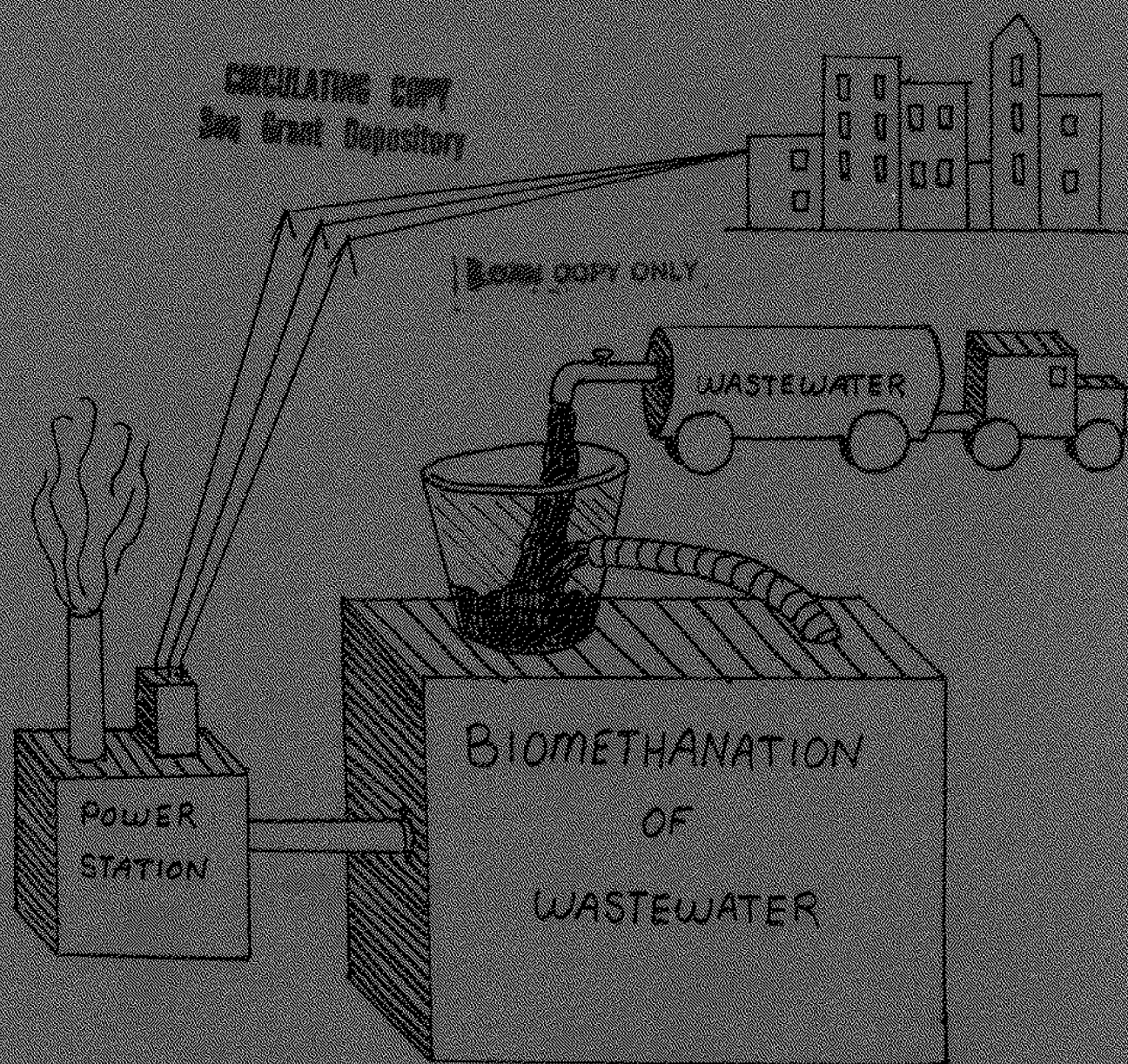


# BIOMETHANATION OF WASTEWATER IN A THREE PHASE FLUIDIZED BED REACTOR

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WASTEWATER TREATMENT IN A THREE PHASE FLUIDIZED BED BIOREACTOR

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ABSTRACT

Aerobic and anaerobic treatment of municipal and industrial wastewater, a major pollutant to marine life, is studied in an upflow three phase Plexiglas fluidized bed bioreactor. Under anaerobic condition useful gaseous by-products, which include methane and hydrogen are produced. A fluidized bed bioreactor has been designed and constructed to operate anerobically. The reactor has been operated continuously and fed with wastewater and nitrogen gas. Both phases fluidize the reactor contents and as a result excellent mixing conditions are achieved within the reactor. The wastewater entering the reactor contained a high level of chemical oxygen demand (COD), which is caused by high concentration levels of organic compounds, e.g., milk, sugar, egg yellow, etc. The reactor design facilitate continuous measurements of temperature, pressure, and pH levels. Sampling and analysis of both gases and liquid products can be performed using gas chromatographs and the chemical oxygen demand test. Results confirmed the presence of methanogenic bacteria within the product stream; this indicate successful digestion of the organic compounds as well as the production of methane gas.

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SUMMARY

The goal of this ocean project was to study the treatment of municipal and industrial wastewater, a major pollutant to marine life, in a three phase fluidized bed bioreactor. A laboratory scale unit was designed based on a literature research of bioconversion and fluidized bed reactors. The fluidized bioreactor was designed, built, and modified. All modifications were done to make the reactor an environment where the methanogenic bacteria could grow and perform effectively.

The basic design of the reactor consisted of two stages, a fluidized bed and a separation tank. The separation tank was added to the system to allow the gases to separate and promote the growth of the methanogens. Computer controls were implemented on the system. Temperature and pressure control of the reactor were both effective. Preliminary research was performed on pH control of the system.

The effectiveness of the reactor for maintaining anaerobic conditions was shown by the result of an autofluorescence test. This test is a powerful method for the recognition of methanogens in a mixed culture. Cell material examined from the apparatus autofluoresced matching the greenish-yellow color described in the literature that is specific to methanogens. This is strong evidence to suggest that methanogens can live and grow in our present experimental set up.

The reactor also performed effectively in digesting the wastewater feed and producing a clean water product. Visual observation indicated that the feed was digested, and the quality of the water product is superior to the feed water quality. Large quantities of gas were also produced during the digestion which possibly could contain methane as a marketable product.

Reactor performance tests have shown that the result of a year long design and modification process has been successful. In the future, the reactor bacteria contents, water product and gas product will be tested with more precise methods to arrive at more quantitative results. At that point, further modifications can be made to the process for its continuous operation. Also scale up measures on our pilot size reactor can be investigated in order to estimate the feasibility of a larger scale unit.

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## 1. INTRODUCTION

Wastewaters are material derived from domestic sewage or industrial processes, which for reasons of public health and for recreational, economic, and aesthetic considerations cannot be disposed of merely by discarding them untreated into convenient lakes or streams. Rather, the undesirable materials in the water must first be either removed or rendered harmless. If the material to be removed is organic in nature, treatment usually involves the activities of microorganisms, which oxidize and convert the organic matter to carbon dioxide. Wastewater treatment usually results in the destruction of pathogenic microorganisms, thus preventing these organisms from getting into rivers or other supply sources. Water treatment can be carried out by a variety of processes, which may be separated broadly into two classes, anaerobic and aerobic [1-5,9-13, 18-20].

The purpose of this ocean project is the study of wastewater treatment in a fluidized bioreactor. A laboratory scale unit was designed based on a literature research of bioconversion and fluidized bed reactors. The unit was built and tested, then modified to improve its performance during lab runs. This report contains a summary of the design, construction, and performance of the fluidized bioreactor, as well as results and conclusions about the project.

## 2. BIOCONVERSION

Anaerobic sewage treatment involves a complex series of digestive and fermentative reactions in which the organic materials are converted into CO<sub>2</sub> and methane gas. The latter can be removed and burned as a source of energy. Since both end products, carbon-dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), are volatile,

the liquid effluent is greatly decreased in organic substances. The efficiency of a treatment process is expressed in terms of the percent decrease of the initial biochemical oxygen demand (BOD); the efficiency of a well-operated plant can be 90 percent or greater, depending on the nature of the organic waste [11,12,18-20].

Anaerobic decomposition is usually employed for the treatment of materials that have much insoluble organic matter, such as fiber and cellulose, or for concentrated industrial wastes. The process occurs in four stages: (1) initial digestion of the macromolecular materials by extracellular polysaccharidases, proteases, and lipases to soluble materials; (2) conversion of the soluble materials to organic acids and alcohols by acid-producing fermentative organisms; (3) fermentation of the organic acids and alcohols to acetate, CO<sub>2</sub>, and H<sub>2</sub>; and (4) the conversion of H<sub>2</sub> plus CO<sub>2</sub> and acetate to CH<sub>4</sub> by methanogenic bacteria [1,3].

Recent survey of methane sources in the atmosphere indicates that 65% are produced by microorganisms. Biogenic methane production is carried out by a highly specialized group of organisms, the methanogenic bacteria, which are obligate anaerobes. Methane production in these organisms is a part of their energy metabolism. Most methanogenic bacteria (or methanogens for short) use CO<sub>2</sub> as their terminal electron acceptor in anaerobic respiration, converting it to methane; the electron donor used in this process is generally hydrogen. The overall reaction of methanogenesis in this pathway is as follows:



Methane formation occurs during the decomposition of such diverse substrates as cellulose, starch and sugars, proteins and amino acids, fats and fatty acids, alcohols, benzoic acid, and a variety of other substances. Although at one time it was thought that methanogenic bacteria attacked some of these

substrates directly, it is now well established that methane formation from these materials requires the participation of other anaerobic bacteria. These other bacteria ferment the substances to either acetate or hydrogen plus  $\text{CO}_2$ , which are then used by the methanogenic bacteria. Thus, methanogenesis from organic carbon is virtually always a process carried out by a mixture of bacteria, none of which can perform a complete process by themselves [1-5].

In most situations, the rate-limiting step in the methane formation from organic materials is not the final reduction of  $\text{CO}_2$  to  $\text{CH}_4$ , but the step involved in the breakdown of the complex organic material into fermentation products, such as acetate and  $\text{H}_2$ . Since carbon-dioxide is very common in anaerobic environments, either in the form of carbonates or derived from bacterial respiration or fermentation processes, methanogenic bacteria are generally limited by the availability of  $\text{H}_2$ . As soon as any  $\text{H}_2$  is formed by a fermentative microorganism, it is quickly consumed by a methanogen. The only situations in which  $\text{H}_2$  ever accumulates in nature are when methanogenesis is inhibited in some way.

Methanogens are quite widespread on earth. Thus, although high levels of methanogenesis are generally only seen in anaerobic environments, such as swamps and marches, the process also occurs in habitats that normally might be considered aerobic, such as forest and grassland soils. In such habitats, it is likely that methanogenesis is occurring in anaerobic pockets, for example, in the midst of soil crumbs. It should be noted that biogenic production of methane by the methanogenic bacteria exceeds considerably the production rate from gas wells and other fossil fuel sources.



### 3. FLUIDIZATION

A fluidized bed reactor, see reference 6, is one in which relatively small particles of catalyst (bacteria flocks in our case) are suspended by the upward motion of either a gas or liquid stream or both. The fluid flows upward through the solid particles at a rate which is sufficient to lift them from a supporting grid, but which is not so large as to carry them out of the reactor. The particles are in constant motion within a relatively confined region of space, and extensive mixing occurs in both the radial and longitudinal directions of the bed, see figure 1.

Several advantages are associated with the use of fluidized bed reactors [5]. A remarkably uniform temperature can be maintained throughout the bed. This property is a consequence of the high degree of turbulence within the bed, the high heat capacity of the solid comprising the bed relative to the gas or liquid phases, and the extremely high interfacial area for heat transfer between the solid and the gas and liquid phases. Another advantage of a fluidized bed operation is that it leads to more efficient contacting of gas, liquid, and solid than many competitive reactor designs. Because the bed particles employed in fluidized beds have very small dimensions, one is much less likely to encounter mass transfer limitations on the reaction rates in these systems than in fixed bed systems [6,7,8].

### 4. EXPERIMENTAL APPARATUS

The process of water biomethanation took place in a three phase fluidized bed reactor under aerobic conditions. Wastewater feed enters the apparatus along with the gas feed, nitrogen, and treated water leaves the process as well as a

gas by-product stream, see figure 2.

The experimental design employs a large recycle stream which maintains a longer residence time for the wastewater feed. The recycle line has an in line rotameter and valve to monitor and control the flow rate through the reactor (see figure 2). Wastewater is continuously pumped into the recycle stream with a 1/10 hp variable speed pump. The wastewater feed line is equipped with a valve and rotameter to maintain and measure the flow rate.

Anaerobic conditions are maintained within the reactor system by sealing the wastewater feed tanks, see figure 3, this was achieved by connecting four feed tanks in series with the last tank open to the atmosphere.

The water product is removed from the recycle stream and is also monitored and controlled with a valve and rotameter. The pressure in the system is the driving force for this stream and no pump is necessary. At steady state conditions the wastewater feed flow rate is the same as the wastewater product.

Feed gas, nitrogen, is added into the recycle stream at the base of the reactor from industrial type gas cylinders. Due to the high pressure of the gas cylinders, care has to be taken when gas is first introduced into the system. Occurrence of strong gas surges can cause permanent damage and breakage of the connecting tubing and leaks throughout the apparatus. The feed gas is monitored and controlled with a rotameter and valve respectively as is the product gas from the reactor.

#### 4.1 INITIAL REACTOR DESIGN

The initial reactor design consisted of a vertical three phase fluidized bed bioreactor constructed out of a plexiglas tube with an inner diameter of 5.08

cm and a height of 71.1 cm for a total volume of 1.44 liters, see figure 3. Aluminum squares (15cm x 15cm x 1cm) were machine fabricated to the ends of the plexiglas tube and sealed with rubber rings and four aluminum rods held in place with four 3/4 inch nuts. The reactor was equipped with six sampling ports spaced evenly down the side of the cylindrical reactor. The sampling ports were fabricated out of copper tube fittings. Holes were drilled and threaded down the side of the reactor and a threaded female adapter was screwed into the reactor with teflon tape to ensure no leakage. A rubber septa was added to the adapter so a syringe may be used to sample the fluid in the bed at the various locations, see figure 2.

Feed gas is added to the recycling liquid prior to entering the reactor and the mixture is passed through the fluidized bed of the reactor. Dispersion beads supported by a screen are located at the lower end of the reactor to equally disperse the gas and liquid over the cross-section of the reactor. The fluidized bed, consisting of glass beads with a diameter of 3.0 mm, rests on a screen that separates them from the dispersion beads. If this second screen was not present between the two types of beads, dispersion and fluidization, then a complex bed would result with two defined layers of fluidization due to the different buoyancy forces of the two types of beads. The mixture then continues through the reactor and is separated at the top. The liquid is returned to the recycle and the gas is taken off as product, see figure 2.

A water jacket is also incorporated in this preliminary design. The jacket surrounds the reactor and is held in place in the same manner as the reactor itself. A water heater is used to heat the water feed to this jacket to the optimum reactor temperature of 35C, which is dictated by bacteria activation. A pump circulates the warm water through the jacket to maintain constant temperature in the reactor

## 4.2 REACTOR MODIFICATIONS

Several successful test runs were made with the initial system design.

However, as the runs become more frequent several problems were faced. This included the following;

- Very poor liquid and gas separation at the top of the reactor, therefore, large amount of gas bubbles escaped through the liquid recycle line. This resulted in drying the recycle pump and complete decay of fluidization level.
- Introduction of the nitrogen gas through the recycle line caused blocking of the feed line and prevented the recycled liquid from reaching the column and as a result termination of fluidization.
- Sealing the water-cooling jacket and preventing water leaks were difficult and tedious to achieve. In addition, reaching the inner parts of the sampling ports was impossible due to the small size of drilled holes.
- Large particles and solid materials in the wastewater caused plugging of all screens and valves and as a result considerable reduction occurred in the liquid flow rate as well as the fluidization intensity.

### 4.2.1 SEPARATION TANK

Separation of the gas and liquid was achieved by allowing the mixture to leave the reactor in two phases and enter a separation tank. The tank has an inner diameter of 12 cm and a length of 110 cm for a total volume of 12.4 liters.

The separation tank lies on an angle of 20 degrees. The feed enters and the gas leaves the tank from the upper end. The liquid continues through the tank and into the recycle from the lower end.

The introduction of the separation tank in the reactor system solved some problems encountered in the initial design.

- Separation of the gas and liquid was achieved very efficiently and as a result the problem of drying the recycle pump was eliminated,
- The pH probe was installed in the side of the tank, the probe is used to monitor both pH and temperature of the liquid,
- A pressure transducer was also installed in the separation tank, to effectively maintain the liquid level with computer control,
- particulates from the fluidized bed that were pneumatically transported from the bed are collected at the lower section of the separation tank, as a result damage of the moving parts in the recycle pump is avoided.

#### 4.2.2 WATER HEATING JACKET

A major modification that was completed on the initial reactor set-up concerned the water heating jacket. The reactor is equipped with six sampling ports which must be accessible from outside the unit. If the preliminary design was used then the septa on the side of the reactor must pass through the heating jacket. It was proposed to fabricate small cylinders out of plexiglas to fit tight against the inner reactor wall and pass through the water jacket. These pieces were fabricated and the idea of using them didn't seem feasible at this point due to the anticipated problems of achieving a perfect and tight sealing. There would be problems in charging the reactor. The water jacket assembly would make it much more difficult to open up the reactor without damaging the set-up.

The modification and simpler solution to maintaining the temperature within the reactor and the system is to allow the recycle to pass through a water bath held at the optimum temperature of 35C. The recycle line was put in a coil and put in a water tank held at 35C with four fish tank heaters, each with a 75W output. The fish tank heaters seem to be a good solution to keep the tank at a constant temperature. The heaters have a very accurate output rate, since they are manufactured and designed to maintain a fish tank at a constant temperature, where fish are very temperature sensitive. The heaters are also very inexpensive as compared to commercial and industrial type heaters advertised in catalogs, costing only \$8/heater. Also, the heaters can be easily hooked up to an interface board so computer control can be completed on the temperature. A computer can control the heaters in such a way that if the temperature in the system gets too high, one or more of the heaters can be turned off. If the temperature gets too low, all the heaters can be turned on and possibly a warning light might be triggered in either case.

The heated water tank is also an ideal location to grow bacteria that can be used to charge the reactor. The constant temperature of 35C keeps an optimum environment for bacterial growth.

#### 4.2.3 SCREENS AND VALVES

A problem was also associated with the screens inside the reactor which is used to separate the distributor beads from the beads within the fluidization section. When the reactor was run with live bacteria, these screens would plug up with particulates made up from bacteria and organic matter. As the screens filled up, the recycle flow rate through the reactor diminishes and the fluidization becomes negligible.

The solution to this problem was simple. The screens and the dispersion beads were removed from the reactor assembly. To prevent the fluidization beads from falling back into the pump casing, during shut-down period, the pump was raised to a higher elevation than the reactor column. The flow rate of the recycle was greatly increased due to the loss of the combined resistances of the two screens and dispersion beads. To avoid pneumatic transport of the fluidization beads, the recycle valve has to be carefully adjusted to attain the appropriate fluidization conditions.

The results of elimination of all screens and the distributor beads was very satisfactory. Fluidization of the reactor contents was very impressive and it covered about  $3/4$  of the reactor height. Dispersion of gas and liquid across the bed cross-section was not effected by the loss of the dispersion beads.

#### 4.2.4 SAMPLING PORTS

Final modifications on the initial reactor design concerns the sampling ports. After more careful consideration of the proximity of the ports to one another it was realized that six ports would not be necessary to take samples from the reactor.

Three of these ports were changed to measure temperature and pressure. A copper-Constantan thermocouple wire was placed through the third septa to monitor the temperature within the system. Pressure transducers were placed on ports one and five to measure the pressure drop across the bed. The pressure drop gives an indication of the fluidization regime occurring in the bed and can be compared to theoretical calculations to determine if channeling is occurring in the reactor.

Both the thermocouple and pressure transducers are capable of being monitored by the computer. An optimum set point of 35C is known for the temperature and an optimum pressure drop can be set theoretically and by monitoring the system behavior to find the best combination of fluidization and residence time. By monitoring the temperature and pressure the computer is capable of sending signals to control the system.

## 5. ANALYSIS OF WASTEWATER AND PRODUCT GAS

### 5.1 CHEMICAL OXYGEN DEMAND

The Chemical Oxygen Demand of a sample determines the quantity of oxygen required for oxidation of the organic matter in the sample, under controlled conditions of oxidizing agents, temperature and time. The Chemical Oxygen Demand (COD) of the samples taken from the reactor were determined using the standard ampule method which is useful in determining the COD of samples with a COD range of 25-900 mg/L.

The apparatus necessary for the conduction of the COD analysis on given samples includes the following: expandable 10 ml ampules with premixed and premeasured reagents needed for the test, a mechanical ampule sealer capable of providing strong, consistent seals, an oven or other device capable of maintaining  $150 \pm 2$  C, and a spectrophotometer.

The sample to be analyzed is first taken from the reactor. Then a 2.5 ml portion is inserted into an ampule that has had its seal broken. The ampule is then sealed using a mechanical sealer. The sealed ampule is then placed in a 150 C oven for two hours, in this time the sample is completely digested by the reagents in the ampule. The COD of the sample is then determined by measuring



the concentration of the Cr(III) ion. This is accomplished indirectly by first measuring the light absorbance at 600 nm in a spectrophotometer. Then the absorbance reading can be converted into mg/L COD through the use of a standard curve.

The standard curve is constructed by using a standard COD solution. The solution is made by taking 8.5034 g of potassium acid phthalate and adding enough water to make one liter of solution. This solution has a COD of 10g/L or 10000mg/L which then can be diluted to a number of COD concentrations. These various COD solutions are then treated like any sample and placed in an ampule, sealed and digested. Once the standard series has been treated the absorbance can be plotted against COD thus creating a standard curve. Through the use of a standard curve the COD of any unknown sample with a COD of 25-900 mg/L can easily be determined.

## 5.2 pH MEASUREMENT

Many biological systems alter the pH of the environment in which they grow. Often the microbes change the pH to the extent that the system becomes too acidic or too basic, halting the growth of other microbes.

In order to monitor the pH and avoid such a situation, a pH probe was installed in the separation tank. The probe was mounted in a manner that allowed for easy removal and replacement of the probe. The probe measures the pH and the temperature of the liquid in the separation tank.

Two major problems were encountered during the pH measurements. During continuous and prolonged operation, it was observed that bacterial growth was progressing the tip end of the measuring electrode. At earlier stages the

bacterial growth was slow, however and as the operation time was continued, a thicker layer of bacterial cells was continuously being formed around the electrode. As a result direct contact between the probe and the liquid was not possible, therefore, the pH readings were no longer representative of the liquid in the tank.

Although the pH probe was rated for industrial use at high pressure, up to 10 atmospheres, the probe was damaged after a short period of installing it on line. The damage is certainly caused by the combined effects of turbulent convective currents as well as pressure head.

### 5.3 GAS ANALYSIS

Analysis of the product gas was performed on an Hewlett Packard, gas chromatograph, model 5730A. The analysis technique is based on measurements of thermal conductivity of the gases forming the sample in absorption column and comparison of the measured data with the standard thermal conductivity measured for the pure components or mixture of known compounds.

This type of analysis is fairly sensitive as well as time consuming, a typical sample analysis usually requires up to 30 min of processing time on the gas chromatograph. In addition, handling of the gas sampling and injection process, in which glass bottles equipped with stopcocks and septum and gas-tight syringes are used, have to be proceed with ultimate care. The following is a list of general rules of thumb and precaution which should be followed during the analysis of the gas samples;

- contamination of the injection syringes is very common, and as a result non-reproducible peaks caused by unknown contaminants usually appear in the sample analysis and are a source of extreme confusion and uncertainty,

- the syringes are equipped with very fine needles which are easily plugged with fine particles from the septum material, on the glass sampling bottle or chromatograph injection port,
- injection septum have to be replaced frequently, i.e., every 10 injections,
- syringes and needles have to be washed with methylene chloride and dried at the same frequency

The first set of data obtained from the gas chromatograph focused on identification of known gas components. As mentioned before this will aid in identifying the composition of the gas samples obtained from the reactor.

Figures 4-7 show the results obtained from injection of pure CO<sub>2</sub>, pure methane, air, and a mixture of CH<sub>4</sub>, CO, H<sub>2</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>. Single component peaks obtained for both CO<sub>2</sub> and CH<sub>4</sub> are shown in figures 4a, and 4b. On the other hand, for the air sample (figure 5) a merged peak for both oxygen and nitrogen was obtained. This behavior is fairly common in analysis of gas samples which contains air. The difficulty in separating O<sub>2</sub> and N<sub>2</sub> in the absorption column is due to the small differences in their physical properties. Also, a similar behavior is shown in the analysis supplied by the manufacturer of the column, see figure 8. In general merged peaks result in difficult quantitative and qualitative analysis of any gas sample.

Figures 6 and 7 are an excellent example on such behavior, as is shown in figure 6, 5 merged peaks are obtained for the gas mixture which contained 5 components. The result of this was the difficulty of obtaining an accurate quantitative measure of the amount of gas injected.

In an attempt to obtain separate peaks, the heating rate during the desorption process in the chromatograph column was increased by a factor of 2, the result was the sharp separation of two peaks, see figure 7. To complete the separation of all peaks, two approaches were thought; the first is to prolong the initial heating time and the second was to use another type of absorption columns.

Pursue of both approaches was considerably slowed by several complications with the injection system. The first of these was the plugging of the injection needles with the septum material, see the above list. In more than one occasion part or non of the sample was injected through, in both events the gas chromatograph have to be left to perform the complete cycle of analysis. Mainly to avoid accumulation of unwanted components and their eventual release during subsequent injections. To eliminate all problems related with the use of gas syringes an automatic gas sampling valve is recommended, see the section on recommendations. The valve is capable of direct injection from the sampling bottle into the absorption column.

## 6. CONTROL OF THE REACTOR SYSTEM

The important variables in a fluidized bioreactor are the system temperature, pH, and pressure, and the input/output flow rates of gaseous and liquid streams [16].

Temperature and pH play an important role in determining the bacterial growth and productivity in bioreactors. The temperature should remain in the range of 35 to 37 C for maximum bacterial growth. The pH should be kept close to the neutral point for optimum bacterial activity.

Pressure determines the regime of fluidization, the intensity of turbulence and mixing in fluidized beds. The pressure does not directly affect the bacteria, but should be monitored because of its stresses on the reactor itself. The control of these parameters has been chosen as the objective of the current study [17].

## 6.1 TEMPERATURE CONTROL

Computer controls were set up to maintain the temperature in the reactor from 25 C to 35 C by controlling the heaters in the constant temperature bath. The temperature in the bath was monitored as well as in the reactor to prevent over heating. An ON/OFF control loop was implemented to switch one or more of the fish tank heaters at the appropriate time. If the temperature in the system exceeded the setpoint, i.e., 35 C, the controlled heaters are turned off. On the other hand, if the temperature dropped below the set point then all the heaters are turned.

The performance of the temperature control experiments was performed only on one heater to avoid cooling of the reaction medium and slowing of the bacterial growth rate. Figure 10, shows a plot of the bath temperature, the ON/OFF control, and the dynamic response of the system. A copy of the SETUP in the LABTECH note book can be found in appendix 2.

One major difficulty was observed in the control loop. Noise was present in the line which caused fluctuations in the control response over a range of 15 C. This caused the heaters to turn on and off rapidly, resulting in excessive wear on the heater. The range of control was increased to avoid this problem.

## 6.2 PRESSURE CONTROL

Three pressure transducers were used to monitor the pressure near the top and bottom of the column, and in the settling tank.

Measured data indicated that the pressure difference in the reactor was too small to measure.

The pressure in the reactor could not be controlled due to a lack of pressure relief valve, but it is highly recommended to implement this type of valve to avoid pressure build up within the tank and the subsequent development of leaks within the system.

## 7. REACTOR OPERATION AND RESULTS

To initiate the experimental runs a rich source of methanogen bacteria was charged into several glass jars (tightly sealed) and was left to ferment for a period of 1 week. The methanogens source was then fed into the reactor unit together with nutrient materials, which included raw eggs, crushed liver, milk, and sugar. After a period of one week the a liquid sample was drawn out of the bed and was tested for existence of methanogens.

Methanogens can be tested for in mixed cultures by passing a certain wavelength of light on the sample and checking the cells for autofluorescence of a specific color. Some material examined from the reactor autofluoresced matching the greenish-yellow color described in the literature, that is specific to methanogens [14]. Methanogens have a very specific mechanism which allows for the production of methane. The mechanism is only performed by these bacteria and two coenzymes involved autofluoresce at a specific wavelength.

These coenzymes are very specific to methanogens making this a powerful method for the recognition of methanogens in a mixed culture. These cells were found attached to organic material and suspended in the fluid. The cells were of all shapes and sizes and several cells are found during to exist during the process of division.

The outcome of the autofluorescence experiment indicates that the methanogens did grow in our present experimental set up. It was originally feared that opening the reactor would destroy the methanogens, which do not survive in the presence of oxygen. However, the reactor had to be opened a few times for design modifications allowing direct air contact with the solution, yet the methanogens were able to survive. Other bacteria in the system react with the oxygen, protecting the methanogens.

The reactor also performed successfully in its ability to digest the wastewater feed and produce a clean water product. This was determined simply by comparing the turbidity of the water feed and product. The feed was a very murky white color. The product was a clean, clear water. The product water will be tested for its exact composition more rigorously in the future, using the COD test. However at the present time it can be seen by observation that the feed was digested, and the quality of the water product is much superior to the feed water quality.

## 8. CONCLUSIONS

A three phased fluidized bioreactor was designed, built, and found to perform effectively during laboratory runs. The testing done to prove the reactor performance were not extensive, however, they do show that the result of a year long design and modification process has been successful.

Methanogenic bacteria is able to exist and grow in our reactor. The feed of a wastewater sample was digested and a clean water sample as well as a large amount of gas were produced.

In the future, the reactor bacteria contents, water product and gas product will be tested with more precise methods to arrive at more quantitative results. At that point, further modifications can be made to the process for its continued improvement. Also scale up measures on our pilot size reactor can be investigated in order to estimate the feasibility of a larger scale unit.

#### 9. RECOMMENDATIONS

1) The diameter of the reactor must be increased either by using the separation tank as the reactor or by using the grooves cut in the capping plate from the previous design of the heating jacket. This will increase the residence time in the reactor. Presently, there is a very small difference between the tube diameter and the reactor diameter.

2) A trip to Newmarket's anaerobic digester should be planned to get an active sample of bacteria. The reactor can then be charged with a living sample of the oxygen sensitive methanogens. The sample fed to the reactor should consist mostly of a liquor(liquid) sample. Clogging problems will exist if particulates are fed. The anaerobic digester should be on line in August. The phone number there is 659-5422.

3) The nitrogen feed should be connected with copper tubing. The nitrogen tank pressure is large and will split Tygon tubing over any length of time.



4) A pressure relief valve should be added to the system. This is a safety measure to prevent seals from blowing and to protect the pH probe. The operating pressure will have to be adjusted to a predetermined set point by data received from the reactor.

5) Control of the pH of the system should be incorporated into the reactor. This is advantageous because it allows for one group of bacteria to prosper and perform more efficiently. Another area of optimization is to find the pH where the bacteria perform the best at digesting the waste water. Presently, corrections should only be made when the pH gets below 4.5 or above 8.0.

6) Screens have shown that they clog with large flocks of bacteria. these large flocks maybe caused by the bacteria clinging to the solid particles in the waste water. If the feed solution is particle free then the screens may be re-introduced in the reactor. But if these flocks are formed by self-flocking bacteria then the screens may not be used. Further experimentation is required with mature colonies of bacteria.

7) One major variable is the type of bead used in the reactor. Changing the bead size, density or shape will effect the amount of fluidization in the bed. Changing the surface area, porosity, texture, or type of material will effect the amount of bacteria filming on the beads. Experimentation with different bead types should be done to detect if reactor performance can be improved.

8) Once the COD and GC measurement techniques are perfected, experimentation should be performed using different types of wastewater to check on the versatility of the system.

9) A feed storage tank should be purchased with the capability of being purged with nitrogen to limit the amount of dissolved oxygen in the feed solution. An effective system for the removal of oxygen being drawn into the tank should be utilized. One way to remove oxygen from the air is to pass the air through a packed bed of copper fillings heated to 150 C.

10) The feed tank and feed solution should be autoclaved. This is done to prevent bacteria from eating the wastewater before it gets into the reactor. This is necessary to prevent variation of the COD in the feed.

11) A filter system should also be put on the air intake to the feed solution to limit the airborne bacteria from entering the solution. This can be done simply with a glass wool plug .

12) It is suggested that the next cylinder of gas that is purchased should contain some CO<sub>2</sub> or H<sub>2</sub>. The addition of these gases would help in the growth of the methanogens.

13) The Tygon tubing should be replaced with Viton tubing, which is oxygen impermeable. The reason this was not done before is because of the high cost of the viton tubing. If this purchase is not financially possible, tygon tubing is sufficient. Although it is oxygen permeable, it is assumed that the oxygen entering the system gets metabolized by other bacteria, protecting the sensitive methanogens.

14) The gas flowmeters should be replaced with larger rotameters that can be kept free of water by check valves.

15) A Plexiglas cover is needed for the constant temperature bath to limit the loss of water due to evaporation.

16) A storage tank is needed for the water product. This is an important recommendation due to the problems caused by the unpleasant smell of the water. The tank should have an airtight lid with a gas exit line leading to the vent to avoid a pressure build-up in the tank.

17) Gas Chromatograph should be equipped with automatic sampling valve to permit proper introduction of gas into GC.

APPENDICES

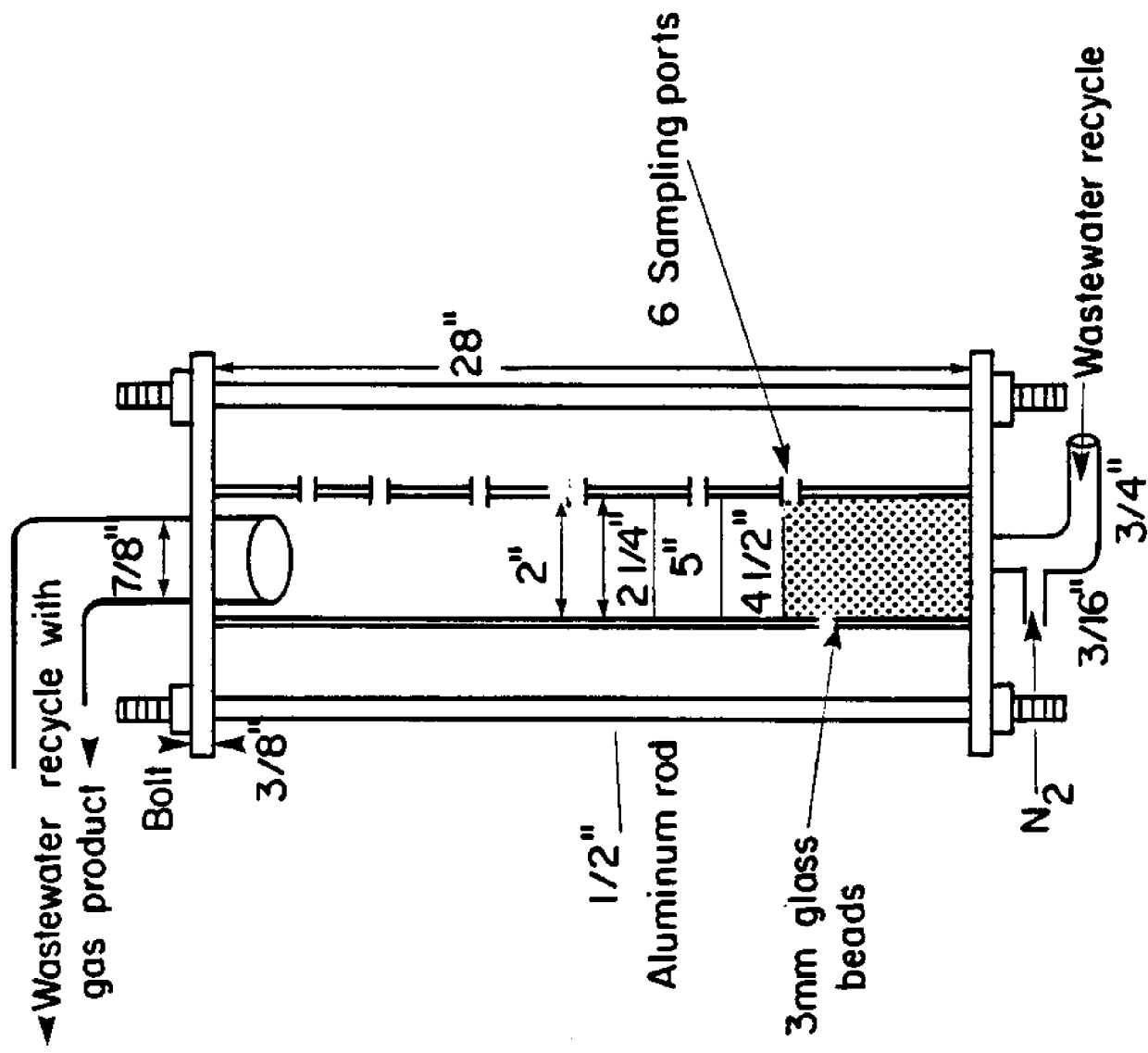


FIGURE 1: DEMENSIONS OF REACTOR

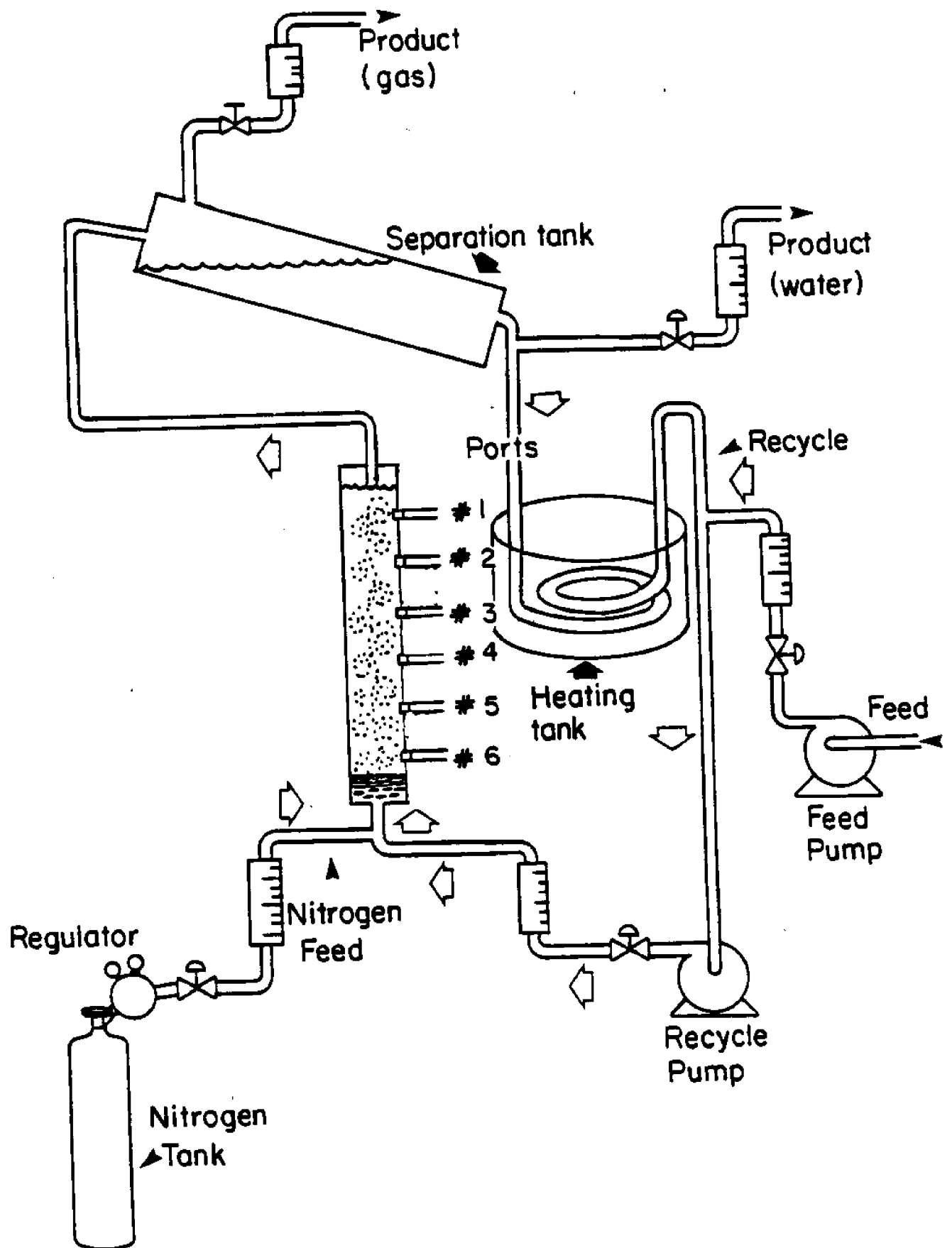
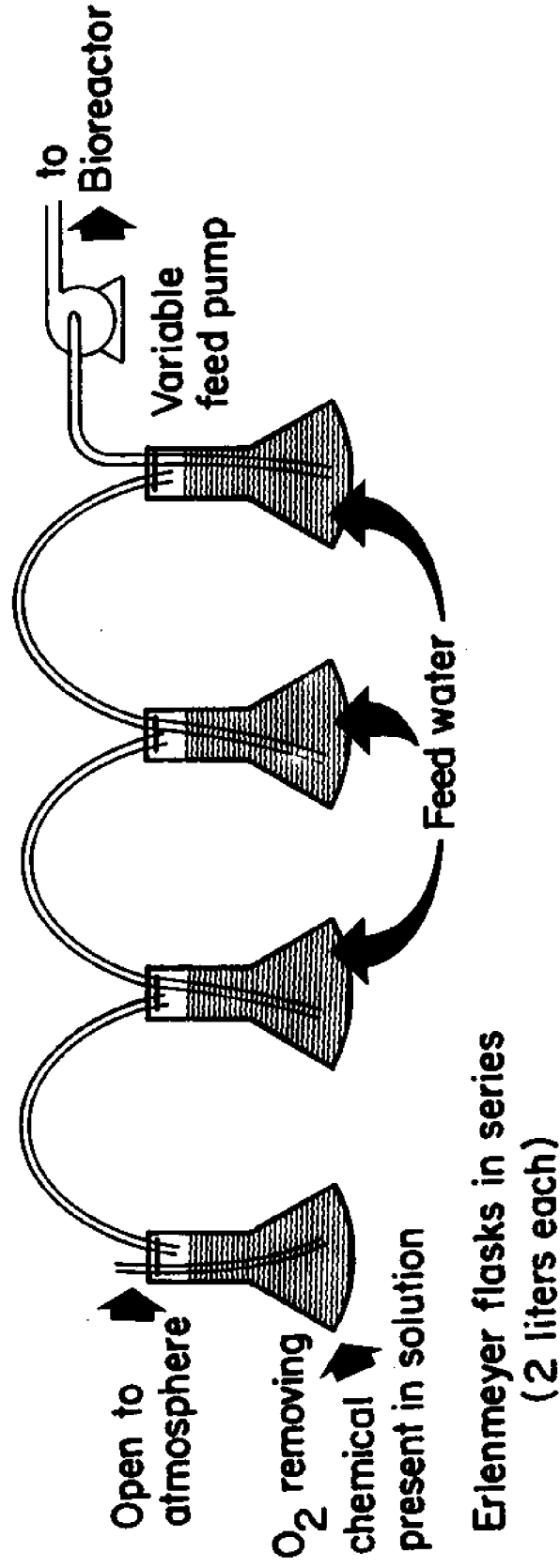
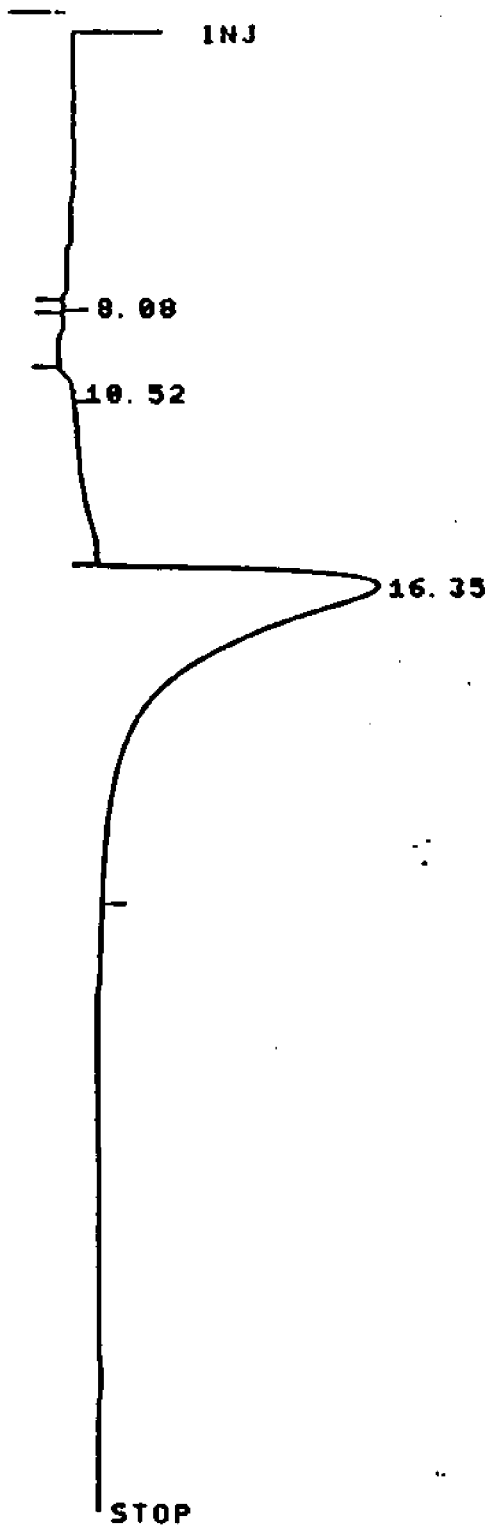


FIGURE 2: FLUIDIZED BED BIOREACTOR

# CLOSED FEED TANK SET UP





RT	TYPE	AREA	AREA %
8.08		69	.042 36
10.52		661	.405 8
16.35		162163	99.55

HP 3380A  
 DLY OFF  
 MV/M .03

STOP OFF  
 ATTN 4

REJECT OFF

Figure 4a: GC results using pure carbon dioxide



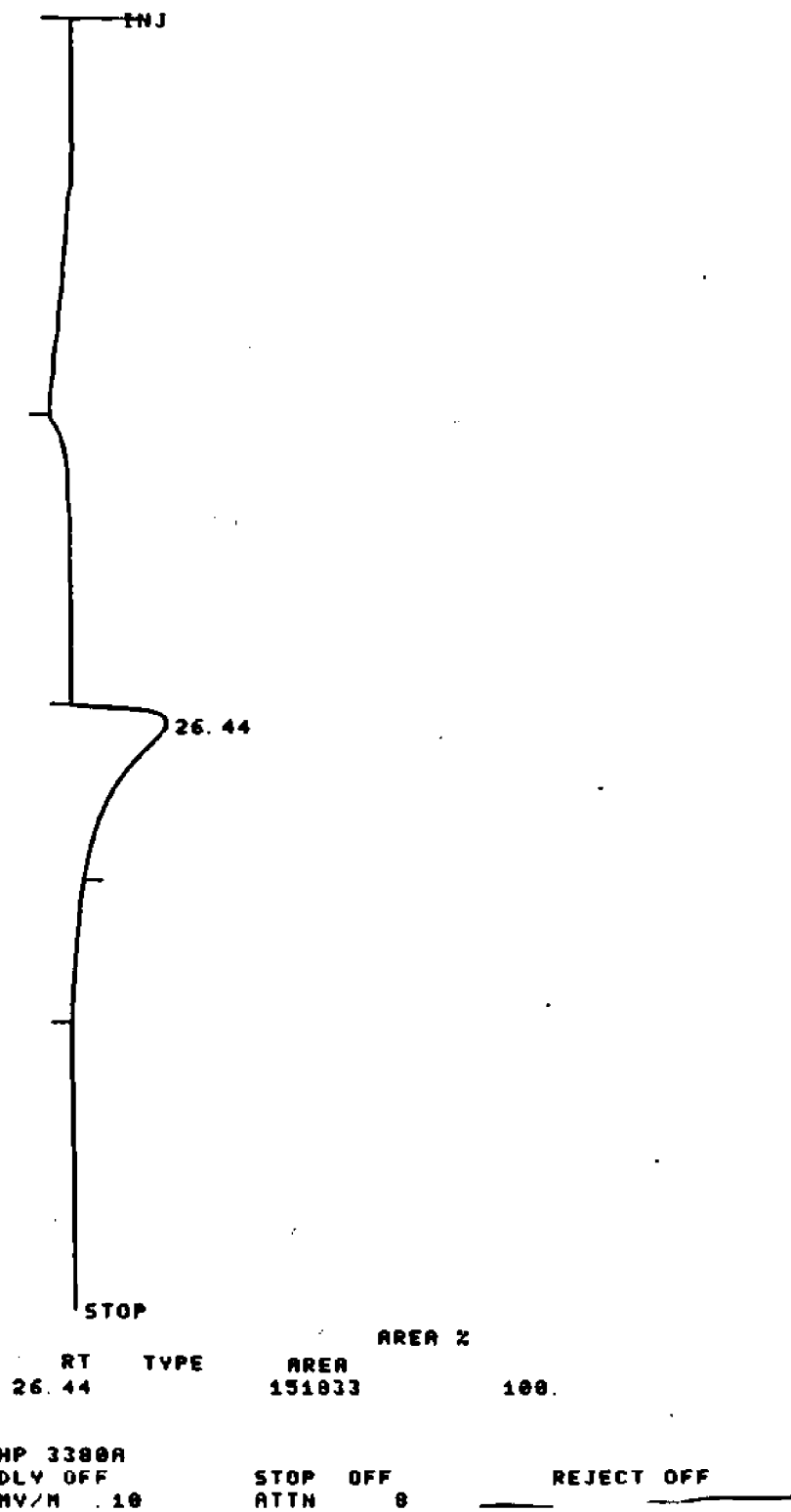
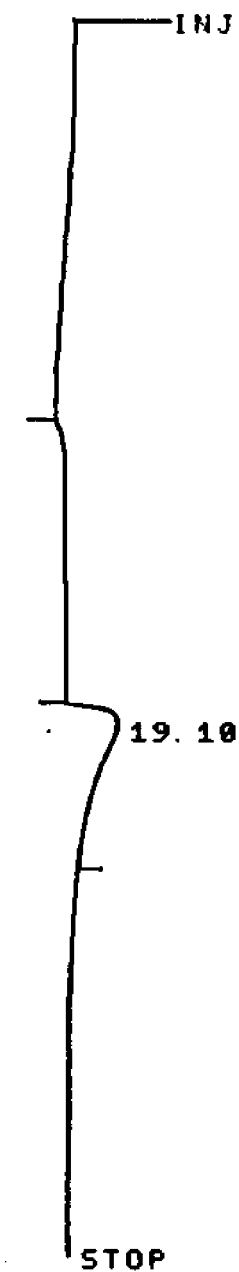


Figure 4b: GC results using pure methane



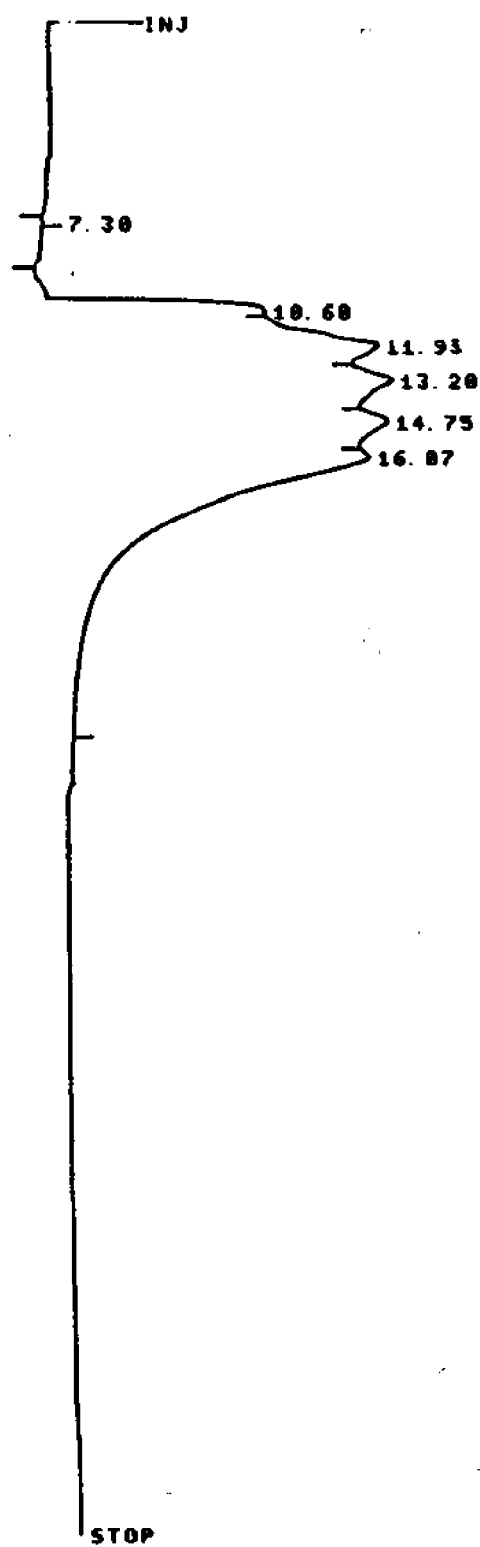
RT	TYPE	AREA	AREA %
19.10		22364	100.

HP 3380A  
 DLY OFF  
 MV/M .03

STOP OFF  
 ATTN 4

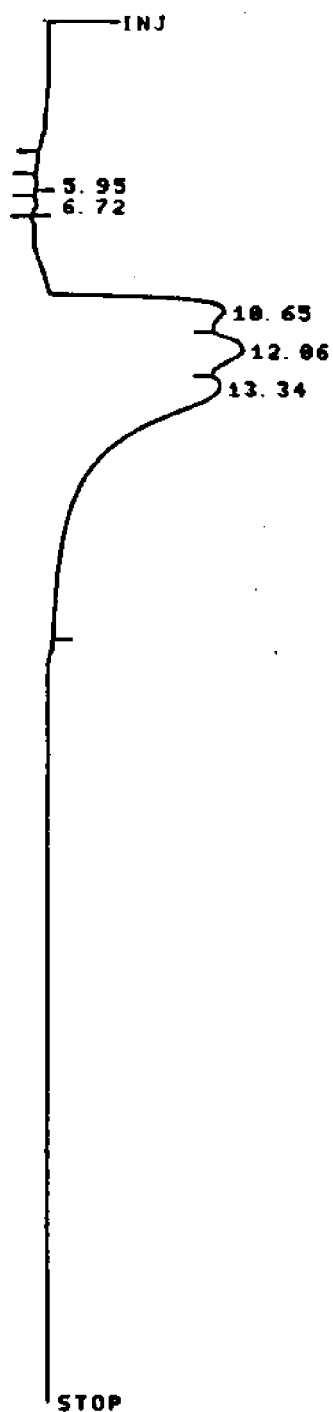
REJECT OFF

Figure 5: GC results\_using air



RT	TYPE	AREA	AREA 2
7.30		188	.813 86
10.60		32398	4.491
11.93	M	151586	21.81
13.20	M	148863	20.63
14.75	M	138330	19.17
16.07	M	258148	34.67

Figure 6: GC results, 5 merged peaks, of a standard mixture of CH<sub>4</sub>, CO, H<sub>2</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>.



RT	TYPE	AREA	AREA %
5.95		274	891.63
6.72		392	131.1
10.65		63257	21.15
12.06	M	89888	30.06
13.34	M	145231	48.57

HP 3380A  
 DLY OFF  
 MV/M 03

STOP OFF  
 ATTN 4

REJECT OFF

Figure 7: GC results, 2 separate peaks, 3 merged peaks, of standard mixture of CH<sub>4</sub>, CO, H<sub>2</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub>.

**Figure C — Permanent Gases,  
Methane, and C2 Hydrocarbons  
on Carbosieve 8-II**

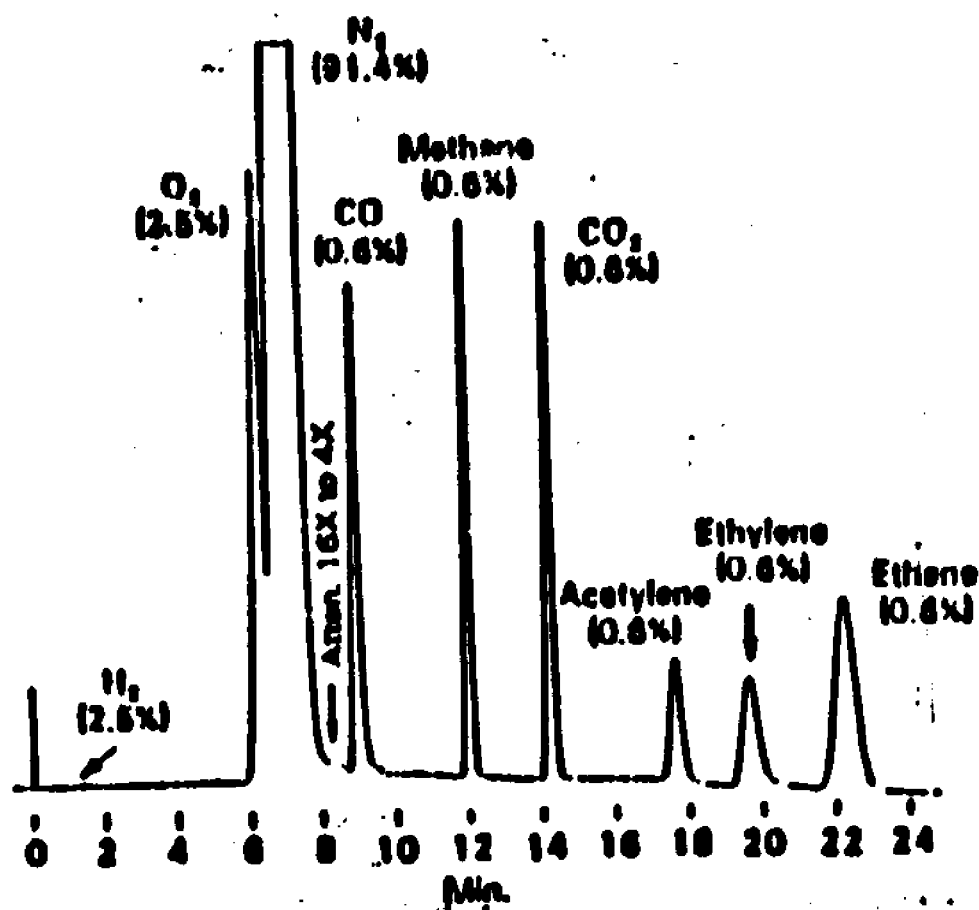


Figure B: GC analysis supplied by the manufacturer of the column

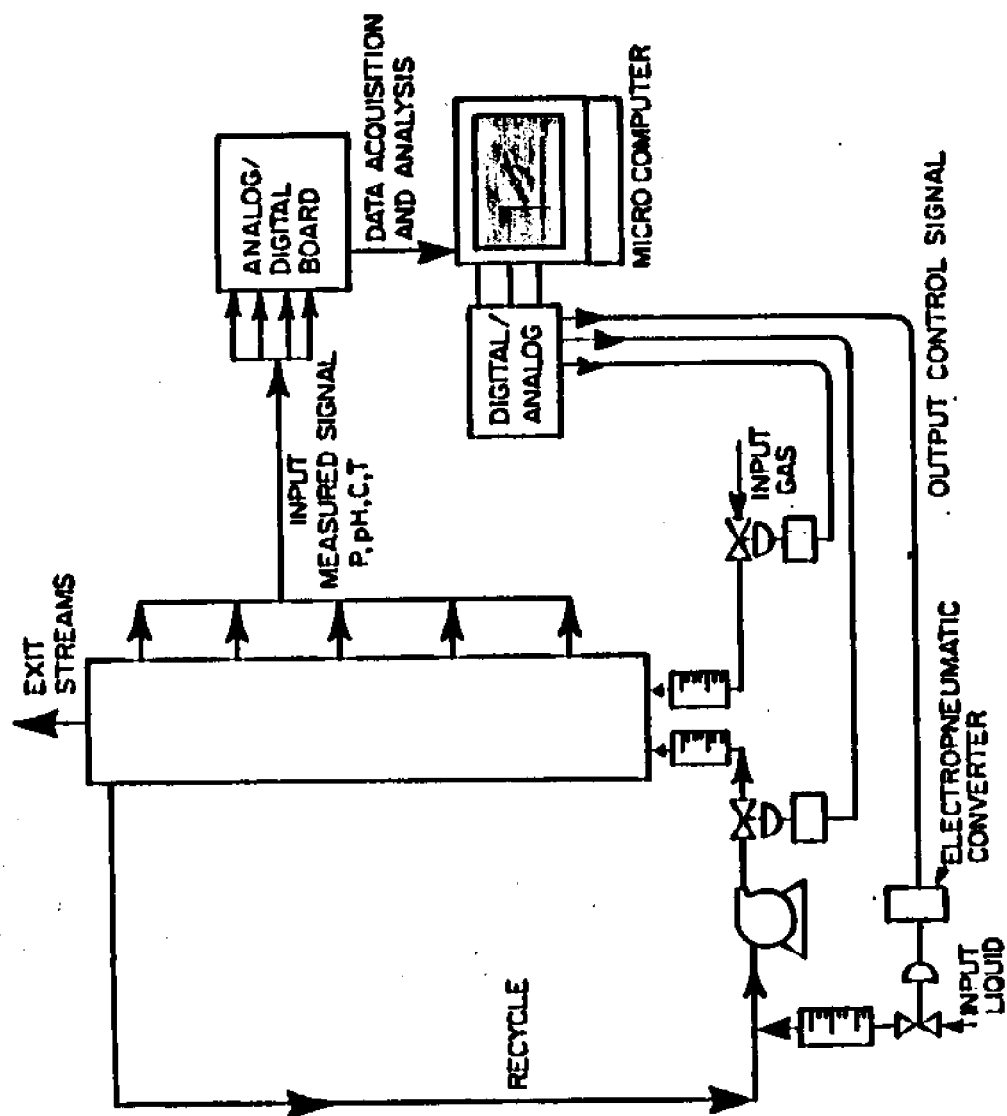


FIGURE 9: FLOW DIAGRAM OF CONTROL LOOP.

Current Value: 1

#### NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels	9
Current Channel(s) [n or n..m]	1
Channel Type	Thermocouple
Channel Name	
Interface Device	1: Dash-8
Interface Channel Number [0..143]	24

Temperature Scale	Celsius
Thermocouple Type	T
Scale Factor	1.000
Offset Constant	0.000
Buffer Size	5000
Number of Iterations	1
Number of Stages [1..4]	1

Sampling Rate, Hz	10.000
Stage Duration, sec. [0.0..1.0E+08]	180.000
Start/Stop Method	Normal
Trigger Channel	1
Trigger Pattern to AND [0..255]	0
Trigger Pattern to XOR [0..255]	0
Current Value: 2	

#### NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels	9
Current Channel(s) [n or n..m]	2
Channel Type	Digital Output
Channel Name	
Interface Device	7: DDA-06
Interface Channel Number [0..2]	1

Loop	Closed
Bit Number [0..7]	7
Upper Limit	30.000
Lower Limit	20.000
Output Polarity	On = High
Loop Type	On / Off
Input Channel	1
Buffer Size	5000
Number of Iterations	1
Number of Stages [1..4]	1

Sampling Rate, Hz	10.000
Stage Duration, sec. [0.0..1.0E+08]	180.000
Start/Stop Method	Normal

Figure 10: Real-Time Computer Output of Bath Temperature, and ON/OFF control.

Current Value: 2

# WINDOW SETUP

Number of Windows [0..15]	2	
Window Number	1	2
Left Limit, x0 [0.0..1.0]	0.150	0.150
Lower Limit, y0 [0.0..1.0]	0.150	0.650
Right Limit, x1 [0.0..1.0]	0.990	0.990
Upper Limit, y1 [0.0..1.0]	0.500	0.990
Y Axis Title	Temp	Pres
X Axis Title	Time, se	Time, se
Length of Time (X) Axis in sec.	60.000	60.000
X Tic Start Value	0.000	0.000
X Tic End Value	60.000	60.000
Number of X Tics [0..11]	7	7
Y Tic Start Value	0.000	0.000
Y Tic End Value	50.000	10.000
Number of Y Tics [0..11]	6	6
Window Color	Black	Black
Scroll Size [0.0..1.0]	1.000	1.000

Current Value: 6

# TRACE SETUP

Number of Traces [0..50]	6				
Trace Number	1	2	3	4	5
Window Number [1..15]	1	1	2	2	2
Line Color	Yellow	Green	White	Yellow	Red
Line Type	Solid	Solid	Solid	Dotted	Dash-Two
Data Point Symbol	None	None	None	None	None
Y Channel Number	1	2	3	6	7
Y Minimum Displayed Value	0.000	0.000	0.000	0.000	0.000
Y Maximum Displayed Value	50.000	50.000	10.000	10.000	10.000
Trace Type	T vs. Y	T vs. Y	T vs. Y	T vs. Y	T vs. Y
For Meters Only:					
Number of Decimal Places	3	3	3	3	3
For Type XY Only:					
X Channel Number	1	2	3	4	5
X Minimum Displayed Value	0.000	0.000	0.000	0.000	0.000
X Maximum Displayed Value	10.000	10.000	10.000	10.000	10.000



Current Value: 2

### TRACE SETUP

Number of Traces [0..50]	6				
Trace Number	2	3	4	5	6
Window Number [1..15]	1	2	2	2	2
Line Color	Green	White	Yellow	Red	Green
Line Type	Solid	Solid	Dotted	Dash-Two	Dash-Two
Data Point Symbol	None	None	None	None	None
Y Channel Number	2	3	4	7	8
Y Minimum Displayed Value	0.000	0.000	0.000	0.000	0.000
Y Maximum Displayed Value	50.000	10.000	10.000	10.000	10.000
Trace Type	T vs. Y	T vs. Y	T vs. Y	T vs. Y	T vs. Y
For Meters Only:					
Number of Decimal Places	3	3	3	3	3
For Type XY Only:					
X Channel Number	2	3	4	5	6
X Minimum Displayed Value	0.000	0.000	0.000	0.000	0.000
X Maximum Displayed Value	10.000	10.000	10.000	10.000	10.000

NOTEBOOK Global Setup Checking

MODE: Normal

```
#####
3 Ch.3Interface3Int.3 Channel 3 Channel 3Duration3 Rate 3 File 3Wd.
3 Mo.3 Device 3Chan3 Name 3 Type 3seconds 3 Hz 3 Name 3#
#####
3 131:Dash-8 3 243 3 Thermocouple3 180.0003 10.0003 3 1
3 237:DDA-06 3 13 3Digital Output3 180.0003 10.0003 3 1
3 330:Dash-8 3 243 3 Analog Input3 180.0003 10.0003 freq1.prn3 2
3 437:DDA-06 3 13 3Digital Output3 180.0003 10.0003 3
4 53 3 3 3 Calculated3 180.0003 10.0003 3
3 631:Dash-8 3 273 3 Analog Input3 180.0003 10.0003 freq1.prn3 2
3 731:Dash-8 3 283 3 Analog Input3 180.0003 10.0003 freq1.prn4 2
3 83 3 3 3 Calculated3 180.0003 10.0003 3 2
3 931:Dash-8 3 183 3 Thermocouple3 180.0003 10.0003 3
#####
```

Setup OK

Current Value: 3

# NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels 9  
Current Channel(s) [n or n..m] 3  
Channel Type Analog Input  
Channel Name  
Interface Device 0: Dash-8  
Interface Channel Number [0..143] 24

Input Range 50V  
Scale Factor 1.000  
Offset Constant 0.000  
Buffer Size 5000  
Number of Iterations 1  
Number of Stages [1..4] 1

Sampling Rate, Hz 10.000  
Stage Duration, sec. [0.0..1.0E+08] 180.000  
Start/Stop Method Normal  
Trigger Channel 1  
Trigger Pattern to AND [0..255] 0  
Trigger Pattern to XOR [0..255] 0  
Time Delay, sec. [0.0..1.0E+08] 0.000  
Current Value: 4

# NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels 9  
Current Channel(s) [n or n..m] 4  
Channel Type Digital Output  
Channel Name  
Interface Device 7: DDA-06  
Interface Channel Number [0..2] 1

Loop Closed  
Bit Number [0..7] 1  
Upper Limit 1.100  
Lower Limit 1.000  
Output Polarity On = High  
Loop Type On / Off  
Input Channel 1  
Buffer Size 5000  
Number of Iterations 1  
Number of Stages [1..4] 1

Sampling Rate, Hz 10.000  
Stage Duration, sec. [0.0..1.0E+08] 180.000  
Start/Stop Method Normal

Current Value: 5

#### NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels	9
Current Channel(s) [n or n..m]	5
Channel Type	Calculated
Channel Name	

Operation	ulimit(X)
X Input Channel	2
Y Input Channel	1
Parameter, r	0.000
Scale Factor	1.000
Offset Constant	0.000
Buffer Size	5000
Number of Iterations	1
Number of Stages [1..4]	1

Sampling Rate, Hz	10.000
Stage Duration, sec. [0.0..1.0E+08]	180.000
Start/Stop Method	Normal

Current Value: 6

#### NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels	9
Current Channel(s) [n or n..m]	6
Channel Type	Analog Input
Channel Name	
Interface Device	1: Dash-8
Interface Channel Number [0..143]	27

Input Range	±5V
Scale Factor	1.000
Offset Constant	0.000
Buffer Size	5000
Number of Iterations	1
Number of Stages [1..4]	1

Sampling Rate, Hz	10.000
Stage Duration, sec. [0.0..1.0E+08]	180.000
Start/Stop Method	Normal
Trigger Channel	1
Trigger Pattern to AND [0..255]	0
Trigger Pattern to XOR [0..255]	0
Time Delay, sec. [0.0..1.0E+08]	0.000

Current Value: 7

# NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels	9
Current Channel(s) [n or n..m]	7
Channel Type	Analog Input
Channel Name	
Interface Device	1: Dash-8
Interface Channel Number [0..143]	28
Input Range	±5V
Scale Factor	1.000
Offset Constant	0.000
Buffer Size	5000
Number of Iterations	1
Number of Stages [1..4]	1
Sampling Rate, Hz	10.000
Stage Duration, sec. [0.0..1.0E+08]	180.000
Start/Stop Method	Normal
Trigger Channel	1
Trigger Pattern to AND [0..255]	0
Trigger Pattern to XOR [0..255]	0
Time Delay, sec. [0.0..1.0E+08]	0.000
Current Value: 8	

# NORMAL DATA ACQUISITION / CONTROL SETUP

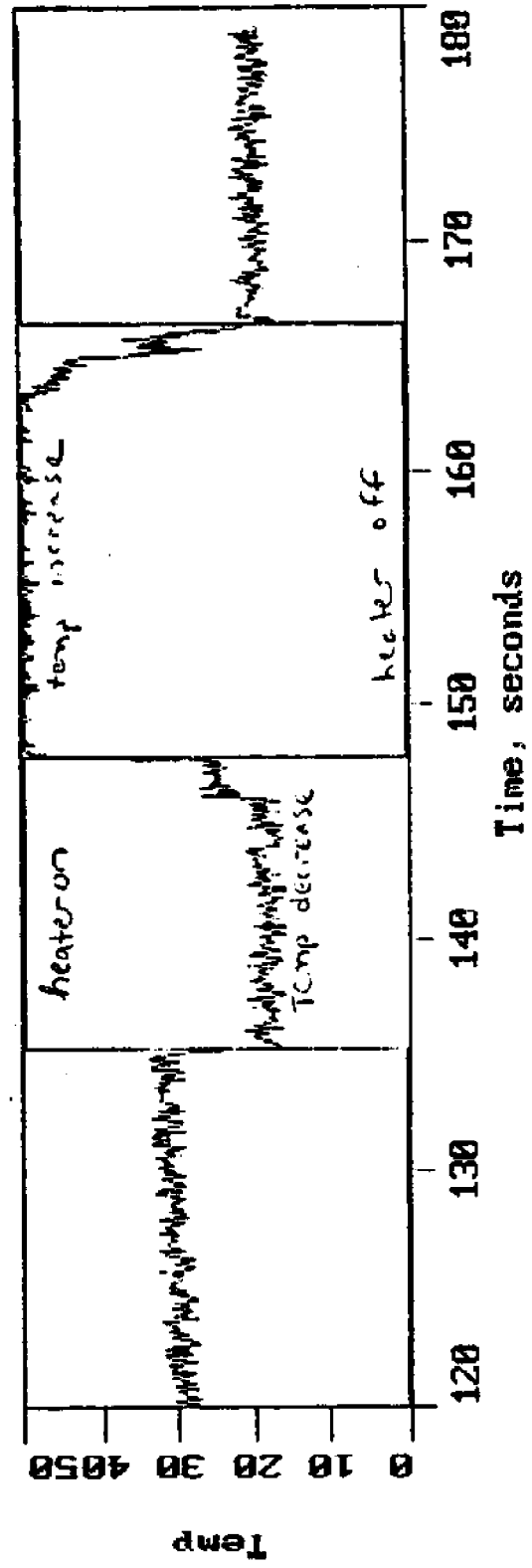
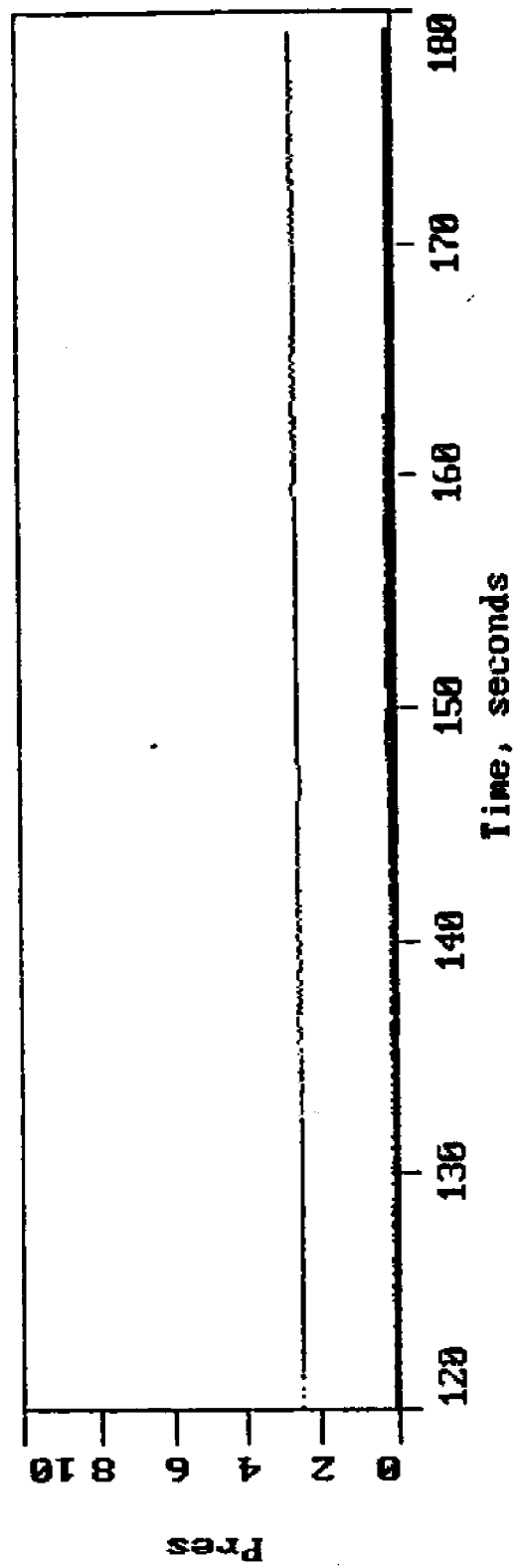
Number of Channels	9
Current Channel(s) [n or n..m]	8
Channel Type	Calculated
Channel Name	
Operation	X-Y
X Input Channel	7
Y Input Channel	6
Parameter, 1	0.000
Scale Factor	1.000
Offset Constant	0.000
Buffer Size	5000
Number of Iterations	1
Number of Stages [1..4]	1

Sampling Rate, Hz	10.000
Stage Duration, sec. [0.0..1.0E+08]	180.000
Start/Stop Method	Normal

Current Value: 4

NORMAL DATA ACQUISITION / CONTROL SETUP

Number of Channels	9
Current Channel(s) [n or n..m]	9
Channel Type	Thermocouple
Channel Name	
Interface Device	1: Dash-A
Interface Channel Number [0..143]	18
Temperature Scale	Celsius
Thermocouple Type	T
Scale Factor	1.000
Offset Constant	0.000
Buffer Size	5000
Number of Iterations	1
Number of Stages [1..4]	1
Sampling Rate, Hz	10.000
Stage Duration, sec. [0.0..1.0E+06]	180.000
Start/Stop Method	Normal
Trigger Channel	1
Trigger Pattern to AND [0..255]	0
Trigger Pattern to XOR [0..255]	0



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