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BIOMETHANATION OF GIANT BROWN KELP MACROCYSTIS PYRIFERA

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ABSTRACT

The results of studies conducted on the anaerobic digestion of the giant brown kelp — Macrocystis pyrifera — in laboratory-scale digesters are presented. Untreated raw kelp sustains a stable fermentation under conventional mesophilic operating conditions with a methane yield of 4.5 SCF/lb volatile solids (VS) of organic matter added and a reduction in organic matter of 50%. A materials and energy balance presented for the kelp biomethanation process shows that 100 pounds of wet kelp as harvested and drained of physical water yields 25 SCF of methane with an energy recovery efficiency of 55.5%. The major biodegradable components of kelp are mannitol and algin, and the refractory components are cellulose and protein. The anaerobic fermentation of kelp was demonstrated as nonlimited by nitrogen or phosphorus. A stable fermentation can be developed with undiluted kelp feed or a kelp feed diluted with seawater. Thermophilic digestion of kelp exhibited unstable performance and lower yields than mesophilic digestion. Inocula derived from anaerobic marine environments did not show better performance than an inoculum derived from a mixture of effluents from domestic sewage sludge and municipal solid waste digesters. Higher methane yields may be possible through post-treatment and recycle of refractory effluent solids. Preliminary studies presented show that heat treatment alone and under acid and alkaline conditions increases the biodegradability of the digested ungasified solids.

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INTRODUCTION

The search for new sources of energy is intensifying as the demand for energy increases and supplies of fossil fuels decrease. One of the possible long-term solutions to this energy shortage dilemma is the conversion of renewable sources of organic matter, such as wastes and biomass, to products that are readily useable as fuels or interchangeable with conventional fuels. Although organic wastes represent a minor supplemental energy resource, land- and water-based biomass could be developed into a major resource (1,2). This fact has led to the concept of land- and water-based energy farms directed at production of sufficient quantities of biomass and their conversion to synthetic fuels to help alleviate the energy shortage. Development of energy farms in the marine environment seems particularly attractive because large areas are available that are not used for food production. Although several processes are being investigated for conversion of biomass to product fuels, microbial conversion to methane (biomethanation) is one of the more attractive methods for materials with high moisture content.

This paper is concerned with work conducted at the Institute of Gas Technology (IGT) on the biomethanation of the giant brown sea kelp (Macrocystis pyrifera). This work was initiated at IGT in 1974 and ultimately became part of the Energy From Biomass Program sponsored initially by the American Gas Association and now the Gas Research Institute through its prime contractor the General Electric Co. (3). The overall objective of this program is to determine the technical and economic feasibility of large-scale commercial production and harvesting of kelp in the open ocean and its conversion to methane and valuable by-products such as food and fertilizer.

The initial objective of IGT's work on the anaerobic digestion of kelp was to establish that it could be fermented at long detention times under conventional conditions without addition of external nutrients. The current objectives include a) identification of factors that limit methane yields and fermentation rates and b) optimization of the process for production of methane at high-energy-recovery efficiencies.

This paper presents some of the results of IGT's kelp fermentation studies, including calculation of theoretical yields, comparison of two different types of kelp feeds, effect of feed particle size, evaluation of potential nutrient limitation, use of seawater for preparation of feed slurries, use of undiluted kelp feeds, comparison of performance of different inocula, effect of temperature, preliminary results of post-treatment studies, and a materials and energy balance for kelp biomethanation.

MATERIALS AND METHODS

Digester Design and Operation

All kelp digestion runs were conducted in 1.5-ℓ glass bottles equipped with feeding and wasting ports, temperature control, continuous mixing, and gas collection systems. The details of these units were described previously (4).

The following steps were followed in the semicontinuous operation used for these studies:

- Gas production was recorded at atmospheric pressure.
- Room temperature and barometric pressure were recorded. (The temperature of the collected gas was assumed to be the same as room temperature.)
- A selected volume (culture volume divided by detention time) of digester effluent was withdrawn and its temperature and pH were measured and recorded.
- The appropriate quantity of kelp was added directly or as a feed slurry (prepared with outgassed water) in a volume equal to that withdrawn.
- When pH control was necessary, 5N NaOH was added with the feed.

This feeding schedule was maintained daily (including weekends and holidays). In addition, the following analyses were conducted weekly to evaluate digester performance: individual and total volatile fatty acids, alkalinity, gas composition, and conductivity. Feed slurries and effluent from steady-state digesters were analyzed for the following parameters: total solids, volatile solids, ash, pH, alkalinity, conductivity, total and individual volatile fatty acids, chemical oxygen demand (COD), total nitrogen, carbon, hydrogen, sulfur, phosphorus, and heat content.

Digester Feeds

Two feed types were used for these studies. Raw kelp (RK) is freshly harvested kelp that is drained of physical water, chopped, ground, and frozen prior to use. Baseline-treated kelp (BLTK) is raw kelp that is mixed with 0.5 weight percent $CaCl_2$ solution, heat treated at 95°C for 30 minutes, drained, pressed in a belt press, and frozen prior to use. The following analyses were conducted on the kelp feeds used in this study: moisture, total solids, volatile solids, ash, heating value, and weight percent carbon, nitrogen, phosphorus, sodium, hydrogen, potassium, and calcium.

Inocula

Inoculum A. Inoculum A was originally derived from a mixture of effluents from an IGT pilot digester receiving municipal solid-waste-sewage sludge and from a municipal high-rate digester. This inoculum was gradually converted from a feed of municipal solid waste/sewage sludge to raw kelp. It has received raw kelp under a variety of

operating conditions since July 1975 and is currently the inoculum used for most of the kelp experimental work reported here.

Inoculum D. Development of Inoculum D was initiated as part of a task to evaluate digestion performance of an inoculum containing organisms principally of marine origin. This inoculum was formed by mixing 180 ml of inoculum received from General Electric's RK-fed digester (originally derived from marine samples), 563 g of (wet weight) anaerobic marine sediment, 188 g of chopped rotting kelp, and 569 ml of IGT's Inoculum A.

Inoculum E. Inoculum E was similar in origin to Inoculum D except that development was conducted at room temperature (instead of 35°C) since that temperature more closely resembles that of the marine environment. This inoculum consisted of 617 g of chopped rotting kelp wrack, 311 g of anaerobic marine sediment, and sufficient anaerobic water to make the total volume 1.5 ℓ. The pH was controlled at 7.1, and raw kelp was gradually added as gas and methane production increased.

Bioassay for Anaerobic Biodegradation Potential

The following procedure was followed to evaluate a bioassay method for evaluation of the effectiveness of various treatment procedures increasing the biodegradability of effluent sludge solids.

Treatment of Effluent Solids. Effluent from a RK-fed digester was placed in a beaker and allowed to settle for 1 hour. The resulting supernatant was decanted and discarded. The solids (about 25% of the original volume) were divided into several 100-ml aliquots. These were adjusted to various pH values with 5N NaOH or HCl, heat treated at 175°C for 1 hour in a pressurized bomb, adjusted to pH 7, and frozen until use in the bioassay.

Bioassay. Several 300-ml Erlenmeyer flasks were each equipped with a stopper and two glass tubes suitable for outgassing. The flasks were connected in series with rubber tubing and outgassed for 15 minutes with helium passed through a gas purifier (Supelco 2-2313) to remove trace amounts of oxygen. Active digesting sludge was collected from a RK-fed digester and transferred anaerobically to each flask at 100 ml per flask; 10 ml of treated effluent solids were also added to the flasks. The tubing connecting the flasks was clamped shut to isolate each flask, and the flasks were incubated at a shaking rate of 150 rpm and temperature of 35°C. Gas production was measured once or twice per day by inserting a needle into the flask stopper connected to a gas burette containing an acid salt solution. The gas volume was recorded and a subsample analyzed for methane and carbon dioxide. The experiment was terminated when the gas production rate in all experimental flasks was equal to the control receiving untreated effluent solids, i.e., about 5 days.

Analytical Procedures

Gas production was determined by daily visual observation of fluid displacement from a gas burette and conversion to standard conditions (60°F and 30 in. of mercury). The fluid consisted of an aqueous solution of 20% sodium sulfate and 5% sulfuric acid. Gas samples were analyzed once per week for methane, hydrogen, carbon dioxide, nitrogen, and oxygen using a Fisher gas partitioner.

Chemical analyses of raw feeds, digester feed, and effluent slurries were performed according to standard analytical procedures listed in Table 1 except for the following procedures that were developed at IGT;

- Carbon-hydrogen analysis
- Heating value
- Potassium, sodium, and calcium
- Volatile fatty acids

Carbon-hydrogen analysis was conducted by the ASTM coal and coke procedure D3178-73.

Heating values were determined using a Parr Model 1241 automatic adiabatic calorimeter system. The unit is standardized to meet ASTM D2015 requirements. A check for completeness of combustion was made by plotting Btu/lb versus percent carbon in the samples. A straight line was obtained with minimal scatter.

Potassium, sodium, and calcium were determined by atomic absorption spectrophotometry following successive acid digestion steps with nitric and perchloric acids.

Volatile fatty acids were determined by flame ionization gas chromatography using a Hewlett-Packard Model 5840A gas chromatograph equipped with an automatic injection system. Samples were prepared for analysis by addition of 0.3 ml of 20% H_3PO_4 per 2-ml sample and centrifuging at 20,000 rpm for 30 minutes. GC operating conditions were as follows: 6 ft x 1/4 in. (OD) glass column packed with Chromosorb 101 (80/100 mesh); N_2 carrier gas, 30 ml/min; H_2, 30 ml/min; air, 250 ml/min; injector, 200°C; oven, 180°C; and detector 250°C. Baseline separation of acetic, propionic, isobutyric, butyric, isovaleric, valeric, and caproic acids is effected by this procedure in 15 minutes. Every 10 samples is followed by a 3% phosphoric acid rinse and a standard containing all seven acids.

Calculations

Equations for calculating the following parameters that appear frequently in this paper are presented below:

Gas Yield

$$G_Y = \frac{G_{SCF}}{VS_{added}}$$

G_Y = gas yield, SCF/lb VS added

G_{SCF} = gas production, SCF/cu ft-day

VS_{added} = volatile solids added, lb/cu ft-day

Table 1. LIST OF STANDARD ANALYTICAL PROCEDURES FOR KELP

Test	Standard Procedure	Reference
Ash	Ignition, gravimetric	APHA-AWWA-WPCF Standard Methods, 14th Edition, Part 208G
Alkalinity	Titrimetric Method	Standard Methods, 14th Edition, Part 403
Carbon Dioxide	Gas Chromatography	Standard Methods, 14th Edition, Part 511B
COD	Dichromate, Oxidation Method	Standard Methods, 14th Edition, Part 508
Conductivity	Conductance Cell and Wheatstone Bridge	Standard Methods, 14th Edition, Part 205
Hydrogen	Gas Chromatography	Standard Methods, 14th Edition, Part 511B
Methane	Gas Chromatography	Standard Methods, 14th Edition, Part 511B
Moisture	Evaporation, Gravimetric	Standard Methods, 14th Edition, Part 208G
Nitrogen (ammonia)	Specific Ion Probe	Standard Methods, 14th Edition Parts 418 and 413J
Nitrogen	Gas Chromatography	Standard Methods, 14th Edition, Part 511B
Nitrogen (organic)	Kjeldahl Digestion and Specific Ion Probe	Standard Methods, 14th Edition, Parts 421, 418, and 413J
Nitrogen (total)	Kjeldahl Digestion and Specific Ion Probe	Standard Methods, 14th Edition, Parts 421, 418, and 413J
pH	Electrometric Method	Standard Methods, 14th Edition, Part 424
Phosphorus	Calorimetric	AOAC Official Method of Analysis, 12th Edition, Section 3.062
Solids (total)	Evaporation, Gravimetric	Standard Methods, 14th Edition, Part 208G
Solids (volatile)	Ignition, Gravimetric	Standard Methods, 14th Edition, Part 208E
Sulfur	Combustion, Gravimetric	ASTM, D3177-75
Suspended Matter (total)	Filtration, Gravimetric	Standard Methods, 14th Edition, Part 208D
Suspended Matter (volatile)	Filtration, Ignition, and Gravimetric	Standard Methods, 14th Edition, Part 208G

Methane Yield

M_Y = (G_Y)(Methane Content)

M_Y = methane yield, SCF/lb VS added

G_Y = gas yield, SCF/lb VS added

Methane Content = mole percent

Volatile Solids Destruction

1. VS destruction = $\dfrac{(G_Y)(\text{VS content})(3.17)}{\%\ \text{C in TS}}$

G_Y = gas yield, SCF/lb VS added

VS content = volatile solids content of total solids,%

3.17 = constant derived from (12.0 lb C/lb mole X 100) ÷ 379 cu ft gas/lb mole

% C in TS = carbon content of total solids, %

2. VS destruction, % = $\dfrac{VS_{in} - VS_{out}}{VS_{in} - VS_{in}\ VS_{out}}$

VS_{in} = volatile solids content of influent, % of total solids expressed as decimal

VS_{out} = volatile solids content of effluent, % of total solids expressed as decimal

Energy Recovery in Methane

E_R = $\dfrac{(G_Y)(M_Y)}{E_{TS}\ /VS}$

E_R = energy recovery in methane

M_Y = methane yield, SCF/lb VS added

E_{TS} = energy content of total solids, Btu/lb

VS = volatile content of influent total solids, %

RESULTS AND DISCUSSION

Characteristics of Raw Feeds

The physical and chemical characteristics of the two feeds (RK and BLTK) used in this work are presented in Table 2. BLTK was a special kelp feed preparation treated with $CaCl_2$ and heat and pressed to remove some of the salts. The purpose of this treatment was to develop a feed with a lower salt content and higher organic content.

Compared with RK, BLTK had higher levels of volatile matter and heating value; higher total carbon, nitrogen, and calcium concentrations; and lower concentrations of ash, sodium, potassium, and sulfur. Little variation was observed in the characteristics of three different lots of RK collected from different locations and on different dates.

The organic constituents of raw kelp (Lot No. 1) reported previously (4) and listed in Table 3 are protein, mannitol, algin, and cellulose which account for 99% of the volatile solids. Minor constituents include laminarin and fucoidin.

Table 2. CHARACTERISTICS OF KELP FEEDS

	RK[a,b]			BLTK[a,c]
Lot No.	1	2	3	1
Date Harvested	Feb. 9 & 10, 1976	Sept. 30, 1976	Oct. 25, 1977	Feb. 9 & 10, 1976
Harvesting Location	Monterey	Soquel Point	Soquel Point	Soquel Point
Proximate Analysis				
Moisture, wt %	89.7	88.8	88.2	75.8
Volatile Solids, wt % dry	54.2	57.9	58.9	72.7
Ash, wt % dry	45.8	42.1	41.1	27.3
Ultimate Analysis, wt % dry				
C	26.6	27.8	28.0	36.1
H	3.74	3.73	3.92	4.68
N	2.55	1.63	1.86	3.32
S	1.09	1.05	1.09	0.87
P	0.48	0.29	0.33	0.46
K	14.4	14.7	14.0	6.4
Na	4.3	3.5	3.6	1.8
Ca	1.05	--	1.4	3.3
Heating Value, Btu/dry lb	4410	4620	4710	6047

[a] Harvested and processed by USDA Western Regional Research Center, Albany, Calif., and shipped to IGT in Trans-Temp containers at -10° to -15°C.

[b] Raw kelp - freshly harvested kelp drained of free water, chopped, and ground in hammer mill equipped with 0.188-in. screen and frozen.

[c] Baseline-treated kelp – raw kelp mixed with 0.5% $CaCl_2$, heat treated at 95°C 30 min., drained, pressed in a belt press, and frozen.

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Maximum Theoretical Yields

To evaluate performance of kelp digestion runs and to provide a basis for establishing target yields, calculations of maximum theoretical yields of methane from the biomethanation of RK and BLTK were made using the data in Table 2. These yields were calculated as follows: Compositional data were used to calculate the empirical formulas of RK and BLTK. Stoichiometric equations for the conversion of each feed to methane and carbon dioxide were determined. The resulting molar yields of methane were expressed as SCF/lb VS added. Because a fraction of organic matter in all bacterial fermentations is converted to bacteria, these yields were corrected for cell synthesis using the data reported by Mc Carty(5) for the anaerobic digestion of pure carbohydrate and protein. The final theoretical methane yields for RK and BLTK were, respectively, 6.50 and 7.24 SCF/lb VS added (Table 4). Corresponding values for volatile solids reduction were 82.2% and 83.7%. It should be recognized that these yields could only be obtained if the organic matter in the kelp feeds were 100% biodegradable.

Table 5 lists several factors that can cause experimental yields to be lower than the calculated theoretical yields. Evaluation of these has been the basis for recent kelp digestion research at IGT.

RK Versus BLTK as a Feed Substrate

During the initial stages of this project, preliminary digestion studies were conducted on two forms of kelp feeds, raw kelp (RK) and $CaCl_2$-treated kelp (BLTK) that was pressed to remove water and salts. The BLTK was selected as a possible alternative to RK because it was thought that the high salt content of the untreated RK would be inhibitory to the biomethanation process. Steady-state performance data for runs receiving RK and BLTK at detention times of 10 and 18 days are presented in Table 6. Methane yields of Runs 26 and 1, which received RK and BLTK, respectively, at a detention time of 10 days, were not significantly different. At a higher detention time of 18 days, however, the methane yield of the RK-fed digester (Run 8) was 31% higher than that of the BLTK-fed digester (Run 101). At both detention times the concentration of volatile acids was higher in the RK digesters. These levels of acids did not appear to result in process inhibition and may represent a source of additional methane through process modification. In view of the stable and high performance of RK-fed runs and the added expense and energy requirement associated with conversion of RK to BLTK, the untreated RK was selected as the feed substrate for more intense study.

Feed Particle Size Reduction

As received from the USDA Western Regional Research Center (WRRC), the raw kelp is drained of physical water, chopped, and ground in a mill equipped with a 0.188-mesh screen. The following run was made to determine if further reduction in particle size would have a significant effect on digestion performance. Although further reduction would not be economically feasible, it was not desirable to have particle size limit the yields of bench-scale studies. Run 118 (Table 7) represents a digester that received RK (as received from WRRC) that was passed twice through an Urschel mill equipped with a 0.03-inch head. This

Table 3. COMPOSITION OF ORGANIC FRACTION OF RAW KELP (Lot No. 1) (4)

Organic Group	Sample Weight, % volatile solids
Protein	29.5
Carbohydrates	
Mannitol	34.5
Algin	26.1
Cellulose	8.8
Laminarin	1.3
Fucoidin	0.4
Total	100.6

Table 4. MAXIMUM THEORETICAL YIELDS FOR BIOMETHANATION OF RK AND BLTK

	RK Lot No. 2	BLTK Lot No. 1
Empirical Formula[a]	$C_{2.32}H_{3.69}O_{1.48}$	$C_{3.01}H_{4.68}O_{1.73}$
Theoretical Methane Yield Based on Stoichiometry, SCF/lb VS added[b]	8.19	8.65
Theoretical Methane Yield Corrected for Bacterial Production, SCF/lb VS added[c]	6.73	7.24
Theoretical Volatile Solids Reduction, %	82.2	83.7

[a] Excluding nitrogen, phosphorus, and sulfur.

[b] Assumes that the reactants are kelp + H_2O and the products are CH_4 + CO_2.

[c] Based on data of Speece and McCarty (7) on enriched sludge digesters receiving either soluble carbohydrate or soluble protein.

Table 5. FACTORS THAT CAUSE EXPERIMENTAL YIELDS TO BE LOWER THAN THEORETICAL YIELDS

- Nutrients are limiting.
- Large particle size limits contact between organisms and substrates.
- Hydraulic detention time is too short to retain critical organisms with long generation times.
- Catabolites of easily metabolized substrates repress decomposition of complex substrates.
- Initial steps of decomposition of certain substrates cannot take place under anaerobic conditions (absence of O_2, NO_3^-, or $SO_4^=$).
- Feed contains inhibitory substances.
- Mixing rate is not optimum.
- Feeding frequency is not optimum.
- Loading is not optimum
- Temperature is not optimum.
- Inoculum lacks organisms necessary for decomposition of feed substrates.

Table 6. COMPARISON OF STEADY-STATE PERFORMANCE OF DIGESTERS RECEIVING RK AND BLTK AT TWO DIFFERENT DETENTION TIMES (Loading, 0.1 lb VS/cu ft-day; Culture Volume, 1.5 ℓ ; Temperature, 35°C)

Run	26	8	1	101
Feed	RK	RK	BLTK	BLTK
Detention Time, days	10	18	10	18
Data Period	1/2-1/31/77	3/17-6/11/77	1/2-1/31/77	7/9-10/8/77
Gas Yield, SCF/lb VS added	5.85	7.65	5.58	5.66
Methane Yield, SCF/lb VS added	3.44	4.45	3.31	3.39
Volatile Solids Reduction, %*	38.6	50.8	35.6	36.2
Total Volatile Acids, mg/ℓ as acetic	855	192	43	29.0
pH	6.8-7.2	6.8-7.2	6.8-7.2	6.8-7.2
Alkalinity, mg/ℓ as $CaCO_3$	3860	4160	3070	4400
Conductivity, μmho/cm	17,500	20,600	8,830	12,000

* Carbon in product gas divided by carbon in feed.

Table 7. COMPARISON OF PERFORMANCE OF CONTROL RUN 116, NUTRIENT EXPERIMENT RUN 117, AND PARTICLE-SIZE EXPERIMENT RUN 118 (RK Feed, L=0.1 lb VS/cu ft-day, DT=12 days, T=35°C, Culture Volume = 1.5ℓ)

Run No.	116	117[c]	118[d]
Date Initiated	1/18/78	1/18/78	1/18/78
Data Period	3/17-6/11/78	4/24-5/14/78	3/6-3/16/78
Detention Times in Progress	12	4.9	4.8
Methane Production Rate, SCF/cu ft culture-day	0.383	0.373	0.399
Gas Yield, SCF/lb VS added	6.62	6.24	6.60
Methane Content, mol %	57.8	59.8	60.5
Methane Yield, SCF/lb VS added	3.83	3.73	3.99
Volatile Solids Reduction, %[a]	45.1	42.6	45.0
Volatile Solids Reduction, %[b]	62.7	49.7	44.8
COD Reduction, %	57.7	59.6	42.8
Total Volatile Acids, mg/ℓ as acetic	485	945	713

[a] Carbon in product gas divided by carbon in feed.

[b] Based on analytical solids data.

[c] Daily addition of NH_4HCO_3 (250 mg/ℓ feed volume as nitrogen) and KH_2PO_4) 250 mg/ℓ feed volume as phosphorus).

[d] RK passed through an Urschel mill equipped with a 0.03-inch head to reduce particle size.

treatment reduced the RK to a puree-type consistency. This run was operated at a loading of 0.1 lb VS/cu ft-day, detention time of 12 days, and temperature of 35°C. The methane yield was not significantly different than that of control Run 116 (Table 7) which was fed RK as received from WRRC under the same operating conditions. These results suggest that the readily biodegradable components of kelp are not tightly bound to the macromolecular structure of the particulate matter of the kelp. If they were, particle-size reduction would have increased the surface area available for microbial attack and resulted in higher methane yields. Since particle-size requirements affect pretreatment process requirements, the effect of larger particle size on performance will be evaluated when a large-scale digester is available for study.

Evaluation of Potential Nutrient Limitation

Certain organic wastes and biomass types require the addition of supplementary nutrients to achieve methane yields responsible for further process development. Table 8 summarizes data obtained at IGT on the carbon, nitrogen, and phosphorus contents of two different lots of RK used for digestion studies. Based on literature values that

Table 8. NUTRIENT LEVELS IN RAW KELP FEEDS

	Lot No. 2	Lot No. 3
C, wt % dry	27.8	28.0
N, wt % dry	1.63	1.86
P, wt % dry	0.29	0.33
C/N	17.0	15.0
Suggested C/N*	11	--
C/P	95.9	84.8
Suggested C/P*	9-52	--

* Higher ratios may result in nutrient limitation. (See Ghosh and Klass (6); Speece and McCarty (7).)

reportedly limited the biomethanation process (6,7), either nitrogen or phosphorus could be limiting the fermentation of kelp. To evaluate the potential nutrient limitations of the kelp digestion process, Run 117 received 250 mg/ℓ feed volume of nitrogen (as NH_4HCO_3) and phosphorus (as KH_2PO_4) on a daily basis. This concentration for each nutrient is commonly used in microbiological growth media containing excess organic substrate and not considered inorganic nutrient limited. Table 7 shows that the methane yield and other performance parameters were not significantly different than those of control 116. It was thus concluded that biomethanation of RK is not limited by either of these nutrients. The absence of a nutrient requirement for fermentation of kelp adds to the list of characteristics making it attractive as a biomass for the biomethanation process.

Performance of Digesters Receiving Undiluted RK and RK Diluted with Seawater

The purpose of this series of experiments was to evaluate the performance of digesters receiving RK without added dilution water at two different loadings and to evaluate the effect of using seawater as a dilution medium for preparation of feed slurries. The absence of a water requirement or the ability to use seawater for feed dilution would reduce process costs.

To evaluate the performance of digesters receiving undiluted feed, Runs 119 and 120 received undiluted RK at loadings of 0.1 lb VS/cu ft-day (equivalent to Run 116) and 0.2 lb VS/cu ft-day, respectively. The detention times, established by the water content (88.81%) and

volatile solids content (57.9%) of the RK, were 40.5 and 20.2 days, respectively. A third digester (Run 121) was operated under conditions identical to those of control Run 116, except that the feed was diluted with seawater (Instant Ocean, Aquarium Systems, East Lake, Ohio.)

A profile of methane yield for each of these runs and the control are shown in Figure 1. Note that each of the three experimental runs began to show signs of inhibition after about two detention times (2θ). This inhibition is apparently related to the buildup of salts to a critically high level. Each of the experimental runs recovered after a period of about 1 month, indicating adaptation of the population to the inhibitory conditions.

Table 9 compares other performance data for these runs. The methane yield of Run 119 receiving undiluted RK at a loading of 0.1 VS/cu ft-day was higher than that of the control. This may be related to the longer residence time of solids in that digester. The methane yield in Run 121 receiving RK diluted with seawater was lower than that of the control. These results suggest that, although a balanced steady-state fermentation can be obtained with feed diluted with seawater, the overall yield will be slightly lower than if the feed is diluted with fresh water. The lower yield observed for Run 120, which received undiluted RK at a loading of 0.2 lb VS/cu ft-day, must be due to the higher loading rather than to the high salt concentration, because the salt concentration was equal to that in Run 119. The latter run also received undiluted RK with no reduction in methane yield.

All three of these experimental runs had high concentrations of volatile acids in the effluent; the concentrations were highest in the two runs receiving undiluted RK, even though performance was stable. Although the high acids might explain the lower yields observed in Runs 120 and 121, the yield of Run 119 was unaffected because it was higher than that of the control.

Performance of Different Inocula

The work reported above was conducted with IGT's Inoculum A derived in 1975 from effluent of digesters operated on domestic sewage sludge and municipal solid wastes. Because kelp contains substrates unique to marine environment (e.g., algin, fucoidin, and laminarin) and has a high salt content, other inocula derived principally from anaerobic marine environments that decompose kelp naturally were investigated.

Table 10 shows that performance of Inoculum D (derived from General Electric's RK-fed digester, decaying kelp, anaerobic marine sediment, and IGT's Inoculum A) was not significantly different than that of IGT's inoculum A after several detention times. Both runs were operated at 35°C.

A second inoculum (E) was developed from a mixture of decaying kelp and anaerobic marine sediment. This culture was developed at room temperature (about 26°C) because that temperature more closely resembles the marine environment. Table 10 shows that steady-state performance of Inoculum E (Run 123) at 26°C was approximately half of that of IGT's Inoculum A (Run 8) incubated at 35°C. Several additional anaerobic marine inocula will be evaluated in this project with the objective of developing inocula that achieve high methane yields at ambient temperatures.

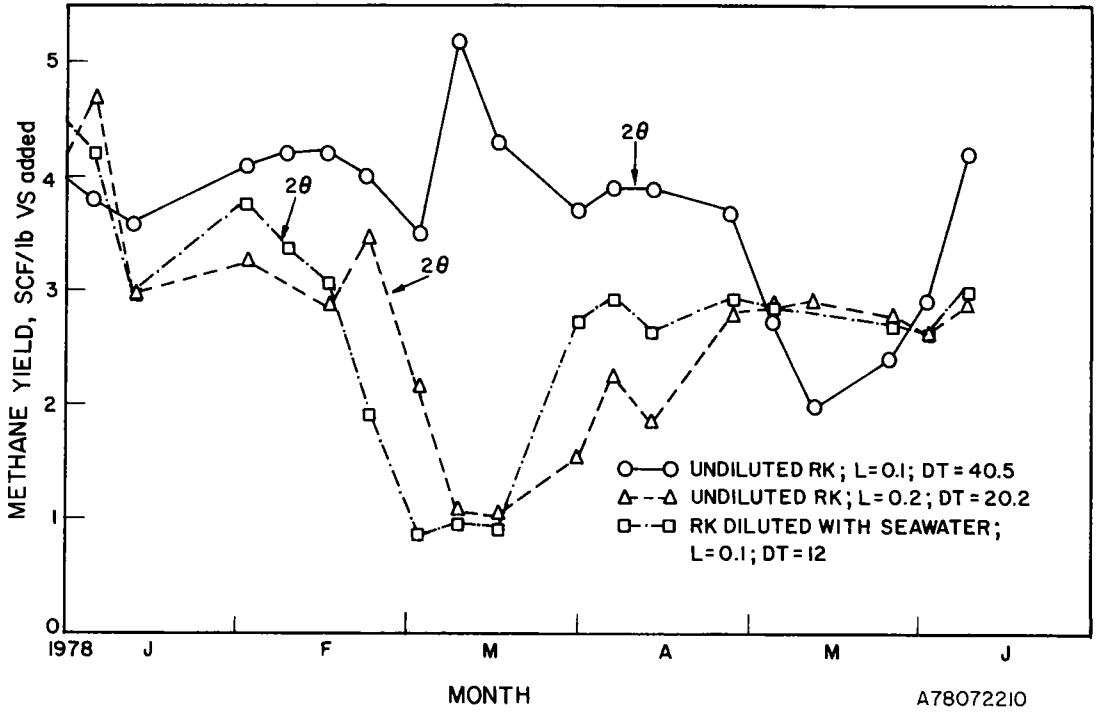

Figure 1. PROFILES OF METHANE YIELD DATA FOR RUNS 119 and 120 RECEIVING UNDILUTED RAW KELP AND RUN 121 RECEIVING RAW KELP DILUTED WITH SEAWATER (θ=1 detention time)

Table 9. COMPARISON OF PERFORMANCE OF CONTROL RUN 116, RUNS 119 AND 120 RECEIVING UNDILUTED RAW KELP, AND RUN 121 RECEIVING RAW KELP DILUTED WITH SEAWATER (35°C, Culture Volume = 1.5ℓ)

Run No.	116	119	120	121
Date Initiated	1/18/78	1/18/78	1/18/78	1/18/78
Data Period	3/17-6/11/78	6/5-6/11/78	5/22-6/11/78	5/22-6/11/78
Detention Times in Progress	12	3.6	7.2	12
Feed	RK	RK[c]	RK[c]	RK[d]
Loading, lb VS/cu ft-day	0.1	0.1	0.2	0.1
Detention Time, days	12	40.5	20.2	12
Methane Production Rate, SCF/cu ft culture-day	0.383	0.420	0.566	0.290
Gas Yield, SCF/lb VS added	6.62	7.04	5.75	5.36
Methane Content, mol %	57.8	59.6	49.2	54.0
Methane Yield, SCF/lb VS added	3.83	4.20	2.83	2.90
Volatile Solids Reduction, %[a]	45.1	46.8	38.2	35.6
Volatile Solids Reduction, %[b]	62.7	63.9	58.2	58.5
COD Reduction,%	57.7	50.8	35.9	44.2
Total Volatile Acids, mg/ℓ as acetic	485	7,700	6,780	2,100

[a] Carbon in product gas divided by carbon in feed.

[b] Based on analytical solids data.

[c] No water added to feed.

[d] Feed diluted with artificial seawater (Instant Ocean, Aquarium Systems, Eastlake, Ohio).

Table 10. MEAN PERFORMANCE DATA FOR NEW INOCULA
RUNS 122, 123, AND IGT'S INOCULUM A RUN 8
(RK Feed L=0.1 lb VS/cu ft-day,
Culture Volume=1.5ℓ)

Run No.	8	122	123
Inoculum	A[a]	D[b]	E[c]
Total Time in Operation, days	843	140	87
Data Period	3/17-6/11	12/5/77-3/16/78	5/22-6/11
Detention Time, days	18	18	18
Temperature, °C	35	35	26
Methane Production Rate, SCF/cu ft culture-day	0.445	0.464	0.219
Gas Yield, SCF/lb VS added	7.65	7.94	4.02
Methane Content, mol %	58.7	52.8	54.4
Methane Yield, SCF/lb VS added	4.45	4.64	2.19

[a] IGT's inoculum derived by mixing effluents from a digester receiving municipal solid waste-sewage sludge and from a municipal high-rate digester.

[b] Marine inoculum derived from mixing 188 g of chopped decaying kelp, 583 g of anaerobic marine sediment, 180 ml of effluent from GE's RK-fed digester, and 569 ml of IGT's Inoculum A.

[c] Marine inoculum derived from mixing anaerobic marine sediment and kelp collected from a decaying kelp wrack pool.

Thermophilic Digestion of Raw Kelp

Several attempts have been made to develop thermophilic cultures that would give high yields and stable performance on RK feed. The performance data of two typical examples of thermophilic runs (29 and SK-4) are compared with mesophilic Run 8 in Table 11. Performance was unstable, methane yields were low, and concentration of volatile acids was high for the thermophilic runs. These results are inconsistent with those obtained with other types of wastes and biomass at LGT. Usually thermophilic temperatures permit operation at higher loadings and lower detention times without reduction in methane yields. Apparently kelp has properties (possibly the high salt content) that prevent development of a healthy thermophilic population.

Component and Energy Balance for Biomethanation of Raw Kelp

Data reported previously (4,8) were used to calculate a balance of the components, carbon, and energy for the biomethanation of raw kelp which is presented in Figure 2. The validity of this balance is

Accounted For: Feed Organic Components 97.3%
Feed Carbon 95.9%
Feed Energy 102%

100 lb Kelp → 35%C, 0.10 VS/cu ft-day, 18-day DT, 47.5% VS reduction → Digested Solids + Gas

89.7 lb H_2O
4.7 lb Ash
5.6 lb VS

Protein	6.25 X 2.65 = 15.9%	Protein	6.26 X 3.20 = 20.0%
	10.3 X 0.16 = 1.65 lb		7.6 X 0.20 = 1.52 lb
Carbohydrate		Carbohydrate	
Mannitol	10.3 X 0.187 = 1.93 lb	Mannitol	7.6 X 0.072 = 0.55 lb
Algin	10.3 X 0.142 = 1.45	Algin	7.6 X 0.029 = 0.22
Cellulose	10.3 X 0.048 = 0.49	Cellulose	7.6 X 0.059 = 0.45
Laminarin	10.3 X 0.007 = 0.07	Laminarin	7.6 X 0.001 = 0.01
Fucoidin	10.3 X 0.002 = 0.02	Fucoidin	7.6 X 0.015 = 0.11
	5.62 lb		2.86 lb
Carbon	10.3 X 0.260 = 2.68 lb	Carbon	7.6 X 0.164 = 1.25 lb
Energy	10.3 X 4,409 = 45,400 Btu	Energy	7.6 X 2,744 = 20,900 Btu

4.7 lb Ash
2.94 lb VS (calc.)

7.44 $\frac{\text{SCF Gas}}{\text{lb VS added}}$ X 5.6 lb VS
= 41.7 SCF Gas
= 0.110 lb mole

Carbon 0.110 X 12.0 = 1.32 lb

Energy 7.44 X 0.598 X 1,012 X 5.6 = 25,200 Btu

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Figure 2. COMPONENT, CARBON, AND ENERGY BALANCE FOR RUN 8

Table 11. COMPARISON OF PERFORMANCE OF RK-FED DIGESTERS OPERATED AT 35°C (Mesophilic) AND 55°C (Thermophilic)

Run No.	8	29	SK-4
Temperature, °C	35	55	55
Data Period	3/17-6/11/78	12/15-3/16/78	3/27-6/23/77
Loading, lb VS/cu ft-day	0.1	0.1	0.2
Detention Time, days	18	18	7
Gas Yield, SCF/lb VS added	7.65	4.69	4.13
Methane Content, mol %	58.2	50.7	52.1
Methane Yield, SCF/lb VS added	4.45	2.38	2.15
Volatile Solids Reduction, %*	50.8	31.2	27.3
Total Volatile Acids, mg/ℓ as acetic	192	4590	4900

* Carbon in product gas divided by carbon in feed.

supported by the fact that 97.4%, 95.9%, and 102%, respectively, of feed organic components, carbon, and energy are accounted for in the products. Of primary importance is the fact that 100 lb wet RK will yield 24.9 SCF of methane. This yield is equivalent to 4.5 SCF CH_4/lb VS added. The digester culture volume that would be required for this daily feed rate and yield would be 56 cu ft. Energy recovery in the product gas is 55.5%, and volatile solids reduction is 47.5%. A comparison of these experimental values for methane yield and volatile solids reduction with the maximum theoretical values reported in Table 4 shows that 67% of the methane yield and 57.8% of the volatile solids reduction have been achieved.

Examination of the organic components in the influent and effluent is useful in identifying the biodegradable and refractory components. For the kelp fermentation, mannitol and algin are the most biodegradable, and cellulose and protein the least biodegradable. It should be pointed out that some of the kelp protein was probably converted to bacterial protein. Laminarin and fucoidin are only minor components of kelp and thus have minimal influence on the overall component balance.

It seems unlikely that further experimentation with conventional operation parameters such as detention time, sludge recycle, or temperature will result in higher methane yields. Higher yields should result, however, through treatment of the refractory components of

kelp to render them more biodegradable. One logical treatment scheme would involve post-treatment of settled solids and the recycle of them back through the digestion process. With this scheme in mind, the screening procedure outlined under Materials and Methods was used to evaluate the effect of heat treatment at 175°C on biodegradability of effluent solids from a RK-fed digester. The results given in Table 12 show that heat treatment alone and heat treatment under alkaline or acid conditions increased biodegradability. This procedure will be used to screen additional post-treatment processes for further evaluation.

Table 12. EFFECT OF HEAT TREATMENT AND pH ON ANAEROBIC BIODEGRADABILITY OF RAW KELP DIGESTER EFFLUENT[a]

Sample No.	Treatment	Accumulative Methane Production, ml[f] 29 hr[e]	53 hr[e]	70 hr[e]	94 hr[e]
1	NT[b]	9.9	20.0	27.4	35.4
2	NT[b]	11.8	21.5	26.1	34.1
3	HT[c]	20.1	33.3	41.7	52.6
4	HT 1[d]	22.0	35.7	43.2	55.8
5	HT 3[d]	16.0	28.6	35.5	45.9
6	HT 11[d]	21.1	35.2	43.1	58.6
7	HT 13[d]	22.9	36.9	43.9	60.2
8	HT 3/HT 11[d]	14.7	28.5	35.4	43.7

a Effluent from RK-fed baseline culture Run 39 was settled for 1 hour. Supernatent (about 75% of total volume) was decanted. Sediment was treated as indicated.

b NT = No Treatment.

c HT = Heat Treatment, 175°C for 1 hour.

d pH of sample prior to heat treatment; all samples were adjusted to pH 7 after heat treatment.

e Incubation Time, hours.

f Not corrected to standard conditions.

CONCLUSION

A stable fermentation was obtained for the mesophilic biomethanation of giant brown sea kelp under conventional conditions in bench-scale fermentors. (i.e., loading, 0.1 lb VS/cu ft-day and detention time, 18 days). The methane yield of 4.5-SCF/lb VS added obtained regularly for this feed substrate is high compared with values reported for other wastes and biomass types composed primarily of carbohydrates, including municipal solid wastes grass, feedlot cattle waste, and dairy manure. (See Table 13.) The references included in Table 13 all contain hard data to document the methane yields presented. It is not uncommon, however to find higher yields in the literature that are not documented with actual data.*

*Note that high methane production rates are not always associated with high methane yields. Ultimately the objective of the kelp biomethane research is to maximize both parameters.

Table 13. PERFORMANCE DATA FOR ANAEROBIC DIGESTION OF VARIOUS TYPES OF BIOMASS

Reference	Biomass Type	Methane Yield, SCF/lb VS added	Methane Prodn. Rate, SCF/ft^3 culture-day	Special Conditions
IGT, 1977	Raw kelp	4.5	0.445	T[c] = 35, L[d] = 0.1, DT[e] = 18
Pfeffer [13]	MSW-Sludge[a]	2.42	—	T = 55, DT = 20
Pfeffer [13]	MSW-Sludge	1.58	—	T = 35, DT = 20
McCarty et al. [12]	MSW-Sludge	3.26	0.750	T = 35, L = 0.23, DT = 15
Ghosh and Klass [6]	MSW-Sludge	3.80	0.530	T = 35, L - 0.14, DT = 12
Klass and Ghosh [11]	Grass mixture	3.10	0.370	T = 35, L = 0.12, DT = 16
Bryant et al. [9]	Feedlot cattle waste	4.10	2.21	T = 60, L = 0.54, DT = 9
Bryant et al. [9]	Feedlot cattle waste	2.74[b]	4.44	T = 60, L = 1.62, DT = 3
Converse et al. [10]	Dairy manure	3.33	0.899	T = 35, L = 0.27, DT = 15

[a] Municipal Solid Waste-Sewage Sludge.

[b] 4.15 SCF CH_4/cu ft culture (highest rate of methane production in the literature).

[c] Temperature, °C.

[d] Loading, lb VS/cu ft-day.

[e] Detention Time, days.

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The studies reported show that the anaerobic fermentation of raw kelp is not limited by nitrogen or phosphorus. Thermophilic digestion of kelp resulted in an unstable fermentation and lower methane yields compared with the mesophilic fermentation. Direct addition of kelp without dilution water or diluted with seawater resulted in retarded digestion after about two detention times, apparently because of the resulting high salt concentrations. Performance gradually returned to normal following a period of adaptation. Two inocula derived from anaerobic marine environments did not show improved performance over IGT's inoculum developed from digesters receiving sewage sludge and municipal solid wastes. A search for an inoculum that will exhibit high-performance at ambient temperatures (about 26°C) is continuing. A materials balance presented for this fermentation showed that most of the methane is derived from decomposition of algin and mannitol and that protein and cellulose represent the major refractory components of the effluent solids. It has not been determined whether the effluent solids protein is associated with kelp or bacteria produced by fermentation. Preliminary studies showed that heat alone and acid and alkaline hydrolysis in the presence of heat increased the biodegradability of the effluent solids.

Studies currently in progress on the biomethanation of kelp are aimed at decreasing the reactor size through optimization of detention time and loading and increasing the methane yield through evaluation of various post-treatment processes, culture optimization, and phase separation. Eventually this information will be used for the design and operation of a large-scale fermentor.

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