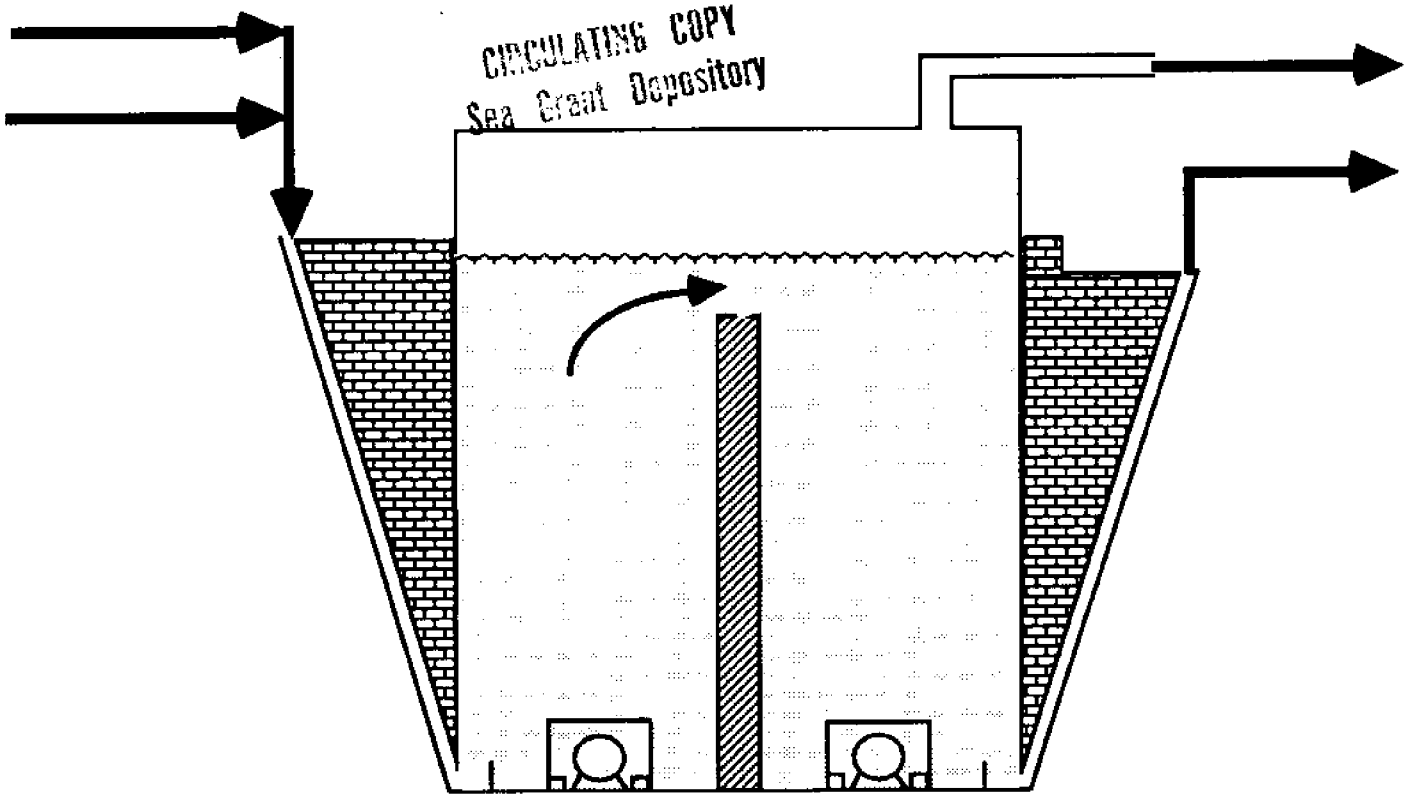
Biomethanation of Seaweed in a Three Phase Fluidized Bed Reactor



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ABSTRACT

The biomethanation of seaweed in a fluidized bed reactor was investigated and an economic analysis of a scale-up process was performed. Bioconversion is the process by which biomass is converted into a desirable product. In this case, the source of biomass is seaweed and the product is methane. This biomethanation process is accomplished in an upflow, three phase fluidized bed fermentor. Both batch and semi-continuous operations were analyzed. The feed solution was a waste stream supplied by Marine Colloids, Me. Effects of several operating parameters on the rate of methane production and its mole fraction in the product gas have been examined. This included the feed flow rate, seaweed concentration in feed, and reaction temperature. A methane mole fraction of 85% has been obtained in the product gas at a feed flow rate of 100 ml/day, seaweed concentration of 10 g/l, reaction temperature of 37 C, and pH of 7.0. Also considered was the scale-up process of the bioreactor for point application industrial processes. An economic analysis of the proposed scaled-up system is presented and discussed.

INTRODUCTION

Recent increase in biochemical technology research and development can be attributed to demands for low cost, renewable, and continuous sources of energy, chemical feedstock, and pharmaceuticals. (Bailley and Ollis(1985), Humphrey (1984), and Webber (1985)). One of the main attractions of biochemical processes is the use of inexpensive and abundant organic waste materials; these include agricultural waste, municipal and industrial wastewater, and seawater vegetation.

Marine biomass offers a potentially vast renewable energy resource for the United States. The area available for growth of marine plants in the U.S coastal waters, including Alaska and Hawaii, has been estimated to be about 908,000 square miles (ref. 2). If one assumes a growth yield of 20 dry tons per acre per year and a heating value of 9 million BTU/dry ton, that area could produce a biomass gross energy equivalent of about 100 quads (ref. 2). (To put these numbers into perspective, the heating value of coal is 2 million BTU/dry ton.)

Bioconversion of fresh seaweed and industrial effluents into methane gas represent a promising approach for production of gaseous fuels. To perform this fermentation process it is necessary to develop a reactor unit which is capable of continuous handling of large feed rates as well as substantial amounts of product gas.

The focus of this study is to develop and operate a three-phase fluidized bed reactor unit to ferment the seaweed. The three phases consist of the seaweed particles, water, and the gaseous products. Bacteria exists within the reactor either attached to the seaweed or floating throughout the liquid medium. Fluidization of the solid particles in the upward flow of a gas-liquid mixture has been studied extensively in the last few years (Muroyama and Fan, 1985). Three-phase fluidized reactors are characterized by excellent mixing, high exchange rates and good control of reactor temperature. Generally,

biochemical reactions are known to be sensitive to small variations in temperature, pH, and local concentration of both the substrate and product material (Hughes et. al., 1982).

Biosynthesis of methane from seaweed is achieved by the combined effect of fermentive, acetogenic, and methanogenic bacteria (Zehnder et. al., 1982). Fermentive bacteria break down complex substrates, i.e., polysaccharides, proteins, and lipids, into organic acids, mainly, and smaller amounts of carbon dioxide and hydrogen. Acetogenic bacteria convert the large acid molecules into either a gaseous mixture of carbon dioxide and hydrogen or into acetic acid. The latter is converted to methane gas and carbon dioxide by methanogens, which are also capable of combining carbon dioxide and hydrogen into methane and water.

BIOMETHANATION

Evidence of methane produced by anaerobic fermentation was first suggested over two centuries ago. Since then, methane production has been recognized in many ecosystems such as, lake sediments, sewage, marshes, and peat bogs. Natural methane fermentation occurs where plants die and decompose in water. The water layer acts as a blanket to exclude oxygen and to promote the growth of many species of anaerobic organisms. Scientists have developed considerable knowledge about the anaerobic bioproduction of methane.

Methane produced by anaerobic fermentation involves the conversion of organic material at modest temperatures (35 C to 39 C), ambient pressures, and nearly neutral pH to methane and carbon dioxide in the absence of exogenous electron acceptors such as oxygen, nitrate and sulfate through a complex series of microbial interactions. The actual mechanism of biodegradation may be broken down into three groups of steps. A different type of bacteria is responsible for each group of steps.

Initially, the organic material, consisting of carbohydrates, proteins and lipids, is too complicated to be reduced to methane by anaerobic fermentation. A species of bacteria known as fermentative bacteria degrade the complex organic substrates to monosaccharides, heavy acids and carbon dioxide, characterized by the following reactions:

$$(C_6H_{10}O_5)_n + H_2O = C_6H_{12}O_6$$

$$C_6H_{12}O_6 = 3CH_3CO_2^- + 3H^+$$

$$C_6H_{12}O_6 = CH_3CH_2CH_2CO_2^- + H^+ + 2CO_2 + 2H_2$$

$$C_6H_{12}O_6 + 2H_2O = CH_3CH_2CO_2^- + H^+ + 3CO_2 + 5H_2$$

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 12H_2$$

The organic fragments are then utilized to obligate hydrogen-producing (proton reducing) acetogenic bacteria to form acetate and hydrogen for consumption by the methanogens. A second group of acetogenic bacteria converts hydrogen and carbon dioxide to acetate and sometimes other acids. The following reactions characterize these steps:

$$C_6H_{12}O_6 + 2H_2O = 2CH_3CO_2^- + 2H^+ + 2CO_2 + 4H_2$$

$$CH_3CH_2CO_2^- + H^+ + 2H_2O = CH_3CO_2^- + H^+ + CO_2 + 3H_2$$

$$CH_3CH_2CH_2CO_2^- + H^+ + 2H_2O = 2CH_3CO_2^- + 2H^+ + 2H_2$$

$$CH_3CH_2OH + H_2O = CH_3CO_2^- + H^+ + 2H_2$$

$$2CO_2 + 4H_2 = CH_3CO_2^- + H^+ + 2H_2O$$

Once the complex organics have been degraded to acetate, the methanogenic bacteria utilize the acetate for energy and growth and by doing so, produce methane gas. The reaction scheme can be characterized as follows:

$$CH_3CO_2^- + H^+ = CH_4 - CO_2$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

$$HCO_3^- + H^+ + 4H_2 = CH_4 + 3H_2O$$

LITERARY SEARCH

Various literary sources have been used to assist in the research of this project. These sources were found by the use of BSR After Dark, in the Main library at The University of New Hampshire. From this research, helpful information was found concerning technical and economic comparisons.

A. Technical Comparison

As previously mentioned, the effects of temperature, pH, and seaweed slurry concentration on the bioconversion process have been investigated. It seems unlikely that further experimentation with these operating parameters will result in higher methane yields (ref. 1). However, other means of improving methane yields are still desirable. Several suggestions pertaining to the current set-up are proposed (see also Recommendations section of report). Some suggestions include the post treatment of the settled solids in the effluent and to recycle them back through the digestion process (ref. 1).

From research conducted by the Institute of Gas Technology (IGT), "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 standard cubic feet of methane with an energy recovery efficiency of

55.5%" (ref. 1). These reported values compare with a calculated value of 22.4 standard cubic feet per pound of solids in Marine Colloid's waste.

Research has also been conducted at IGT with unconventional digesters. As referenced in Fannin (ref. 3), utilization of digester designs that promoted long solids retention times improved the anaerobic digester performance significantly. From these studies it was found that methane yields and production rates increase as the solids retention time and organic loading increase. Based on these reports, further investigation concerning the effects of retention time on methane yield should be considered.

B. Economic Comparison

A secondary goal of this project was to investigate the economic feasibility of seaweed as a source for methane production. Based on literature, seaweed as a biomass source depends on the supply available and its uses in other industries.

As previously mentioned, the area available for growth of marine plants in the United States coastal waters has been estimated to be about 908,000 square miles. The success of a full scale marine biomass to energy process depends on ocean farming or harvesting (ref. 3). As can be seen, the potential to use seaweed as an energy resource in the United States is apparent, but other economic avenues exist. In other countries marine biomass is wasted. For instance, in Japan, algae is not used to the fullest extent. Therefore the concept of bio-fuel production is investigated instead of letting this energy source rot away (ref. 6). According to studies conducted by Sivalingam (ref. 6), the feasibility of biomass to energy production is promising and can be used efficiently where the marine biomass just goes to waste.

APPROACH

The purpose of this study was to determine the feasibility of using anaerobic digestion to treat a waste stream containing seaweed. As previously mentioned, the waste stream originates from Marine Colloids in Maine. The stream contains 7 % solids in the form of shredded seaweed. Because the seaweed contains large amounts of carbon and hydrogen, it may be referred to as volatile solids.

In order to evaluate the feasibility, a lab scale fluidized bed bioreactor was designed and constructed to perform experiments on bioconversion. A batch reactor was also made in order to perform preliminary tests to obtain basic rate data, and various guidelines for the fluidized bed reactor operation.

The importance of temperature and pH are also realized in this study. Unless the temperature is maintained around 37 degrees centigrade, and the pH around neutrality, the biomethanation process will not take place. A computer controlled heat exchanger was used to maintain the reactor temperature. Similarly, the pH was maintained by a computer controlled mechanism.

Three types of analysis were necessary in order to fully characterize the material balance of the system. The first was an elemental composition test on a dried sample of waste from Marine Colloids. This revealed a 33%, 5.9%, by weight of carbon, and hydrogen respectively. Analysis was performed in the UNH instrument lab in Parsons Hall using a Perkin Elmer 240 B Elemental Analyzer.

The product gas composition was determined on a Hewlett Packard 5730A gas chromatograph with a permanent gas column. The gas produced by the reactor collected in the top of the Fluidized Bed Reactor. There it bled into a glass sampling bottle. A .6 ml sample was withdrawn from an injection port in the side of the bottle. (see appendix 6 for gas chromatograph operation)

The liquid within the reactor was tested for the presence of light organic acids using the gas chromatograph equipped with an organic acids column. Liquid was withdrawn from a faucet in the recycle line of the reactor and injected in the gas chromatograph.

EXPERIMENTAL SECTION

A. Fluidized Reactor

The bioreactor used was a 13 liter upflow fluidized bed reactor. A 1/8 horsepower March centrifugal pump (model AC-5C-MD) circulates the slurry through the main reaction vessel (ID = 4.5" , OD = 5", height = 4'). A recycle line descends from the side of the column, (9 inches from the top) and passes through a heat exchanger and returns to the recycle pump.

B. Heat Exchanger

The heat exchanger was made from a 10 gallon stainless steel tank. It has a hot and cold water feed line and an exit hole in the bottom to prevent overflow. The flow out of the heat exchanger is controlled with a solenoid valve. It may be directed to recycle to the water heater or be dumped down a drain. The hot water used in the heat exchanger was generated on site in a 30 gallon tank with a 1500 watt heating coil. The hot water was pumped into the heat exchanger using a 1/12 hp Gorman-Rupp centrifugal pump, (model 12523-050). The cold water feed line to the heat exchanger was turned on an off using a 1/4 inch ID solenoid valve. Similarly the water feed to the hot water heater was turned on and off using a 1/4 inch ID solenoid valve.

C. Gas Collection System

The product gas collects at the top of the column and bleeds into a gas collection bottle. One end of the gas collection bottle is attached to the top of the column and the other is submerged in a water lock to prevent air contamination. (see next page for reactor schematic)

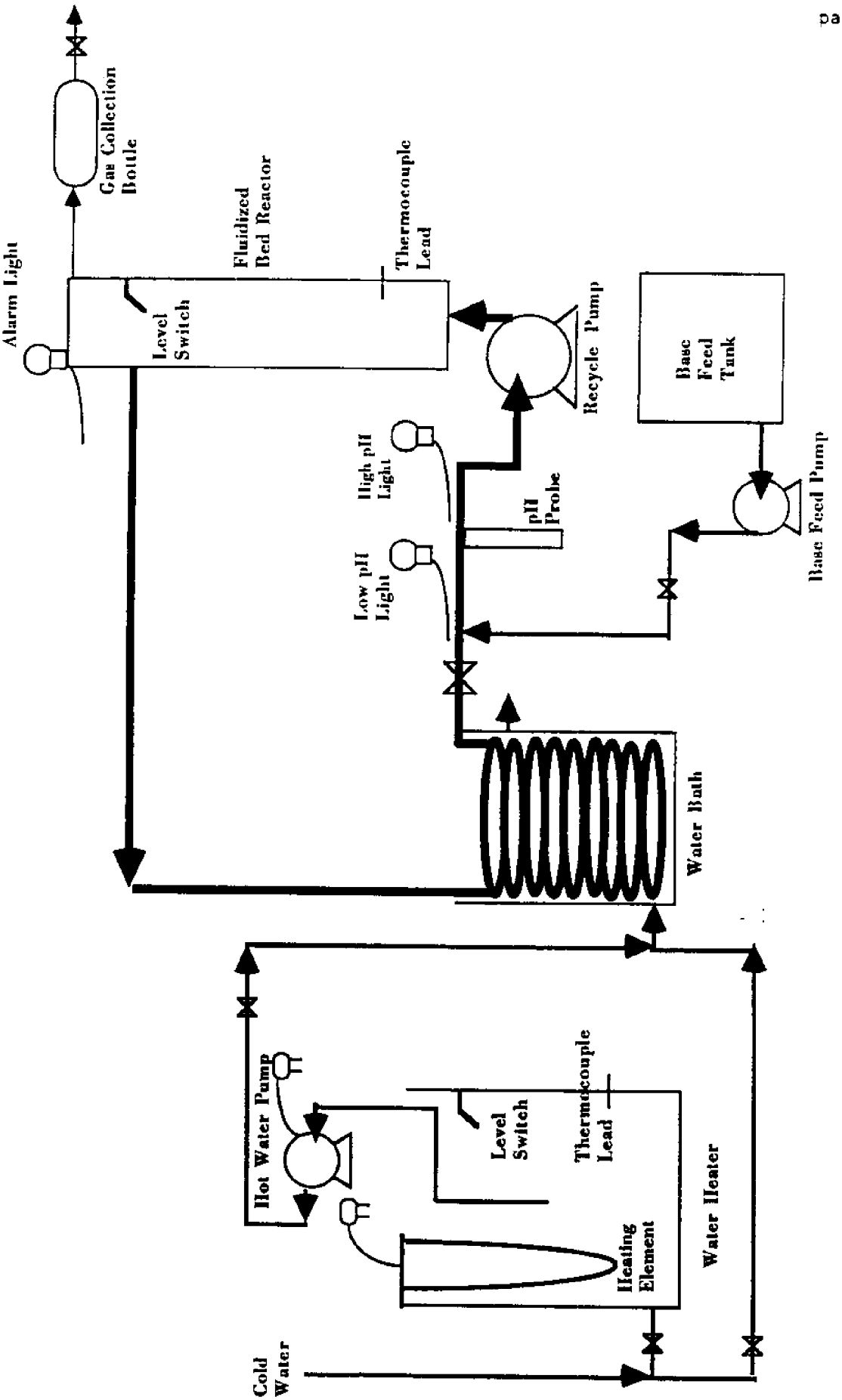


Figure 1
Experimental
Setup

The product gas flow was difficult to measure in the reactor. A devise was made which trapped the gas in a collection vessel filled with water. The gas displaced a nearly equal volume of water which was measured in a graduated cylinder. The major problem was the reactor produced such a small amount of gas that it took several days to accurately measure the gas flow.

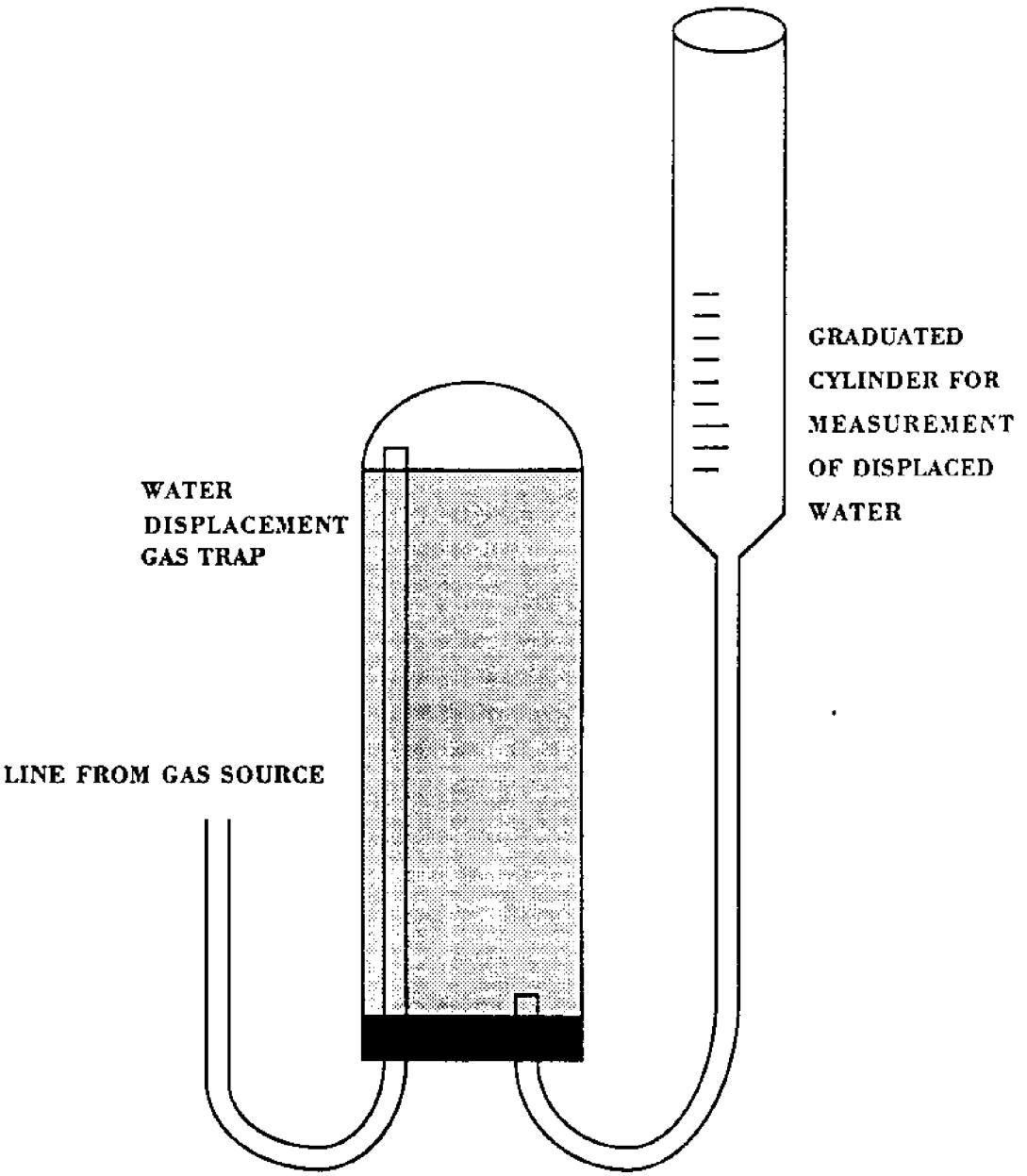


Figure 2. Gas Measurement Apparatus

D. Measurement Devices

pH must remain neutral in the reactor for biomethanation to occur. To monitor the pH, an Omega pHE 7151-15PT-100 pH probe was installed directly downline of the solenoid valve which let into the system. Base was pumped from a four liter flask into the system using a Cole-Parmer Master Reflex Pump (#7553-30).

A T type thermocouple was inserted near the base of the column to measure reactor temperature. The level of the reactor contents was monitored by an Omega F-90 float activated microswitch. Similarly the temperature and level of the hot water heater was monitored by a T type thermocouple and Omega microswitch. All the data received from the thermocouples, pH probe, and level switches may be recorded on a file with real time measurement using the IBM computer with Labtech Notebook software. See also Control Hardware System and appendix 5.

E. Batch Reactor

The batch reactor took place in a four liter flask. This flask was heated and stirred by a magnetic stirrer, heating plate. The temperature of the reactor was measured by a T type thermocouple.

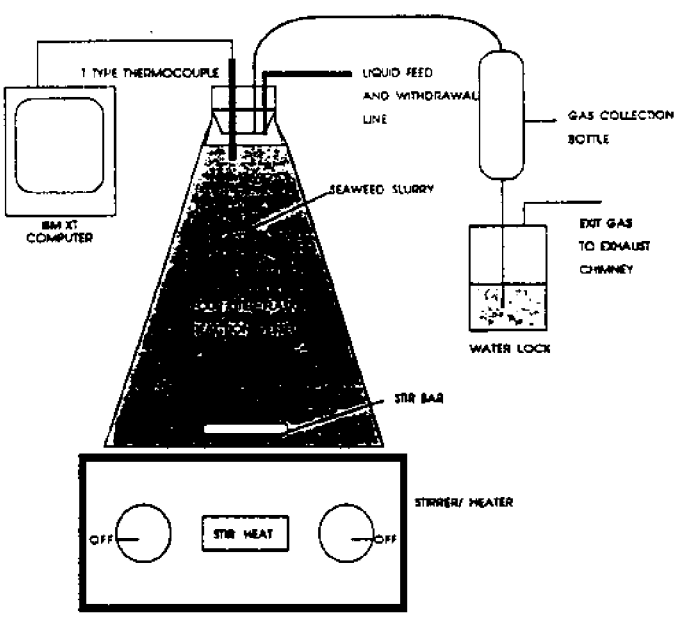


Figure 3. Batch Reactor

F. Control Hardware

The method used to provide control of the temperature and pH of the system was through simple feedback control loops. The measured variables were the temperature and pH of the reactor contents. These were measured using thermocouples and an immersed pH probe respectively. The thermocouple sent out a millivolt signal which was amplified 200 times on a Metrabyte EXP-16 multiplexer board before it was sent to the Dash-08 A/D board, where it was converted to a digital signal.

The pH signal was in the range of 0 to 1.4 volts DC, and was wired into a Metrabyte Dash-08 A/D board. Within the computer, channels were setup using a software called Labtech Notebook or NB, to compare the measured variables with predetermined setpoints. If the values deviated, a digital signal was sent out through a DDA-06 output to an ERB-24 relay board which would open or close the circuit of a valve or pump to correct the error in the system. All controlled equipment was either on or off (see appendix 5 for control logic and loop design).

EXPERIMENTAL PROCEDURE

A. Fluidized Bed Reactor

The first step was to fill the reactor with the waste from the Marine Colloids plant. Because of the thickness of the slurry, water was added to ease the pumping requirement. Specifically a mixture of three parts water, one part waste was used. The bacteria was supplied from marine mud, collected at Adam's Point in the Great Bay Estuary. To introduce the bacteria into the system, approximately one tablespoon of mud was mixed in with the slurry. Furthermore, sugar was added into the reactor to consume the free oxygen that is present in the reactor head immediately after charging.

Once the reactor was charged, the recycle pump, and computer control systems were started. The computer control maintains the reactors temperature at 37 C and the pH in the range of 6.7 to 7.2. Once per day, the gas composition was analyzed to monitor the transient behavior of the system. Furthermore, once the system reaches steady state, i.e., the methane mole fraction in the product gas reaches its maximum value, continuous operation begins.

To operate the reactor in a continuous mode, once each day a specified volume of the slurry is withdrawn from the reactor, and an equal volume of fresh slurry is added.

Occasionally, it was desired to check for the presence of organic acids. This was done by withdrawing a small sample of liquid from the reactor and injected into a gas chromatograph equipped with an acids column. Additionally, to determine the solid composition at any time, a small sample was removed, dried and then sent to the UNH instruments lab in Parson Hall.

B. Batch Reactor

The batch reactor was charged with a mixture of three parts water to one part seaweed waste. The magnetic stirrer was started, and the heating plate turned on to maintain the temperature at 37 C. Daily gas composition measurements were made until the system stopped making methane.

DATA ANALYSIS

A. Fluidized Bed Reactor

While operating with a slurry containing ground seaweed in water, data was collected that indicated a product gas which contains up to 85 molar percent methane can be produced under the appropriate conditions. The transient behavior of the system lasted approximately ten to twelve days as the system reached steady state. Once peak methane production was achieved,

continuous operation was attempted. The mole fraction of methane began to drop off due to a poor loading technique, which permitted air to enter the system each time fresh slurry was added. This explains the decrease of methane in the product gas. (appendix 4 contains experimental data)

Samples of the spent liquid slurry are injected into a liquid acids column in the chromatograph. Although samples have been taken, no reliable results can be reported. In order to fully characterize the biomethanation process, all streams (gas and liquid) must be analyzed. However, it is encouraging to note the high percentage of methane in the product gas. Although all material balances could not be completed due to the acids reading, theoretical scale-up, using methane mole percent in the gas, was performed.

B. Batch Reactor

The data analysis and conclusions concerning the batch reactor are similar to that of the fluidized bed. Using ground seaweed in water approximately two weeks elapsed before significant amounts of methane were noticed. Mole percent of methane in the product gas reached a high of 74%. The batch reactor data indicated what the approximate residence time would be for complete solid degradation. In the case of seaweed, this was approximately 50 days. The waste from Marine Colloids was digested in approximately 35 days. (see appendix 4)

A batch reactor charged with waste from Marine Colloids was operated at 20 C due to the heating system malfunctioning. Although the methane mole percent never rose above 2.4 % there was a significant solids reduction after slightly over one month of operation. This indicates that it is very critical for the temperature to be at 37 degrees centigrade for biomethanation to occur, but solid degradation may occur at lower temperatures.

CONCLUSIONS AND RECOMMENDATIONS

The data indicates that gas with useful amounts of methane can be produced using the upflow fluidized bed reactor. The biomethanation process only takes place at specific temperatures and pressures, however. If the temperature is greater or lower than 37 C the process will not produce significant amounts of methane, although solid degradation will still occur.

Based on the data, a residence time of 40 days has been chosen to ensure complete degradation of the biomass. (data in appendix 4)

If work does continue with the present biomethanation process, several suggestions should be considered. First, a fresh sample should be obtained from Marine Colloids, and a run should be made on the new reactor. Now that the system has an operational temperature and pH control system, very reliable results can be obtained. Furthermore, due to modifications to the reactor, it is now possible to make slurry withdrawal and addition easily without contaminating the system.

Presently, our system would take approximately 12 days to restart if it had a failure that deactivated the bacteria. One area that should be investigated would be the development of a technique for rapid digester start-up or recovery to minimize the economic impact of large-scale digester failure. (Fannin ref. 2) For example one might keep a supply of inoculated waste ready to seed the system if it fails. Alternatives such as this must be examined and developed.

SCALE UP OF FLUIDIZED BED REACTOR

One of the problems many industries must face today is the expense of waste disposal. A company in Maine, Marine Colloids, extracts carrageenin from seaweed. The carrageenin is a valuable food additive used widely in the food industries. Once the carrageenin is removed the spent seaweed is discharged in

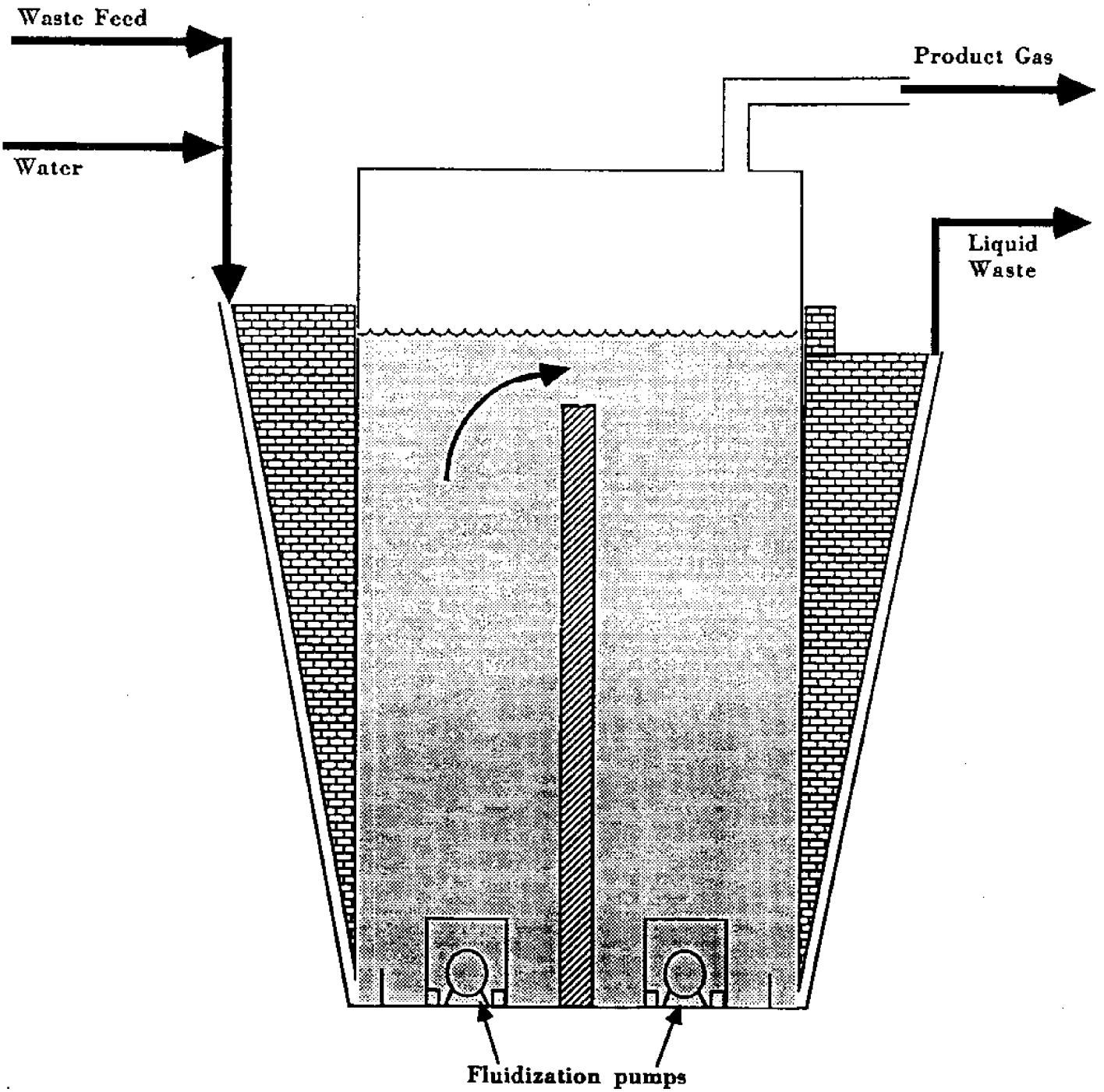
a slurry which contains 7% solids by weight. For years they have disposed of their waste, approximately 1530 cubic meters per year, in an open pit. Recent inquiry by the EPA, has forced them to search for alternative methods of waste disposal. The possibilities investigated were aerobic digestion, mechanical filtration and drying, and anaerobic digestion. The following sections will focus on our efforts to determine the feasibility of installing an anaerobic digestor to help take care of the waste disposal problem at Marine Colloids.

A. DESIGN OF REACTOR

The main process vessel of the digestor was designed to be built in ground. A pipe will be built to collect the waste stream from the plant and dump it directly to the base of the reaction tank. The exit stream originates from the base of the second half and empties into a vessel/truck, at ground level for shipment to a waste treatment facility. The tanks dimensions are approximately 6 meters in diameter and 18 meters high. It is split by a central weir that rises 13 meters from the base of the column. The weir functions as a baffle to prevent any of the waste stream from short circuiting through the reactor in a time shorter than the designed residence time. Under each half of the reactor are pumps which will provide the mixing and fluidization within the column. Heat may be added to the reactor through a steam coil which is submerged in the slurry. Furthermore, an equal volume of water is added to the waste stream which enters the reactor to reduce the viscosity and allow for easier mixing within the reaction vessel.

(see figure 4 on following page)

Figure 4
Reactor Scale-up



B. Approach

The waste stream originating from Marine Colloids consists of 4.93 cubic meters per day of a 7% solid solution. Based on an elemental analysis of the solids performed at the UNH instruments lab, there is approximately 33 % by weight of carbon and 5.9 % of hydrogen. By making a simple stoichiometric equation, the volume of methane produced was approximated conservatively assuming that hydrogen was the limiting element (see appendix 3 for calculation of methane yield). Next based on previous data and literature, a residence time of 40 days was used to determine the size of the vessel. After costing the process using methods explained in reference 6, a cost summary was made based on one operating year. The results were then compared to the alternate disposal schemes and to values obtained in other related studies. (see appendix 1 for calculation details and annual cost summary)

C. Results

The anaerobic digestor designed offers the ability to produce over 35,000 standard meters cubed of methane from the solids in Marine Colloid's waste stream. The capital required to build the plant comes to approximately $226,000. The yearly total expenses are $168,000. Based on a methane value of $ 0.16 /cubic meter (obtained from Palmer Gas Company), this translates to a processing cost of $ 110 /cubic meter of waste. This does not include further filtration and treatment of the digestor waste stream which is unknown at the present time. The annual cost breakdown reveals that 16.5 % of the operating cost is due to capital expenses, 33.9 % is due to labor related costs, and 1.1 % is due to utility costs. A processing cost of $ 133/cubic meter of waste was calculated for a proposed filtration and drying technique.

D. Discussion and Conclusions

The economic analysis was not encouraging. The total methane revenue generated at present market prices was $5,600. This does not even scratch the surface of the yearly operating costs. The only way to improve the economics of the plant would be to increase the processing capacity. Unfortunately, the amount of available biomass is limited by Marine Colloid's waste stream.

The results of the scale up were also dependant on the assumptions made. Obviously if a smaller residence time is required, the capital costs will be reduced, but only by a maximum of 16.5 %. Similarly, if more methane can be produced, the revenue from sales will be increased. Because labor related expenses account for 33.9 % of the annual total expense, this estimation may be incorrect.

The amount of methane produced is limited by the available carbon in the waste stream. Since the amount of biomass in the waste steam is fixed, methane production could only be increased by small amounts if techniques are improved and the efficiencies are increased. Similarly, if the residence time can be shortened and a smaller reactor built, it would only result in a slight decrease in the annual total expense. If it turns out that the waste leaving the digestor needs no further treatment, then the system becomes more feasible.

The alternative disposal method investigated involved filtration of the slurry, followed by further drying of the solid residue. Complete flow sheet and sample calculations may be found in appendix 2.

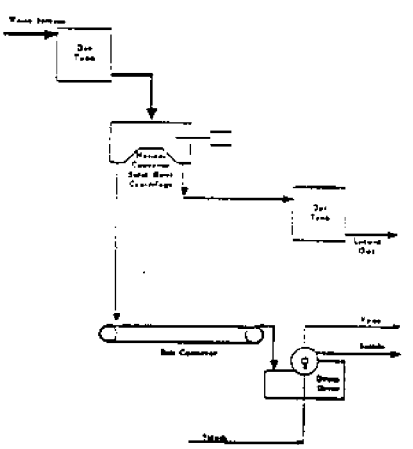


Figure 5
Alternate Scheme

E. Recommendations

The first area which must be further investigated is more experimentation with samples of Marine Colloid's waste. The sample which we used was old and possibly partially degraded through decay. This would reduce the amount of methane which could be produced from the sample. A new sample should be obtained and fed into the digestor for data collection and analysis.

Another foggy area, lies in the economics of alternative schemes. The various techniques that Marine Colloids are considering should be examined more thoroughly and compared to our scale up to determine the most reasonable scheme.

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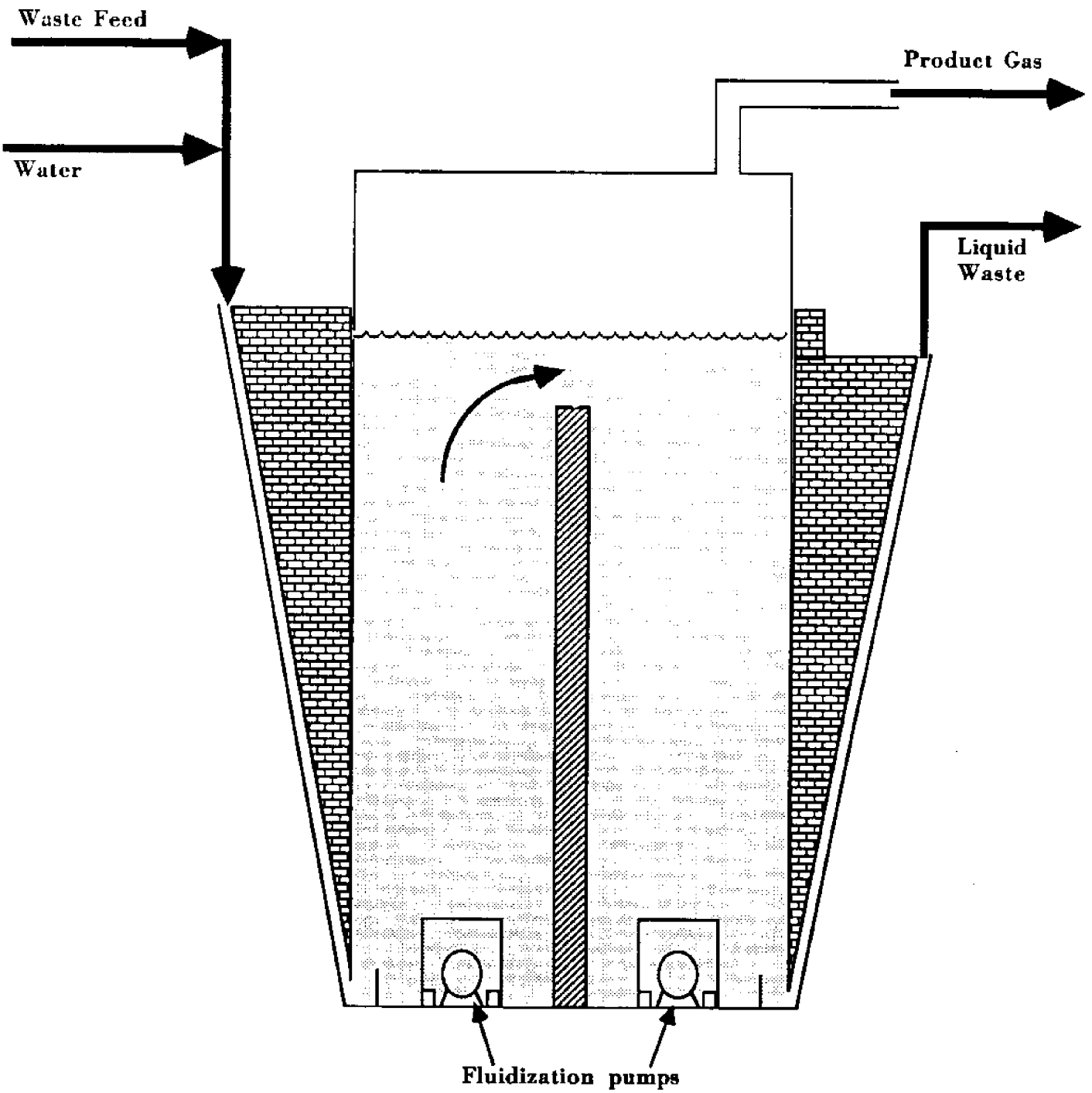
APPENDIX I

Reactor Scale-up



Appendix I Method of Scale up

First we must make Assumptions as to how the reactor operates.

1) 40 day residence time
2) Operating factor = .85 (plant operates 310 days/yr)
3) Add an equal volume of H_2O to slurry to aid in mixing

Determine how much waste we must process per day

1530 m^3/yr → 4.93 m^3 of waste/day

with H_2O added → 9.88 m^3/day

Liquid volume within Reactor : 40 days (9.88 m^3/days) = 395.2 m^3

Add 110 m^3 head to reactor for methane collection

Reactor volume = 505 m^3

Reactor Dimensions

$D/L = 1/3$

$505\ m^3 = \pi d^2 L = \pi D^3\ 3/4$

$D = 5.97$ m

$L = 17.92$ m

Cost = \$131,670 (from reference 6)

2 Pumps are required for fluidization.

Each pump must produce 1.4 Kw in order to fluidize

Cost for both pumps = \$47,250 (reference 6)

A heat exchanger will be needed to maintain the optimum Temperature

Cost = \$2000 (reference 6)

Determine the steam required to heat the system

$q = k_R S A (\Delta T_{overall})$

$\Delta T_{overall} = 37 - 13.5 = 23.2^\circ C$

↑ Ground Temperature

$A = 392\ m^2$

$k_R = .8\ W/m^\circ C$ (thermal conductivity of earth)

$S = \frac{2\pi L}{\ln(\frac{2L}{r})} = 45.3\ m$

$q = 329.6\ kW = \dot{m}_{steam} h_{fg}$

$\dot{m}_{steam} = 0.138$

purchased at .009 $/kg

$P = 15\ psig$

$T = 120.5^\circ C$

$h_{fg} = 2386\ KJ/kg$

Cost for year = $32,759 /yr

Total Grass Roots Cost

$C_{GR} = \$225,840$

operating labor: 1 person/shift → $25,000 /yr

Utilities: H_2O → 27.1 $/yr (0.01771 $/m³)

Electricity: 1,844.5 $/yr (.09 $/KWHR)

Steam: 32,759 $/yr (.009 $/kg)

Yearly Operating Costs (see Cost summary Sheet)

Annual Total Expense = $168,000 /yr

Processing Cost = 109.7 $/m³

The processing cost does not include further filtration and drying costs. These are conservatively estimated at 80 $/m³ that additional treatment could potentially raise total processing costs to 190 $/m³

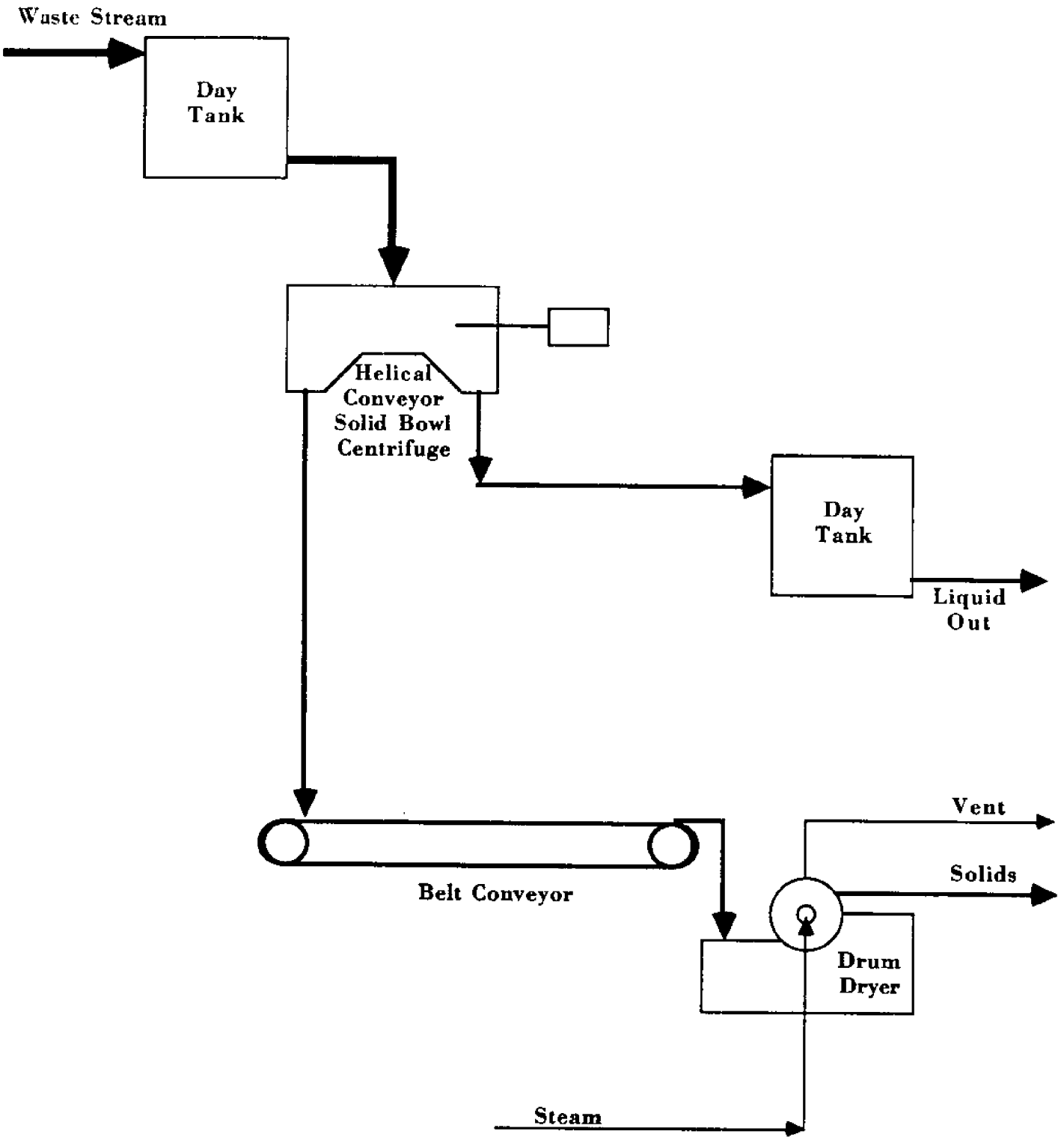
OPERATING COSTS OF PROPOSED SCALE UP

Fixed Capital	$ 108,500
Working Capital	$ 16,300
Total Capital Investment	$ 124,800

	$/yr	
Manufacturing Expenses		
Direct		
Raw Materials	0	
By-Product Credits	(5600)	
Operating Labor	25,000	
Supervisory and Clerical Labor	3,800	
Utilities		
Steam (1.1 barg at 0.009 $/kg)	32,700	
Electricity (0.09 $/KWHR)	1,800	
Process Water (0.02 $/kg)	100	
Waste Disposal (0 $/kg)	0	
Maintenance and Repairs	13,600	
Operating Supplies	2,000	
Laboratory Charges	3,800	
Patents and Royalties	5,000	
Total Direct Manufacturing Expenses	82,000	82,000
Indirect		
Overhead	25,400	
Local Taxes	3,400	
Insurance	1,600	
Total Indirect Manufacturing Expenses	30,400	30,400
Total Manufacturing Expense		112,400
Depreciation		22,600
General Expenses		
Administrative Costs	7,600	
Distribution and Selling Costs	16,800	
Research and Development	8,400	
Total General Expenses	32,800	32,800
TOTAL Expense		167,800
PROCESSING COST (per cubic meter of feed)		$ 110

APPENDIX II

Alternate Scheme



APPENDIX II - ALTERNATE SCHEME

The waste from the plant will first be sent to a holdup tank The tank was designed to hold up to one days worth of waste.

Volume = $5 m^3$
Cost = $2992 (from reference 6)

From the holding tank, the waste will flow into a helical conveyor Solid bowl centrifuge. This was chosen because of its ability to separate the waste.

Cost = $40,000
Power = 12.01 KW/hr
Power Cost = 335 $/yr at $0.09/KWHR

It was assumed that the two streams leaving the reactor have the following compositions.

Solid Stream	Liquid Stream
70% solids	100% liquid
30% liquid	

The liquid stream moves into another holdup tank with the same cost and volume as the one above. This liquid waste can then be sent to a wastewater treatment plant. The cost of this treatment was found to be 0.25 $/m³ which comes to 345 $/yr.

The Solids stream is dumped onto a belt conveyor

Length = 10 m
Width = 0.5 m
Cost = $15,320.

The belt conveyor deposits the solids into a drum dryer.

Cost = $163,800

The drum dryer is heated by steam.

Steam flow rate = 0.0014 kg/s = 36,890 kg/yr

Cost for steam = 332 $/yr at $0.009 $/kg

The liquid in the solids stream is vented off, and the solids can be brought to sanitary landfill. The cost for dumping the waste was estimated at 50 $/ton.

Total Grass Roots Cost:

C_{tot} = $337,100

Operating labor: 1 person/shift = $25,000/yr

Waste disposal: Liquid = $339 9/yr

Solids = $8441/yr

$8781/yr

Yearly Operating Costs (see cost summary sheet):

Annual Total Expense = $203,500/yr

Processing Cost = $133.0/m³

COSTING FOR ALTERNATE WASTE DISPOSAL SCHEME

Fixed Capital	$ 337,200
Working Capital	$ 50,600
Total Capital Investment	$ 487,800

	$/yr	
Manufacturing Expenses		
Direct		
Raw Materials	0	
By-Product Credits	(0)	
Operating Labor	25,000	
Supervisory and Clerical Labor	3,800	
Utilities		
Steam (1.1 barg at 0.009 $/kg)	300	
Electricity (0.09 $/KWHR)	300	
Process Water	0	
Waste Disposal	8,800	
Maintenance and Repairs	20,200	
Operating Supplies	3,000	
Laboratory Charges	3,800	
Patents and Royalties	6,130	
Total Direct Manufacturing Expenses	71,400	71,400
Indirect		
Overhead	49,000	
Local Taxes	5,100	
Insurance	2,400	
Total Indirect Manufacturing Expenses	56,500	56,500
Total Manufacturing Expenses		127,900
Depreciation		33,700
General Expenses		
Administrative Costs	12,200	
Distribution and Selling Costs	20,400	
Research and Development	10,200	
Total General Expenses	42,800	42,800
TOTAL Expense		203,400
WASTE DISPOSAL (per cubic meter of waste)		$ 134

APPENDIX III

Theoretical Methane Yield (Based on Stoichiometry)

345 kg of Volatile Solids per Day:

33% by weight of carbon
5.9% by weight of hydrogen

2.75 moles of carbon per 5.4 moles of hydrogen
Assume all hydrogen in biomass will combine with carbon to form CH_4

$$C_{2.75}H_{5.4} \longrightarrow 1.475\ CH_4 + 1.275\ C \qquad \text{(Hydrogen is limiting)}$$

23.6 weight percent of the biomass ultimately turns to methane
Therefore 81.42 kg/day is converted to methane.

$$81.42\ \text{kg} \left\{ \begin{matrix} (61.1\ \text{kg C}) \\ 5.09\ \text{kg mol } CH_4/\text{day} \end{matrix} \right.$$

$$\left(5091.6\ \frac{\text{gmoles } CH_4}{\text{day}}\right)\left(22.4\ \frac{\text{std l}}{\text{mol}}\right) = 114.5\ \text{std m}^3/\text{day of } CH_4$$

$$(114.5\ \text{m}^3/\text{day})(310\ \text{days operating/yr}) = \underline{35,356\ \text{m}^3/\text{yr}}$$

Methane Yield per kilogram of volatile solids:

$$\frac{81.42\ \text{kg}}{1\ \text{kg}} = \frac{114.5\ \text{m}^3\ CH_4}{x}$$

$$\underline{x = 1.4\ \text{m}^3/\text{kg of volatile solids} = x = 22.4\ \text{ft}^3/\text{lb volatile solids}}$$

DATA TABLE 1 Fluidized Bed Reactor (first trial) (charged with seaweed)

Day	Elapsed Time Hours	Percent Composition CO2	CH4	Solid Product Weight Fraction C	N	H	Temperature Degrees C AM	PM	pH
1	24	2.11	0.09	.2192	.0154	.0305	---	---	---
2	48	9.47	1.58	-----	-----	-----	44.8	47.8	6.62
3	72	6.51	2.09	-----	-----	-----	44.1	42.3	6.66
6	144	9.26	12.24	-----	-----	-----	48.6	---	6.95
7	168	5.53	9.06	-----	-----	-----	45.7	41.8	6.93
8	192	5.68	12.03	.3196	.0199	.0477	38.6	43.1	6.97
9	216	6.97	20.03	-----	-----	-----	37.6	45.9	7.21
10	240	7.55	24.07	.2931	.0208	.0455	38.1	46.8	6.93
13	312	9.89	49.14	.3061	.0211	.0459	41.1	41.0	7.00
14	336	7.70	45.65	-----	-----	-----	37.6	40.4	7.11
* 15	360	7.53	48.37	.3258	.0231	.0482	39.9	44.8	6.94
16	384	6.96	34.80	-----	-----	-----	39.5	42.5	6.81
* 17	408	8.97	44.32	-----	-----	-----	41.5	41.9	6.88
* 20	480	8.37	32.04	-----	-----	-----	42.0	48.3	7.00
21	504	11.35	35.00	-----	-----	-----	46.7	---	6.95
* 22	528	10.61	34.41	-----	-----	-----	45.4	43.8	7.02
** 23	552	10.21	34.60	-----	-----	-----	42.6	43.5	6.99
* 27	648	10.99	32.01	-----	-----	-----	49.8	41.5	6.87
28	672		28.00	-----	-----	-----	38.1	---	---

* denotes days in which 200 ml of slurry was removed then 200 ml of fresh feed was added

** indicates that on this day the system was filled with slurry. approximately two liters was required.

DATA TABLE 2 Batch Reactor (charged with seaweed)

Day	Time Hours	Gas Percent Composition CH4	CO2	Temperature Degrees C
1	24	0.00	0.98	33.4
2	48	0.00	3.51	30.7
3	72	0.00	5.73	29.0
4	96	0.00	25.20	28.5
5	120	0.00	25.13	28.5
8	192	0.00	50.93	41.7
9	216	0.00	24.07	----
10	240	0.00	-----	37.5
11	264	0.00	32.56	40.5
12	288	0.00	21.18	37.8
15	360	0.74	5.88	42.1
16	384	4.07	10.42	30.0
17	408	5.90	11.51	29.5
18	432	9.42	12.88	35.8
21	528	55.96	29.10	37.8
22	552	67.99	24.07	27.6
23	576	68.20	19.00	39.8
24	600	73.91	14.00	36.9
25	624	61.62	12.91	31.3

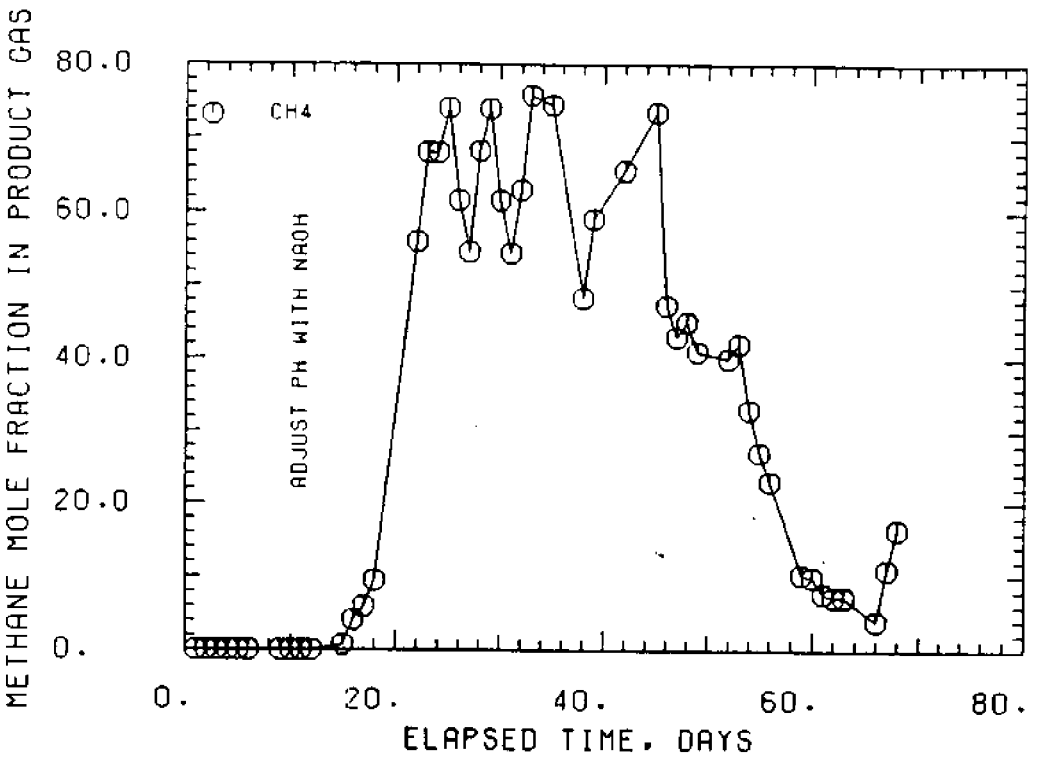


FIGURE : TRANSIENT MOLE FRACTIONS IN BATCH, T=40+/-2 C

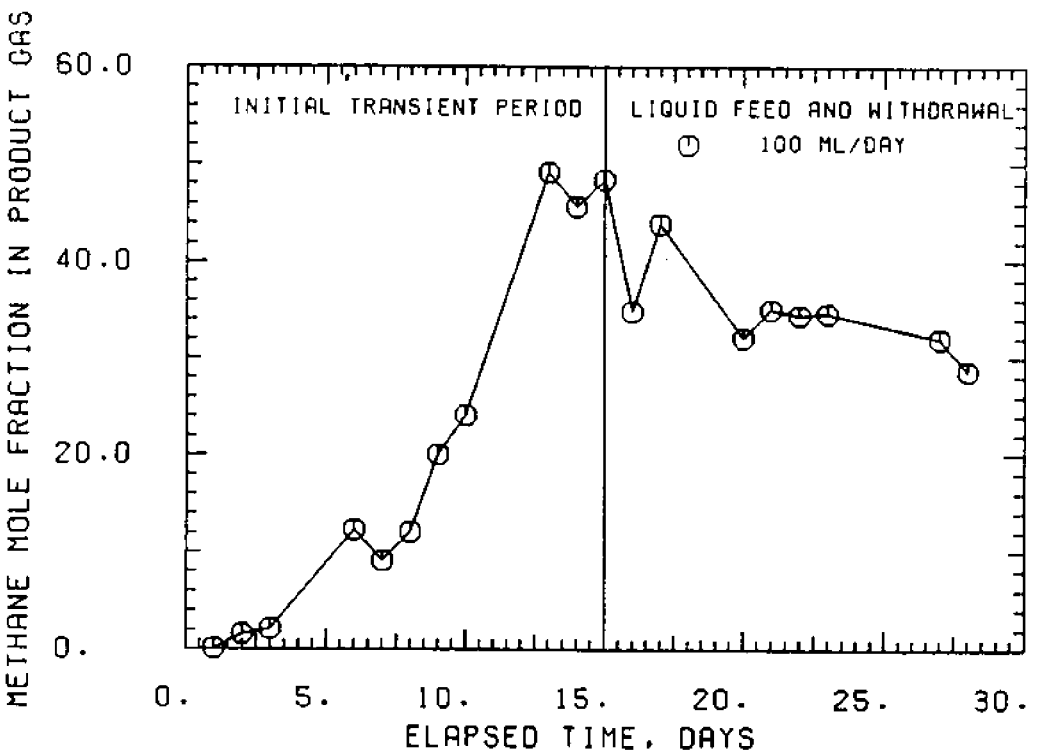


FIGURE : CH4 MOLE FRACTION IN THREE-PHASE FLUIDIZED SEAWEED BIOREACTOR, T=40+/-2 C

DATA TABLE III Fluidized Bed Reactor Second Trial
Continuation of Batch Run

DAY	FBR % CH4	FBR % CO2	FBR pH	BATCH % CH4	BATCH % CO2	Day of Batch Run
26	55.96	29.10		32.01	10.21	26
27	67.99	24.07		28.00	--	27
28	--	1.00	7.50	68.20	19.30	28
29	--	0.45		73.91	14.94	29
30	--	--	6.87	61.60	12.90	30
(beginning of FBR second trial)				(continuation of Batch)		
1	1.13	22.30	6.20	54.40	11.40	31
2	2.50	23.00		63.00	14.70	32
3	1.70	34.40	5.94	75.80	19.20	33
4	2.41	31.62		80.30	21.30	34
5	2.10	13.20	10.93	74.50	18.97	35
8	15.20	26.80		48.30	17.70	38
9	36.00	25.80	6.58	59.10	20.80	39
10	48.00	31.00	6.72	61.00	22.00	40
11	72.60	22.30		66.30	15.90	41
12	84.70	21.00		65.60	15.50	42
15	83.90	18.50		73.40	16.90	45
16	70.00	16.40		47.30	10.80	46
17	68.50	16.70		43.00	9.50	47
18	1.90	17.70	7.10	45.00	10.20	48
19	5.10	31.00		41.00	10.10	49
22	--	8.40		40.00	11.00	52
23	--	0.70		42.00	11.00	53
24	--	0.77		33.00	8.50	54
25	--	0.90		27.00	9.00	55
26	--	3.00		23.00	8.30	56
29	--	--		10.30	3.70	59
30	--	0.36		9.90	3.60	60
31	--	5.70		7.70	3.00	61
32	--	9.70		7.20	4.60	62
33	0.03	13.30		7.20	4.70	63
34	**	**	7.69	**	**	64
35	**	**		**	**	65
36	--	10.00		4.00	2.20	66
37	0.07	9.50		11.00	5.10	67
38	--	26.00		16.40	20.83	68

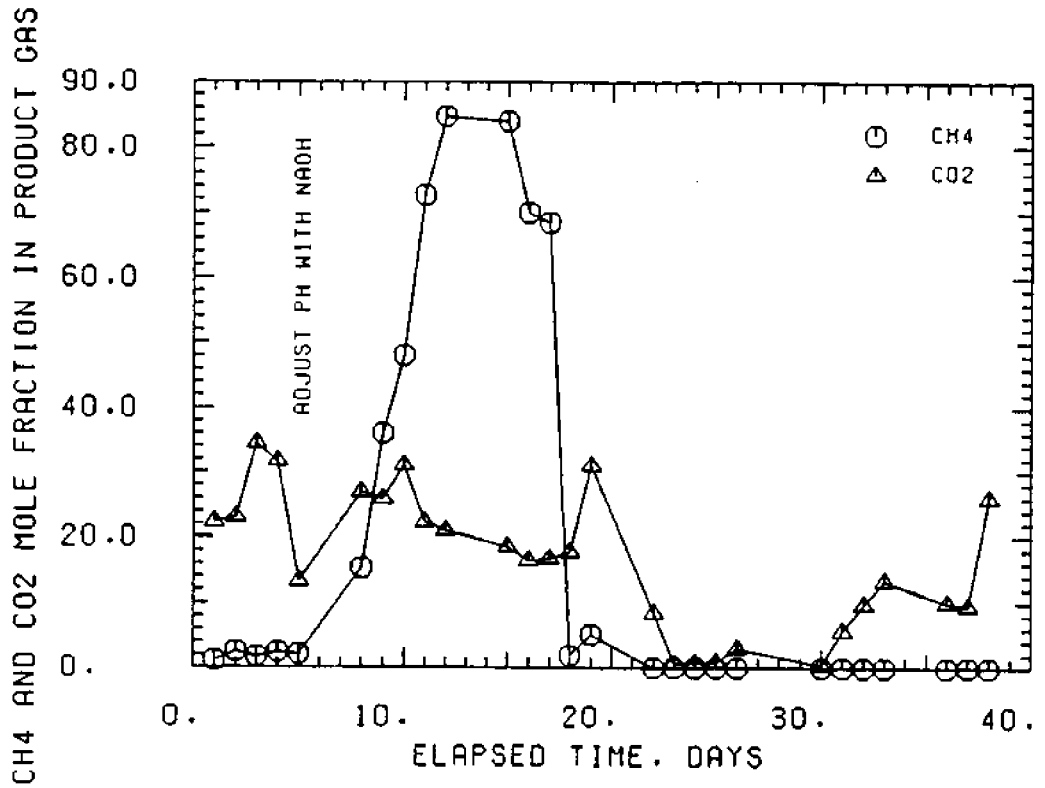


FIGURE : TRANSIENT MOLE FRACTIONS IN FBR, 2ND TRIAL

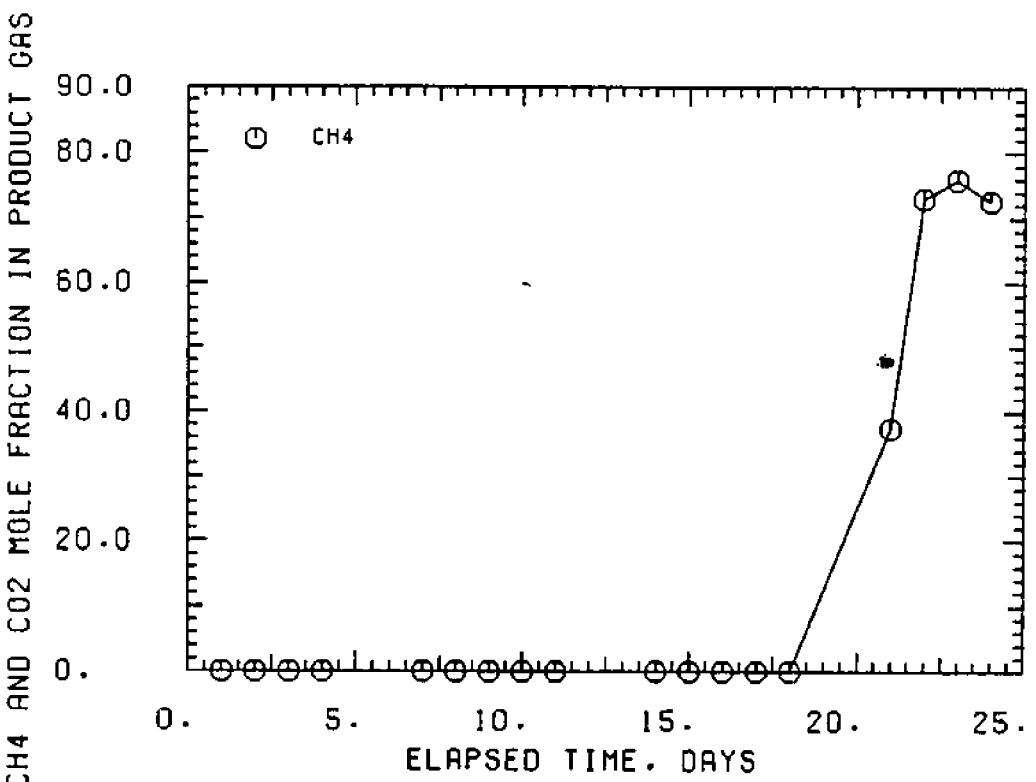


FIGURE : TRANSIENT MOLE FRACTIONS IN FBR,
FBR CHARGED WITH MARINE COLLOID WASTE

DATA TABLE IV Fluidized Bed and Batch Reactor Charged With Three Parts Water One Part Marine Colloid Waste

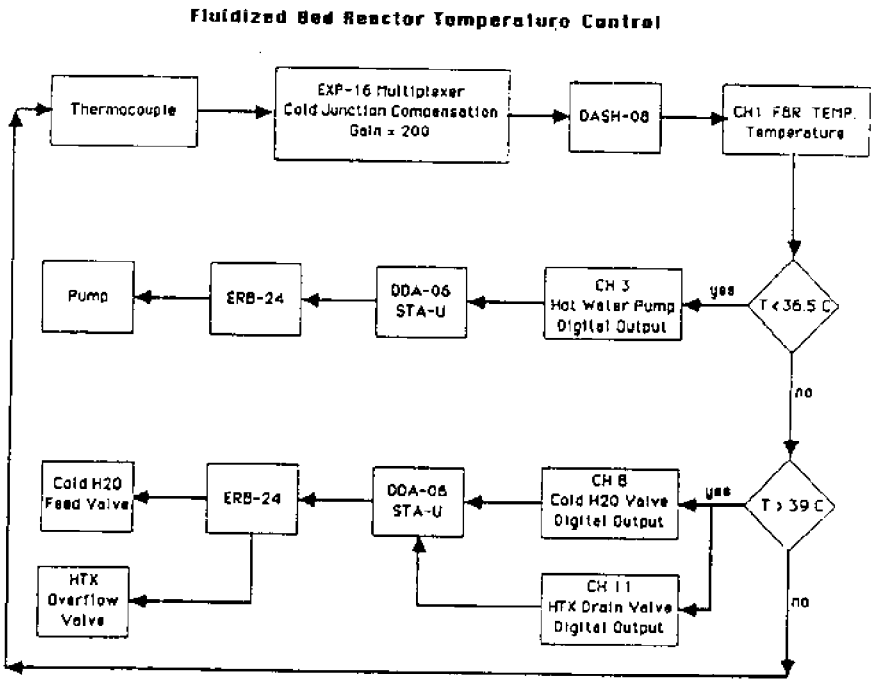
Day	Fluidized Bed Reactor T = 37 C Mole Fraction of Methane	Batch Reactor T = 20 C Mole Fraction of Methane
1	0.0	0.0
2	0.0	0.0
3	0.0	0.0
4	0.0	0.0
7	0.0	0.0
8	0.0	0.0
9	0.0	0.0
10	0.0	0.0
11	0.0	0.0
14	0.0	0.8
15	0.0	1.2
16	0.0	1.8
17	0.0	1.6
18	0.0	2.4
21	37.4	1.8
22	73.0	2.0
23		1.9
24		1.6
25		2.0
28		1.3
29		1.2
30		0.8
31		1.2
32		1.4
35		0.0
36		0.6
37		0.0

Appendix 5

CONTROL LOOP DESIGN

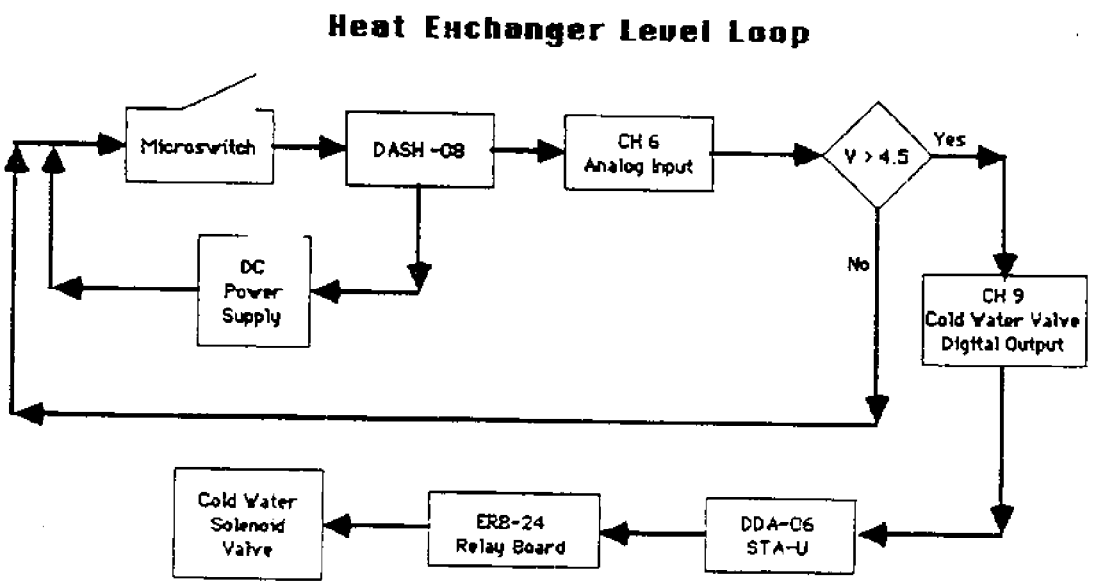
A. Temperature

The temperature control loop was the most important of our objectives. The measured variable was the reactor temperature. It was measured by installing a T type thermocouple into the bed and connecting it to an exp-16 board with a cold junction compensator. The manipulated variables included the hot water and cold water flow rate. These were controlled simply by turning the required stream on or off depending on the need of the reactor. The thermocouple signal was received by Notebook in a Thermocouple channel. There it was converted to a temperature and subsequently read by two Digital Output channels. The setpoints in the Digital Output channels determined which control unit would operate. A pump controlled the hot water flow rate, and it would begin operating if the reactor temperature fell below 36.5 C. A solenoid valve on a water inlet hose would open to allow cooling water to flow into the heat exchanger if the system's temperature rose above 39 C.



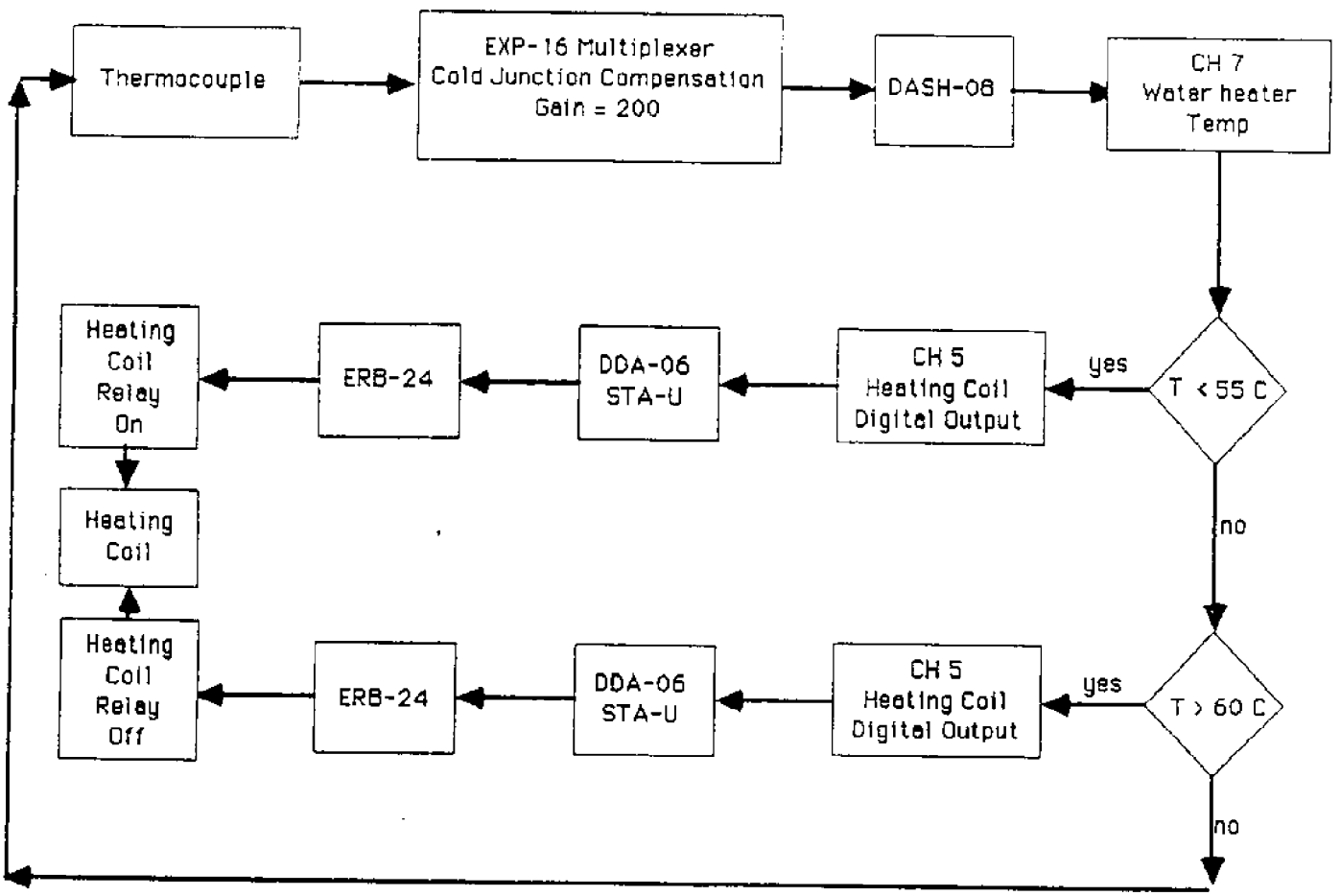
B. Heating Tank Safety Loops

As a safety measure, two feedback control loops were installed on the hot water heater. The purpose of the safety loops were to prevent the heating coil from being exposed, to prevent the pump from burning out and to try to reduce energy usage. The control objectives were to maintain a tank temperature of 55 C to 60 C and an adequate liquid level in the tank. The measured variables were the temperature of the tank and the level within the tank. The temperature was measured by a T type thermocouple which was again read by Notebook on a Thermocouple channel. The Digital Output channel compared the temperature with the range of acceptable tank temperatures. When the temperature rose above 60 C the heating coil was turned off to conserve energy. The level was monitored by a float activated microswitch. A 5 volt DC current was applied to a circuit that was completed if the float became low enough to activate the switch. Once the circuit was completed, Notebook received a the digital equivalent of a 5 volt signal through an Analog Input channel. This was the indication to open a solenoid valve to allow feed water to enter the tank. (temperature control loop on next page)



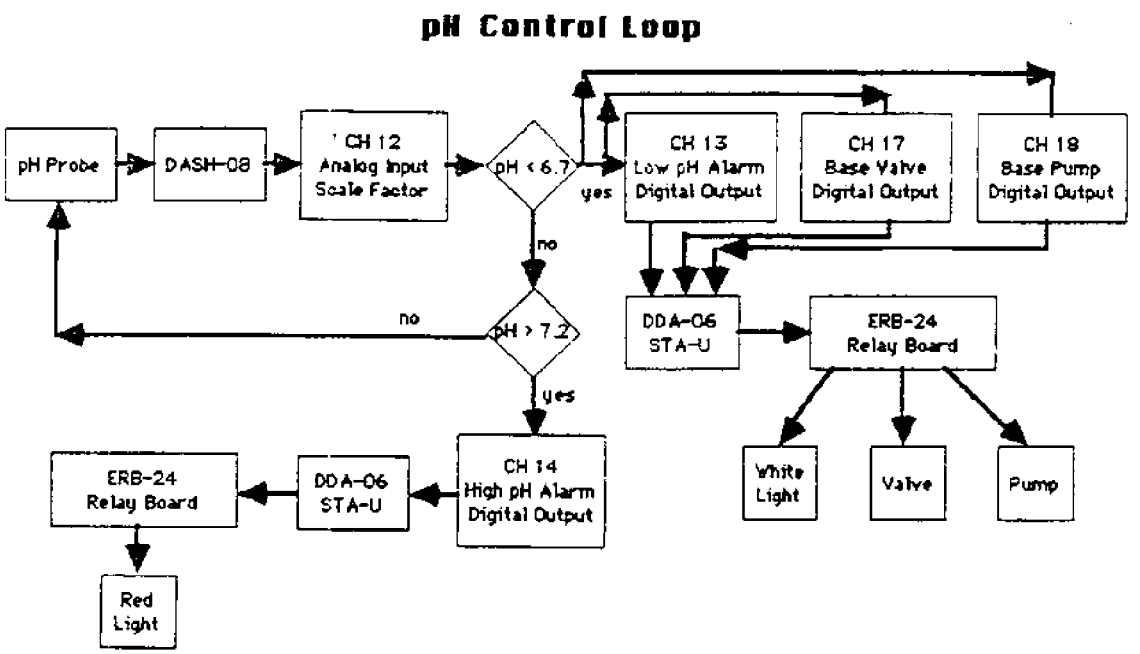
Flow diagram of level control loop for water heater.

Heat Exchanger Temperature Control



C. pH

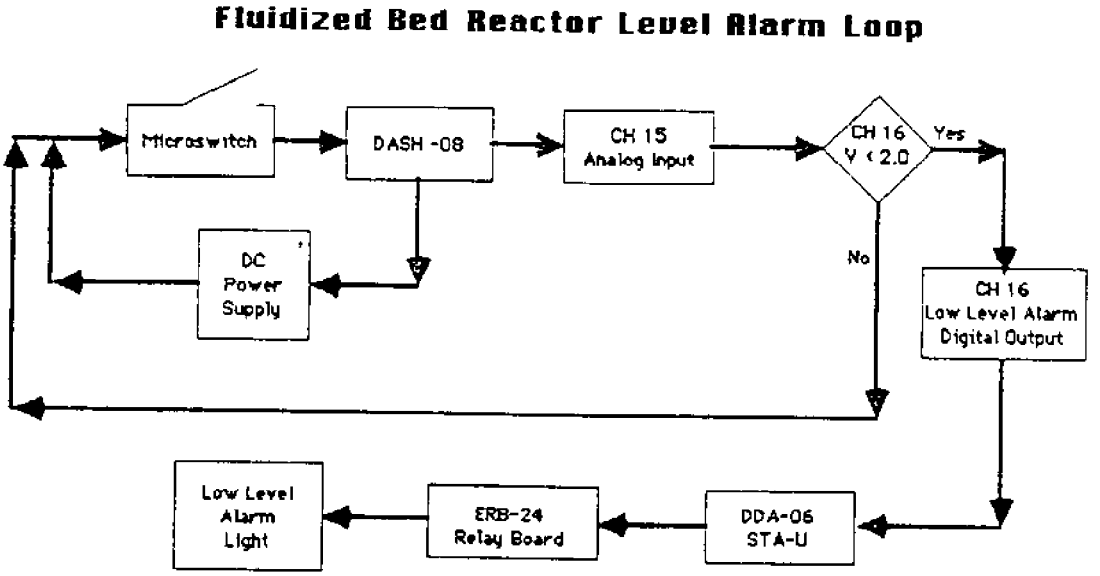
The pH of the system was measured using an immersed pH probe installed in the recycle line. Its analog signal was received by a Dash-08 board and then sent to the comparator. The control objective was to maintain the pH of the slurry within the range of 6.7 to 7.2. The signal was read by notebook through an Analog Input channel and multiplied by a scale factor of 10. Four Digital Output channels compared the pH value with their setpoints. All the channels operated on alarm mode. When the pH became too acidic, a white light was activated, a solenoid valve opened and a pump fed base into the reactor. If the pH became overly basic, a red light turns on. All of the lights and pumps were connected to the digital output relay board which received signals from the computer through the DDA-06 board.



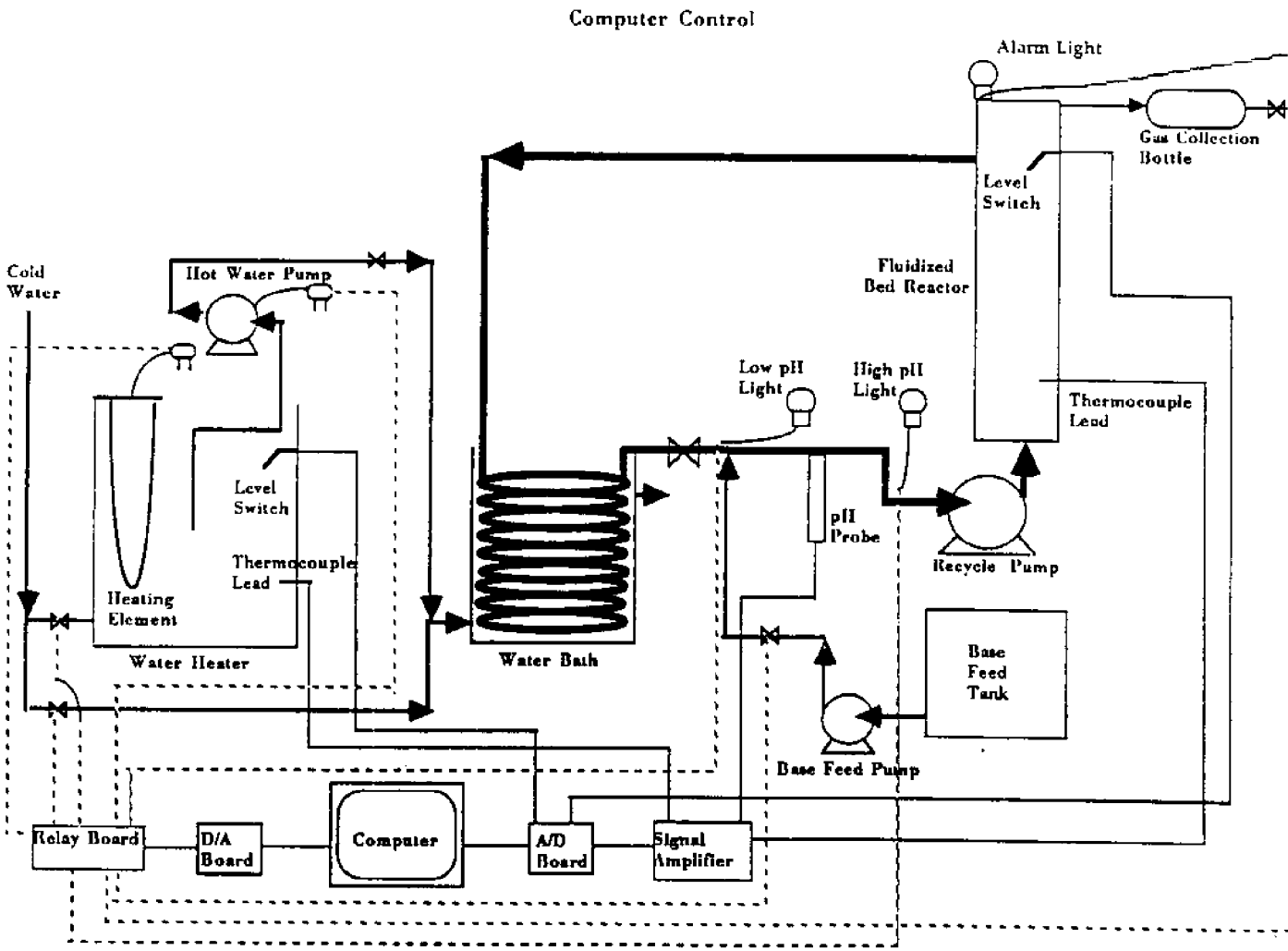
Flow diagram of pH control loop.

D. Reactor Level

To prevent the recycle pump from being damaged, the level within the bioreactor had to be maintained at a satisfactory level. A float activated microswitch monitored the level within the reactor. If it fell too low closing the switch, a red alarm light turns on. Its Notebook control logic was identical to that of the hot water heater level switch.



Logic of reactor level control loop.


Computer Control
Alarm Light
Gas Collection Bottle
Level Switch
Fluidized Bed Reactor
Cold Water
Hot Water Pump
Low pH Light
High pH Light
Thermocouple Lead
Level Switch
pH Probe
Recycle Pump
Thermocouple Lead
Heating Element
Water Heater
Water Bath
Base Feed Tank
Base Feed Pump
Relay Board
D/A Board
Computer
A/D Board
Signal Amplifier

Appendix 6

GAS ANALYSIS

The product gas stream analysis was performed on a Hewlett Packard 5730A Gas Chromatograph (G.C.). This analysis gave the molar composition of the product gas.

Before the G.C. could be used to analyze the gases, it was necessary to determine the composition of a standard mixture, and to adjust the machine so it will collect results which are useful. To begin this preparation, a temperature program was recommended. The program starts with an initial temperature of 60 C, holding for 8 minutes, then increasing at a rate of 32 C/min until final temperature of 220 C is reached. The presence of gas in a column is indicated by a peak on the recorder. By choosing the correct temperature program the peaks will be separate and distinct, plus each run will not endure longer than necessary.

The next adjustment required was the attenuation, which adjusts the height and size of the peaks. The greater the attenuation the smaller the peak. Depending on the size of a sample, the attenuation may be adjusted so the peaks don't exceed the size of the paper. For our purposes, the log setting provided the best size peaks.

The remaining settings; detector power (3), detector 1 temperature (200C), detector 2 temperature (200 C), injection port temperature (250C), and sample size (.6 ml), are all set according to the column in which the analysis is being done on. Although these settings may be changed, it is not recommended because the results may not correlate to the standard run. With these settings the following peak times were found; hydrogen at 1 minute, air at 4 minutes, carbon monoxide at 5.3 minutes, methane at 11 minutes, carbon dioxide at 14 minutes and ethane at 26 minutes.

The standard is very important. Each column is catalogued with a copy of its standard curve, which identifies the gas peaks in their order of appearance and gives their residence time in the column. When an experimental run is performed and a peak is recorded, its identity may be determined by looking on the standard curve for the gas which has the same residence time.

For experimental purposes, a gas standard was made in which the mole fraction of each gas is known. From this, the composition of an unknown gas may be calculated using a simple ratio.

$$\frac{\text{area of standard gas X}}{\text{mole fraction of standard gas X}} = \frac{\text{area of experimental gas X}}{\text{mole fraction of experimental gas X}}$$

The gas standard used, contained:

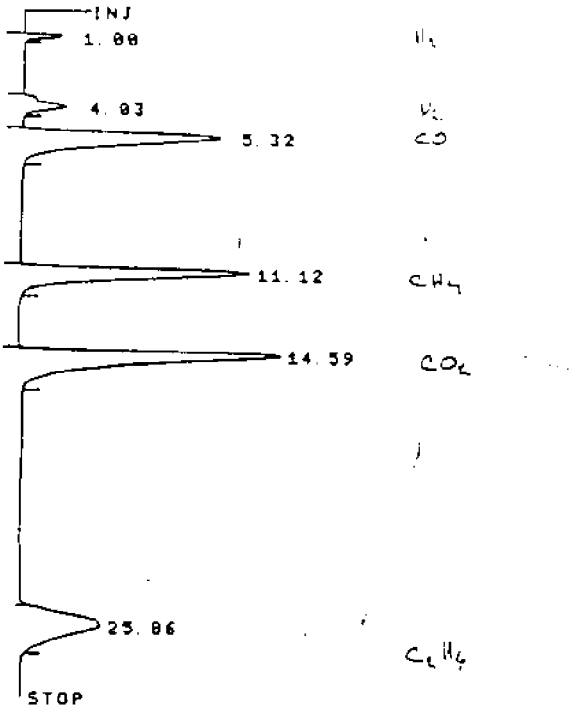
22.96%	CH_4
20.83%	CO_2
31.50%	H_2
Balance	C_2H_6, C_2H_4, Air

To operate the G.C. a sample of the product gas is withdrawn by a gas-tight syringe from the sampling bottle, and injected into the chromatograph column. Instantaneously and after the sample injection is completed, the temperature program and the integrator recorder are started simultaneously. The analysis cycle is completed by the use of an automatic stop timer which is set at 30 minutes, slightly longer than the temperature program. The output results are analyzed by using the peak areas to determine the molar composition of the gas.

There are several important factors that are necessary for accurate results. 1) The carrier gas flow rate, (helium), must be the same for each column. If it is not , the results will not be reproducible. 2) If the carrier gas flow changes from run to run the residence time will drift. Less

flow = longer residence time. 3) In order to obtain accurate mole fractions, the gas samples must be exactly the same size each time. Increasing the gas sample, will increase the area of the peak. 4) The rubber septum must be changed frequently, and as often as every 4 to 5 runs to prevent leakage. A leaky septum will cause the Helium flow rate to change. A change in the flow rate during a run, will cause the base line to drift. Instead of a clear line with several sharp peaks, a wavy baseline with many false and merged peaks will result. 5) Finally, it is very common for the syringes to become clogged with small pieces of the septum. When this occurs, the sample size is reduced or sometimes there is no injection. To prevent this a syringe with a side port needle was purchased and it has operated without a flaw.

.6 ml Standard Sample

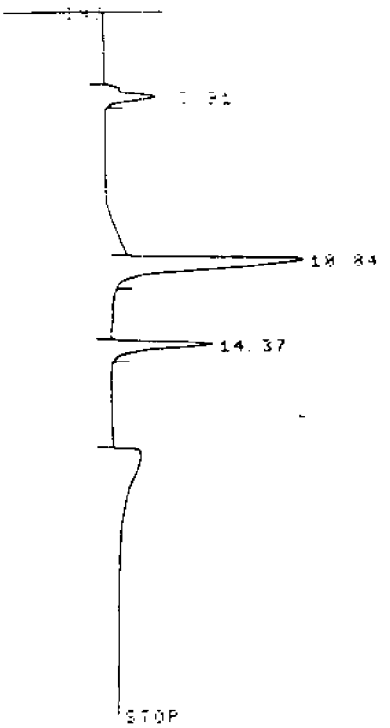


AREA %

RT	TYPE	AREA	AREA %
1.00		680	.561 3
4.03		1661	1.371
5.32		26706	22.04
11.12		31570	26.06
14.59		51681	42.66
25.86		8855	7.309

HP 3380A
DLY OFF
MV/M .10
STOP 30
ATTN LOG
REJECT OFF

FBR Sample 4/26/88



AREA %

RT	TYPE	AREA	AREA %
[illegible]		[illegible]	[illegible]

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