon, hydrogen, nitrogen, phosphorous, sulfur ammonia-nitrogen, amino acids, and biogasification potential assays. The mannitol analyses were performed by the Western Regional Research Center Laboratory (WRRC) using the periodic acid method described by Cameron, et al.[20]

The calculations for gas production, gas yield, methane yield, volatile solids reduction, STR digester contents replacement, and rate of digester feed addition are also described in Appendix A.

Retention Time Determination

The hydraulic retention time (HRT) was determined by calculating the number of days required for displacement of a fluid volume equal to that of the culture volume. When the feed was diluted, the HRT could be reduced while maintaining a constant loading rate. When undiluted feed was used, as in most of the experimental digesters used in this study, the HRT was related to the VS content of the feed and to the digester loading rate. As the VS content of the feed increased, a specified digester loading rate was maintained by adding a lower feed volume, which resulted in a longer HRT. As the digester loading

rate was increased, a larger feed volume was added to the digester, and the HRT decreased. Consequently, the HRT at a given loading rate can vary with individual kelp lots that have different VS concentrations.

The HRT and the solids retention time (SRT) in a well-mixed system, such as an STR, were the same. In such a system, the time required for replacement of the digester contents was determined by the following expression:

$$\frac{C_t}{C_o} = e^{-t/\theta} \qquad (1)$$

where —

C_t = concentration at time t
C_o = initial concentration
t = time, days
θ = retention time, days

Using such an expression, it can be determined that three retention times are needed to replace 95% of the digester contents. Based on this observation, three hydraulic retention times were considered as the minimum time required to attain steady-state operation in STR digesters.

In other systems, such as the USR, the solids were retained in the digester longer than the liquid portion of the feed, and the time required for replacement of the digester contents would not be determined by the above expression.

Provided the concentration and density of the suspended solids within the reactor and in the effluent can be determined, the SRT can be calculated as follows:

$$SRT = \frac{TSS_R * RV * D_R}{TSS_E * EV * D_E} \qquad (2)$$

where —

SRT = solids retention time, days

TSS_R = percent TSS concentration in reactor

TSS_E = percent TSS concentration in reactor effluent

RV = reactor volume (m^3 or ft^3)

EV = effluent volume per day (m^3 or ft^3 per day)

D_R = density of solids in reactor (g/mL)

D_E = density of solids in reactor effluent (g/mL)

If one were to assume a linear distribution of the solids within the reactor, then TSS_R could be estimated as the average of the TSS in the influent and effluent. Using this approach, the SRT in a USR digester operated at a loading rate of 1.6 kg VS/m^3day (0.10 lb VS/ft^3-day) was estimated to be about 300 days. This was about six times greater than the HRT. Since the assumption of a linear TSS distribution throughout the reactor may not hold, a better measure to TSS_R can be obtained by sampling a homogeneously mixed digester. Although some gas mixing occurs, the solids within the digester are not uniformly distributed and a higher concentration is present near the inlet to manually mix the digester prior to sampling. This special mixing was, however, avoided to minimize the disruption of ongoing experiments. Instead, TSS_R estimates were made from samples taken from three depths within the reactor. The TSS concentration at each sampling depth was weighted for the sample volume represented and the mean TSS concentration was determined and multiplied by the reactor volume.

Kelp Feeds Studied

Kelp harvested on three different occasions was used in this study. These kelp lots were harvested in Southern California by the U.S. Department of Agriculture, WRRC, Albany, California. Kelp Lot 53 was used in most of the experimental studies performed during this reporting period. The two remaining lots, 54 and 59, were also harvested by WRRC and were used for specific tasks and also for baseline screening studies to evaluate their performance in anaerobic digestion prior to utilization in experimental studies. All kelp lots were drained of water, chopped, ground, and frozen prior to use.

In order to evaluate the performance of each kelp lot during anaerobic digestion and to provide a basis for establishing target methane yields, the maximum theoretical yields for these kelp lots were calculated. These calculations were based on the empirical formula of each kelp lot determined from compositional analyses. Ignoring nitrogen and sulfur, and assuming that the carbon, hydrogen, and oxygen in the feed reacted with water to form CO_2 and CH_4, the following equation was used:

$$C_nH_aO_b + (n - \frac{a}{4} - \frac{b}{2})\ H_2O = (\frac{n}{2} - \frac{a}{8} + \frac{b}{4})\ CO_2 + (\frac{n}{2} + \frac{a}{8} - \frac{b}{4})\ CH_4 \qquad (3)$$

Methane yields were expressed as SCM/kg (SCF/lb) VS added.

Fresh feed slurries were prepared each day by rapidly thawing frozen cartons of feed, mixing the contents of the carton, and weighing the required amounts of each feed constituent. In the studies using diluted feed, the raw feed was diluted to the required volume with oxygen-free (purged with argon) distilled water. Thawed cartons of feed were stored at 4° to 5°C for a period of not more than 7 days. Any feed that had been thawed but not used within 7 days was discarded.

Results and Discussion

Feed Characteristics

The physical and chemical characteristics of kelp vary and are affected by the conditions of growth as well as the methods of harvesting, handling, and storage. Kelp variability, which has been documented in several previous reports and publications,[3-6,11,12,14] can have substantial effects on anaerobic digester process performance and stability. The effects of nitrogen and such organic components as mannitol have been well documented at SRT's of 15 to 18 days. Numerous unanswered questions about kelp compositional variability and its affect on anaerobic digestion, especially at longer SRT's remain unanswered.

In this study, kelp harvested on three different occassions was analyzed for major physical and chemical characteristics, shown in Table 2. The total solids (TS) content in each lot ranged from 11.8% to 12.9%. The volatile solids (VS) content, which is an estimate of the organic matter, ranged from 57.9% to 63.9% of the TS. The ash, or non-organic matter, is the residue remaining after volatilization of the VS. The ash content in these kelp lots, ranging from 36.1% to 42.1% of the TS, is higher than that of most other biomass feeds studied in anaerobic digestion. For example, the ash content of the TS, is about 13.9% to 17.9% for water hyacinth, 5.5% for napier grass, and only about 1.0% to 2.0% for hybrid poplar.[21]

Previous studies with other kelp lots have shown that the ash is composed mainly of chlorine (105,000 to 125,000 ppm), potassium (94,000 to 150,000 ppm), sodium (29,000 to 32,000 ppm), and calcium (11,500 to 16,000 ppm).[7] The

Table 2. CHARACTERISTICS OF THE KELP FEED USED DURING THE REPORT PERIOD

Kelp Feed Lot No.	53	54	59
TS, %	12.6	11.8	12.9
Moisture, %	87.4	88.2	87.1
VS, % of TS	60.2	57.9	63.9
Ash, % of TS	39.8	42.1	36.1
Elements, % of TS			
Carbon	29.8	25.7	29.7
Hydrogen	4.0	3.3	4.2
Nitrogen	2.0	2.2	1.7
Phosphorus	0.3	0.3	0.2
Sulfur	0.9	1.2	0.2
Mannitol, % of TS	21.4	15.4	18.7
Heating Value, kJ/kg dry wt (Btu/lb dry wt)	11,300 (4860)	10,100 (4340)	11,420 (4910)
Empirical Formula	$C_{2.48}H_{4.05}O_{1.65}$	$C_{2.14}H_{3.33}O_{1.59}$	$C_{2.48}H_{3.17}O_{1.76}$
Stoichiometric Methane Yield, SCM/kg (SCF/lb) VS added	0.52 (8.4)	0.44 (7.1)	0.48 (7.7)

kelp inoculum used in these studies was previously demonstrated to respond well to salt adaptation, without demonstrating inhibitory effects.[8]

The total solids and volatile solids contents of Lots 53 and 59 were similar and were higher than those of Lot 54. The nitrogen content was higher in Lots 53 and 54 than in Lot 59. The carbon-to-nitrogen (C/N) ratio in Lots 53, 54, and 59 were 11.7, 14.6, and 17.5, respectively. Our previous studies with kelp demonstrated that C/N ratios exceeding 15 were nutrient limited in baseline digestion at 15 to 18-day HRT's.[22] The mannitol contents of Lot 59 (18.7% of TS) and Lot 54 (15.4% of TS) were lower than in Lot 53 (21.4% of TS). Kelp Lot 53, which had both high mannitol and high nitrogen contents, was used for most of the experimental work reported in this study.

Task 1. Anaerobic Digestion Process Development and Techniques Study

Upflow Solids Reactor Studies

The objective of this study was to evaluate the performance of USR's to determine the feasbility of this design for process definition and scale-up for the anaerobic digestion of kelp.

Previous studies had demonstrated extremely stable kelp digestion and a methane yield of 0.37 SCM/kg (6.0 SCF/lb) VS added in USR's studied at a loading rate of 1.6 kg VS/m^3-day (0.10 lb VS/ft^3-day). The methane production rate in that digester operated under those conditions was, however, only about 0.6 vol/vol culture-day. The thrust of the work performed with USR digesters in this study was to increase the methane production rate by increasing the loading rate without proportionally decreasing the methane yield. The loading rate was increased at 1.6 kg VS/m^3-day (0.1 lb VS/ft^3-day) increments until digester destabilization was observed.

USR digesters were operated at 35°C with once-a-day feeding using undiluted kelp Lot 53 at loading rates of 3.2, 4.8, 6.4, 8.0, 9.6, and 11.2 kg VS/m^3-day (0.20, 0.30, 0.40, 0.50, 0.60 and 0.70 lb VS/ft^3-day). The USR digester was not completely mixed and solids moved through a gradient from the bottom to the top of the digester. Unreacted solids remained in the digester until they were either degraded or washed out. One consequence of retaining high concentrations of unreacted solids is that the effective reactor volume available to receive new feed substrate was reduced. Thus, the effective loading rate in the USR was increased by displacement of the culture with these unreacted solids. During this study, no measures were taken to physically remove these unreacted solids. The loading rates were, however, reported as the amount of organic matter added per total culture volume. Thus, the reported loading rates are a very conservative estimate of the actual effective loading rate. Unless measures are employed for removing unreacted solids, however, the reported values will be a reliable basis for determining reactor costs.

In this study, data were reported as steady state after three HRT's when stable digester performance and good materials balanced were observed. These conditions were achieved at kelp loading rates of 4.8, 6.4, 8.0, and 9.6 kg VS/m^3-day (0.30, 0.40, 0.50, and 0.60 lb VS/ft^3-day). USR performance at each

of the several loading rates studied was extremely stable and demonstrated good methane yields and materials balances (Appendix B).

Solids Retention Time

The SRT in USR and STR digesters at several loading rates is shown in Table 3. The data used for these determinations are presented in Appendix C. In the STR's the SRT was estimated to be the same as the HRT, which decreased from 50 to 8.5 days as the kelp loading rate was increased from 1.6 to 9.6 kg VS/m^3-day (0.10 to 0.60 lb VS/ft^3-day). In the USR, on the other hand, the SRT exceeded the HRT by about 2.7 to 3.8 times at loading rates ranging from 4.8 to 9.6 kg VS/m^3-day (0.30 to 0.60 lb VS/ft^3-day).

Table 3. SOLIDS AND HYDRAULIC RETENTION TIMES IN USR AND STR AT SEVERAL LOADING RATES USING KELP LOT 53

Loading Rate, kg VS/m^3-day (lb VS/ft^3-day)	Hydraulic Solids Retention Time, USR and STR	Solids Retention Time, USR	Solids Retention Time, STR
	days	days	days
1.6 (0.10)	50	*	50
3.2 (0.20)	25	*	25
4.8 (0.30)	17	66	17
6.4 (0.40)	12	45	12
9.6 (0.60)	10	28	10
11.2 (0.70)	8.5	23	8.5

*Not measured.

Thus, the passive settling that occurred in the USR digesters promoted longer solids than hydraulic retention times. The relationship between the SRT and the methane yield in both STR and USR digesters is illustrated in Figure 6. The SRT had an important effect on the methane yield in both digester types when below about 30 days. However, beyond about 30 days, increases in the SRT had only slight effects on the methane yield. After an

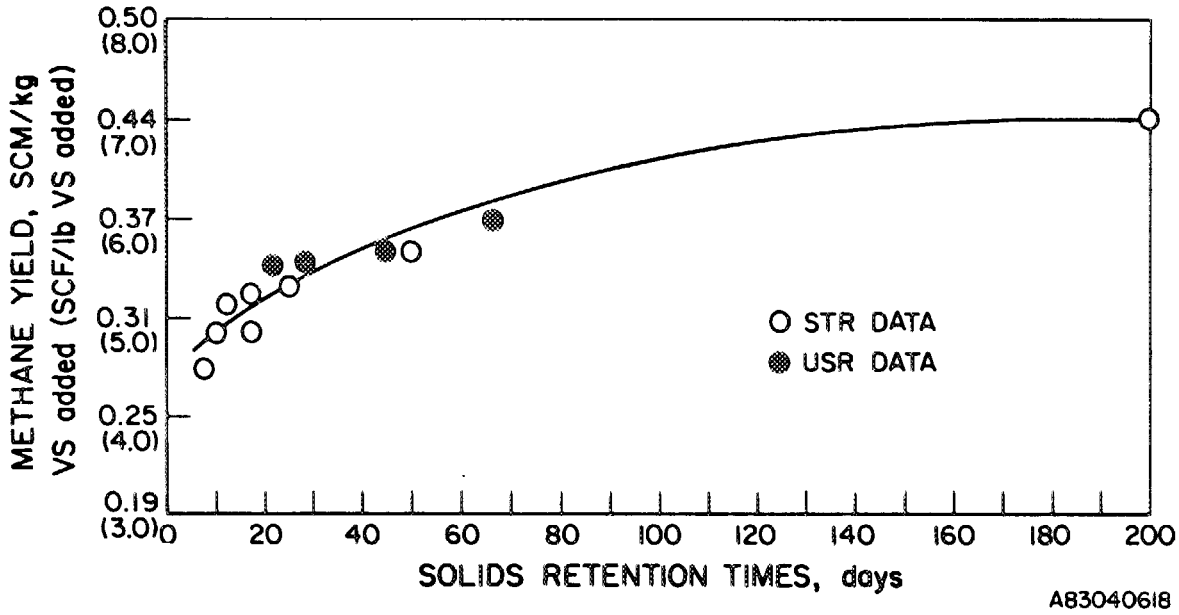

Figure 6. RELATIONSHIP BETWEEN SRT AND METHANE YIELD IN DIGESTERS RECEIVING KELP LOT 53 WITH ONCE-A-DAY FEEDING

SRT of about 200 days, however, a methane yield of about 0.42 SCM/kg (6.8 SCF/lb) VS added was achieved.

These data indicate that long SRT's are probably more important to high methane yields than the reactor design. However, in the STR digesters, the SRT was the same as the HRT, whereas the SRT exceeded the HRT in USR digesters. One important advantage of the USR over the STR digester is that high SRT's can be achieved without correspondingly larger reactor volumes and resulting capital expenditures. Thus, at similar loading rates, the SRT in the USR can be expected to be longer than that of the STR.

Reactor Performance

The performance of the anaerobic digesters was evaluated regularly by monitoring digester gas production, gas composition, pH, temperature and volatile acids. Gas production, pH and temperature were determined daily whereas the gas composition and volatile acids were determined once per week. (A few typical samples of chromatographs for gas and volatile acids analysis and computer print out for hydrogen sulfide analysis are illustrated in Appendix D.) Using these analyses as criteria, it was found that the anaerobic digestion of kelp in USR digesters was generally quite stable at loading rates ranging from 1.6 to 9.6 kg VS/m^3-day (0.10 to 0.60 lb VS/ft^3-day). Digestion in STR's under the same conditions was generally less stable, especially at higher loading rates. Steady-state data for USR and STR reactors at several loading rates are shown in Appendix B and performance curves for digesters evaluated in this study are illustrated in Appendix E.

The methane yield of the USR and STR digesters at increasing kelp loading rates is shown in Figure 7. The methane yield in the USR's exceeded that in the STR's at all loading rates studied, with the greatest difference of about 22% at the highest loading rate of 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day). The methane yield decreased from 0.37 to 0.34 SCM/kg (6.0 to 5.5 SCF/lb) VS added in the USR's and from 0.35 to 0.28 SCM/kg (5.6 to 4.5 SCF/lb) VS added in the STR's. That is, the methane yield decreased by about 24% in the STR digesters compared to only about 9% in the USR digesters as the loading rate was increased from 1.6 to 9.6 kg VS/m^3-day (0.10 to 0.60 lb VS/ft^3-day).

The methane production rates of the two digester types compared at the several loading rates studied are illustrated in Figure 8. The rate in the

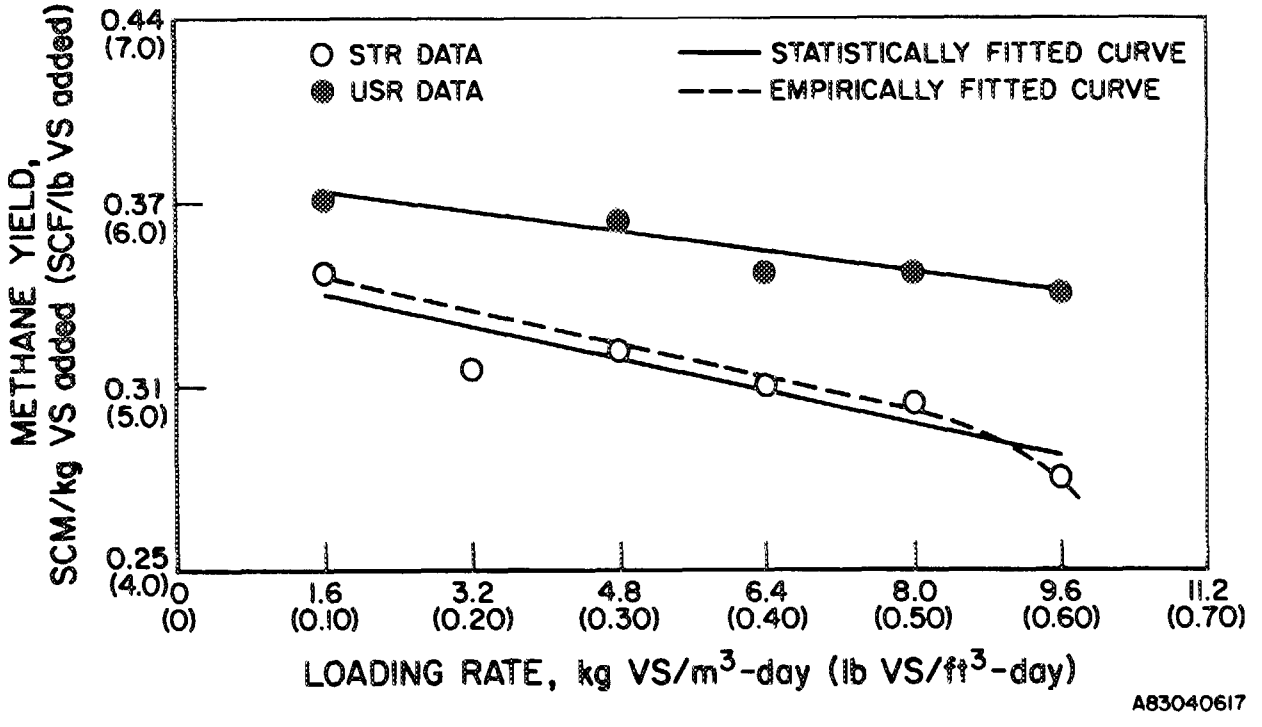

Figure 7. METHANE YIELD IN STR AND USR DIGESTERS RECEIVING KELP LOT 53, AT SEVERAL LOADING RATES

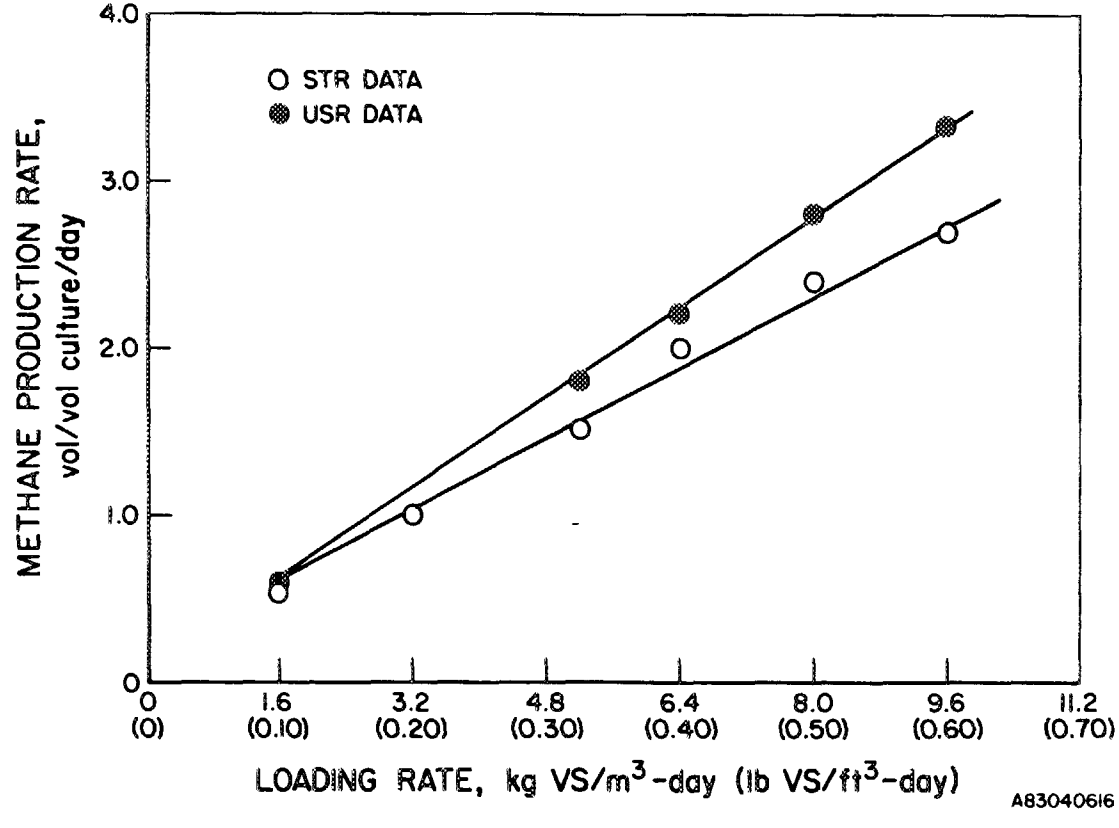

Figure 8. METHANE PRODUCTION RATE IN STR AND USR DIGESTERS RECEIVING KELP LOT 53, AT SEVERAL LOADING RATES

USR digesters increased from 0.6 to 3.3 vol/vol culture-day while that of the STR digesters increased from 0.6 to 2.7 vol/vol culture-day when the loading rate was increased from 1.6 to 9.6 kg VS/m^3-day (0.10 to 0.60 lb VS/ft^3-day). The methane production rate in the USR digesters at the highest loading rate studied exceeded that of the STR digesters by about 22%. Furthermore, that rate of the increase in methane production in the USR digesters exceeded that of the STR digesters, especially at the higher loading rates.

One important measure of digester stability is the volatile acid concentration in the digester effluent. Higher volatile acids concentrations indicate that these products of kelp hydrolysis and acetogenesis are not being converted to methane as rapidly as they are produced. Thus, a high volatile acids concentration suggests an imbalance between the number of acid- and methane-forming bacteria and greater digester instability.

The volatile acids concentrations in the USR and STR digesters at kelp loading rates ranged from 1.6 to 9.6 kg VS/m^3-day (0.10 to 0.60 lb VS/ft^3-day) and are as shown in Figure 9. At the lowest loading rate the volatile acids concentration in both the USR and STR digesters was 100 mg/L as acetic. As the loading rate in each digester was increased to 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day), the volatile acids concentration increased in the STR digesters but not in the USR digesters. The upper limit volatile acids concentrations ranged from 800 to 1800 mg/L as acetic in the STR digesters, but did not exceed 100 mg/L as acetic in the USR digesters. At the highest kelp loading rate, the volatile acids concentrations in the USR digester increased to an upper limit of 800 mg/L as acetic, but in the STR digester this level was as high as 5200 mg/L. These data clearly indicate that above a loading rate of 1.6 kg VS/m^3-day (0.10 lb VS/ft^3-day) the performance of the USR digesters was more stable than that of the STR digesters. Furthermore, although some destabilization was observed in the USR digesters at the highest kelp loading rate of 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day), significant instability occurred under similar conditions in the STR digester.

Second-Stage Reactor Studies

USR digesters promote longer SRT's and, hence, improve solids biodegradation over reactors that do not promote solids retention. However, at high loading rates the probability of additional washout of unreacted solids increases. Such washout can reduce the conversion efficiency and resulting methane yields.

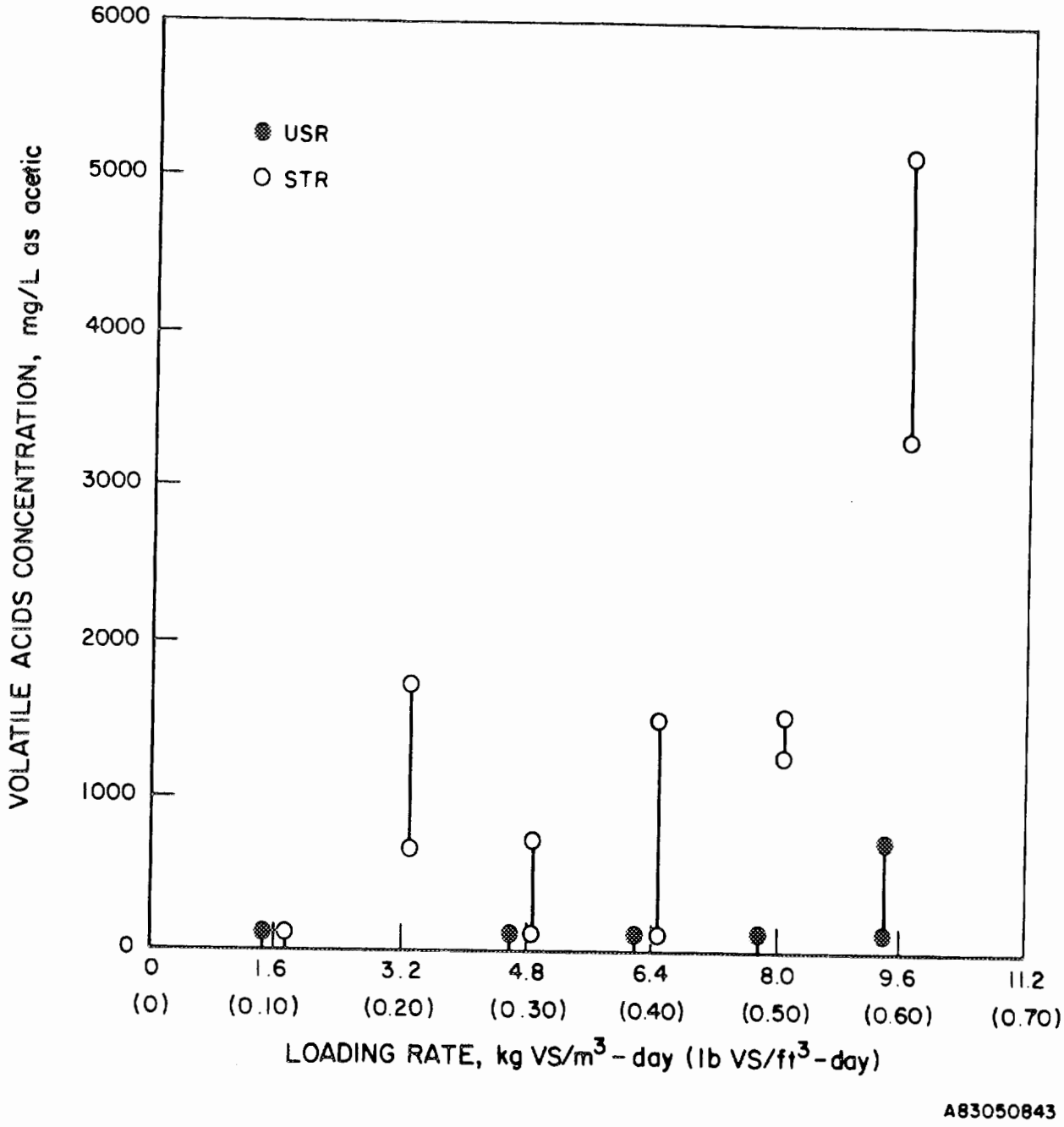

Figure 9. VOLATILE ACIDS CONCENTRATION IN USR AND STR DIGESTERS RECEIVING KELP LOT 53 AT SEVERAL LOADING RATES

One approach to recovering the methane from the unreacted residues is through the addition of second-stage reactors to the USR's. For the second-stage reactors to be effective, they need to retain microorganisms and unreacted residues for sufficient durations to increase biodegradation and methane yields. The addition of second-stage reactors can, however, reduce the overall loading and methane production rates by increasing the overall reactor size. If the kelp feed is expensive, on the other hand, it may be cost effective to improve the methane yield, even at the expense of the methane production rate. If the second-stage reactors offer such advantages as increased microorganism retention, then it is conceivable that the addition of a second-stage reactor could be used to maintain a given methane yield at a higher overall loading rate than could be achieved in a single-stage USR.

Studies conducted with IGT in-house support on fluidized bed (FBR) and packed bed (PBR) reactors demonstrated improved performance over STR's when operated under the same conditions (Appendix F). Using diluted kelp in an FBR, for example, the methane production rate was increased from 0.8 to 3.8 vol/vol culture-day as the loading rate was increased from 2.6 to 18.3 kg VS/m^3-day (0.16 to 1.14 lb VS/ft^3-day) and the hydraulic retention time was decreased from 7 days to 1 day. The methane yield was stable, ranging from 0.30 to 0.31 SCM/kg (4.8 to 4.9 SCF/lb) VS added. The digester study was terminated at an HRT of 1 day because of feed clogging. Based on available data, the HRT could have been further decreased, and the methane production rate further increased, with slight modification of the reactor design.

The PBR was fed a solution with a mixed total volatile acids concentration of approximately 25,000 mg/L. The methane production rate in this reactor increased from 1.6 to 3.8 vol/vol culture-day as the HRT was decreased from 7 days to 1 day. The methane content of the collected gas ranged from about 63 to 68 mol % over all loading rates studied.

Based on these attached-film reactor studies, PBR and FBR designs were used for two-stage reactor evaluations. It was anticipated that increased loading rates in the USR digesters would increase the probability of washout of unreacted residues that could clog the PBR digester. Hence, the FBR and another reactor design, the upflow sludge blanket reactor (USBR), that had not previously been studied in our laboratory, were used at higher kelp loading rates.

Initial studies were performed using a PBR as the second stage of a USR-PBR digestion system. The PBR second stage was intended to promote digester stability and improve conversion rates by providing a large microorganism population in the USR effluent. During these studies, USR digester instability was anticipated after the loading rate exceeded 4.8 kg VS/m^3-day (0.30 lb VS/ft^3-day). In order to promote greater digester stability at higher loading rates, the culture was recirculated between the USR and PBR stages. The USR effluent was recycled between the two stages at about 30 mL/min for approximately 8 hours/day, which represented an exchange of about 2.4 USR culture volumes/day. An effluent volume equal to that of the feed was wasted prior to the once-a-day feeding. The system was started at a loading rate of 1.6 kg VS/m^3-day (0.10 lb VS/ft^3-day) and demonstrated a methane yield of about 0.38 SCM/kg (6.1 SCF/lb) VS added and the VA concentration in this digester was very low (<100 mg/L as acetic).

When the loading rate in this interactive digestion system was increased to 4.0 kg VS/m^3-day (0.25 lb VS/ft^3-day), the effective loading rate in the first-stage USR was 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day). High gas production in the USR after the once-a-day feeding caused increased agitation of the solids within the digester. To reduce the probability of pumping system clogging, the culture was not recirculated for about 18 hours after feeding. The culture was recirculated at about 30 L/min for approximately 6 hours, resulting in an exchange of about 1.8 USR culture volumes/day. At a loading rate of 4.0 kg VS/m^3-day (0.25 lb VS/ft^3-day), as shown in Appendix G, the methane yield in the interactive system was about 0.34 SCM/kg (5.4 SCF/lb) VS added and the volatile acids concentration ranged from 100 to 800 mg/L as acetic. Culture interaction between the USR and PBR was discontinued and the system was operated as a two-stage digestion system without effluent recirculation. Following this operational change, the loading in the first-stage USR remained at 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day) and the gas collection system was modified to collect the gas from each of the two stages separately. The second-stage digester, which continued to receive the effluent of first-stage USR digesters, experienced solids clogging in the support medium.

The clogging of the PBR was caused by the suspended solids carried in the USR effluent. In order to reduce the probability for clogging the second-stage digester, the PBR was replaced by an FBR with sand at the attachment

medium. The surface area of the sand support medium was estimated to be about 9.3 to 12.1 m^2 (100 to 130 ft^2). The FBR employed had been operated previously on kelp diluted to 3.5% TS at a 1-day HRT.[3] This digester had been stored for five months at room temperature before it was placed into operation as the second stage of a two-stage system. Prior to attachment of this FBR, the loading rate in the USR was increased to 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day). The FBR digester was fed once a day by pumping the effluent directly from the first-stage USR into the FBR. After feeding, the sand support medium was fluidized by recirculating the culture through the digester at a rate of about 3.8 L/min (1 gpm).

The FBR second-stage digester demonstrated very stable performance when operated on the effluent from a USR receiving kelp at a loading rate as high as 9.6 kg VS/m^3-day (Appendix G). The effective loading rate in the FBR second-stage digester was 4.5 kg VS/m^3-day (0.28 lb VS/ft^3-day) and the combined methane yield of the USR-FBR system was 0.37 SCM/kg (6.0 SCF/lb) VS added. The HRT in the FBR digester was about 5.7 days but, based on our experience described above, it can be further decreased by reducing the reactor size relative to the USR first stage. These data suggest that the operation of the FBR as a second-stage digester can be further optimized through increasing the loading rate by decreasing the reactor size without a substantial adverse effect on the overall performance of the two-stage system.

Studies were initiated to evaluate second-stage digesters containing no added support media operated on the effluent from a USR digester. USR digestion improved the settling characterstics of the digesting kelp. The settling characteristics of the effluent were substantially better than those at a depth of 1/3 culture volume (Appendix H). Based on these observations, a second-stage USR was operated and evaluated using the effluent from a first-stage USR. The physical properties of this effluent, however, promoted entrapment of the produced gas in the second stage. This produced a buoyant sludge at the top of the digester that could not easily be wasted through the effluent ports. Instead, the liquid component of the digester was selectively wasted while the sludge-associated solids remained in the digester. The solid-gas mixture that built up in the digester was not removed through normal operations.

The operation of this digester was discontinued and a set of baffles was installed to promote gas/solids separation. Such baffles are required in soluble feed digesters, such as the USBR. After baffle installation, this digester was restarted as a second-stage digester and was operated as a USBR. This USBR, operated on the effluent from the USR receiving kelp at a loading rate of 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day), had an effective loading rate of 2.7 kg VS/m^3-day (0.17 lb VS/ft^3-day). The performance of this second-stage digester was very stable and the methane yield in the USR-USBR two-stage system is shown in Appendix H and was about 0.38 SCM/kg (6.0 SCF/lb) VS added.

Stirred Tank Reactor Studies

Effect of Feeding Frequency

Two STR's were studied at several loading rates to determine the effect of feeding frequency on the performance of the digestion process and to use the data for evaluation of STR process kinetics.

One STR was fed from a refrigerated reservoir via an autofeeder described in an earlier report.[3] Timers were used to control the frequency and duration of each feeding cycle. The other STR received feed once a day from the same feed reservoir. The performance of these digesters at a loading rate of 4.0 kg VS/m^3-day (0.25 lb VS/ft^3-day) is given in Appendix I. The methane yield in the frequently fed (45 times a day) digester was about 0.32 SCM/kg (5.3 SCF/lb) VS added compared to about 0.32 SCM/kg (5.1 SCF/lb) VS added in the feed digester fed once a day, indicating similar performance in these digesters at this loading rate.

At a higher loading rate of 4.8 kg VS/m^3-day (0.30 lb VS/ft^3-day), also shown in Appendix H, the methane yield in the frequently-fed (30 times/day) digester was about 0.36 SCM/kg (5.8 SCF/lb) VS added compared with only about 0.32 SCM/kg (5.2 SCF/lb) VS added in the once-a-day-fed digester. The loading rate in these two digesters was increased to 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day). The once-a-day-fed STR remained stable with a methane yield of about 0.31 SCM/kg (5.0 SCF/lb) VS added and a volatile acids concentration of <100 mg/L in the effluent.

Both reactors became destabilized due to equipment malfunction. Although both digesters showed substantial recovery and restabilization after

initiating corrective measures, our previous data suggest that cultural destabilization may have an effect on future digester performance. To eliminate the possible influences of culture differences on the studies comparing once-a-day and frequently fed digesters, one culture, the frequently fed digester, was split into two subcultures for continuation of this study. The frequently fed digester was anaerobically divided into two 5-L subcultures. One subculture was fed once an hour while the other was fed about once a day. Both digesters remained at a kelp loading rate of 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day) and were fed from a common refrigerated mixed reservoir. The performance of these digesters during a recovery period of approximately five retention times are given in Figure 10. It is apparent that the once-a-day-fed recovered faster than the frequently-fed digester. After completing about five to six retention time periods, both STR's became very stable. The performance of once-a-day-fed and frequently-fed digesters was almost identical whether determined prior to destabilization or after destabilization and recovery (Appendix I). Deriving the culture from a destabilized frequently-fed digester had no effect on performance. Likewise, the frequency of digester feeding after stabilization also appeared to have no effect on digester performance at this loading rate.

Kinetic Modeling of STR Kelp Digestion

The objective of this part of the study was to establish a data base for employing a kinetic model to predict 1) biodegradable effluent substrate concentration as a function of retention time, and 2) methane yield and production rate as a function of organic loading. In addition to providing data which delineate process limiting factors, these experiments provide a uniform basis for comparison of test feed digester kinetics with those of other feedstocks.

The kinetic model used was developed by Monod[23] for growth kinetics, applied to bacterial growth in continuous culture by Herbert, et al.[22] and applied to continuous stirred tank reactor digester kinetics by several investigators.[23-25] The model describes effluent substrate concentration as a function of retention time.

$$\theta = \frac{1}{\hat{\mu}} + \frac{K}{\hat{\mu}} \left(\frac{1}{S}\right) \qquad (4)$$

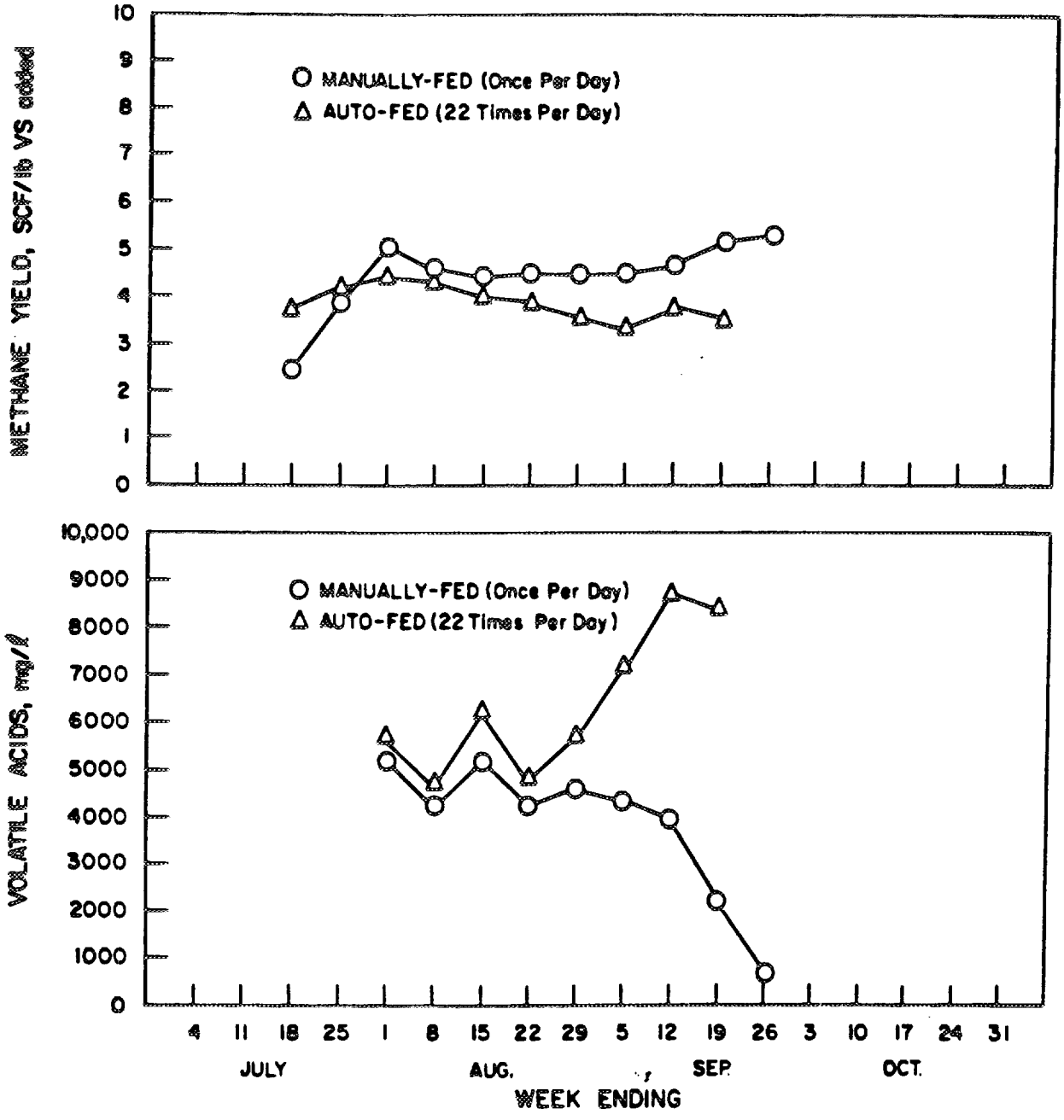

Figure 10. PERFORMANCE OF FREQUENTLY FED AND ONCE-A-DAY FED DIGESTERS AT A LOADING RATE OF 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day)

where —

θ = retention time, days

$\hat{\mu}$ = maximum specific growth rate, $days^{-1}$

K = saturation coefficient, g/L

S = effluent biodegradable substrate concentration, g/L

Experimental data required for this model are the biodegradable substrate concentration as a function of retention time.

$$S = V - V_o (1 - \beta) \quad (5)$$

where —

V_o = influent volatile solids concentration, g/L

V = effluent volatile solids concentration, g/L

β = ultimate biodegradability coefficient, decimal %

The kinetic data were determined by operating digesters on kelp Lot 53 at different loading rates ranging from 1.6 to 8.0 kg VS/m^3-day (0.10 to 0.50 lb VS/ft^3-day). The hydraulic retention times corresponding to these loading rates were 50, 25, 20, 16.5, 12.5 and 10 days. The data used for kinetic studies are given in Appendix J. The biodegradability coefficient (β) was determined by bioassay and was 0.80 for kelp Lot 53. The maximum specific growth rate ($\hat{\mu}$) and the saturation coefficient (K) was determined by plotting the inverse of effluent biodegradable substrate concentration as a function of retention time. As shown in Figure 11, the digestion of kelp followed the Monod kinetic model up to the retention time of about 25 days which corresponds to a loading rate of 3.2 kg VS/m^3-day (0.20 lb VS/ft^3-day) and is shown with the solid line. Beyond that, a deflection from the straight line occured, as expected, when the biodegradable substrate concentration fell below the minimum concentration required for the organism to reproduce.[23,22]

Since the kinetic parameters depend on the growth rate of microorganisms, microorganism concentration in the digester, and the biodegradable substrate concentration in the digester, a deviation from the straight line at low loading rates was anticipated. However, the part of the plot showing the digester performance at low loading rates (shown with the dotted line) cannot be considered to describe the performance of the digester at a normal range of loading rates, 3.2 to 8.0 kg VS/m^3-day (0.20 to 0.50 lb VS/ft^3-day). Using the data which follow the model, a maximum specific growth rate of 1.72/day

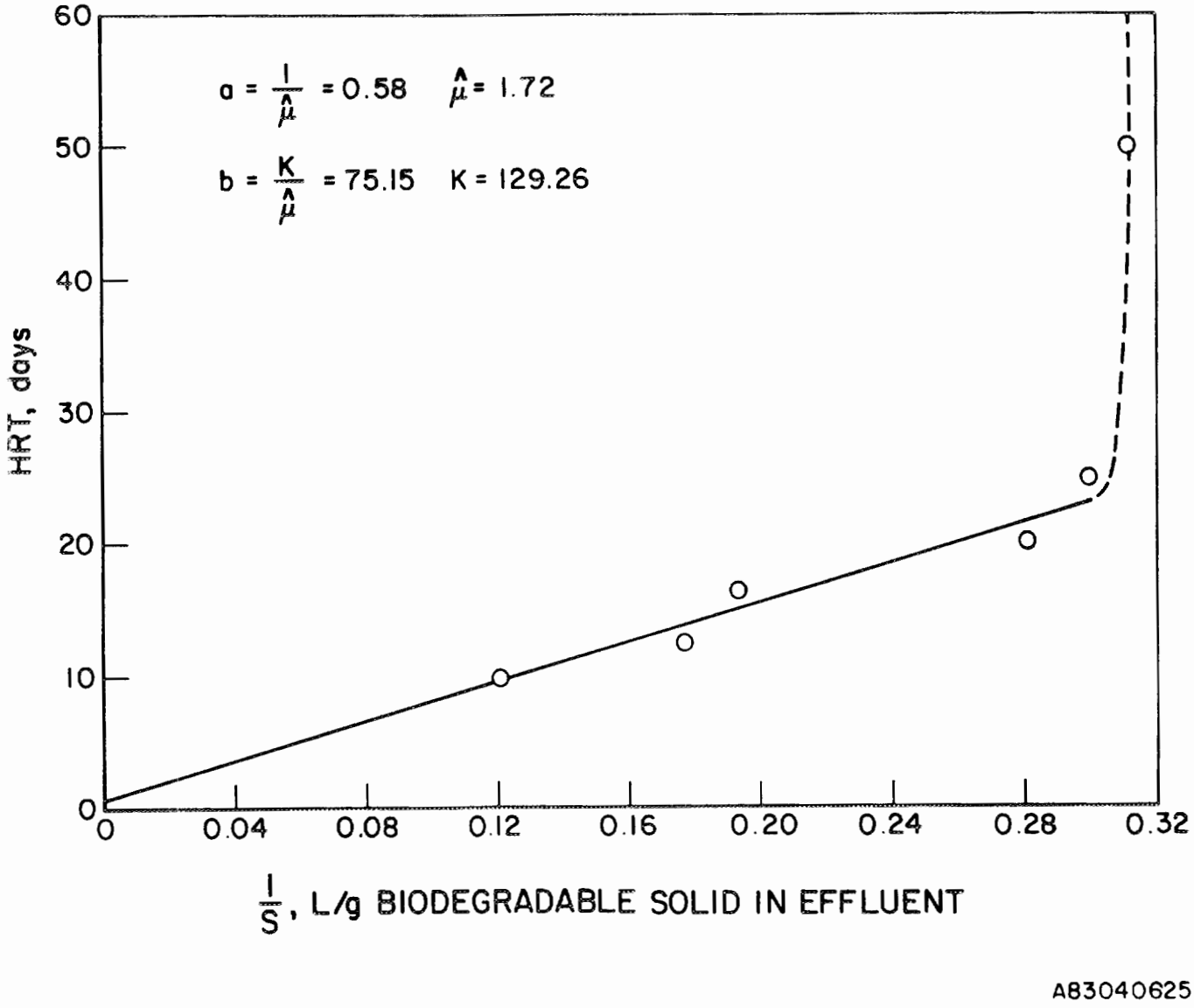

Figure 11. BIODEGRADABLE EFFLUENT SOLIDS CONCENTRATION AT SEVERAL HRT'S

and a saturation coefficient of 129.3 kg/m^3 (or g/L) was obtained for kelp digestion in the STR. Table 4 gives the kinetic parameters developed during this study.

A major focus of our research was to optimize the anaerobic digestion process for the production of methane. Accordingly, the goal was to maximize methane yields and methane production rates. Using Equations 4 and 5, an equation for methane yield (Y_M) and methane production rate (R_m) was developed as a function of organic loading. Appendix J shows the derivation of equations for methane yield, as follows:

$$Y_m = \frac{R_m}{L_o} = \alpha \left[\frac{S_o \hat{\mu} \theta - (S_o + K)}{L_o \theta^2 \hat{\mu} - L_o \theta}\right] \quad (6)$$

where —

Y_m = methane yield, L/g VS added

L_0 = loading, g VS/L culture volume-day^{-1}

α = methane yield coefficient, L CH_4/g biodegradable substrate

and methane production rate, as follows:

$$R_m = \alpha \left[\frac{(S_o \hat{\mu} \theta) - (S_o + K)}{\theta^2 \hat{\mu} - \theta}\right] \quad (7)$$

where —

R_m = methane production rate, vol CH_4/vol culture-day

α = methane yield coefficient, L CH_4/g biodegradable substrate

S_0 = influent biodegradable substrate concentration, g/L = V_0 (β)

Equations 6 and 7 can be further simplified by putting the values of α, $\hat{\mu}$ and K given in Table 4. Thus, Equations 8 and 8 can be used to calculate the methane yield 0.06 SCM/kg (1.0 SCF/lb) VS added and the methane production rate (vol/vol culture-day).

$$Y_M = \alpha \left[\frac{16.02\ \beta\theta^2 \hat{\mu} - (16.02\ \beta\theta + K/L}{\hat{\mu}\ \theta^2 - \theta}\right] \quad (8)$$

and methane production rate (R_m), Equation (4)

Table 4. KINETIC PARAMETERS FOR KELP DIGESTION IN STR's

Maximum Specific Growth Rate ($\hat{\mu}$), $days^{-1}$	1.72
Saturation Coefficient (K), kg/m^3	129.26
Biodegradability Coefficient (β)	0.80
Methane Yield Coefficient (α), m^3 CH_4/kg Biodegradable Substrate Destroyed	0.43

$$R_m = \alpha \left[\frac{16.02\ \beta\ L\ \theta^2\ \hat{\mu} - (16.02\ \beta L\theta + K}{\hat{\mu}\ \theta^2 - \theta}\right] \quad (9)$$

where —

α = methane yield coefficient, $\frac{m^3\ CH_4}{kg\ biod.}$ substrate destroyed

θ = retention time, days

where L_o is expressed as 16.02 kg VS/m^3-day (1.0 lb VS/ft^3-day).

Task 2. Anaerobic Digestion Process Stability Study

The objective of this task is to evaluate factors that affect process stability and to recommend approaches for optimizing digester start-up and recovery procedures. This objective could be achieved by identifying the products or factors which are toxic to the microorganism and are able to imbalance the anaerobic digestion process, and studying the effect of kelp composition on its biodegradability.

Inoculum Source

The objectives of these studies were to evaluate the effect of inocula derived from two sources on kelp Lot 53 biodegradation. These studies were performed in triplicate using anaerobic biodegradability potential (ABP) assays in 250 mL serum bottles. These inoculum sources were a municipal sludge digester maintained at 35°C and a kelp inoculum stock digester maintained at room temperature. This kelp inoculum was originally derived from a mixture of the effluents from a digester receiving municipal solid waste/sewage sludge and from a municipal high-rate digester that has been fed raw kelp since 1975 under a variety of operating conditions. The ABP bioassays using each inoculum were incubated at 35°C and the results of the two 60-day bioassays are shown in Figure 12.

The 60-day methane yield was about 0.42 SCM/kg (6.8 SCF/lb) VS added using kelp inoculum and was about 0.43 SCM/kg (6.9 SCF/lb) VS added using the sludge inoculum. The maximum achievable methane yield using either inoculum was not substantially different. The rate at which high methane yields were achieved, however, was substantially higher using the sludge inoculum, which came from a digester operated at 35°C, than using the kelp-adapted inoculum, which had been maintained at room temperature. After a 6-day retention time,

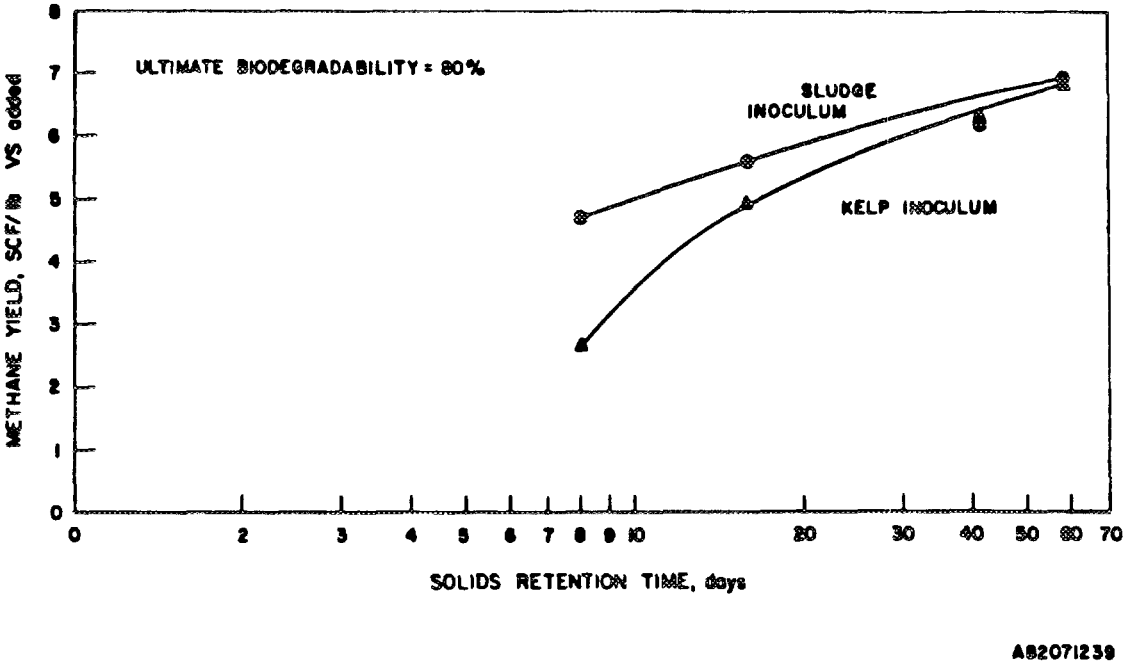

Figure 12. ANAEROBIC BIOGASIFICATION POTENTIAL OF KELP LOT 53 USING TWO INOCULA

for example, the bioassays receiving the sludge inoculum had achieved a methane yield of about 0.29 SCM/kg (4.7 SCF/lb) VS added while a yield of only about 0.16 SCM/kg (2.5 SCF/lb) VS added was attained using the kelp inoculum. About 90% of the ultimate biodegradability was achieved after 32 days in the bioassay using the mesophilic inoculum and after 36 days using the kelp inoculum. Because the kelp inoculum was developed and maintained at a lower temperature, it is likely to contain organisms growing at a slower rate. Consequently, a digester started with such an inoculum is expected to demonstrate a longer lag period before achieving maximum performance.

The ultimate biodegradability and methane yield was also calculated from a stock culture STR digester which was operated at 0.0016 kg VS/m^3-day (0.025 lb VS/ft^3-day) loading rate. The methane yield in this digester, which had an effective HRT of 200 days, was about 0.42 SCM/kg (6.8 SCF/lb) VS added. This further confirms that the ultimate biodegradability of kelp Lot 53 is about 80%.

Anaerobic Digestion Toxicity

Fermentation Products

The objectives of this experiment are to determine the composition and concentration of fermentation products toxic to anaerobic digestion and to initiate studies to develop fermentation-product-tolerant bacteria.

Studies were performed to increase the fermentation product concentrations in an anaerobic digester. An STR digester was induced to perform as an acid-phase digester by continually increasing the kelp loading rate until gas production decreased to a minimum level while the volatile acids concentration in the effluent increased to a maximum concentration. After the digester reached its maximum volatile acids concentration, the pH was adjusted during the once-a-day feeding to 7.0.

At a kelp loading rate of 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day), the feed was diluted with about 150 mL of 2.5-N sodium bicarbonate and 50 mL of 5-N sodium hydroxide solution. This dilution decreased the effective HRT from 8.5 to about 7 days. Under these operating conditions, volatile acids concentrations as high as about 40 g/L were achieved. Further, the volatile acids concentrations, shown in Appendix I, were maintained at about 22 to 28 g/L over more than 20 HRT's. As previously reported, acetic acid was the major

component of these volatile acids, followed by propionic and then butyric acids.[3]

A VS balance of this acid-phase digester (Appendix I) shows that about 92% of the feed VS was accounted for by the experimental and analytical procedures used. About 27% of the feed VS was accounted for in the gas while 65% was removed through the effluent. Of the gas, 23.4% of the VS was in the form of CO_2, while about 3.4% was in the form of methane.

Experiments were continued to study the effects of kelp fermentation products on the ability of a culture to produce high concentrations of volatile acids. A digester received kelp at a loading rate of 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day) and was supplemented with 10 g/L volatile acids as acetic. The volatile acids concentration maintained in the digester ranged from 50 to 60 g/L as acetic acid. These data indicate that the volatile-acids-producing ability of the bacteria in this culture remained despite high concentrations of their products.

Oxygen

The objective of this experiment was to determine the oxygen concentrations that promote kelp digester instability. As discussed under Task 1, significant digester instability occurred in the frequently fed digester that was operated on feed that was stored in a refrigerated mixed reservoir. The amount of oxygen trapped in the feed from this reservoir was significantly greater than that trapped in the feed stored under refrigeration without being mixed. This was determined by placing refrigerated kelp feeds from the mixed reservoir and from an unmixed container into serum stoppered bottles. Both bottles were vigorously agitated and then the oxygen content in the gas space was determined. The amount of oxygen observed in the gas over the kelp from the stirred reservoir was about six times greater than that from the bottle containing the kelp from the nonstirred reservoir. Further incubation of these bottles at 35°C for 2 hours showed that about four times as much CO_2 was produced by the feed from the stirred than from the nonstirred reservoir. These data suggest that a greater amount of oxygen was available for aerobic respiration in the kelp from the stirred reservoir.

These data indicate that a greater amount of oxygen is likely to enter the digesters fed from a mixed than from an unmixed reservoir unless such

mixing is done under anaerobic conditions. The digester performance data do suggest, however, that greater instability resulted when the digester was fed about once an hour than when fed once a day. It is also possible that during the once-a-day feeding more trapped oxygen escapes from the culture into the gaseous atmosphere, while during the more frequent feeding a greater amount of oxygen is absorbed over a 24-hour period into the culture, thus increasing oxygen toxicity and digester instability. This hypothesis of the effect of oxygen toxicity on digester performance needs further evaluation.

Effects of Kelp Composition

Nitrogen Forms

Anaerobic digestion can be unstable with low methane yields and production rates when nitrogen is limited. The amount of nitrogen required for nonlimiting cell growth depends upon the metabolic requirements of the microbial population within the anaerobic digester. Cell synthesis requirements are probably affected by the rate of microorganism washout and the need to replace these organisms for utilization of available substrate.

The amount of substrate, for example, utilized for cell synthesis is higher during very low retention times and decreases as the retention time increases. This concept was illustrated by Speece and McCarty[28] who showed that the amount of substrate required for cell maintenance increased as the retention time decreased.

Our previous studies demonstrated that nitrogen was limiting to kelp digestion when the carbon-to-nitrogen ratio in the feed exceeded 15:1.[22] The studies that verified this nitrogen requirement were performed in STR digesters operated at a 15 to 18-day retention time at a loading rate of 1.6 kg VS/m^3-day (0.10 lb VS/ft^3-day) under mesophilic conditions. If the cell synthesis requirements for digesters with shorter retention times are indeed greater than those with longer retention times, it is likely that a similar relationship exists with biologically available forms of nitrogen.

Reactors that promote longer SRT's have lower cell synthesis requirements and, consequently, lower energy and nutrient requirements. The ammonia nitrogen concentration in the effluent from both USR and STR digesters operated at 35°C at SRT's ranging from 7 to 200 days and at loading rates ranging from 0.4 to 9.6 kg VS/m^3-day (0.02 to 0.60 lb VS/ft^3-day) is

illustrated in Figure 13. The ammonia nitrogen concentration in the effluent of a stirred tank reactor operated at an SRT of about 7 days was about 110 to 220 mg/L. In a USR operated at an SRT of about 66 days, however, the ammonia nitrogen concentration was about 750 to 770 mg/L. The digester operating at an SRT of approximately 200 days had an ammonia nitrogen concentration of about 790 to 810 mg/L in the effluent. A nitrogen balance performed on a USR digester operated at a loading rate of 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day) and a 12-day HRT, for example, showed that virtually all of the feed nitrogen was accounted for in the digester effluent and gas. Almost 98% of the feed nitrogen was accounted for in the digester effluent (Appendix K).

These data indicate that the ammonia concentration in this digester was derived from sources within the feed and support the hypotheses that either the nitrogen requirements for anaerobic digestion can be reduced or additional bound ammonia nitrogen is made available by increasing the SRT. These data suggest that a lower carbon-to-nitrogen ratio may be required in feeds that are digested in reactors that promote longer SRT's and that the ammonia-enriched effluent from such reactors will have a higher value as a potential fertilizer.

Experiments were performed to evaluate the fate of the ammonia nitrogen in the effluent of a USR kelp digester. Measurements of effluent contained in an open vessel demonstrated a steady loss of ammonia upon storage at room temperature (Appendix K). In two experiments, the average ammonia nitrogen content was observed to decrease by 64%, from about 580 to 210 mg/L, after five days of storage. These experiments were repeated in a closed vessel and both total and ammonia nitrogen were measured. A slight decrease in the ammonia concentration was observed after the first day (from 520 to 490 mg/L), after which the concentration steadily increased to 540 mg/L after 5 days, and then to 560 mg/L after 10 days, but the total nitrogen content remained relatively stable.

A somewhat similar observation was made when ammonia nitrogen was run on another digester effluent stored in a closed vessel purged with different gases. One container was used as a control and not purged with any gas, the second one was purged with an 80:20 ratio of helium and oxygen and the third one was purged with an 80:20 ratio of nitrogen and oxygen. As shown in Appendix K, Table K-3, slight increases were observed in NH_3-N concentration

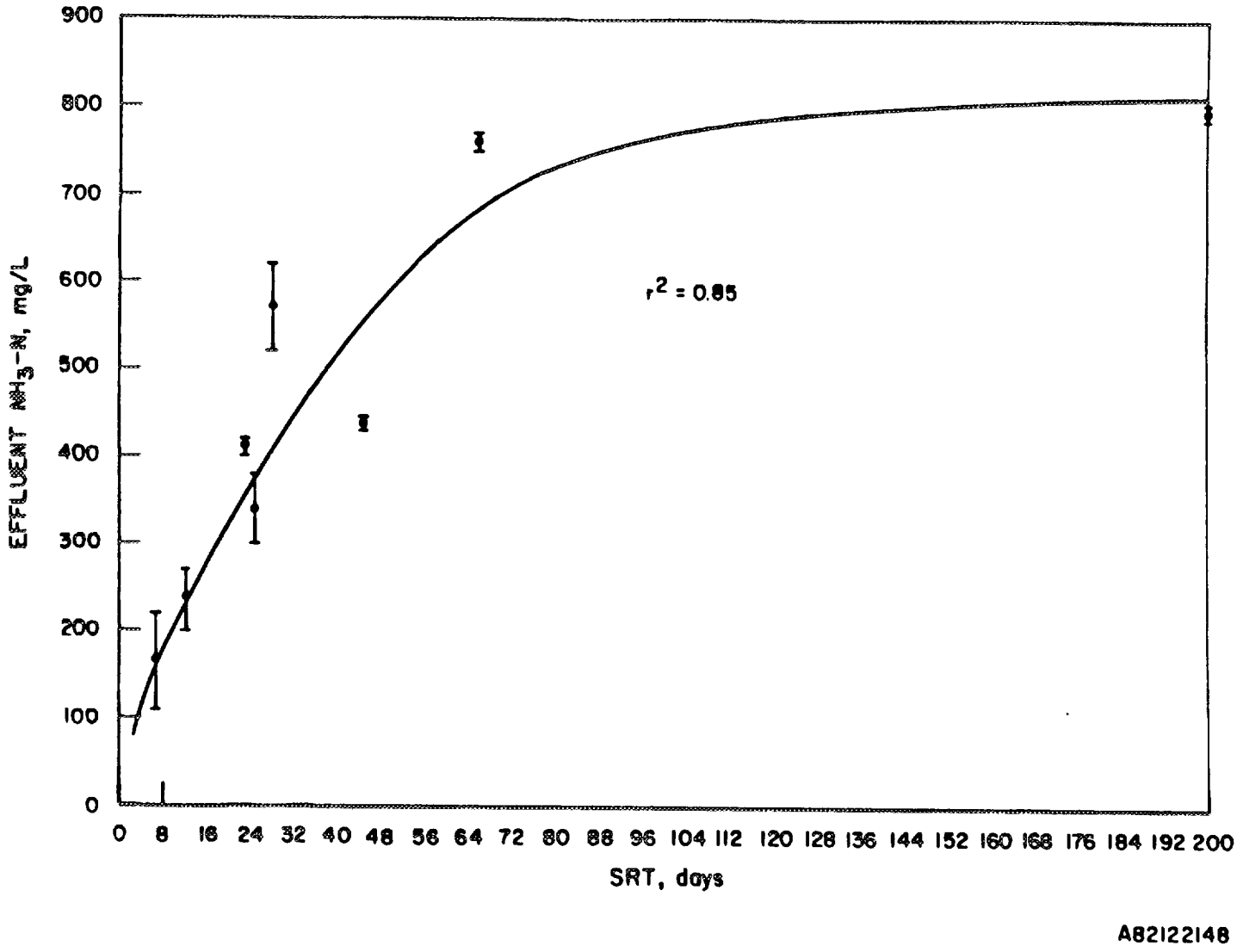

Figure 13. RELATIONSHIP BETWEEN SRT AND AMMONIA NITROGEN IN KELP DIGESTER EFFLUENT

(from 700 to 760 mg/L) over 12 days of storage whereas the total N concentration remained constant.

In order to evaluate amino acids degradation and utilization during kelp digestion, feed and effluent samples were compared to determine their relative concentrations (Appendix K). Kelp Lot 53 contained a total amino acids concentration of about 11.2 mg/g wet wt or about 9% of the TS. Glutamic acid and alanine were the most predominant amino acids in the feed at concentrations of 2.4 and 2.0 mg/g, respectively. A steady-state analysis of the effluent of a USR digester being operated on this kelp feed at a 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day) loading rate was performed. Comparing the amino acids composition in the feed to that observed in the digester effluent showed that alanine and glutamic acid were the only amino acids that were significantly reduced in concentration during digestion. Based on the relative predominance of glutamic acid and alanine and upon their relatively high percent reduction in the digester effluent, the effect of nitrogen availability in the form of these amino acids on the anaerobic digestion of kelp should be studied further.

Organic Composition

The organic composition of biomass feeds has an important impact on the biodegradability and methane yield at relatively short SRT's. The organic composition varied substantially among different kinds of biomass plants of the same species grown under different conditions. With kelp, algin and mannitol were the two major organic components. As shown in Figure 14, the relative concentrations of mannitol and algin in most kelp lots studied were somewhat inversely related. The mannitol concentration ranged from 5.2% to 24.0% while the algin concentration ranged from 12.4% to 19.5%.

Anaerobic digestion studies conducted in stirred tank reactors at a 15 to 18-day SRT and at 35°C demonstrated that the mannitol concentration in each kelp lot had a significant impact on the fraction of the theoretical methane yield that was achieved experimentally. The data were derived from kelp lots having different natural mannitol concentrations and from a single kelp lot with a natural mannitol concentration of 9.06% with supplements of added mannitol.

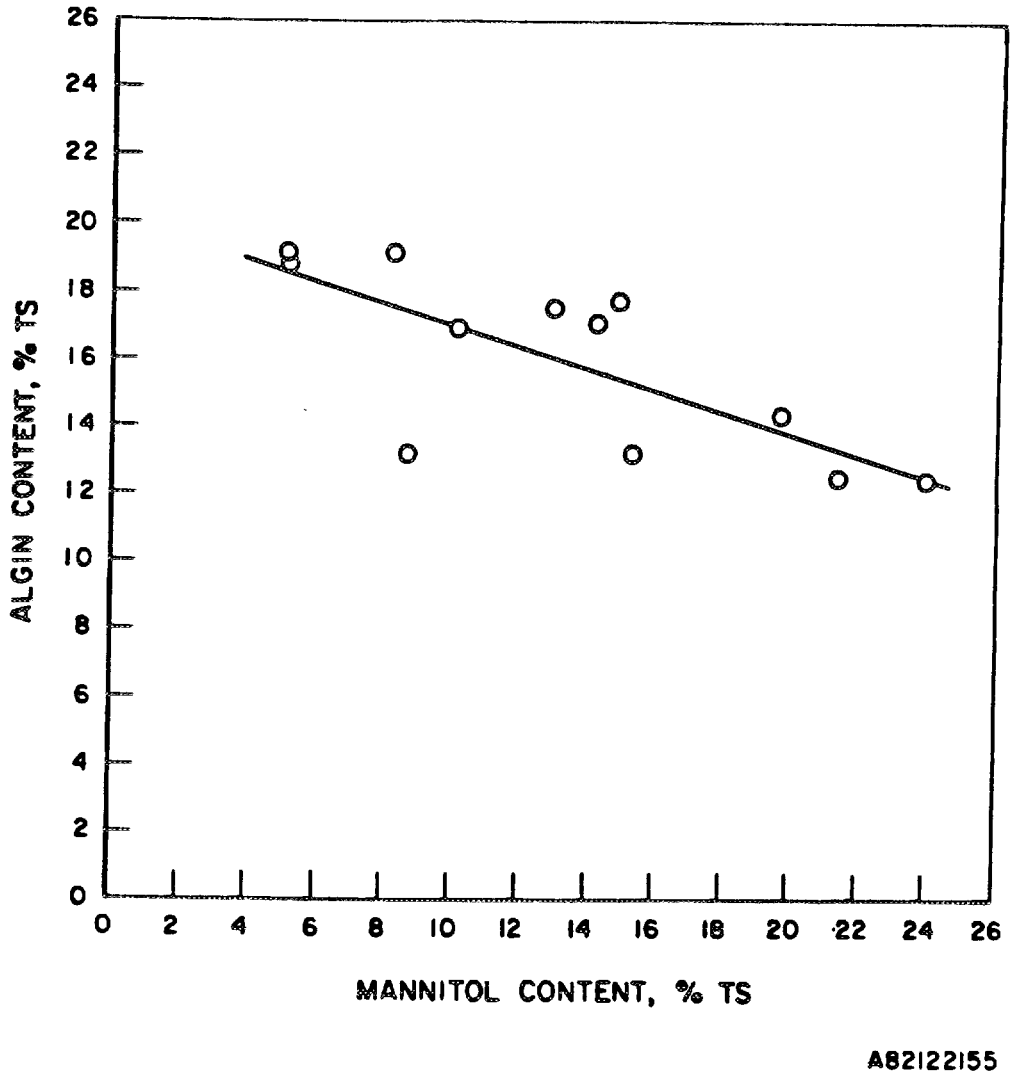

Figure 14. RELATIONSHIP BETWEEN ALGIN AND MANNITOL IN KELP LOTS USED IN ANAEROBIC DIGESTION

A log curve demonstrated with $r^2 = 0.92$ is plotted in Figure 15. The equation illustrating the relationship between mannitol concentration and methane yield is:

$$Y_E = Y_T (0.055 + 0.19 \ln X_m) \quad (10)$$

where —

Y_E = experimental methane yield, 0.06 SCM/kg (SCF/lb) VS added

Y_T = theoretical methane yield, 0.06 SCM/kg (SCF/lb) VS added

X_m = mannitol concentration, % dry wt

The fraction of the theoretical methane yield achieved experimentally increased logarithmically with the mannitol content.

The relative biodegradability of mannitol and algin was evaluated using an anaerobic biodegradability potential (ABP) assay. Figure 16 shows that both the rate of degradation and the ultimate methane yield were higher for mannitol than for algin. Within 3 days, about 58% of the 60-day methane yield was achieved with mannitol compared to only about 43% for algin. Within 20 days, about 98% of the 60-day methane yield was achieved with mannitol compared to only about 92% for algin. The calculated theoretical methane yield for algin is about 0.31 SCM/kg (4.9 SCF/lb) VS added compared to about 0.42 SCM/kg (6.7 SCF/lb) VS added for mannitol. Although the algin did degrade more slowly than mannitol, it had a lower expected methane yield and was not found to be refractory.

Since the rate of conversion of algin was slower than that of mannitol, a longer SRT is required for algin than for mannitol degradation.

Major Achievements

Solids retention time was shown to have a marked effect on the methane yield during the anaerobic digestion of kelp when below about 30 days.

Methane yields as high as about 0.42 SCM/kg (6.8 SCF/lb) VS added were, however, demonstrated at SRT's of about 200 days in a mesophilic stirred tank reactor. This methane yield is about 81% of the stoichiometric theoretical yield attainable with the kelp lot studied.

At a loading rate as high as 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day), with once-a-day feeding, a 6-L USR showed a methane yield of about 0.34 SCM/kg

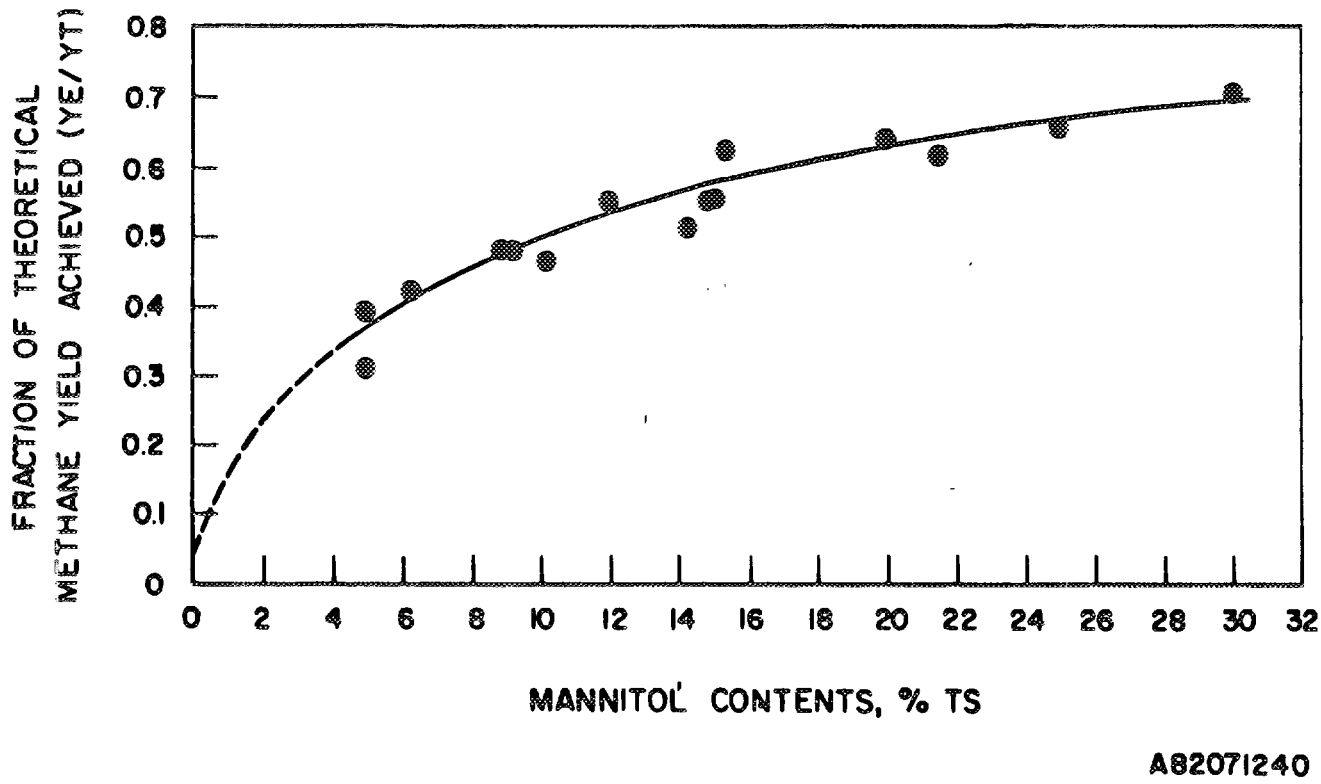

Figure 15. FRACTION OF THEORETICAL METHANE YIELD ACHIEVED EXPERIMENTALLY AT DIFFERENT KELP MANNITOL CONCENTRATIONS (15 to 18-Day SRT and 35°C)

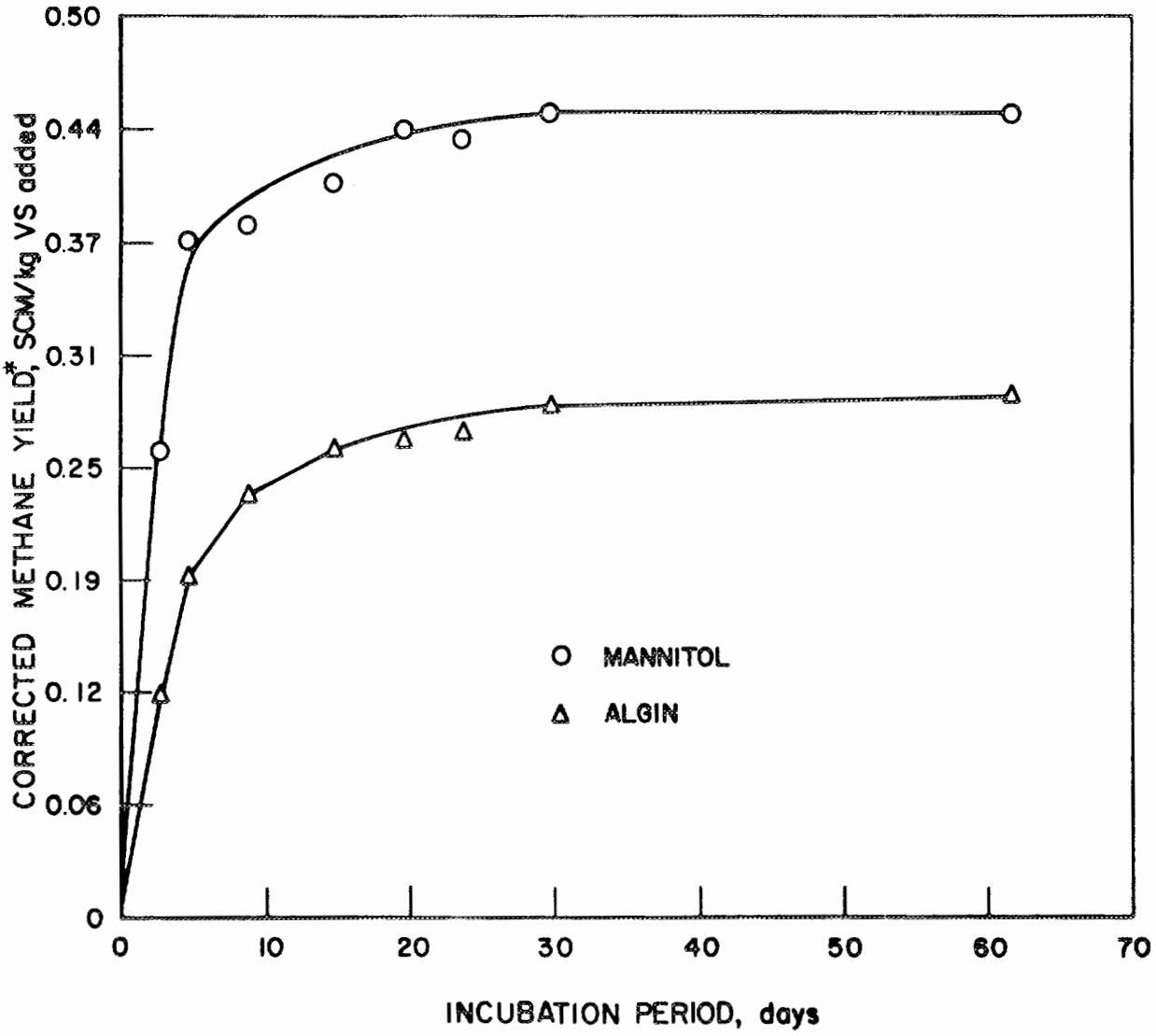

Figure 16. BIODEGRADABILITY OF MANNITOL AND ALGIN
(60 Days at 35°C)

(5.5 SCF/lb) VS added and a methane production rate of about 3.3 vol/vol culture-day.

At loading rates up to 6.4 kg/m^3-day (0.40 lb VS/ft^3-day), increasing the frequency of an STR digester from once to 25 times a day had no significant effect on digester performance.

Kelp digestion in STR's followed Monod kinetics up to a retention time of about 25 days. The kinetics profile suggested that, at longer SRT's, the biodegradable substrate concentrations were below the minimum concentration level needed for nonlimited organism growth.

An acid-phase digester was maintained and studied at a loading rate of 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day) with daily pH adjustment to 7.0. Volatile acids concentrations were maintained between 22 and 28 mg/L as acetic over several HRT's. Furthermore, additional studies demonstrated that the volatile acids production ability of bacteria could be maintained even in the presence of volatile acids concentrations as high as 50 to 60 mg/L as acetic in an adapted culture.

The ammonia nitrogen concentration in kelp digester effluent increased with SRT. These concentrations ranged from 110 to 220 mg/L at an SRT of 7 days to 800 to 810 mg/L at an SRT of 200 days. These data suggest that the cell synthesis requirements for digesters decrease or that additional ammonia is released at longer SRT's and indicate that the effluent from such digesters may have a higher fertilizer value and should be stored in closed containers to prevent ammonium volatilization.

The fraction of the theoretical methane yield achieved experimentally with kelp was found to increase logrithmically with the mannitol content.

CONCLUSIONS

Kelp is a potentially abundant, highly biodegradable biomass form that can be used in anaerobic digestion to produce methane. Long SRT's are probably more important to high methane yields than reactor design. For example, at long SRT's of 200 days under mesophilic conditions, 81% of the theoretical methane yield is attainable with kelp in STR's. Longer SRT's are, however, achievable in USR's than in STR's because the solids are passively retained longer than the liquid portion of the feed. Thus, utilization of USR designs will enable smaller reactor sizes and resultant lower capital costs. Methane yields of 0.37 SCM/kg (6.0 SCF/lb) VS added can be achieved in stable digestion. Using USR's, organic loading rates of as high as 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day) and methane production rates of more than 3.3 SCM/m^3-day (SCF/ft^3-day) can be achieved. The performance of kelp, in terms of loading rates, methane yields, methane production rates, and process stability, is among the best ever reported for particulate forms of biomass.

In addition to improved performance in terms of methane yields and process stability, longer SRT's also promote higher concentrations of ammonia-nitrogen in the digester effluent. The data suggest that the cell synthesis requirements for digesters decrease or that additional ammonia is released at longer SRT's and indicate that the effluent from such digesters may have a higher fertilizer value.

The organic composition of kelp can vary substantially, depending on the conditions of growth and harvest. Mannitol and algin are two important organic components whose concentrations in kelp are somewhat inversely related. There is a correlation between the percent of the theoretical methane yield achieved experimentally and the mannitol content of kelp digested at 35°C and at 15 to 18-day SRT's.

Since the theoretical methane yield of algin is substantially lower than that of mannitol, kelp lots that have higher concentrations of algin relative to mannitol can be expected to have lower methane yields. These observations emphasize the importance of controlling the growth of kelp to be used for methane production in order to maximize the mannitol and minimize the algin content. The optimum algin to mannitol ratio may, however, be determined by establishing the optimum systems costs that can be achieved using the value of both the energy and by-products from the process.

Kelp is a very promising species for large-scale methane production from renewable biomass. Although considerable progress has been demonstrated in the anaerobic digestion of kelp, further research is needed in several important areas. The design of the upflow solids reactor and a second-stage reactor needs further evaluation and optimization. These studies should include large-scale demonstration reactors to enable the evaluation of materials handling, process control, and effluent utilization options. Further work is needed on the effect of feed composition and inocula development on anaerobic digestion. In addition, different operating conditions, including two-phase digestion, may affect process performance and stability and methods for process control need further study.

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LIST OF ABBREVIATIONS

Abbreviations	Meaning
ABP	Anaerobic biodegradability potential
BFR	Baffle flow reactor
C/N	Carbon-to-nitrogen ratio
D_E	Density of solids in reactor effluent
D_R	Density of solids in reactor
ETU	Experimental test unit
EV	Effluent volume per day
FBR	Fluidized bed reactor
HRT	Hydraulic retention time
PBR	Packed bed reactor
RV	Reactor volume
SCF	Standard cubic foot: at 30 in Hg pressure and 60°F
SCM	Standard cubic meter: at 760 mm Hg pressure and 15.6°C
SRT	Solids retention time
STR	Stirred tank reactor
TS	Total solids
TSS	Total supsended solids
TSS_E	Percent TSS concentration in reactor effluent
TSS_R	Percent TSS concentration in reactor
USBR	Upflow sludge blanket reactor
USR	Upflow solids reactor
VA	Volatile acids
VS	Volatile solids
WRRC	Western Regional Research Center

LIST OF CONVERSION FACTORS

To Convert From	Multiply By	To Obtain
Pound (lb)	0.4536	Kilogram (kg)
Cubic foot (ft^3)	0.0283	Cubic meter (m^3)
British Thermal Unit (Btu)	1055	Joule (J)
lb VS/ft^3-day	16.02	kg VS/m^3-day
SCF/lb VS added	0.0624	SCM/kg VS added
Btu/lb	2.326	kJ/kg
Pound per square inch (psi)	6.895	Kilopascal (kPa)

APPENDIX A.
Analytical Methods and Performance Calculations

ANALYTICAL METHODS AND PERFORMANCE CALCULATIONS

Determination of Digester Gas Composition

The digester gas composition was determined using a Fisher/Hamilton Model 29 Gas Partitioner. Helium at a flow rate of 60 mL/min was used to separate the digester gas, which contains mainly carbon dioxide and methane, and sometimes carbon monoxide, nitrogen, and oxygen. This gas chromatographic method used at IGT is described in Standard Methods, 15th Ed. (1981), pp. 527-529.

Analysis of Volatile Fatty Acids

The gas chromatography procedure used for this study employs a Hewlett-Packard Model 5840 A gas chromatograph, equipped with an automatic injector. Samples and standards are prepared by addition of 0.3 mL 20% H_2PO_4 per 2 mL sample. The samples are centrifuged at 20,000 rpm for 30 min, and the supernatant is transferred to 2-mL vials sealed with crimp seal caps and then refrigerated until analysis. Gas chromatographic separation and analysis is accomplished using a 6-ft X 1/4-in. (OD) glass column packed with 80/100 mesh Chromasorb 101. Other conditions are as follows: N_2 carrier gas, 30 mL/min; H_2; 30 mL/min; air, 250 mL/min; injector, 200°C; oven 180°C; detector, 250°C. Baseline separation of acetic, propionic, isobutyric, butyric, isovaleric, valeric, and caproic acids is effected by this procedure in 15 min. Every 10 samples are followed by a 3% phosphoric acid rinse and a standard containing all seven acids. Residues accumulate after several hundred analyses on the glass wool plug of the injection side of the column. This causes baseline drift and a broad interfering injection peak. Replacement of the glass wool and reconditioning of the column at 250°C restore normal performance.

Analysis of Hydrogen Sulfide in Gas Phase

Samples of digester gas were collected using a glass gas syringe. The sample was transferred to a 56.2-μL gas sample loop attached to a Perkin-Elmer gas chromatograph equipped with a flame photometric detector. Separation was effected by a Porapak QS (80/100 mesh) in a 5-ft high X 18-in. OD Teflon-lined stainless steel column using the following conditions: He carrier, 25 mL/min; column temperature program of 35°C for 6 min at 200°C at 10°/min.

Alkalinity

The alkalinity of the digester effluent was determined by potentiometric titration to a preselected pH, 3.7 or lower. The effluent was titrated against 0.02N sulfuric acid and the alkalinity was expressed in terms of mg/L $CaCO_3$. The procedure used is described in Standard Methods, 15 Ed. (1981), pp. 253-257.

Conductivity

The conductivity of the digester effluent was determined by using a Yellow Spring Instrument Model 31 conductivity bridge. A Pyrex cell with a cell constant K = 1 was used and the result was expressed in μmhos/cm. The procedure used is described in Standard Methods, 15th Ed. (1981), pp. 70-73.

Soluble Carbon Analysis

Total carbon in aqueous samples was determined in an Oceanography International Corporation Model 05248-HR Direct Injection Module combustion instrument. The Direct Injection Module (DIM) comprised an oxygen purification train consisting of a heated cupric oxide catalyst tube, a carbon dioxide removal tube, and a flow meter. The combustion train consists of a vertically-mounted combustion tube, a sample filament, and a high-temperature internally contained combustion furnace. Carbon-containing compounds were volatilized from the sample filament without being converted to carbon dioxide, and swept into the high-temperature, internal combustion furnace area by the oxygen carrier gas (144 cm^3/min) where quantitative conversion to carbon dioxide occurred. An electronic integrator displayed a number directly proportional to the intensity and duration of the carbon dioxide passing through the IR analyzer. Particulates were removed from samples by centrifugation at 48,200 G's for 15 min, and a 50 μL sample was injected into the filament with a rapid inward movement of the syringe plunger and immediate syringe withdrawal from the septum after injection. The elapsed time required to integrate a CO_2 peak from a typical 50 μL injection was about 1 min.

A calibration curve, integrated IR units versus carbon concentration, was prepared by injections of standard solutions. The total carbon concentration of sample injections was determined by comparing integrated units of the unknown to the standardization curve.

Moisture, Volatile Solids, and Ash

Moisture was determined as the weight lost after a well-mixed sample had been dried to a constant weight in an oven at 103° to 105°C. The procedure for ash involves initiation of a dried sample at 550° ± 50°C. We start the analysis with a cold oven, bring the temperature to the specified level, and maintain it for 1 hour. Volatile solids represent the difference between dry weight and ash determined by this procedure. Experiments in this laboratory have shown that errors can result from 1) placing a sample in a hot oven, 2) higher ignition temperatures, and 3) longer ignition times. Ash is determined by the difference between dry weight and ash.

Heating Value

One-gram samples of dried feedstock were charged to the bombs of an automatic adiabatic calorimeter system, pressurized to 35 atm with oxygen, and fired. The temperature difference between firing and 13 minutes after firing was multiplied by the heat capacity (cal/°C) of the calorimeter with the particular bomb used to determine the total heat released. A fuse wire correction (cm wire burned X 2.3 cal/cm) was applied to obtain the net heat released by the sample. This net heat was divided by the sample, which was then multiplied by 1.8 to obtain higher heating value (Btu/lb).

Carbon and Hydrogen

The carbon/hydrogen analysis used is essentially ASTM Coal and Coke Procedure D-3178-2. A weighed quantity of dried sample was burned in a closed system, and the products of combustion were fixed in an adsorption train after complete oxidation and purification from interfering substances. The method gave the total percentage of carbon and hydrogen in the sample, as analyzed, including the carbon in carbonates and the hydrogen in the moisture and water in hydrated silicates. Major modifications of the ASTM method included omission of a guard tube, which was the second water adsorber, and the inclusion of an adsorption bulb containing manganese dioxide between the water and carbon dioxide adsorption bulbs for removing the oxides of sulfur and nitrogen.

Nitrogen

A scaled down (1:10) version of the ASTM Kjeldahl Method was used to determine the nitrogen content in feedstock samples. In this procedure,

nitrogen was converted to ammonium salts by destructive digestion of the sample with a hot catalyzed mixture of concentrated sulfuric acid and potassium sulfate containing 5% $CuSeO_3$ and H_2O. After decomposition of these salts in a hot alkaline solution, the ammonia was recovered by distillation and determined by titration.

Phosphorus

The sample was digested by using a wet-heated ashing procedure with nitric acid followed by perchloric acid. The rehydrated sample was filtered, and the filtrate was employed in subsequent analyses. Phosphorus was determined according to the AOAC Official Method of Analysis. After water, ammonium molybdate, hydroquinone, and solium sulfide were added, phosphorus concentration were determined calorimetrically.

Sulfur

Sulfur was determined by the Eschka Method as described in ASTM Method D-3177-75. A weighed sample and Eschka mixture (calcined magnesium oxide and anhydrous sodium carbonate) were ignited together, and the sulfur was precipitated from the resulting solution as barium sulfate. The precipitate was filtered, ashed, and weighed.

Ammonia Nitrogen

The distillation and titration procedure described in Standard Methods, 15th Ed, (1981), pp. 361-62, was used for ammonia nitrogen determinations. Samples were buffered to pH 9.5 with a borate buffer and distilled into a boric acid solution. The ammonia nitrogen concentrations were determined titrimetrically with standard 0.02N H_2SO_4.

Amino Acids

Amino acids analysis were performed by acid hydrolysis followed by gas liquid chromotography.

Biogasification Potential Assay

The procedure described by Chyncweth, et al.,[21] was used to determine the anaerobic biodegradability of kelp. The kelp feeds were weighed and quantitatively transferred to 250 mL Wheaton serum bottles prepared in triplicate. A sample of the feed was retained for solids analyses. Approximately 180-220 mg feed volatile solids were added per reactor, which provided a measurable

amount of methane (10 to 100 mL) during the incubation period. The bottles were outgassed with 30:70 volume ratio of CO_2/N_2, which was passed through a heated, reduced copper column for oxygen removal. Simultaneously, a defined nutrient medium, containing macronutrients, trace elements, and vitamins, was purged with 30:70 volume ratio of CO_2/N_2.

The seed inoculum was obtained from a sewage sludge or a stock kelp inoculum digester. The inoculum was anaerobically transferred to the outgassed nutrient medium, resulting in a tenfold inoculum dilution. While the diluted inoculum was being purged and mixed, a 100-mL aliquot was anaerobically transferred to the serum bottle containing the feedstock resulting in a feed/inoculum volatiles solids ratio of approximately one. Throughout the addition of the growth medium/inoculum to the serum bottles, samples were taken for solids analyses to ensure the introduction of similar amounts of solids into the reactors during preparation. The reactors were purged for an additional ten minutes, rubber-stoppered, crimp-sealed, and incubated at 35°C in an inverted position to minimize gas leaks.

Gas production and gas composition measurements were typically performed at 3, 7, 10, 20, 30, and 60 days. Gas production measurements were performed with a glass syringe equipped with a 20-gauge needle. The assay bottles were equilibrated to room temperature before measuring gas production. The sample syringe was lubricated with deionized water and flushed with a CO_2/N_2 mixture prior to gas reading. Gas volume determinations were made by allowing the syringe plunger to equilibrate between the bottle and atmospheric pressure. At the termination of the test period, the quantity of methane within the assay volume was added to that wasted during incubation and sampling, and the methane yield was determined.

Gas composition analysis for CO_2, N_2, and CH_4 was performed on a Fisher-Hamilton (Model No. 29) gas chromatograph. At the termination of the 60-day incubation period, the reactor contents were analyzed for pH and volatile fatty acids to check for an imbalanced fermentation and total and volatile solids concentrations to enable calculation of volatile solids reduction and effluent solids recovery. An inoculum control and a positive control (AVICEL cellulose) were incubated concurrently with each bioassay group. These analyses enabled determination of methane yield, methane production rate, volatile solids reductions, and solids material balances.

Performance Calculations

Equations for calculating the following parameters that appear frequently in this report are presented as follows:

Gas Production

$$G_{SCM} = \left(\frac{P - pH_2O}{T + 273.16}\right)\left(\frac{288.72}{762.00}\right)(Gm)\ (0.001)$$

G_{SCM} = gas production, standard cubic meter (762 mm Hg, 15.56°C)

G_m = measured gas production, L

P = atmospheric pressure, mm Hg

T = temperature, °C

pH_2O = vapor pressure of water at temperature (T), mm Hg

Gas Yield

$$Gy = \frac{G_{SCM}}{VS\ added}$$

Gy = gas yield, SCM/kg VS added

VS added = volatile solids added, kg/m^3-day

Methane Yield

My = (Gy) (Methane content)

My = methane yield, SCM/kg VS added

Methane Content = mol % of methane in the gas produced, 1/100

Volatile Solids Reduction

$$VS\ Reduction\ \% = \frac{VS_i - VS_o}{VS_i - VS_i \cdot VS_o} \times 100$$

VS_i = feed volatile solid content of total solids, % TS as decimal

VS_o = effluent volatile solid content of total solid, % TS as decimal

Replacement of Digester Contents as a Function of Time

$$\frac{C_t}{C_o} = e^{-t/\theta}$$

C_t = concentration at time t

C_o = initial concentration

t = time, days

θ = retention time, days

Conversion of Loading to Feed Weight (Wet) Added Daily

$$F = \frac{(L)(CV)}{(TS)(VS)}$$

F = wet feed weight added daily, g

L = loading, kg VS/m^3-day

CV = culture volume, L

TS = feed total solid, % of net weight as decimal

VS = feed volatile solid, % of toal solid as decimal

APPENDIX B.
USR Digester Performance Data

Table B-1. PERFORMANCE DATA AND OPERATING CONDITIONS FOR USR DIGESTER AT A LOADING RATE OF 4.8 kg VS/m^3-day (0.30 lb VS/ft^3-day) (Feed, Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	5
Data Period	8/2-9/5/82
HRT, days	17
SRT, days	66
No. HRT's in Progress	6.8
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.66 $\pm$ 0.01 (10.52 $\pm$ 0.23)
Methane Content, mol %	54.7 - 57.4
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.37 (5.9)
Methane Production Rate, vol CH_4/vol culture-day	1.8
Total Volatile Acids, mg/L as acetic	<100
Mean Caustic Added, meq/L feed	0

Table B-2. VOLATILE SOLIDS BALANCE FOR USR AT A LOADING RATE OF 4.8 kg VS/m^3-day (0.30 lb VS/ft^3-day)

	VS, g	Percent
Input		
Feed	24.03	100.0
Total	24.03	100.0
Output		
Methane	5.95	24.8*
Carbon Dioxide	12.94	53.9*
Liquid Effluent	5.58	23.2
Total Accounted	24.47	101.9
Not Accounted for by Experimental and Analytical Procedures	-0.44	-1.9
Total	24.03	100.0

*These combined products represent a 78.7% conversion of the volatile solids.

Table B-3. PERFORMANCE DATA AND OPERATING CONDITIONS FOR A USR DIGESTER AT A LOADING OF 6.4 kg VS/m^3-day (0.40 lb Vs/ft^3-day) (Feed, Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	6
Data Period	5/24-6/12/82
HRT, days	12
SRT, days	45
No. of HRT's in Progress	6.2
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.64 $\pm$ 0.04 (10.3 $\pm$ 0.6)
Methane Content, mol %	54.5-56.0
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.36 (5.7)
Methane Production Rate, vol CH_4/vol culture-day	2.3
Total Volatile Acids, mg/L as acetic	$\leq$100
Mean Caustic Added, meq/L feed	0

Table B-4. VOLATILE SOLIDS BALANCE FOR USR AT A LOADING RATE OF 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day)

	VS, g	Percent
Input		
Feed	38.04	100.0
Total	38.04	100.0
Output		
Methane	9.14	24.0
Carbon Dioxide	20.44	53.7
Liquid Effluent	6.96	18.3
Total Accounted	36.54	96.1
Not Accounted for by Experimental and Analytical Procedures	1.50	3.9
Total	38.04	100.0

Table B-5. PERFORMANCE DATA AND OPERATING CONDITIONS FOR USR DIGESTER AT A LOADING RATE OF 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day) (Feed, Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	6
Data Period	8/9-8/29/82
HRT, days	10
SRT, days	28
No. of HRT's in Progress	6.2
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.64 $\pm$ 0.04 (10.2 $\pm$ 0.60)
Methane Content, mol %	54.9 - 56.3
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.35 (5.6)
Methane Production Rate, vol CH_4/vol culture-day	2.8
Total Volatile Acids, mg/L as acetic	<100
Mean Caustic Added, meq/L feed	0

Table B-6. VOLATILE SOLIDS BALANCE FOR USR AT A LOADING RATE OF 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day)

	VS, g	Percent
Input		
Feed	48.05	100.0
Total	48.05	100.0
Output		
Methane	11.42	23.8*
Carbon Dioxide	25.00	52.0*
Liquid Effluent	13.80	28.7
Total Accounted	50.22	104.5
Not Accounted for by Experimental and Analytical Procedures	-2.17	-1.45
Total	48.05	100.0

*These combined products represent a 75.8% conversion of the volatile solids.

Table B-7. PERFORMANCE DATA AND OPERATING CONDITIONS FOR USR DIGESTER AT A LOADING RATE OF 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day) (Feed, Kelp Lot 53; Temperature, °C)

Culture Volume	6
Data Period	9/27-12/5/82
HRT, days	10
SRT, days	26
No. of HRT's in Progress	7
Gas Yield SCM/kg VS added (SCF/lb VS added)	0.63 ± 0.01 (10.13 ± 0.10)
Methane Content, mol %	54.2 - 57.6
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.36 (5.7)
Methane Production Rate vol CH_4/vol culture-day	2.8
Total Volatile Acids, mg/L as acetic	<200
Mean Caustic Added, meq/L feed	0

Table B-8. VOLATILE SOLIDS BALANCE FOR USR AT A LOADING RATE OF 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day)

Input	VS,g	Percent
Feed	48.05	100.0
Total	48.05	100.0
Output		
Methane	11.52	24.0*
Carbon Dioxide	24.78	51.6*
Liquid Effluent	13.71	28.5
Total Accounted	50.01	104.1
Not accounted for by Experimental and Analytical Procedures	- 1.96	- 4.1
Total	48.05	100.0

*These combined products represent 75.6 % conversion of the volatile solids.

Table B-9. PERFORMANCE DATA AND OPERATING CONDITIONS FOR USR DIGESTER AT A LOADING RATE OF 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day) (Feed, Kelp Lot 53: Temperature, °C)

Culture Volume, L	6
Data Period	9/6-10/24/82
HRT, days	8.3
SRT, days	23
No. of HRT in Progress	5.5
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.62 ± 0.02 (9.96 ± 0.30)
Methane Content, mol %	53.8 - 56.9
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.34 (5.5)
Methane Production Rate, vol CH_4/vol culture-day	3.3
Total Volatile Acids mg/L as acetic	100 - 800
Mean Caustic Added, meq/L feed	0

Table B-10. VOLATILE SOLIDS BALANCE FOR USR AT A LOADING RATE OF 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day)

	VS,g	Percent
Input		
Feed	57.66	100.0
Total	57.66	100.0
Output		
Methane	13.10	22.7*
Carbon Dioxide	29.05	50.4*
Liquid Effluent	18.20	31.6
Total Accounted	60.35	104.7
Not accounted for by Experimental and Analytical Procedures	- 2.69	- 4.7
Total	57.66	100.0

*These combined products represent a 73.1 % conversion of the volatile solids.

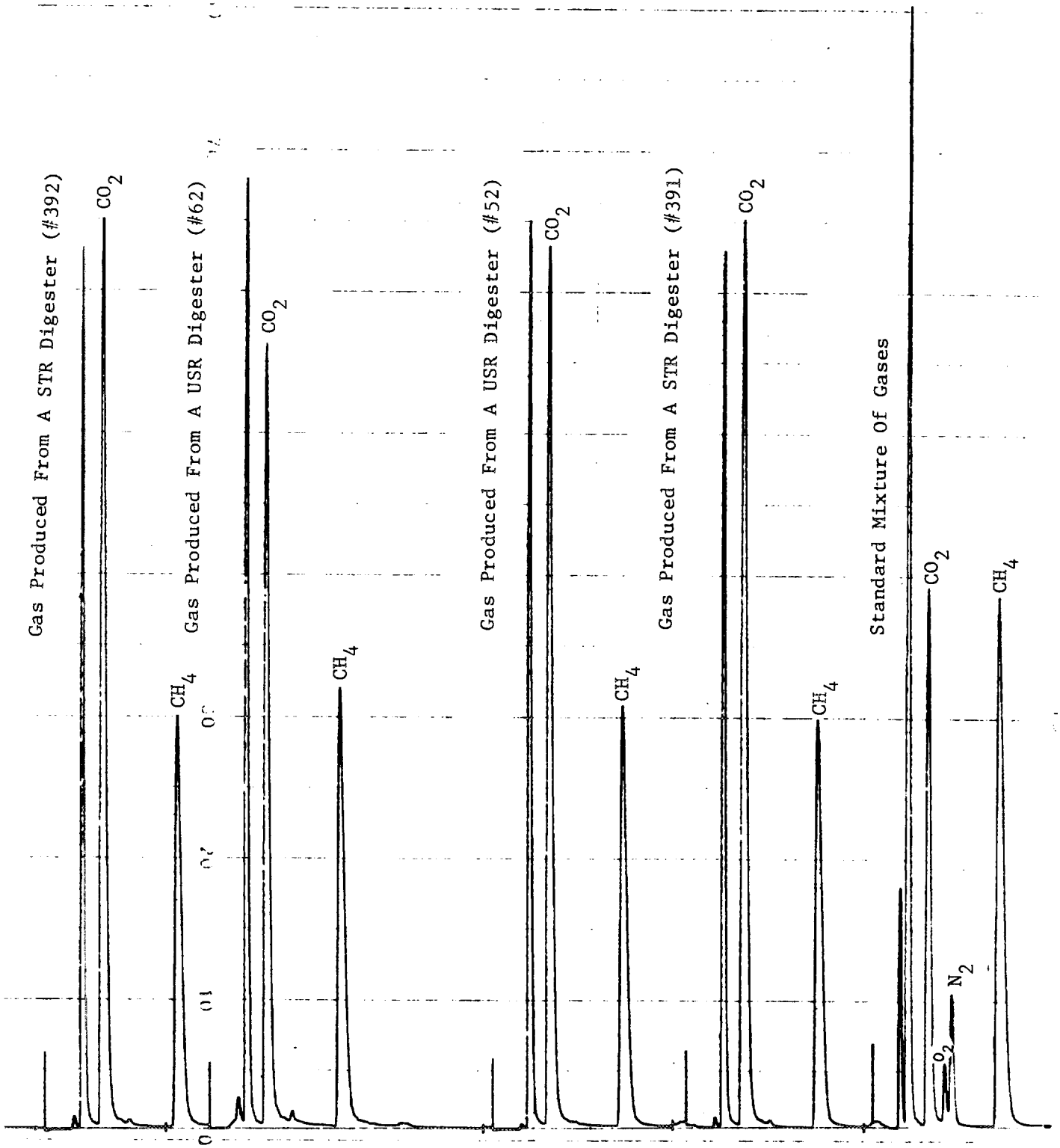
APPENDIX C.
Solids Retention Time Determination in USR Digesters

Table C-1. SOLIDS RETENTION TIME IN USR DIGESTERS OPERATED WITH ONCE-A-DAY FEEDING

Loading Rate, kg/m^3-day (lb/ft^3/day)	4.8 (0.30)	6.4 (0.40)	8.0 (0.50)	9.6 (0.60)
HRT, days	17	12.5	10	8.5
Reactor Volume, L	5	6	6	6
Effluent Removed, L/day	0.30	0.48	0.60	0.72
TSS_R, %	6.0	8.8	6.7	0.72
TSS_E, %	1.4	2.5	2.4	2.4
Density of TSS_R, g/mL	1.04	1.05	1.05	1.06
Density of TSS_E, g/mL	1.03	1.03	1.03	1.05
SRT, days	66	45	28	23

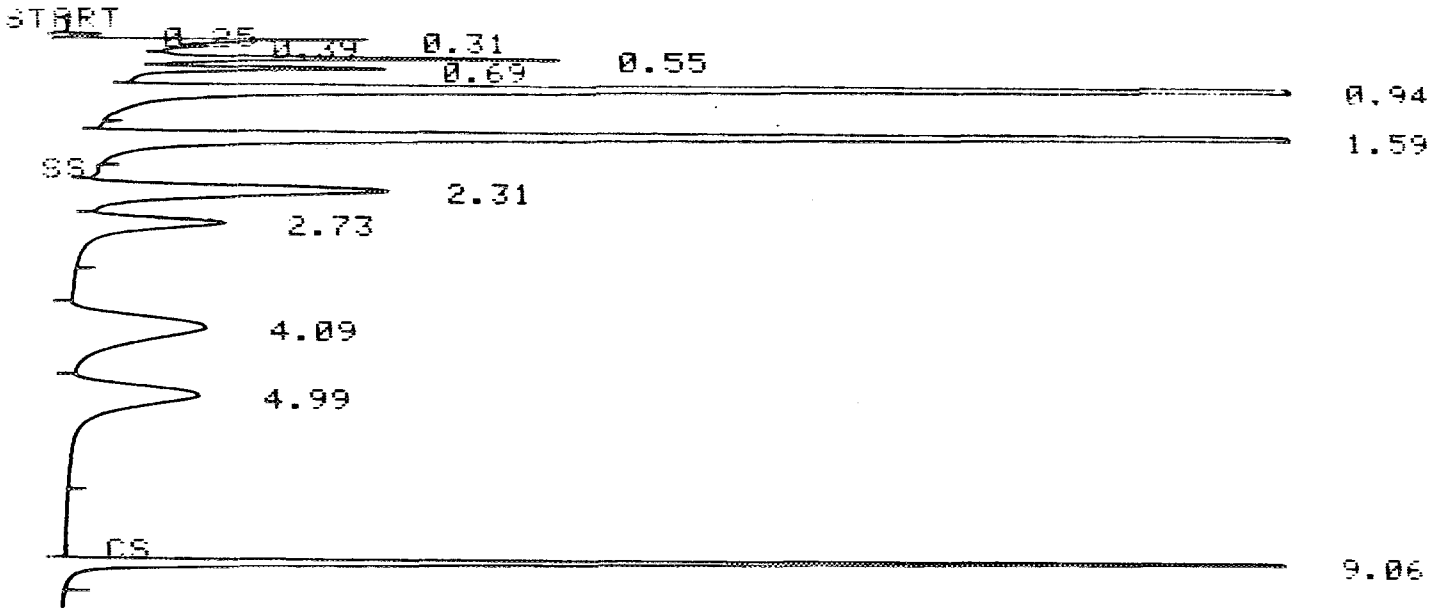
APPENDIX D.
Digester Gas Composition and Volatile Acids Profile

TYPICAL CHROMATOGRAPH OF GAS COMPOSITION ANALYSIS



TYPICAL CHROMATOGRAPH OF VOLATILE ACIDS

ANALYSIS

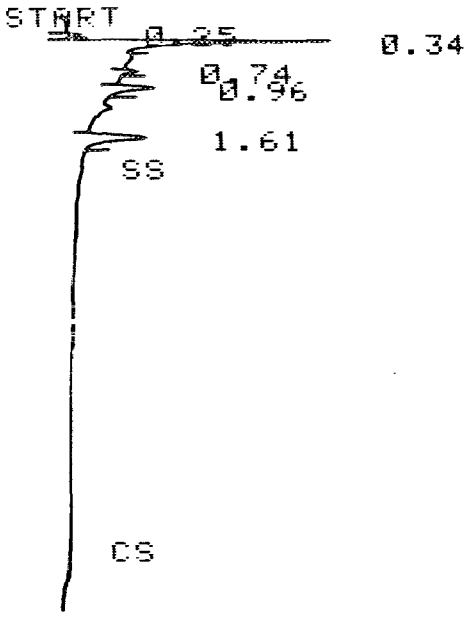


HP RUN # 3 NOV/18/82 TIME 15:11:37
ID:30558-00 BOTTLE 3
AREA %

Standard Mixture Of Volatile Acids

RT	AREA	AREA %	
0.25	610	0.054	
0.31	10930	0.974	
0.39	7924	0.706	
0.55	27260	2.429	
0.69	21410	1.908	
0.94	142600	12.709	acetic acid
1.59	126500	11.274	propionic acid
2.31	38490	3.430	isobutyric acid
2.73	19870	1.771	butyric acid
4.09	40360	3.597	isovaleric acid
4.99	35310	3.147	valeric acid
9.06	650800	58.000	caproic acid

DIL FACTOR: 1.0000 E+ 0

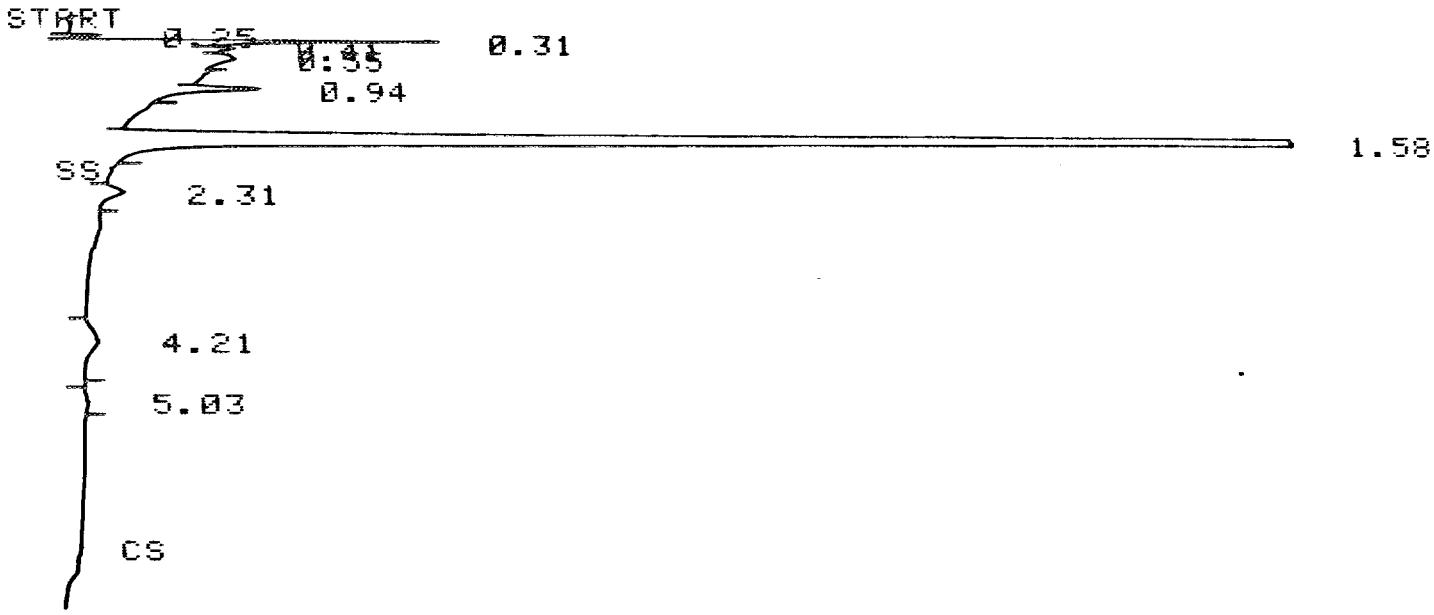


HP RUN # 11 NOV/18/82 TIME 17:29:58
ID:30558-00 BOTTLE 11
AREA %

Effluent Sample Of A USR Digester

RT	AREA	AREA %	
0.25	220	1.336	
0.34	10100	61.357	
0.74	295	1.792	
0.96	1963	11.925	acetic acid
1.61	3883	23.589	propionic acid

DIL FACTOR: 1.0000 E+ 0



HP RUN # 9 NOV/18/82 TIME 16:55:21
ID:30558-00 BOTTLE 9
AREA %

Effluent Sample Of A STR Digester

RT	AREA	AREA %	
0.25	469	0.182	
0.31	14020	5.433	
0.41	6784	2.629	
0.55	10600	4.108	
0.94	3556	1.378	acetic acid
1.58	217100	84.134	propionic acid
2.31	2085	0.808	isobutyric acid
4.21	2974	1.153	isovaleric acid
5.03	452	0.175	valeric acid

DIL FACTOR: 1.0000 E+ 0

HYDROGEN SULFIDE ANALYSIS

RESULTS

SAMPLE	DETECTOR	CONC.H2S (+/- 10%)
KELP (7-29-82 3:30 PM)	FPD	4600 PPM VOL.
KELP (7-30-82 3:30 PM)	TCD	3400 PPM VOL.

FPD-FLAME PHOTOMETRIC DETECTOR (SULPHUR MODE)

TCD-THERMAL CONDUCTIVITY DETECTOR

CHROMATOGRAPHIC METHOD FOR HYDROGEN SULFIDE DETERMINATION IN BIOMASS DIGESTER GAS

INSTRUMENT:	PERKIN-ELMER #1B GAS CHROMATOGRAPH #10 DATA CONSOLE
COLUMN:	5 FT. TEFLON LINED STAINLESS STEEL PORPAK QS
METHOD:	SEE ATTACHED SHEET
DETECTOR:	FLAME PHOTOMETRIC (SULPHUR MODE) THERMAL CONDUCTIVITY
STANDARDS:	210 PPM H2S IN NITROGEN(AIRCO RARE AND SPECIALTY GASES) 500 PPM H2S IN NITROGEN(SCOTTY IV ANALYZED GASES)

CALIBRATION DATA

FLAME PHOTOMETRIC DETECTOR

1 ML GAS SAMPLING LOOP

SAMPLE	PRESSURE.(TORR)	AREA UNITS
210 PPM STD	750	18.4
210 PPM STD	750	19.5
210 PPM STD	495	11.5
210 PPM STD	754	18.4
KELP (7-29-82 3:30 PM)	145	79.8

THERMAL CONDUCTIVITY DETECTOR (HIGH SENSITIVITY)

1 ML GAS TIGHT SYRINGE

500 PPM STD	1 ATM	6.5
500 PPM STD	1 ATM	6.7
KELP (7-30-82 3:30 PM)	1 ATM	44.5

APPENDIX E.
Digester Performance Curves

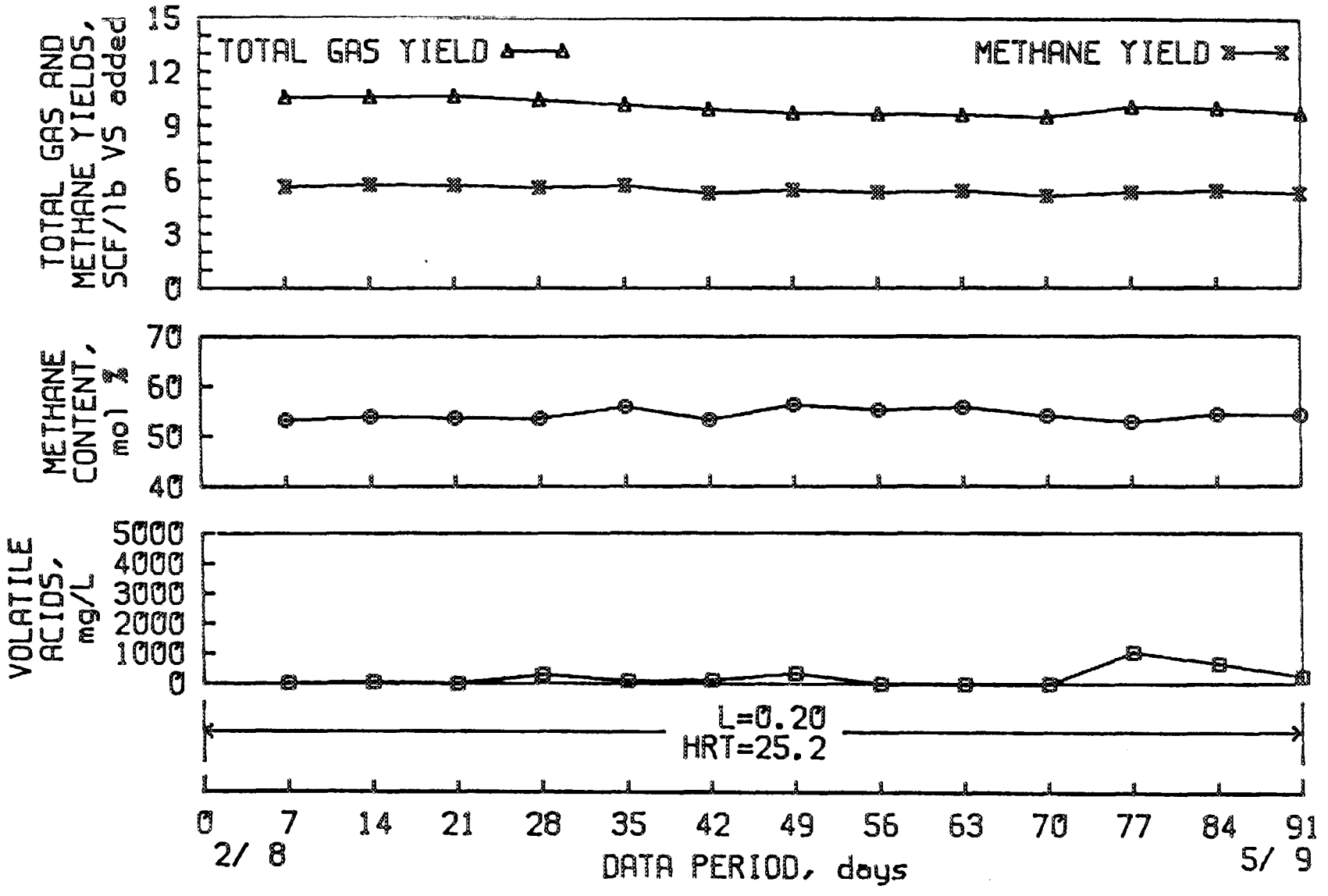


Figure E-1. PERFORMANCE CURVES OF USR RECEIVING KELP LOT 53 AT 3.2 kg VS/m^3-day (0.20 lb Vs/ft^3-day) LOADING RATE
(Culture Volume-6L; Temperature-35°C; Digester No. 52)

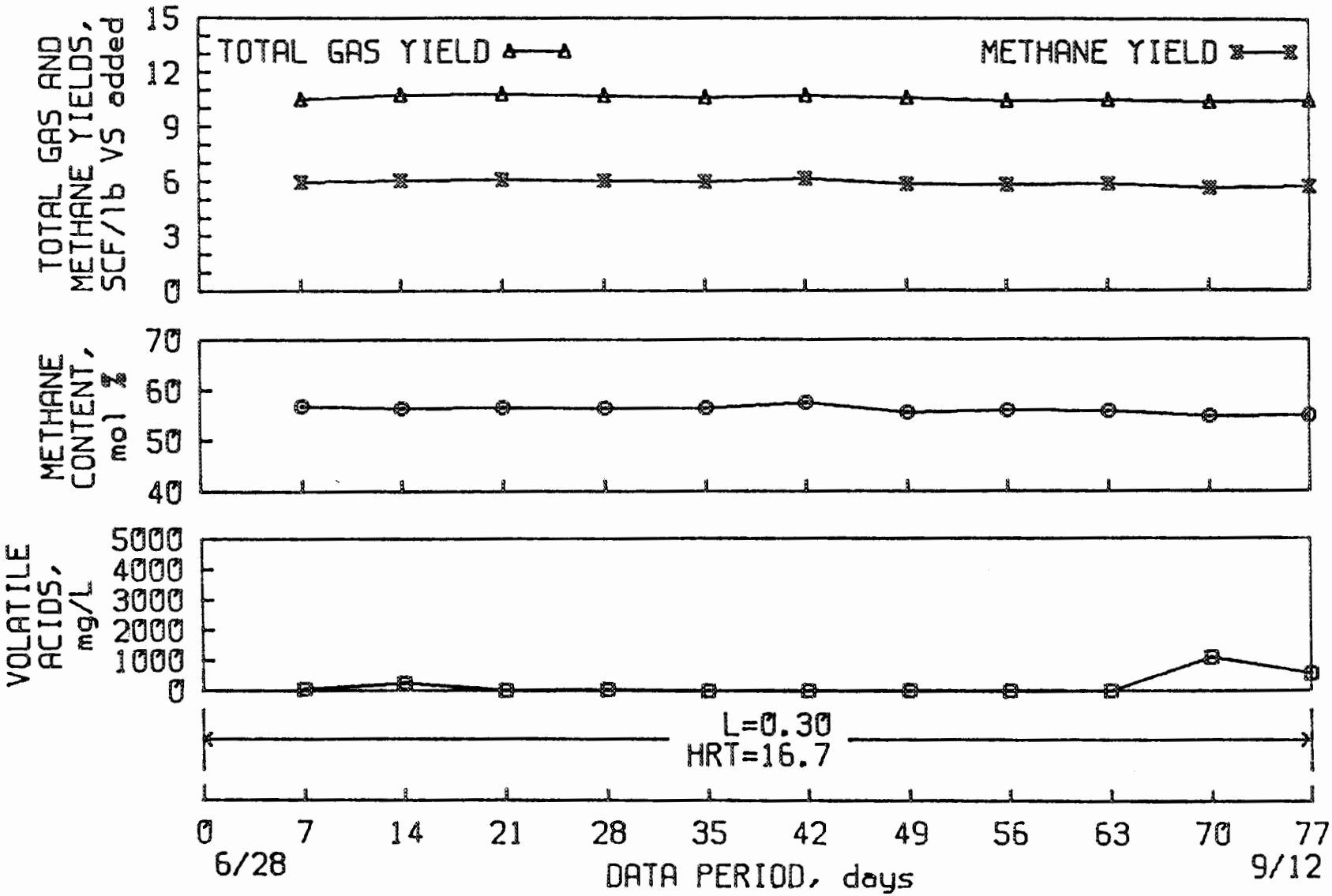


Figure E-2. PERFORMANCE CURVES OF USR RECEIVING KELP LOT 53 at 4.8 kg VS/m^3-day (0.30 lb VS/ft^3-day) LOADING RATE
(Culture Volume-6L; Temperature-35°C; Digester No. 52)

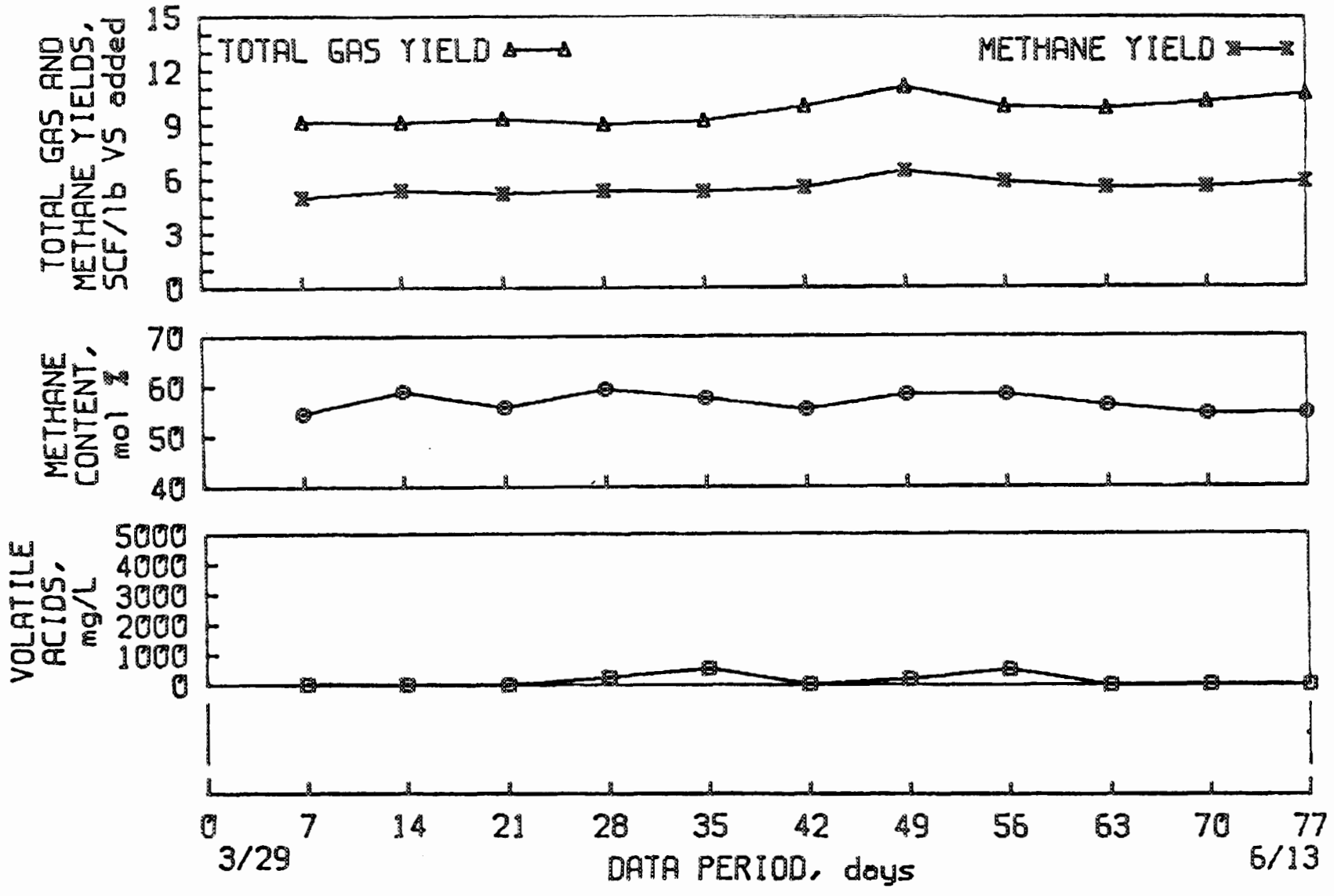


Figure E-3. PERFORMANCE CURVES OF USR RECEIVING KELP LOT 53 AT 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day) LOADING RATE
(Culture Volume-6L; Temperature-35°C; Digester No. 62)

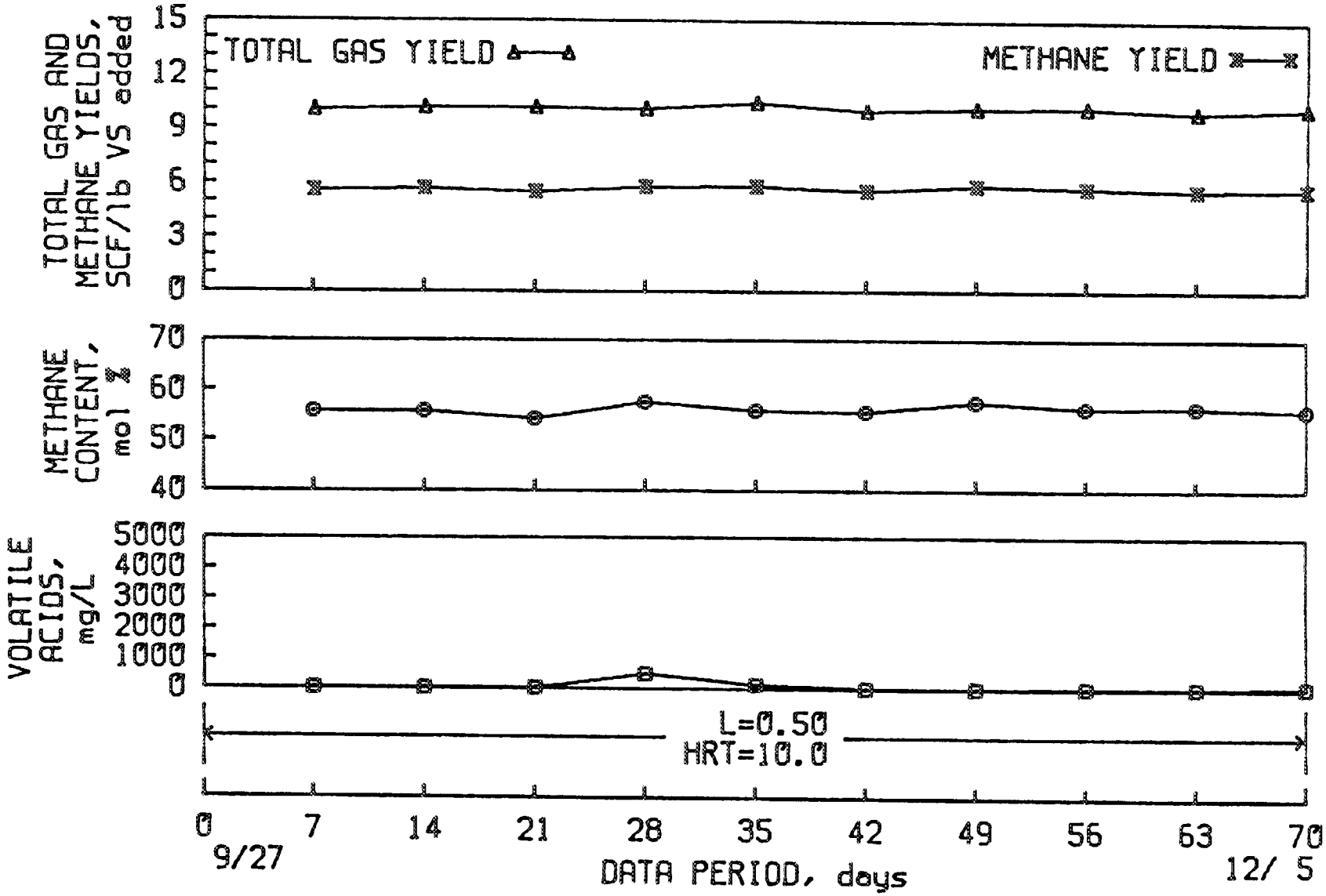


Figure E-4. PERFORMANCE CURVES OF USR RECEIVING KELP LOT 53 AT 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day) LOADING RATE
(Culture Volume-6L; Temperature-35°C; Digester No. 52)

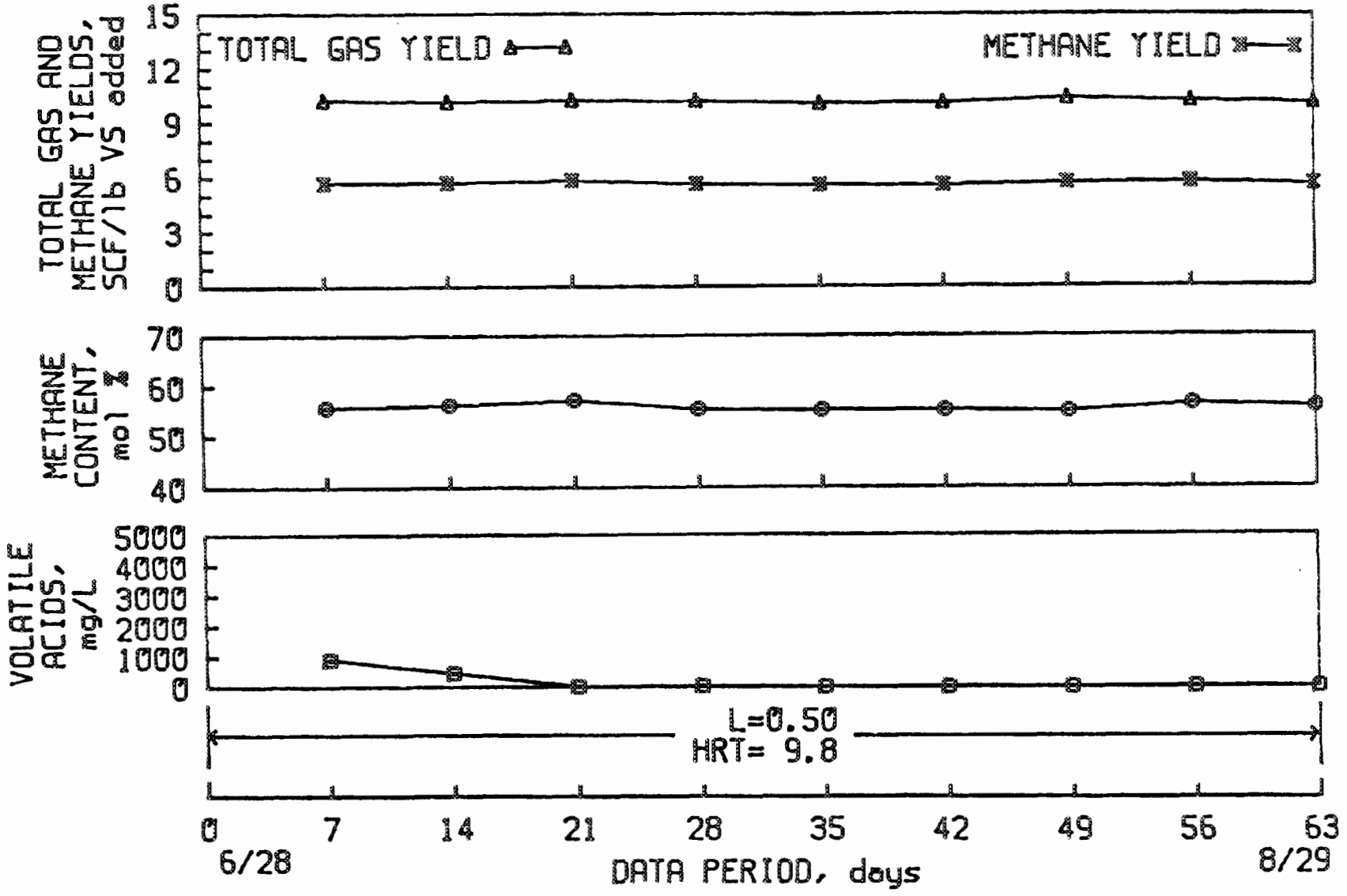


Figure E-5. PERFORMANCE CURVES OF USR RECEIVING KELP LOT 53 AT 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day) LOADING RATE
(Culture Volume-6L; Temperature-35°C; Digester No. 62)

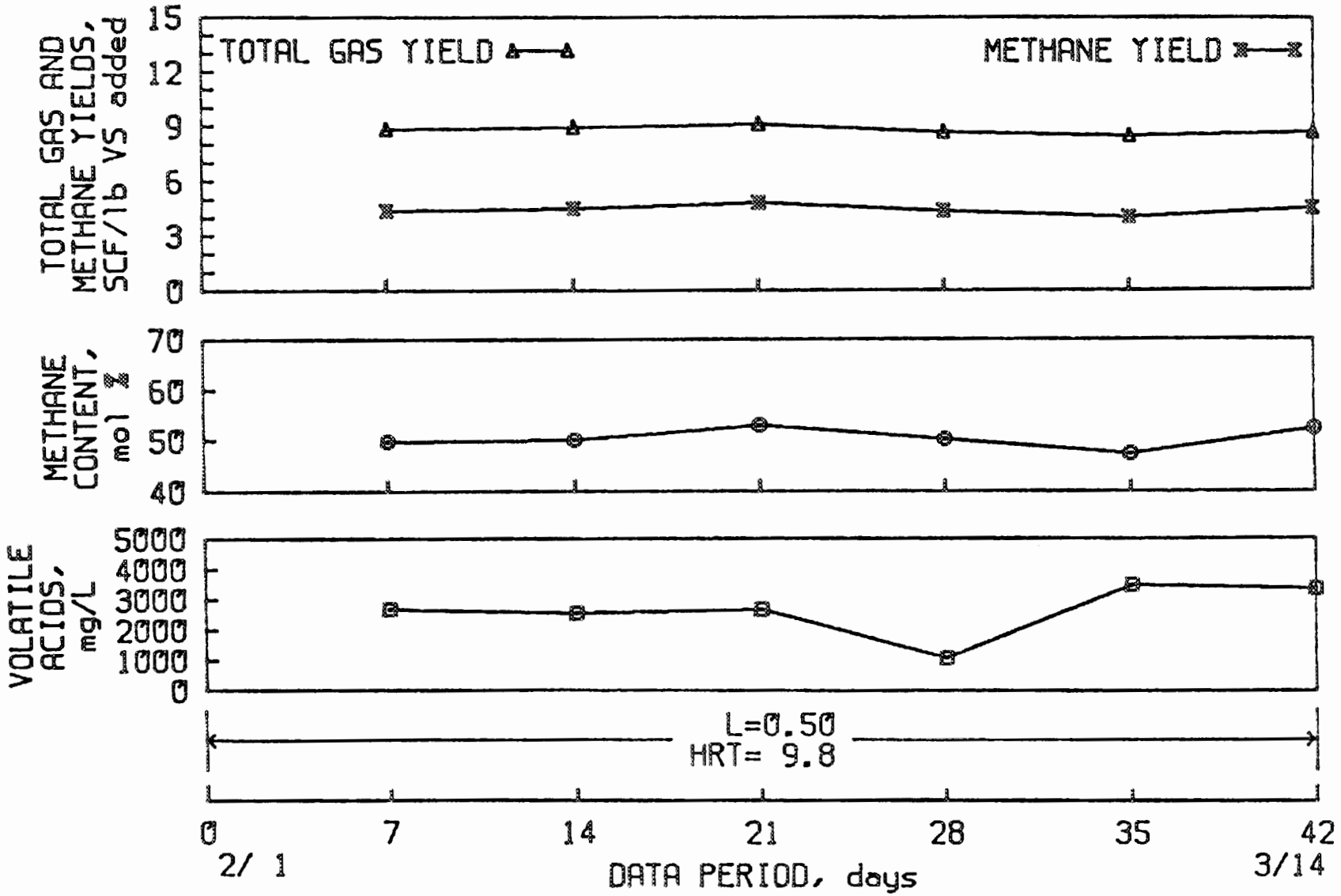


Figure E-6. PERFORMANCE CURVES OF USR RECEIVING KELP LOT 53 AT 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day) LOADING RATE
(Culture Volume-6L; Temperature-35°C; Digester No. 62)

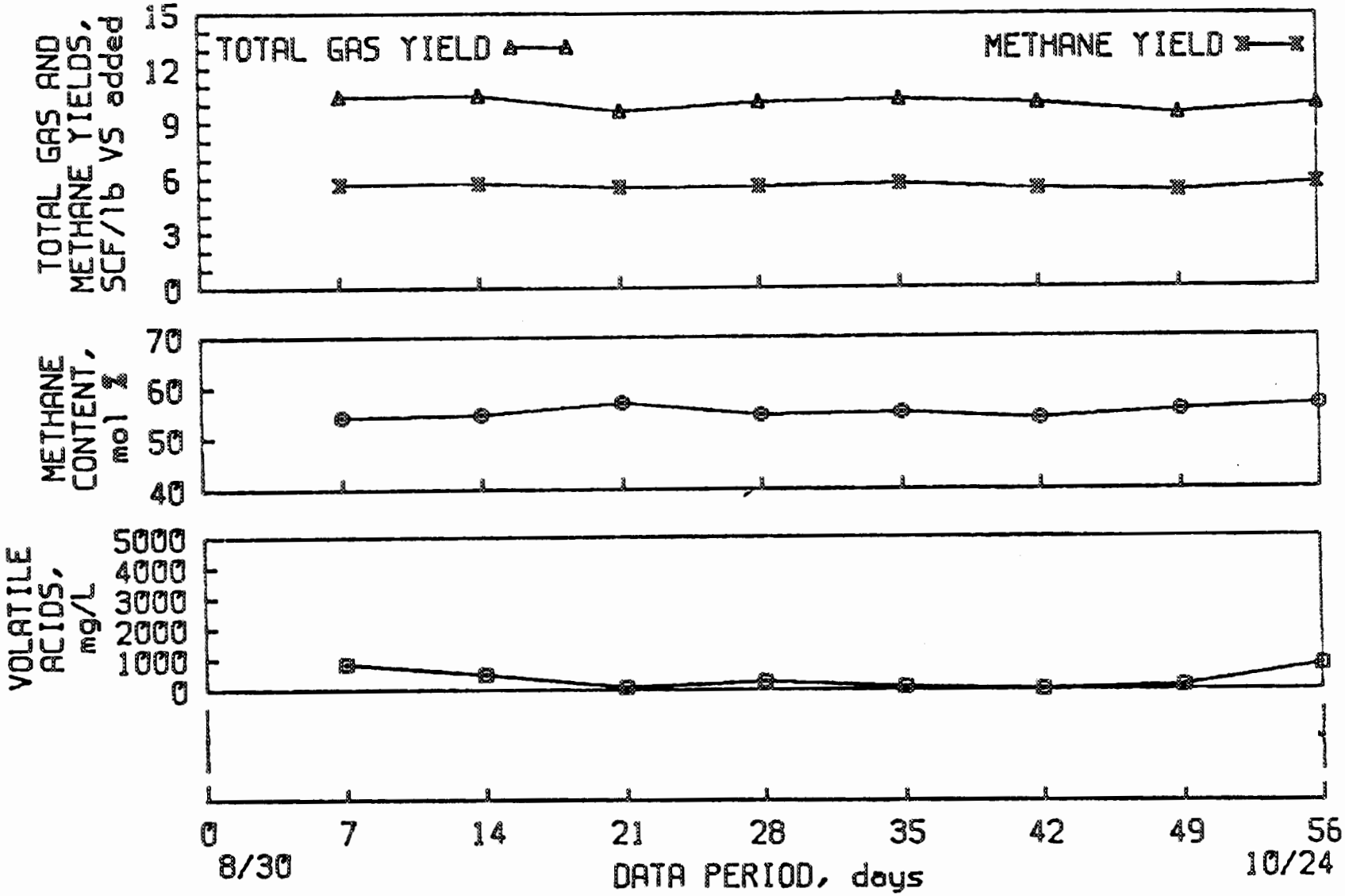


Figure E-7. PERFORMANCE CURVES OF STR RECEIVING KELP LOT 53 (UNMILLED) AT 8.0 kg VS/m^3-day (0.50 lb VS/ft^3-day) LOADING RATE (Culture Volume-7L; Temperature-35°C; Digester No. 41)

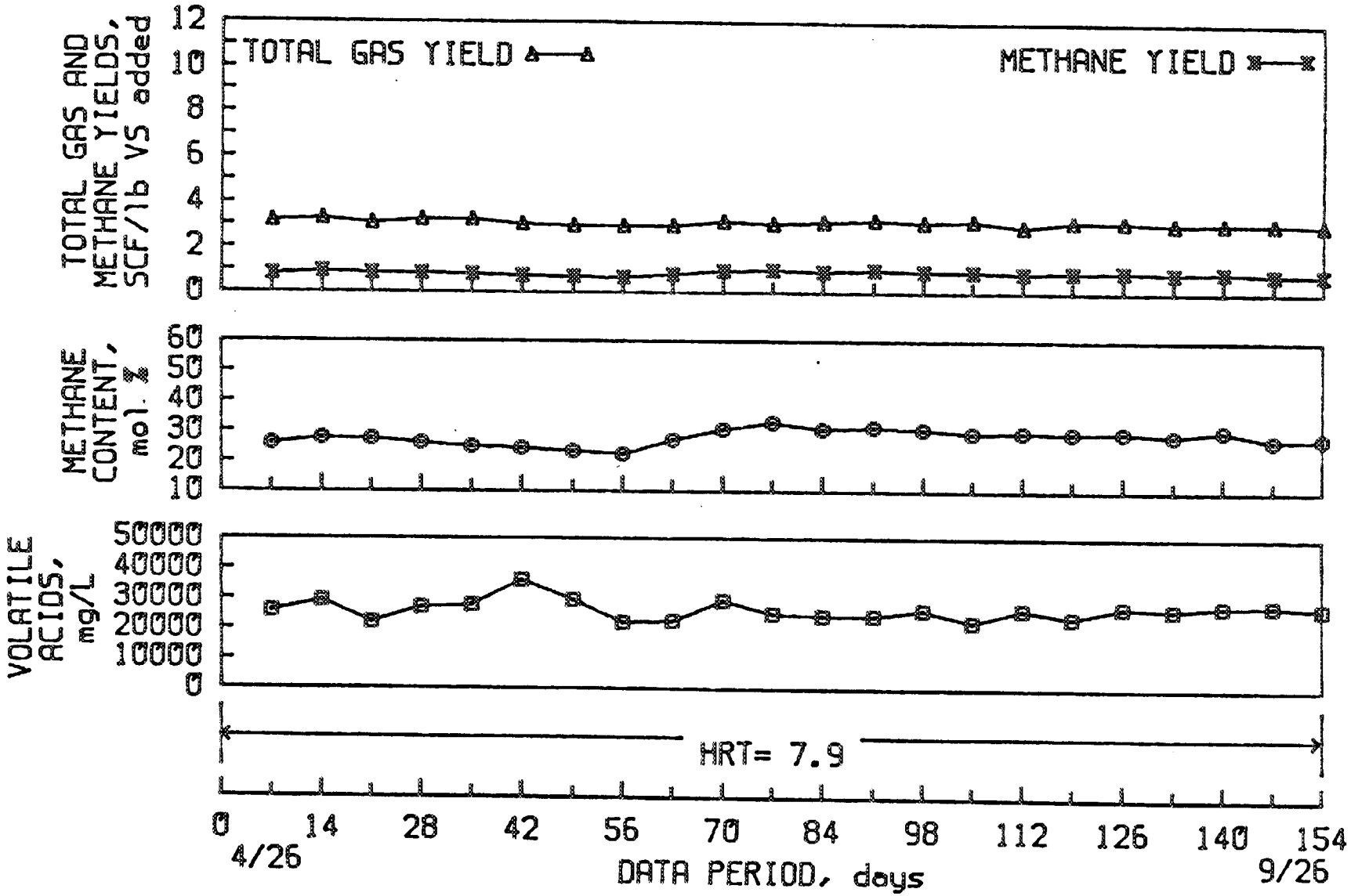


Figure E-8. PERFORMANCE CURVES OF STR RECEIVING KELP LOT 53 (UNMILLED) AT 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day) LOADING RATE (Culture Volume-5L; Temperature-35°C; Digester No. 41)

APPENDIX F.
IGT-Supported Studies

IGT-SUPPORTED STUDIES

Three experiments were initiated last year to evaluate the performance of certain conventional and unconventional digesters at very high loading rates. The experimental plan for these studies included increasing the loading rates, while maintaining good methane yields, to the maximum limit prior to digester destabilization and failure. The excellent performance of these digesters, however, permitted loading rate increases beyond the levels expected and, consequently, prevented the completion of these experiments during 1981. Although these experiments were deleted from the GRI 1982 work plan, the successful completion of these experiments were determined to be of sufficient value to developing biomass anaerobic digestion techniques that they were continued using IGT in-house funds. These experiments, which included the study of a stirred tank reactor digester, a fluidized-bed reactor, and a packed-bed reactor at high loading rates, are described below.

Stirred Tank Reactor. The 10-L STR used in this study was previously started on unmilled kelp Lot 53 at a loading rate of 4.8 kg VS/m^3-day (0.30 lb VS/ft^3-day). The performance of this digester at this loading was very stable with a methane yield of about 0.30 SCM/kg (4.8 SCF/lb) VS added and a methane production rate of about 1.4 vol/vol culture-day. At an increased loading rate of 5.6 kg VS/m^3-day (0.35 lb VS/ft^3-day), the methane yield remained at about 0.30 SCM/kg (4.8 SCF/lb) VS added, but the methane production rate increased to about 1.7 vol/vol culture-day. During this quarter, the loading rate in this digester was increased to 6.4, 8.0, and finally to 9.6 kg VS/m^3-day (0.40 and 0.50, and 0.60 lb VS/ft^3-day). The steady-state performance of this digester at 6.4 and 8.0 kg VS/m^3-day (0.40 and 0.50 lb VS/ft^3-day) is shown in Table F-1. The methane yields at loading rates of 6.4 and 8.0 kg VS/m^3-day (0.40 and 0.50 lb VS/ft^3-day) were about (4.5 and 4.4 SCF/lb) VS added, respectively, and the respective methane production rates were about 1.8 and 2.2 vol/vol-day. These methane production rates are the highest achieved to date on this program in an STR digester. The volatile acids concentrations remained below 4000 mg/L as acetic at both loading rates. The digester will be operated at 0.60 lb VS/ft^3-day until either digester instability or steady-state performance is demonstrated.

Fluidized Bed Reactor. A fluidized-bed reactor, shown in Figure F-1, with sand as the microorganism support medium, was studied, using a feed

slurry with a constant total solids concentration, at decreasing hydraulic retention times (HRT) of 7, 5, 3, 2 and 1 days. The performance data and operating conditions in Table F-2 show that, as the HRT was decreased, the effective loading rate increased from 0.16 to 1.14 lb VS/ft^3-day. The methane yield remained relatively stable, about 4.8 to 4.9 SCF/lb VS added, at HRT of 7 to 3 days. At a 2-day HRT, the methane yield dropped to about 4.4 SCF/lb VS added and at a 1-day HRT the methane yield dropped to 3.3 SCF/lb VS added. By increasing the loading rate without greatly sacrificing the methane yield, the methane production rate increased from 0.8 vol/vol culture-day at a 7-day HRT to 3.8 vol/vol culture-day at a 1-day HRT. The total volatilize acids concentration increased from about 100 to 300 mg/L as acetic at a 7-day HRT to about 4000 mg/L as acetic at a 1-day HRT.

The loading rate of 1.14 lb VS/ft^3-day and methane production rate of 3.8 vol/vol culture-day are the highest yet observed in this program in any reactor design. Efforts to decrease the HRT below 1 day using the seawater-diluted feed was not successful because the high amount of solids fed during the once-a-day feeding caused a clogging problem that prevented culture recycling and digester fluidization. Our experience suggests that the HRT can be further reduced and the methane production rates further increased by slight digester modification and by the use of an autofeeder to permit frequent feeding throughout each 24-hour period.

These encouraging results demonstrate that high loading and methane production rates are achievable with a kelp particulate feed diluted in seawater. Realization of the full potential of this design for kelp digestion will require further research. Such research should examine both basic and applied research questions relating to this design. One important potential application of the FBR may be as a second-stage digester using the solids-containing effluent from a first-stage digester.

Packed-Bed Reactor. A packed-bed was operated as the methane phase of a two-phase digester. The digester was fed the effluent supernatant of an STR digester operated on kelp Lot 53. The volatile acids concentrations in the supernatant feed was adjusted to approximately 25,000 mg/L total volatile acids using a stock solution of volatile acids. The composition of this stock volatile acids solution was based on the previously observed composition of an acid-phase digester that contained about 20,000 mg/L as acetic volatile acids

concentration. This stock feed solution was composed of acetic, butyric, propionic, caproic, valeric, isovaleric, and isobutyric acid, in order of descending concentration.

The methane yield, shown in Table F-3, was based on the volatile acids concentration in the feed and ranged from about 7.6 to 3.1 SCF/lb VS added at HRT's of 7 days to 1 day, respectively. The methane production rate in this system increased from 1.6 to 3.8 vol/vol culture-day as the HRT was decreased from 7 days to 1 day. The volatile acids concentrations in the effluent were about 2000 to 3000 mg/L at a 7-day HRT and about 11,000 to 13,000 mg/L as acetic at a 1-day HRT. The loading rate, expressed in terms of total volatile acids added, ranged from about 0.21 to 1.22 lb VA/ft^3-day at 7 and 1-day HRT's, respectively. The methane content of the collected gas ranged from about 63 to 68 mol % over all loading rates studied.

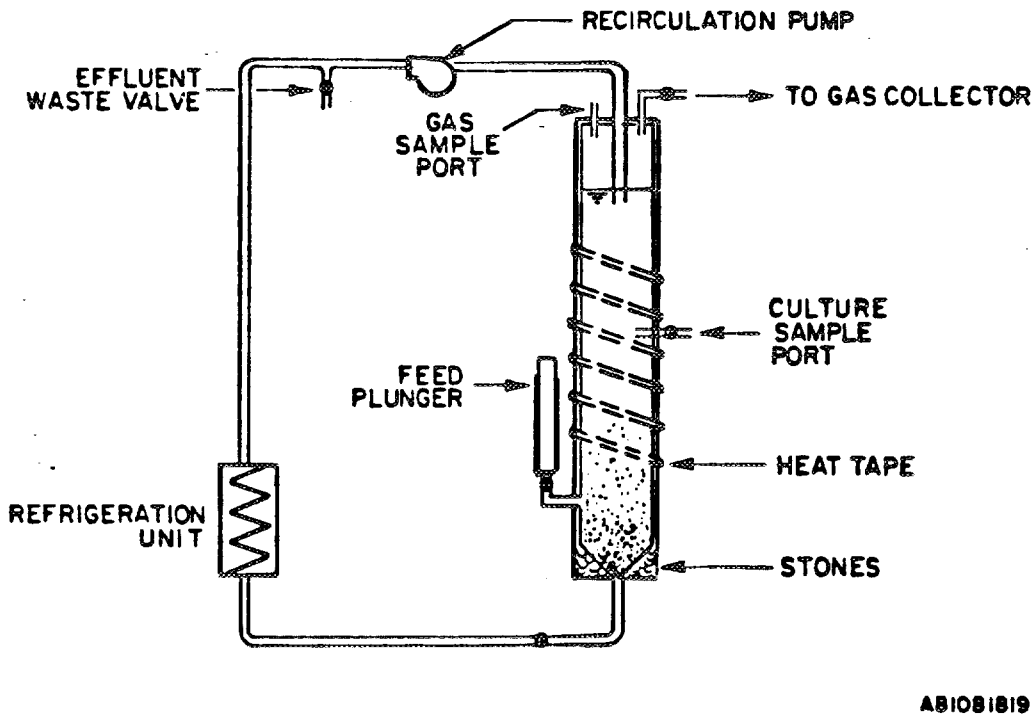


Figure F-1. FLUIDIZED BED REACTOR SYSTEM

Table F-1. PERFORMANCE DATA AND OPERATING CONDITIONS FOR STR DIGESTER AT 0.40 AND 0.50 lb VS/ft^3-day LOADINGS
(Feed, Kelp Lot 53; Temperture, 35°C)

Digester No.	41	
Digester Design	STR	STR
Culture Volume, L	10	7
Loading, lb VS/ft^3-day	0.40	0.50
Date Initiated	11/1/81	2/2/82
Data Period	1/11-1/31/82	3/1-3/17/82
HRT, days	12	10
No. of HRT's in Progress	5.0	4.4
Gas Yield, SCF/lb VS added	8.6 ±0.1	8.6 ±0.1
Methane Content, mol %	52.5-53.1	50.1-52.2
Methane Yield, SCF/lb VS added	4.5	4.4
Methane Production Rate, vol CH_4/vol culture-day	1.8	2.2
Total Volatile Acids, mg/L as acetic	2400-3700	3300-3700
Mean Caustic Added, meq/L feed	0	0

Table F-2. PERFORMANCE DATA AND OPERATING CONDITIONS FOR FLUIDIZED BED REACTOR AT DIFFERENT HYDRAULIC RETENTION TIMES AND LOADING RATES (Feed, 3% TS Feed Slurry in Simulated Seawater; Temperature, 35°C)

Digester No.	63				
Digester Design	FBR				
Culture Volume, L	4				
HRT, days	7	5	3	2	1
Date Initiated	12/21/81	1/13/82	2/8/82	2/19/82	7/8/82
Data Period	1/4-1/12/82	1/18-1/31/82	2/8-2/18/82	2/19-2/25/82	3/8-3/12/82
Loading, lb VS/ft^3-day	2.6 (0.16)	0.22	0.38	0.57	18.3 (1.14)
No. of HRT's in Progress	3.3	3.8	3.7	3.5	5.0
Gas Yield, SCF/lb VS added					
Average	8.3	8.3	8.1	7.3	5.6
Range	7.9-8.8	7.8-8.7	7.6-9.6	6.5-8.0	5.4-5.8
Methane Content, mol %	57.0-58.0	57.4-60.0	59.7-60.4	60.4-60.7	57.8
Methane Yield, SCF/lb VS added	4.8	4.9	4.9	4.4	3.3
Methane Production Rate, vol CH_4/vol culture-day	0.8	1.1	1.9	2.5	3.8
Total Volatile Acids, mg/L as acetic	100-300	100-200	600-700	600-1500	4000
Mean Caustic Added, meq/L feed	35	70	110	100	100

Table F-3. PERFORMANCE DATA AND OPERATING CONDITIONS FOR PACKED BED REACTOR AT DIFFERENT HYDRAULIC RETENTION TIMES AND LOADING RATES (Feed, STR Digester Effluent Supernatant With Total Volatile Acids Concentration Adjusted to Approximately 25,000 mg/L)

Digester No.	54				
Digest Design	PBR				
Culture Volume, L	4				
HRT, days	7	5	3	2	1
Date Initiated	12/14/81	1/18/82	2/8/82	2/18/82	2/25/82
Data Period	1/4-1/17/82	1/18-2/7/82	2/8-2/17/82	2/18-2/24/82	2/25-3/1/82
Loading, lb VA/ft^3-day	0.21	0.28	0.46	0.67	1.22
No. of HRT's in Progress	5.0	4.0	3.2	3.5	5.0
Gas Yield, SCF/lb VA added	11.44	12.5	11.5	7.9	4.7
Methane Content, mol %	65.1-67.7	63.5-66.9	63.3-63.4	68.5	66.1
Methane Yield, SCF/lb VA added	7.6	8.1	7.6	5.4	3.1
Methane Production Rate, vol CH_4/vol culture-day	1.6	2.3	3.5	3.6	3.8
Total Volatile Acids, mg/L as acetic	2000-3000	2000-3000	4000-5000	5000-9000	11,000-13,500
Mean Caustic Added, meq/L feed	180	60	110	140	90

APPENDIX G.
Second-Stage Digester Performance Data

Table G-1. PERFORMANCE DATA AND OPERATING CONDITIONS FOR USR-PBR TWO-STAGE INTERACTIVE SYSTEM AT A LOADING RATE OF 4.0 kg VS/m^3-day (0.25 lb VS/ft^3-day)* (Feed, Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	
USR	6.0
PBR	3.5
Date Initiated	1/25/82
Data Period	3/1-3/28/82
HRT, days	20
No. of HRT's in Progress	5.2
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.59 ± 0.01 (9.40 ± 0.20)
Methane Content, mol %	56.5 - 57.8
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.34 (5.4)
Methane Production Rate,** vol CH_4/vol culture-day	1.4
Total Volatile Acids, mg/L as acetic	100 - 800
Mean Caustic Added, meq/L feed	0

* Loading in the first stage (USR) was 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day).

** Methane production rate is based on both stages.

Table G-2. PERFORMANCE DATA AND OPERATING CONDITIONS FOR FBR DIGESTER AS SECOND STAGE OF TWO-STAGE SYSTEM (Feed, Effluent of USR Operated at a Loading Rate of 0.50 lb VS/ft^3-day* With Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	4
Data Period	8/16-8/29/82
HRT, days,	6.7
No. of HRT's in Progress	4.7
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.15 ± 0.01 (2.38 ± 0.11)
Methane Content, mol %	61.2 - 62.1
Methane Yield, SCM/kg VS added (SCF/lb VS added)**	0.37 (6.0)
Total Volatile Acids, mg/L as acetic	<100
Mean Caustic Added, meq/L feed	0

*Loading rate in the FBR was 3.2 kg VS/m^3-day (0.20 lb/VS ft^3-day).

**Combined yield for first and second stages.

Table G-3. PERFORMANCE DATA AND OPERATING CONDITIONS FOR FBR DIGESTER AS A SECOND-STAGE OF TWO-STAGE SYSTEM (Feed, Effluent of USR Operated at a Loading Rate of 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day]* With Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	4
Data Period	9/6-9/26/82
HRT, days	5.7
No. of HRT's in Progress	3.5
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.14 ± 0.01 (2.20 ± 0.11)
Methane Content, mol %	61.0-62.0
Methnae Yield, SCM/kg VS added (SCF/lb VS added)**	0.37 (6.0)
Total Volatile Acids, mg/L as acetic	< 100
Mean Caustic Added, meq/L feed	0

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* Loading rate in FBR was 4.5 kg VS/m^3-day (0.28 lb VS/ft^3-day).

** Combined yield for first and second stages.

Table G-4. PERFORMANCE DATA AND OPERATING CONDITIONS FOR USBR DIGESTER AS SECOND OF TWO-STAGE SYSTEM (Feed, Effluent of USR Operated at a Loading Rate of 8.0 kg VS/m^3-day [0.50 lb VS/ft^3-day]* With Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	6
Data Period	11/22-12/5/82
HRT, days	10.4
No. of HRT's in Progress	5.8
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.15 ± 0.02 (2.40 ± 0.37)
Methane Content, mol %	5.43-57.7
Methane Yield, SCM/kg VS added** (SCF/lb VS added)**	0.37 (6.0)
Total Volatile Acids, mg/L as acetic	< 100
Mean Caustic Added, meq/L feed	0

*Loading rate in USBR digester was 2.7 kg VS/m^3-day (0.17 lb VS/ft^3-day).

**Combined yield for first and second stages.

APPENDIX H.
Digester Effluent Settling Characteristics

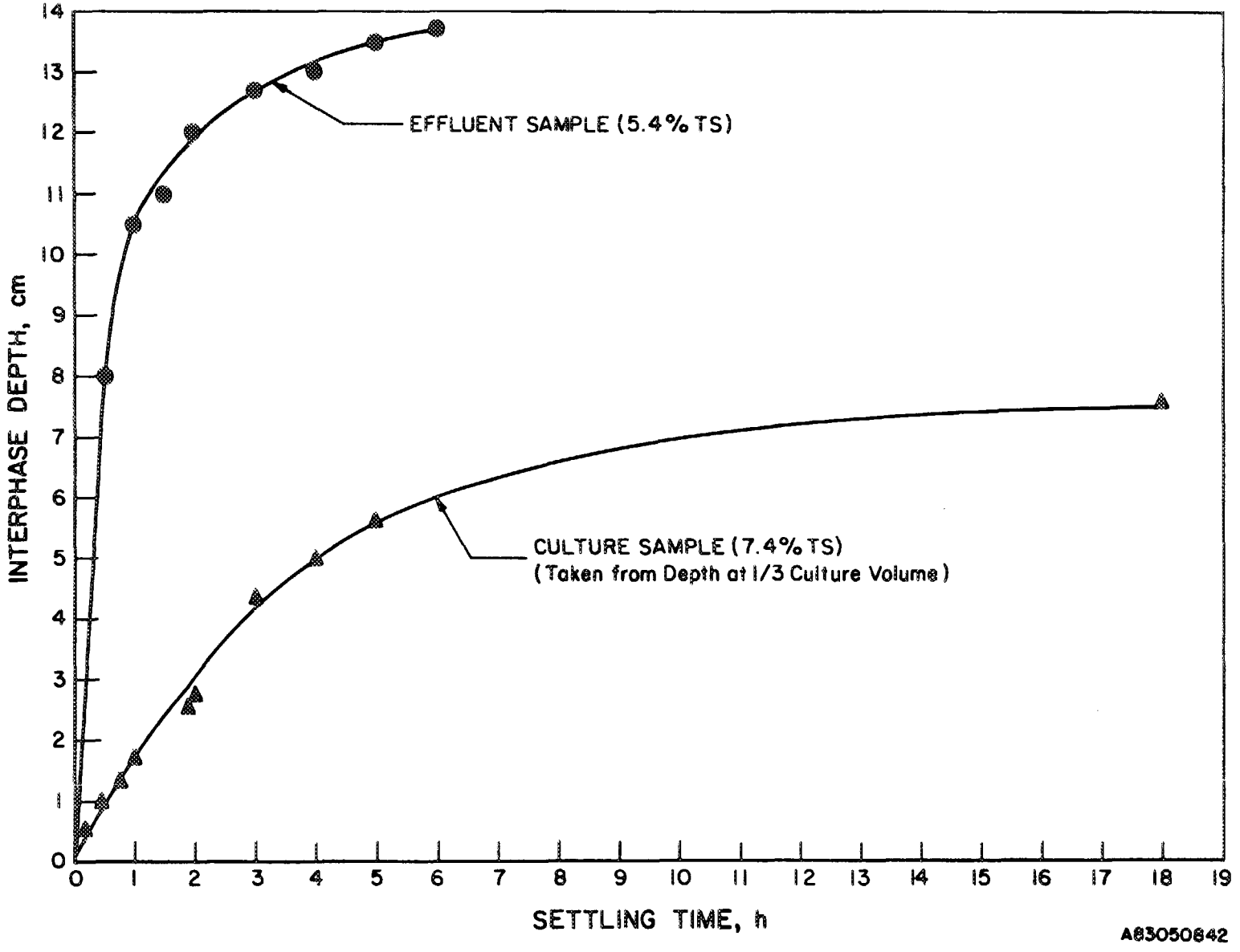

Figure H-1. SETTLING CHARACTERISTICS OF CULTURE AND EFFLUENT OF USR OPERATED AT A LOADING RATE OF 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day)

APPENDIX I.
STR Performance Data

Table I-1. PERFORMANCE DATA AND OPERATING CONDITIONS FOR FREQUENTLY FED AND ONCE-A-DAY FED DIGESTERS AT A LOADING RATE OF 4.0 kg VS/m^3-day (0.25 lb VS/ft^3-day)(Feed, Kelp Lot 53; Temperature, 35°C; Culture Volume, 7-10L)

Feeding Fequency, times/day	45	1
Data Period	12/19/81-1/17/82	
HRT, days	20	20
No. of Retention Times in Progress	9.8	9.8
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.60 ± 0.02 (9.6 ± 0.3)	0.58 ± 0.01 (9.3 ± 0.2)
Methane Content, mol %	52.2-56.7	54.1-55.5
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.32 (5.2)	0.32 (5.1)
Methane Production Rate, vol CH_4/vol culture-day	1.3	1.3
Total Volatile Acids, mg/L as acetic	100-300	300-1500
Mean Caustic Added, meq/L feed	0	0

Table I-2. PERFORMANCE DATA AND OPERATING CONDITIONS FOR FREQUENTLY FED AND ONCE-A-DAY FED DIGESTERS AT A LOADING RATE OF 4.8 kg VS/m^3-day (0.30 lb VS/ft^3-day)(Feed, Kelp Lot 53; Temperature, 35°C; Culture Volume, 7L)

Feeding Frequency, times/day	30	1
Data Period	2/15-3/14/82	2/15-3/14/82
HRT, days	17	17
No. of HRT's in Progress	3.3	3.3
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.68 ± 0.01 (11.1 ± 0.2)	0.61 ± 0.01 (9.8 ± 0.1)
Methane Content, mol %	52.0-52.8	52.6-53.6
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.36 (5.8)	0.32 (5.2)
Methane Production Rate, vol CH_4/vol culture-day	1.7	1.6
Total Volatile Acids, mg/L as acetic	100-600	100-900
Mean Caustic Added, meq/L feed	0	0

Table I-3. PERFORMANCE DATA AND OPERATING CONDITIONS FOR FREQUENTLY FED AND ONCE-A-DAY FED STR DIGESTERS AT A LOADING RATE OF 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day)(Feed, Kelp Lot 53; Temperature, 35°C, Culture Volume, 5L)

Culture Volume, L	7*	5**	5**
Data Period	5/10-6/30/82	11/8-12/12/82	9/13-12/12/82
Feeding Frequency, times/day	1	25	1
SRT, days	12.5	12.5	12.5
No. of HRT's in Progress	7.8	22	22
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.57 ± 0.01 (9.20 ± 0.10)	0.55 ± 0.01 (8.87 ± 0.19)	0.56 ± 0.003 (9.00 ± 0.05)
Methane Content, mol %	52.6-55.2	54.5-55.5	53.6-58.6
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.31 (5.0)	0.31 (4.9)	0.31 (5.0)
Methane Production Rate, vol CH_4/vol culture-day	2.0	2.0	2.0
Total Volatile Acids, mg/L as acetic	100-300	100-200	100-200
Mean Caustic added, meq/L feed	0	0	0

*Digester performance before digester imbalance.

**Digester performance after digester imbalance and recovery; culture derived from frequently-fed digester.

Table I-4. PERFORMANCE DATA AND OPERATING CONDITIONS FOR STR AS AN ACID-PHASE DIGESTER AT A LOADING RATE OF 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day)(Feed, Kelp Lot 53; Temperature, 35°C)

Culture Volume, L	7
Data Initiated	3/18/82
Data Period	7/5-9/12/82
HRT, days	7
No. of HRT's in Progress	25.4
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.19 ± 0.002 (3.11 ± 0.04)
Methane Content, mol %	28.5-32.6
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.06 (0.94)
Methane Production Rate, vol CH_4/vol culture-day	0.56
Total Volatile Acids, mg/L as acetic	22,270-27,740
Mean Caustic Added, meq/L feed	690-750

Table I-5. VOLATILE SOLIDS BALANCE FOR STR AT A LOADING RATE OF 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day)

	VS, g	Percent
Input		
Feed	73.00	100.0
Total	73.00	100.0
Output		
Methane	2.48	3.4*
Carbon Dioxide	17.09	23.4*
Liquid Effluent	47.53	65.1
Total Accounted	67.10	91.9
Not Accounted for by Experimental and Analytical Procedures	5.90	8.1
Total	73.00	100.0

*These combined products represent a 26.8% conversion of the volatile solids.

Table I-6. PERFORMANCE DATA AND OPERATING CONDITIONS FOR STR DIGESTER RECEIVING KELP LOT 53 AT 9.6 kg VS/m^3-day (0.60 lb VS/ft^3-day) ADDED LOADING RATE

Digester No.	392
Digester Design	STR
Culture Volume, L	5
Loading, kg VS/m^3-day (lb VS/ft^3(day)	9.6 (0.60)
Date Initiated	2/14/83
Data Period	3/14-4/17/83
HRT, days	8.4
No. of HRT in Progress	7.5
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.52 ± 0.001 (8.36 ± 0.09)
Methane Content, mol %	53.8-54.7
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.28 (4.52)
Methane Production Rate, vol CH_4/vol culture-day	2.71
Total Volatile Acids, mg/L as acetic	3270-5250
Mean Caustic Added, meq/L feed	0

Table I-7. PERFORMANCE DATA AND OPERATING CONDITIONS FOR STR RECEIVING KELP LOT 53 AT 0.40 kg VS/m^3-day (0.025 lb VS/ft^3-day) LOADING RATE

Digester No.	50
Digester Design	STR
Culture Volume, L	50
Loading, kg VS/m^3-day (lb VS/ft^3-day)	0.40 (0.025)
Data Period	9/20-10/10/82
HRT, days	200
Gas Yield, SCM/kg VS added (SCF/lb VS added)	0.78 (12.45)
Methane Content, mol %	54.8
Methane Yield, SCM/kg VS added (SCF/lb VS added)	0.43 (6.82)
Methane Production Rate, vol CH_4/vol culture-day	0.27
Total Volatile Acids, mg/L as acetic	<100
Mean Caustic Added, meq/L feed	0

APPENDIX J.
STR Kinetics Data and Calculations

Kinetics

It is assumed that digestion of kelp follows mixed second-order reaction kinetics with respect to substrate and organism concentrations, and that the kinetics for the rate-limiting fermentation step can be represented by the Monod equation for microbial growth:

$$\mu = \frac{\hat{\mu}\, S}{K + S} \tag{1}$$

where —

μ = growth rate for the rate-limiting reaction step, $days^{-1}$

$\hat{\mu}$ = maximum specific growth rate constant, $days^{-1}$

K = saturation coefficient, g/L

S = effluent biodegradable substrate concentration, g/L.

The rates of change of bacterial cell mass and substrate concentrations in STR systems without solids recycle are governed by the following two differential equations:

$$\frac{dM}{dt} = \hat{\mu}M - \frac{M}{\theta} \tag{2}$$

and —

$$\frac{dS}{dt} = -\dot{F} + \frac{S_o - S}{\theta} \tag{3}$$

where —

S_o = influent biodegradable substrate concentration, g/L

M = cell mass concentration, g/L

$\dot{F}$ = volumetric substrate utilization rate, g/L-day

t = time, days

θ = hydraulic retention time, days.

Under steady state conditions —

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

Equation 2 yields —

$$\theta = \frac{1}{\hat{\mu}} \tag{4}$$

Combine Equations 1 and 4:

$$\theta = \frac{1}{\hat{\mu}} + \frac{K}{\hat{\mu}}\left(\frac{1}{S}\right) \tag{5}$$

Equation 5 represents a straight line with an intercept of $1/\hat{\mu}$ and a slope of $K/\hat{\mu}$ that may be used to evaluate the kinetic constants ($\hat{\mu}$ and K) for kelp feeds.

Because of the complexity of the kelp, it is not possible to determine the effluent biodegradable substrate concentration (S) directly. Values for S can be determined, however, according to the following equation:

$$S = V - V_o(1 - \beta) \tag{6}$$

when —

$$S_o = \beta V_o$$

where —

V = effluent volatile solids concentration, g/L

V_o = influent volatile solids concentration, g/L

β = feed biodegradability factor.

Values of β will be obtained from 60-day anaerobic biogasification potential (ABP) assays.

Process Kinetic Model

The methane yield (Y_M) can be predicted by the following equation:

$$Y_M = \frac{\alpha(S_o - S)}{V_S} \tag{7}$$

where —

α = methane yield coefficient, LCH_4/g biodegradable substrate destroyed

V_S = volatile solids added, g/L

From Equation 5 —

$$S = \frac{K}{(\hat{\mu}\theta - 1)} \tag{8}$$

Put the value S from Equation 8 into Equation 7 and put $V_s = L\theta$; the equation for methane yield becomes —

$$Y_m = \alpha \frac{S_o\mu\theta - (S_o + K)}{L\mu\theta^2 - L\theta} \quad (9)$$

where —

L = loading, g volatile solids/L culture-day.

The methane production rate (R_M) can be predicted as given below:

$$R_M = Y_m * L \quad (10)$$

Substitute the value of Y_M from Equation 9 into Equation 10:

$$R_M = \alpha \frac{S_o\mu\theta - (S_o + K)}{\mu\theta^2 - \theta} \quad (11)$$

With appropriate substitutions, Equations 9 and 11 can be modified to obtain process models relating digester methane production rate and methane yield to the system constants $\hat{\mu}$, K, β and α and selected operating variables such as loading, retention time, and feed volatile solids concentration as given below:

- Substitute for $S_o = \beta V_o$ to obtain R_M and Y_M as a function of feed volatile solids concentration and retention time —

$$Y_M = \alpha \frac{\beta V_o\mu\theta - (\beta V_o + K)}{L\theta^2\mu - L\theta} \quad (12)$$

$$R_M = \alpha \frac{\beta V_o\mu\theta - (\beta V_o + K)}{\theta^2\mu - \theta} \quad (13)$$

- Substituting for $V_o = 16.02\ (L\theta)$*, Equations 12 and 13 may be rewritten to obtain R_M (in vol CH_4/vol culture-day) and Y_M (in SCF/lb VS added) as a function of loading (in lb VS/ft^3-day) and retention time (days) —

$$Y_M = \alpha \frac{16.02\ \beta\theta^2\mu - (16.02\ \beta\theta + K/L)}{\theta^2\mu - \theta} \quad (14)$$

$$R_M = \alpha \frac{16.02\ \beta\ L\theta^2\mu - (16.02\ \beta\ L\theta + K)}{\theta^2\mu - \theta} \quad (15)$$

* 16.02 is a factor to convert from metric to English units.

Table J-1. DATA USED IN STR KINETIC STUDIES[a]

Loading Rate, kg VS/m^3-day (lb VS/ft^3-day)	HRT, days	Culture Volume, L	Methane Yield, SCM/m^3-day (SCF/ft^3-day)	VS, g/L	VS, g/L	$\frac{1}{VS - VS_o(1 - \beta)}$	Methane Produced, L	g VS Destroyed[b]	α, L Methane Produced/ g VS Destroyed[b]
1.6 (0.10)	50	10	0.35 (5.6)	79.66	19.13	0.313	5.55	12.38	0.45
3.2 (0.20)	25	7	0.33 (5.3)	79.66	19.21	0.305	7.38	17.10	0.43
4.0 (0.25)	20	7	0.32 (5.1)	79.66	19.46	0.283	8.92	21.13	0.42
4.8 (0.30)	16.5	7	0.32 (5.2)	79.66	21.10	0.193	10.94	25.26	0.43
6.4 (0.40)	12.5	7	0.31 (5.0)	79.66	21.59	0.177	13.88	33.14	0.42
8.0 (0.50)	10	5	0.31 (4.9)	79.66	24.20	0.121	11.94	28.74	0.42

[a] $\beta = 0.80$, determined by anaerobic biogasification assays.

[b] Biodegradable VS.

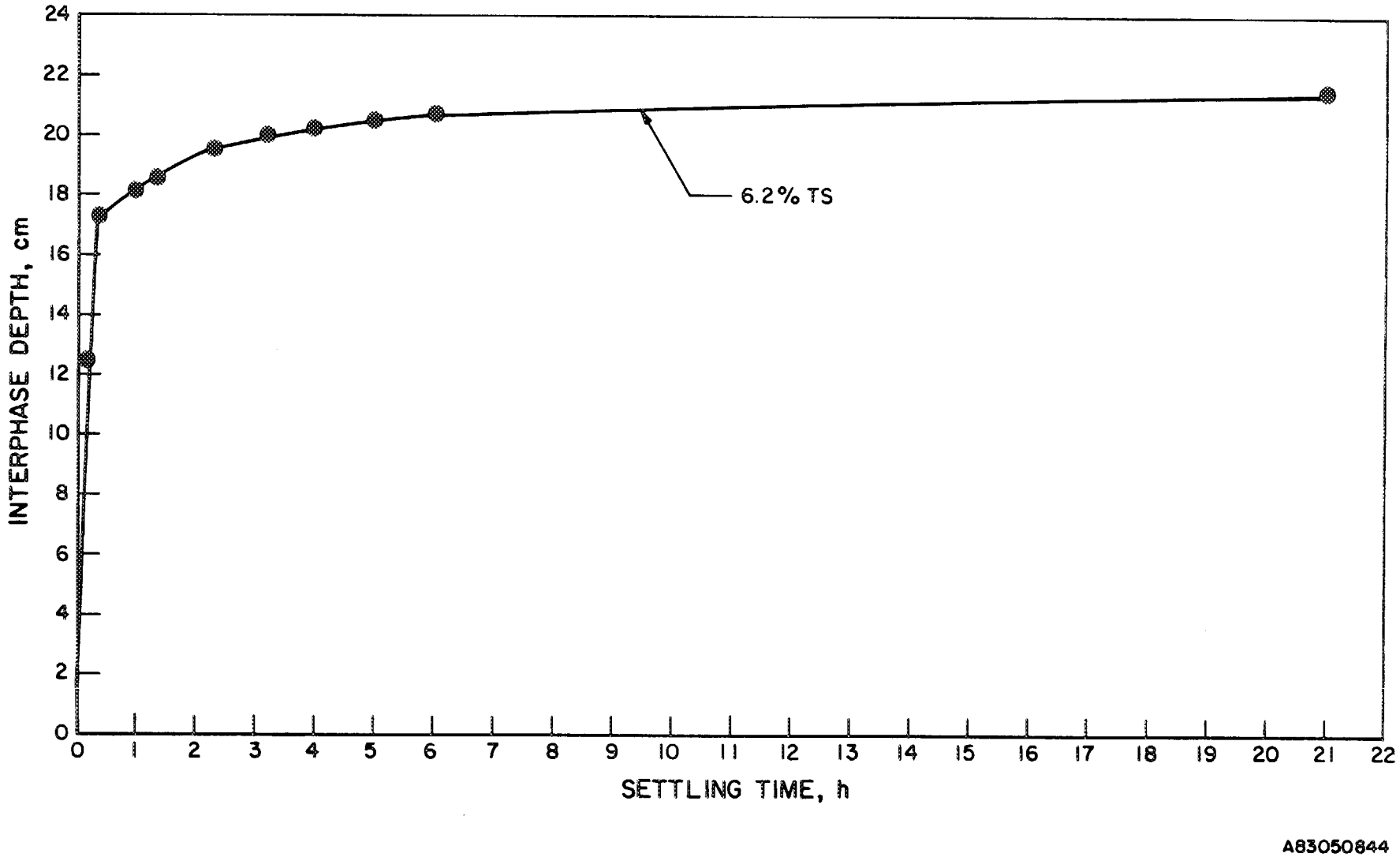

Figure J-1. SETTLING CHARACTERISTICS OF EFFLUENT OF STR OPERATED AT A LOADING RATE OF 0.4 kg VS/m^3-day (0.025 lb VS/ft^3-day)

APPENDIX K.
Nitrogen in Digester Effluent

Table K-1. EFFECT OF STORAGE ON AMMONIA NITROGEN IN A DIGESTER EFFLUENT STORED IN AN OPEN VESSEL

Lapsed Time, days	NH_3-N, mg/L
1	580
2	530
3	470
4	380
5	210

Table K-2. EFFECT OF STORAGE ON AMMONIA AND TOTAL NITROGEN IN A DIGESTER EFFLUENT STORED IN A CLOSED VESSEL

Lapsed Time, days	NH_3-N, mg/L	N, wt %
0	520	0.12
1	490	0.12
3	505	0.13
5	540	0.15
10	560	0.17

Table K-3. EFFECT OF STORAGE ON AMMONIA NITROGEN AND TOTAL NITROGEN IN USR DIGESTER EFFLUENT STORED IN A CLOSED VESSEL*

	Purge Gases					
	Helium/O_2		Nitrogen/O_2		No Purge Gas	
Days	NH_3-N, mg/L	N, wt %	NH_3-N, mg/L	N, wt %	NH_3-N, mg/L	N, wt %
0	700	0.21	700	0.21	700	0.21
1	730	0.17	730	0.17	700	0.17
2	670	0.17	720	0.20	700	0.20
5	720	0.17	720	0.19	700	0.22
9	730	0.18	750	0.21	730	0.17
12	760	0.17	760	0.18	--	--

* Room temperature storage in a closed vessel; the headspace of each vessel was purged with the specified gas mixture after each sampling.

Table K-4. AMINO ACIDS PROFILE IN KELP LOT 53 AND IN EFFLUENT OF A USR OPERATED AT A LOADING RATE OF 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day)

Amino Acid	Kelp Lot 53 mg/g	USR* Loading, mg/g	% Reduced
Alanine	2.0	0.8	60
Valine	0.5	0.7	−40
Glycine	0.5	0.6	−20
Isoleucine	0.3	0.6	−100
Leucine	0.6	0.9	−50
Proline	0.4	0.4	0
Threonine	0.5	0.6	−20
Serine	0.5	0.6	−20
Methionine	0.2	0.3	−50
Hydroxyproline	0.04	< 0.01	—
Phenylalanine	0.4	0.6	−50
Asparatic Acid	1.2	1.5	−25
Glutamic Acid	2.4	1.4	42
Tyrosine	0.3	0.5	−67
Lysine	0.7	0.8	−14
Histidine	0.2	0.2	0
Arginine	0.3	0.3	0
Cystine	0.2	0.3	−50
Total	11.2	11.1	

* USR operated at 0.4 lb VS/ft^3-day.

Table K-5. NITROGEN BALANCE IN USR DIGESTER OPERATED AT A LOADING RATE OF 6.4 kg VS/m^3-day (0.40 lb VS/ft^3-day) ON KELP LOT 53

	N,g	Percent
Input		
Feed	1.28	100.0
Total	1.28	100.0
Output		
Liquid Effluent	1.25	97.7
Gas Phase	0.05	3.9
Total Accounted	1.30	101.6
Not Accounted for by Experimental and Analytical Procedures	−0.02	1.6
Total	1.28	100.0