COLLECTION, ANALYSIS, AND UTILIZATION OF BIOGAS GENERATED BY THE ANAEROBIC TREATMENT OF CRAB PROCESSING WASTEWATER

by

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(ABSTRACT)

Energy recovery from the anaerobic treatment of crab processing wastewater was investigated. Biogas from two laboratory-scale, upflow anaerobic filters (Systems A and B) was collected and analyzed to determine percent by volume composition of methane (CH_4), carbon dioxide (CO_2), and hydrogen sulfide (H_2S). Biogas produced by System A (upflow anaerobic bed filter) produced biogas averaging 68, 28, and 1.5 % CH_4, CO_2, and H_2S, respectively. System A average gas production ranged from 6.3 to 15.8 liters per day (L/d) (6.6 to 10.0 L gas/L feed) for COD reductions ranging from 11,000 to 27,000 milligrams per day (mg/d) and COD loadings ranging from 16,700 to 43,600 mg/d. System B (upflow anaerobic packed filter) produced biogas averaging 68, 28, and 1.4 % CH_4, CO_2, and H_2S, respectively. System B average gas production ranged from 7.5 to 19.5 L/d (7.1 to 11.9 L gas/L feed) for COD reductions ranging from 11,700 to 28,700 mg/d and COD loadings ranging from 16,100 to 48,500 mg/d.

A pilot-scale biogas collection system was constructed to collect, treat (remove H_2S), store, and utilize the biogas produced by an anaerobic/aerobic crab processing wastewater treatment system treating between 15 and 30 gallons per day (gpd). Biogas

was produced by a 190 gallon upflow anaerobic bed filter and a 190 gallon anaerobic clarifier operated in series. Preliminary results indicated biogas production rates comparable to maximum average gas production rates of the laboratory-scale systems at approximately 10 L gas/L feed. Biogas was stored in a 120 gallon tank at up to 12 pounds per square inch (psi) following removal of hydrogen sulfide. Biogas was then burned in a modified natural gas hot water heater to produce heated water for maintaining the anaerobic reactors at 35°C.

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CHAPTER I. INTRODUCTION

Concern over regulations limiting discharge levels for biochemical oxygen demand (BOD), total suspended solids (TSS), and ammonia (NH_3/NH_4^+-N) has stimulated interest among many small seafood processors in developing economical, efficient, and low maintenance wastewater treatment systems. High rate anaerobic treatment was selected for study due to its ability to reduce high levels of BOD typically found in seafood processing wastewater, while requiring a relatively small reactor size when compared to typical aerobic treatment systems. The decision to use anaerobic treatment also provided an opportunity for energy recovery in the form of methane. For example, a crab processor might use the methane to offset or eliminate current energy requirements for boilers, automated crab cleaning equipment, lighting, heating, etc.

The crab processing wastewater treated in this study was generated by the steaming of live blue crabs (*Callinectes sapidus*). Crab processing begins as live blue crabs are received at a crab processing facility by boat or truck. The crabs are first passed through a reel washer to remove sand, dirt, and other materials from the body of the crab. The crabs exit the reel washer and are immediately collected in large perforated metal baskets. Three baskets, containing approximately 1,200 pounds (lbs) of live crabs, are then stacked in a retort. The crabs are then steamed at 15 pounds per square inch gauge (psig) and 120°C for 10 to 15 minutes. Approximately 50 gallons of crab processing wastewater, with a chemical oxygen demand (COD) from 9,300 to 33,700 milligrams per liter (mg/L), is generated per 1,200 lbs of live crabs (Diz and Boardman,

1994). The typical crab processor performs 6 to 20 cooking cycles per day, which yield 400 to 1,000 gallons of crab cooker wastewater (Boardman *et al.*, 1993).

The generation of energy, while degrading the vast quantities of organic waste material generated in today's society, make anaerobic treatment very promising as not only a means of organic waste stabilization, but also as an alternative energy source. The stabilization of organic materials in an anaerobic environment and the subsequent use of the methane by product is by no means a recent development. Anaerobic treatment dates back as far as 100 years. Cameron of Exeter, England constructed a tank he called a "septic tank" which provided preliminary treatment for approximately 60,000 gallons of wastewater per day. The methane gas produced was used for heating and lighting at the treatment facility (McCarty, 1982e). One hundred years later, anaerobic treatment for the sole purpose of producing methane, is still not economically feasible with existing prices for fossil based fuels (Frank and Smith, 1993b). This includes the operation of "energy farms" dedicated to growing biomass feedstocks such as *Sorghum*, *Pennisetum*, and *Succharum* species for anaerobic methane production (Frank and Smith, 1993a). Biogas production may, however, be economical when it is a by-product of another process, such as waste treatment (Frank and Smith, 1993b). Modern day wastewater treatment plants often collect and utilize the biogas produced by the anaerobic digestion of sludge.

This study focused on collection, analysis, treatment, storage, and utilization of biogas generated by the anaerobic treatment crab cooking waters. Thus, this research was divided into two overlapping phases. Phase I consisted of the collection and characterization of biogas derived from the laboratory-scale, anaerobic treatment of crab

processing wastewater. The primary goal of Phase I was to determine the relative composition of the biogas in terms of percent by volume CH_4, CO_2, and H_2S, as well as the volume of biogas generated. Phase II consisted of constructing a pilot-scale biogas collection, treatment, storage, and utilization system linked to an anaerobic biological treatment system treating crab processing wastewater. The goal of Phase II was to determine if a biogas system could be constructed and operated so as to be economical and practicable for the crab industry.

CHAPTER II. LITERATURE REVIEW

Anaerobic Treatment

Anaerobic treatment is a biological process whereby complex organic compounds are broken down into simple molecular components followed by the subsequent production of methane and carbon dioxide. Anaerobic treatment involves a very complex ecosystem made up of a variety of anaerobic microorganisms. (Figure 1)

The first stage of the anaerobic treatment process involves the hydrolysis of complex organic compounds (i.e. carbohydrates, proteins, lipids) into simple organic compounds (i.e. sugars, amino acids, fatty acids). Fermentative bacteria are responsible for this stage. The fermentative bacteria produce enzymes capable of hydrolyzing complex organic materials and producing simple materials which can be further assimilated by the bacterial cells (Novaes, 1986).

The second stage involves the conversion of these simple materials to hydrogen (H_2), carbon dioxide (CO_2), acetate, and longer chain fatty acids by the anaerobic bacteria called acidogens. In the third stage, the long chain fatty acids are converted into acetate, H_2, and CO_2 by the acetogens, also referred to as H_2-producing or proton (H^+) reducing acetogenic bacteria. Homoacetogenic bacteria, a special group of acetogenic bacteria, convert a portion of the H_2 and CO_2 to acetate (Novaes, 1986).

In the final stage, the substrates produced in the second and third stages are consumed by the methanogenic bacteria. Carbon dioxide is reduced to CH_4 by the CO_2

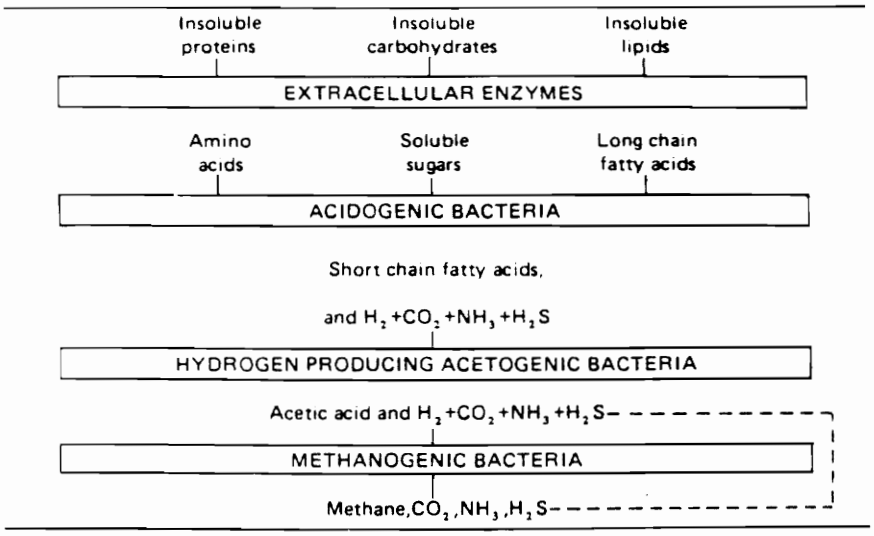

Figure 1. Stages of anaerobic treatment and gas production (Anderson, 1982).

reducing methanogenic bacteria. Acetate is decarboxylated to CH_4 and CO_2 by the acetoclastic methanogenic bacteria.

Methane Production Pathways

CO_2 reducing methanogens. Most methanogens are capable of utilizing H_2 to reduce CO_2 to CH_4 as follows (Thauer *et al.*, 1993):

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad [1]$$

Of the five orders of methanogenic bacteria in the proposed taxonomy, four consist mainly of species that can utilize H_2 and CO_2. The hydrogen and carbon dioxide are generally produced by other anaerobic bacteria such as the acidogens and acetogens, with the hydrogen being quickly consumed by the methanogens. Hydrogen is typically the electron donor for the reduction of CO_2 to CH_4 as shown in reaction [1]. However, formate can also be used as an electron donor for CO_2 reduction. (Boone *et al.*, 1993)

Acetoclastic methanogens. The other main route of methane production is acetate degradation by acetoclastic methanogens. Acetate is cleaved, with the carboxyl group being oxidized to CO_2 and the methyl group being reduced to methane. Acetoclastic methanogenesis can be represented as follows (Karhadkar *et al.*, 1987):

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad [2]$$

Methylotrophic methanogens. Methylotrophic methanogens are a broader group of methanogens, including those that decarboxylate acetate, that produce methane from compounds containing methyl groups. The methyl groups from compounds such as methanol, trimethylamine, and dimethyl sulfide are reduced to methane. Hydrogen is often the electron donor for this reaction. (Keltjens and Vogels, 1993)

Mesophilic vs. Thermophilic Treatment

Anaerobic treatment is typically divided into two temperature regimes: mesophilic and thermophilic. The mesophilic range is generally considered from 85 to 100°F, or approximately 30 to 40°C. The thermophilic range is generally considered from 120 to 135°F, or approximately 50 to 60°C. (McCarty, 1964b) The higher temperatures of the thermophilic range allow for higher loading rates than the mesophilic temperatures and generally result in increased organic stabilization for similar loadings and retention times (Harmon *et al.*, 1993; Chynoweth and Isaacson, 1987). Disadvantages of operating in the thermophilic range include a narrower optimum temperature range, as well as the additional energy required for maintaining high system temperatures (Chynoweth and Isaacson, 1987).

Advantages and Disadvantages of Anaerobic Treatment

Anaerobic treatment offers several advantages over conventional aerobic treatment. Sludge production is significantly reduced due to the lower cell yield inherent under anaerobic conditions (McCarty, 1964a; Parkin and Speece, 1983; Anderson *et al.*, 1977). Higher cell growth in aerobic systems represents a transfer of organic waste material to cellular material without stabilization. However, anaerobic systems transfer a large portion of the waste material to methane gas. This results in 80 to 90 % stabilization rates for anaerobic systems compared to approximately 50 % for aerobic systems (McCarty, 1964a). Lower cell yield also translates into lower nutrient requirements for anaerobic treatment systems (McCarty, 1964a; Parkin and Speece, 1983). Another advantage of anaerobic treatment is the absence of a need for energy for oxygen transfer.

In addition, anaerobic treatment produces energy in the form of methane gas (McCarty, 1964a; Parkin and Speece, 1983). Anaerobic treatment systems are capable of maintaining a viable cell population even after prolonged periods of zero loading, while aerobic systems will typically require reseeding (McCarty, 1964a; Anderson *et al.*,1982).

Two main disadvantages are associated with anaerobic treatment. One disadvantage is the relatively slow growth rate of methanogens. The slow cell growth results in longer start-up times (when seed sludge is not available), susceptibility of systems to upsets caused by shock loadings and toxicants, and fluctuations in temperature. This disadvantage can be overcome in many situations by careful control of bacterial solids retention time (Parkin and Speece, 1983). Another disadvantage of anaerobic treatment is the requirement for maintaining relatively high temperatures necessary for efficient system operation (McCarty, 1964a).

Conversion of waste organic matter to a source of energy (i.e. biogas) is perhaps the most attractive of the advantages associated with anaerobic treatment. Biogas is a mixture of CH_4 and CO_2, with small amounts of H_2S (Stafford, 1980). The CH_4 content ranges from 50 to 80 % by volume (Camargo, 1986; Wise, 1981; Stafford *et al.*, 1980; Rohlich *et al.*, 1977; Auerbach, 1973; Gunnerson and Stuckey, 1986; Orth, 1982). The remainder of the biogas is primarily CO_2. Hydrogen sulfide also may be present in amounts ranging from 0.1 to 5 % or higher (Soto and Lema, 1991; Wheatly, 1980). Biogas will produce a stable blue flame and can be burned in most gas burning appliances (i.e. generators, boilers, hot water heaters, internal combustion engines) with little or no modification (Rohlich *et al.*, 1977; Auerbach, 1973; Fredericks and Boll,

1980). The CH_4 content of the biogas is the sole contributor of calorific value (i.e. heating value).

A mixture of 60 % CH_4 and 40 % CO_2 has a calorific value of approximately 600 British thermal units per cubic foot (Btu/ft^3) at 25°C and atmospheric pressure, as compared to 978 Btu/ft^3 for pure CH_4. Natural gas is comprised of 97-98 % CH_4 with propane and butane as the balance; resulting in a calorific value of approximately 1,000 Btu/ft^3 (Dehart, 1995). Upon combustion, H_2S can form sulfur dioxide and sulfur trioxide, which can then react with moisture to form sulfuric acid resulting in damage to burner assemblies or engine parts. If the gas is used in engines, removal of H_2S has been suggested when concentrations exceed from 0.25 to 0.7 % to prevent corrosion (Rohlich *et al.*, 1977). Some suggest concentrations of not more than 1 % are acceptable (Dohne, 1980). Specific manufacturers generally set limits for H_2S. Removal of H_2S may be advisable regardless of the way the gas is used because of its extremely toxic nature (Dohne, 1980). Removal of CO_2 will increase the heating value per unit volume of the gas. However, economics of CO_2 removal must be considered on a case by case basis. Carbon dioxide removal is generally only required when the gas is intended for use in a public supply system (Dohne, 1980).

Gas Scrubbing

Caustic Scrubbing

Caustic scrubbing can be used to accomplish removal of both CO_2 and H_2S from

biogas. Sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide ($Ca(OH)_2$) are commonly used for this purpose. Carbon dioxide is removed in carbonate forming reactions as follows:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad [3]$$

$$Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3 \quad [4]$$

Extending contact time will also result in the removal of H_2S by the carbonate formed in reaction [3] as follows (Rohlich, 1977):

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3 \quad [5]$$

Caustic Scrubbing can be very costly for small systems not capable of regenerating the spent caustic solutions.

Water Scrubbing

Water scrubbing can be used for the removal of CO_2. This process takes advantage of the solubility of CO_2 in water. This process does have disadvantages. Water requirements are high (i.e. 24.2 gallons of water per 2.45 ft^3 of CO_2 at 20°C and 1 atmosphere). Increased pressures and decreased temperatures will increase the solubility of CO_2 in water, thereby increasing CO_2 removal efficiency. However, increased pressures will also lead to corrosion problems in compressors. In addition, the acid water may pose a disposal problem. (Rohlich, 1977)

Monoethanolamine Process

The monoethanolamine (MEA) process is widely used in the natural gas industry for the removal of both CO_2 and H_2S from natural gas (Stafford *et al.*, 1980). The gas is forced upward through a packed tower against a countercurrent flow of aqueous low

temperature MEA. Carbon dioxide and hydrogen sulfide are absorbed by the MEA solution. The contaminated MEA solution is then passed through a stripping tower where, upon heating, the CO_2 and H_2S are released.

Iron Sponge

The use of "Iron Sponge" is a relatively simple and economical method for the removal of H_2S from biogas (Connelly GPM, 1994). "Iron Sponge" consists of hydrated iron oxide ($Fe_2O_3 \bullet H_2O$), wood fiber, soda ash (Na_2CO_3), and limestone prior to use. The reaction effecting the removal of H_2S from biogas is as follows:

$$Fe_2O_3 \bullet H_2O + 3H_2S \rightarrow Fe_2S_3 + 4H_2O + \text{heat} \qquad [6]$$

The hydrated iron oxide reacts with H_2S under slightly alkaline conditions (pH 8-9) to produce ferric sulfide (Fe_2S_3), water and modest heat. The spent "Iron Sponge" is regenerated as shown in reaction [7].

$$2Fe_2S_3 + 3O_2 + 2H_2O \rightarrow 2\,Fe_2O_3 \bullet H_2O + 6S + \text{heat} \qquad [7]$$

Ferric sulfide, in the presence of oxygen and sufficient moisture, is converted back to iron oxide with the evolution of elemental sulfur and significant heat. The life of the "Iron Sponge" is usually limited to a single regeneration and reuse, as the efficiency of the sponge decreases with increasing amounts of elemental sulfur (Connelly GPM, 1994).

The removal of H_2S under neutral to slightly acidic conditions is undesirable because of the formation of ferrous sulfide (FeS) shown in reaction [8].

$$Fe_2O_3 \bullet H_2O + 3H_2S \rightarrow 2FeS + S + 4H_2O + \text{heat} \qquad [8]$$

The ferrous sulfide can also be converted back to hydrated iron oxide as shown in reaction [9].

$$4FeS + 3O_2 + 2H_2O \rightarrow 2Fe_2O_3 \bullet H_2O + 4S \quad [9]$$

However, at the elevated temperatures generated by the reaction of iron oxide with hydrogen sulfide, ferrous sulfide is converted to iron disulfide (FeS_2), as shown in reaction [10].

$$FeS + S \rightarrow FeS_2 \quad [10]$$

Iron disulfide is inert and not reoxidized to iron oxide. Ferrous sulfide will also create acidic conditions in the presence of water. The addition of a soda ash and water mixture to the "Iron Sponge" during the operation and regeneration of the sponge will help to prevent this condition. Slaked lime ($Ca(OH)_2$) addition is not recommended because of reaction with CO_2, rendering the slaked lime inactive as calcium carbonate. (Stafford, 1942a)

Several factors affect the life of the "Iron Sponge". Various grades of sponge are available; from a CH grade with approximately 9 pounds of dry basis Fe_2O_3 per bushel (1 bushel = approximately 1.25 ft^3 loose or 1 ft^3 installed) to a Cl grade with approximately 15 pounds of Fe_2O_3 per bushel (Taylor, 1956b). The denser grades typically result in a slightly longer time between revivification (Taylor, 1956c). Continuous versus periodic regeneration of the "iron Sponge" has a significant effect on the overall capacity of the sponge remove sulfur from the gas. Continuous regeneration is accomplished by the addition of enough air (three percent) to supply a few tenths of a percent oxygen to the sponge to catalyze the transformation of Fe_2S_3 to Fe_2O_3 with liberation of elemental sulfur. Continuous regeneration of the CH grade sponge can result in as much as 22.5 pounds of sulfur removed per cubic foot of sponge compared to five

pounds of sulfur removed per cubic foot of sponge without continuous regeneration. (Taylor, 1956d)

Membrane Separation

Carbon dioxide and hydrogen sulfide can also be separated from the methane component of biogas using membrane separation processes (Wise, 1981). These processes rely on the different diffusion speeds of CH_4, CO_2, and H_2S through a membrane. Membrane separation often requires gas pressurization of 350 to 400 psi.

Nutrient Limitations

Nutrient limitations can have a wide range of effects on the microbial population in an anaerobic treatment system. Nutrient limitations can slow cellular growth, lower treatment efficiency by limiting substrate utilization, and halt cellular growth completely; all resulting in a decrease or cessation of methane production (Chynoweth and Isaacson, 1987). Nutrient requirements for methanogens include (decreasing order of importance): nitrogen, sulfur, phosphorus, iron, cobalt, nickel, molybdenum, selenium, riboflavin, and vitamin B_{12} (Speece, 1985).

The nutrients of most importance are nitrogen, sulfur, and phosphorus. Ammonia appears to be a source of nitrogen for all methanogens. Most methanogens use sulfide as a sulfur source, while some can utilize cysteine. (Takashima and Speece, 1990) Understanding the nutrient limitations of the methanogens will not necessarily result in a "healthy" anaerobic treatment system. A nutrient that is limited for other anaerobic

microorganisms in the system, such as the acidogens and acetogens, will directly affect the methanogens, resulting in system upset (Chynoweth and Isaacson).

The relative amounts of carbohydrates, proteins, and fatty acids in the waste being treated will ultimately increase or decrease cell production, hence have an effect on possible nutrient limitation. The synthesis of new cells from a high carbohydrate waste is much greater than cell synthesis from a high protein or fatty acid waste. This relationship is shown in Figure 2. The higher cell synthesis from the high carbohydrate waste will increase the chances of a nutrient limitation as greater numbers of cells compete for existing nutrients.

Ammonia Inhibition

Significant levels of total ammonia are typically present when wastes containing a high proportion of proteinaceous material are anaerobically degraded. The amount of protein in the waste being treated, in addition to the pH in the anaerobic reactor, contribute to the overall effect that ammonia will have on the anaerobic system. Ammonia will be present in the anaerobic environment as either ammonium ion (NH_4^+) or as dissolved ammonia gas (NH_3). The relative concentration of each depends on the pH. Ammonium ion and ammonia gas will be in equilibrium based on the following equations:

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad [11]$$

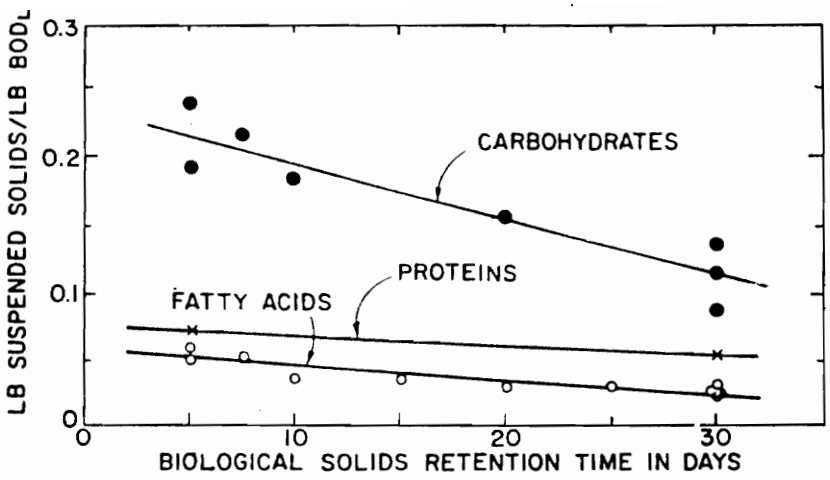

Figure 2. Biological solids production resulting from methane fermentation (McCarty, 1964a).

$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]} \quad [12]$$

For a K_a = 1.13E-9 at 35°C, the free ammonia (NH_3) concentration will be approximately 0.1, 1, and 11 % of the total ammonia (NH_3 + NH_4^+) concentration at a pH equal to 6, 7, and 8, respectively (Anderson *et al.*, 1982). According to McCarty (1964c), "The ammonia gas is inhibitory at a much lower concentration than the ammonium ion." The pH range from 6.6 to 7.6, considered acceptable for stable operation of anaerobic systems, favors the less toxic ammonium ion (McCarty, 1964b).

Total ammonia concentrations of from 1,500 to 3,000 mg/L at pH values above 7.4 to 7.6 may result in NH_3 concentrations that can become inhibitory. At total ammonia concentrations above 3,000 mg/L, inhibition can occur regardless of pH, because of NH_4^+ toxicity (McCarty, 1964c). Sathananthan (1981) reported no inhibition at pH 7 and total ammonia concentration of 7,000 mg/L, indicating possible acclimation to the ammonium ion. Sathananthan (1981) also reported inhibition at pH 7.5 and total nitrogen concentrations of between 2,000 and 3,000 mg/L and inhibition at free ammonia concentrations of greater than 80 mg/L regardless of pH. McCarty and McKinney (1961) reported failure of acetate utilizing methanogens at free ammonia concentrations exceeding approximately 150 mg/L as N. Parkin *et al.* (1983) reported acclimation of a submerged anaerobic filter to a maximum level of 6,000 mg/L NH_4^+-N at pH levels not exceeding 7.5.

Velsen (1979) reported acclimation of a digested sewage sludge to an ammonia nitrogen concentration of 5,000 mg/L following a 50 day lag period. In addition, results

with the same digested sewage sludge indicated a threshold level between 1,210 mg/L and 2,360 mg/L, supporting the results of Melbinger and Donnellon (1971) who reported ammonia nitrogen inhibition at concentrations above 1,700 to 1,800 mg/L when the ammonia nitrogen concentration increased faster than the acclimation of the methanogens. Soto *et al.* (1991) reported acclimation of a mesophilic sludge to fish canning wastewaters with ammonia concentrations reaching 4,000 mg/L, only after 38 days of adaptation.

Sulfide Inhibition

The presence of sulfurous compounds, such as sulfate and sulfite, in wastewaters can have an inhibitory effect on the anaerobic treatment process. In addition to sulfate and sulfite, the presence of sulfur containing organic compounds can contribute to the overall sulfur levels when these compounds are anaerobically degraded. Sulfur reducing bacteria utilize sulfate (SO_4^{2-}) as an electron acceptor in the oxidation of hydrogen and acetate; the same substrates utilized by the methanogens. The reduction of sulfate to hydrogen sulfide yields more energy than that derived by the methanogens in the reduction of carbon dioxide and acetate decarboxylation, and is therefore favored [equations 13 - 16].

Methanogenesis:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \; ; \; \Delta G = -135 \text{ kJ} \qquad [13]$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \; ; \; \Delta G = -28.5 \text{ kJ} \qquad [14]$$

Sulfate Reduction:

$$SO_4^{2-} + 4H_2 \rightarrow H_2S + 2H_2O + 2OH^- \; ; \; \Delta G = -154 \text{ kJ} \quad [15]$$

$$SO_4^{2-} + CH_3COOH \rightarrow H_2S + 2HCO_3^- \; ; \; \Delta G = -43 \text{ kJ} \quad [16]$$

Hence, theoretically sulfate reducing bacteria will outcompete the methanogens (Karhadkar *et al.*, 1987; Anderson *et al.*, 1982; Sarner *et al.*, 1988; Velsen, 1979).

Parkin *et al.* (1983) reported inhibition of unacclimated batch systems by 50 mg/L S^{2-}. McCarty (1964c) stated that up to 200 mg/L soluble sulfides can be tolerated in continuous systems with acclimation, while concentrations exceeding 200 mg/L are toxic. Rinzema and Lettinga (1988) reported stable granular sludge anaerobic degradation of propionate in the presence of excess sulfate at total sulfide concentrations of 700 mg/L, as long as H_2S was kept below 100 mg/L S. Soto *et al.* (1991) investigated H_2S toxicity in the anaerobic treatment of fish canning wastewater. They reported an inhibition threshold of H_2S at 40 mg/L S (1.5 % H_2S in the gas phase) and an increase to 50 % inhibition at 133 mg/L S (5 % H_2S in the gas phase) at pH 7.0 to 7.2.

Therefore, there is evidence supporting two mechanisms of inhibition of methanogenesis due to hydrogen sulfide formation: indirect inhibition of methanogenesis due to competition between the methanogens and sulfur reducing bacteria for the same substrates, and direct inhibition of methanogenesis due to the action of soluble sulfides on cellular functions.

Karhadkar *et al.* (1987) attempted to determine if inhibition is caused by competition for substrates and/or by sulfide inhibition of cellular functions. They reported

greater total methane production in batches with 40 and 80 mg/L sulfide as S added compared to a control (< 5 mg/L sulfide as S), indicating that sulfide is growth limiting below a certain concentration. Increasing inhibition was observed in batches with 160 mg/L (as S added) and greater sulfide concentrations. Batches with sulfate added showed no inhibition at up to 5,000 mg/L sulfate, reportingly ruling out the possibility of competition for substrates. Karhadkar also reported 20 mM molybdate caused inhibition to both sulfate reduction and methanogenesis.

Soluble sulfides will exist in their various forms in solution based on pH as expressed in reactions [17] and [18] and in Figure 3.

$$H_2S \rightleftharpoons HS^- + H^+ \qquad [17]$$

$$HS^- \rightleftharpoons S^{2-} + H^+ \qquad [18]$$

For the typical range of pH involved in anaerobic treatment, reaction [18] is displaced to the left and S^{2-} is negligible. Therefore, reaction [17] is of greater importance, with the relative amounts of HS^- and H_2S being dependent on pH.

Soluble H_2S will be in equilibrium with H_2S in the gas phase according to Henry's law as shown in reaction [19].

$$\begin{array}{l} H_2S_{gas} \\ \uparrow \\ H_2S_{aq} \rightleftharpoons HS^- + H^+ \end{array} \qquad [19]$$

Increased gas production will shift the equilibrium to the left, as the partial pressure of H_2S in the gas phase drops, thus, increasing the transfer of H_2S from the liquid to gas phase. This equilibrium relationship is the basis for a H_2S toxicity reduction procedure in which gas is removed from the reactor, washed to remove H_2S, and returned to the

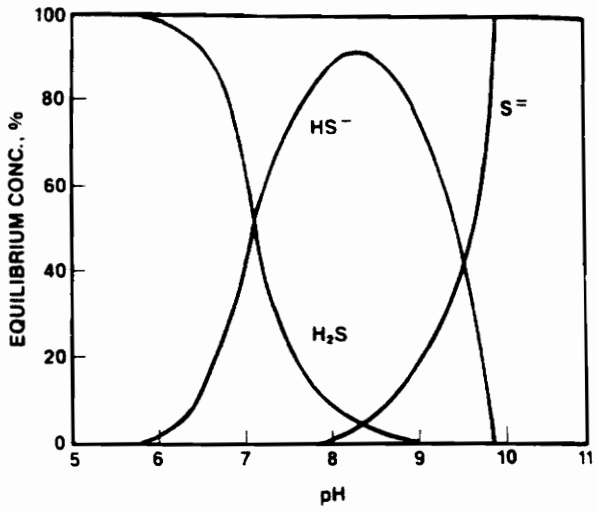

Figure 3. Sulfide species as a function of pH (Sarner *et al.*, 1988).

reactor (Sarner *et al.*, 1988). This method promotes the removal of the reportedly toxic unionized H_2S from the liquid phase , thereby reducing sulfide inhibition (Rinzema and Lettinga, 1988).

Gas Production

The volume of CH_4 produced by anaerobic treatment of organic waste is directly related to the degree of waste stabilization achieved. As stated by McCarty (1964a) "...the ultimate oxygen demand of the waste being degraded is equal to the ultimate oxygen demand of the methane gas produced. The ultimate oxygen demand of methane is given by reaction [20].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad [20]$$

Two moles of oxygen is required to completely oxidize one mole of methane to carbon dioxide and water. As stated above, the converse of this is also true. In other words, if the amount of stabilization achieved, in terms of COD reduction of the waste , is known, an estimate of the methane production can be made. Theoretically, one gram of COD reduced will produce 350 ml of CH_4 at standard temperature and pressure (STP) (STP: 0°C, 1 atmosphere) based on reaction [20]. This is equivalent to 5.62 ft^3 of methane per pound of COD stabilized. In the same manner, if the volume of methane produced is measured, the theoretical degree of waste stabilization can be calculated.

Gas Storage

Biogas is typically stored in one of three pressure ranges: low pressure storage (0 to 60 inches of water column) (Stafford *et al.*, 1980; Dohne, 1980; Hobson *et al.*, 1981; Ru-Chen, 1982), medium pressure storage (100 to 350 psi) (Stafford *et al.*, 1980; Dohne, 1980; Hobson *et al.*, 1981), and high pressure storage (2,000 psi and up) (Dohne, 1980; Hobson *et al.*, 1981).

Low Pressure Gas Storage

Low pressure gas storage includes the following types: fixed dome, floating cover, and membrane type storage devices (Gunnerson and Stuckey, 1986; Ru-Chen 1982).

Fixed dome. The fixed dome reactor allows the gas pressure to increase within the reactor headspace, thus displacing a portion of the reactor contents into an elevated effluent chamber. An example of the fixed dome type reactor is shown in Figure 4a. The effluent chamber is typically designed to allow the liquid level to reach a maximum of 1.0 to 1.5 meters (m) (40 to 60 inches (in.)) above the liquid level in the reactor, thereby allowing for a gas pressure from 1.0 to 1.5 m (40 to 60 in.) of water column pressure. (Ru-Chen, 1982)

Floating cover. The floating cover reactor consists of two major parts. The reactor walls and bottom are typically constructed of brick or concrete. The reactor cover is made from materials such as steel, polyethylene, and fiberglass. As gas is produced, the cover slides upward on a central guide or on vertical channels constructed along the reactor walls. An example of the floating cover reactor is shown in Figure 4b. The gas

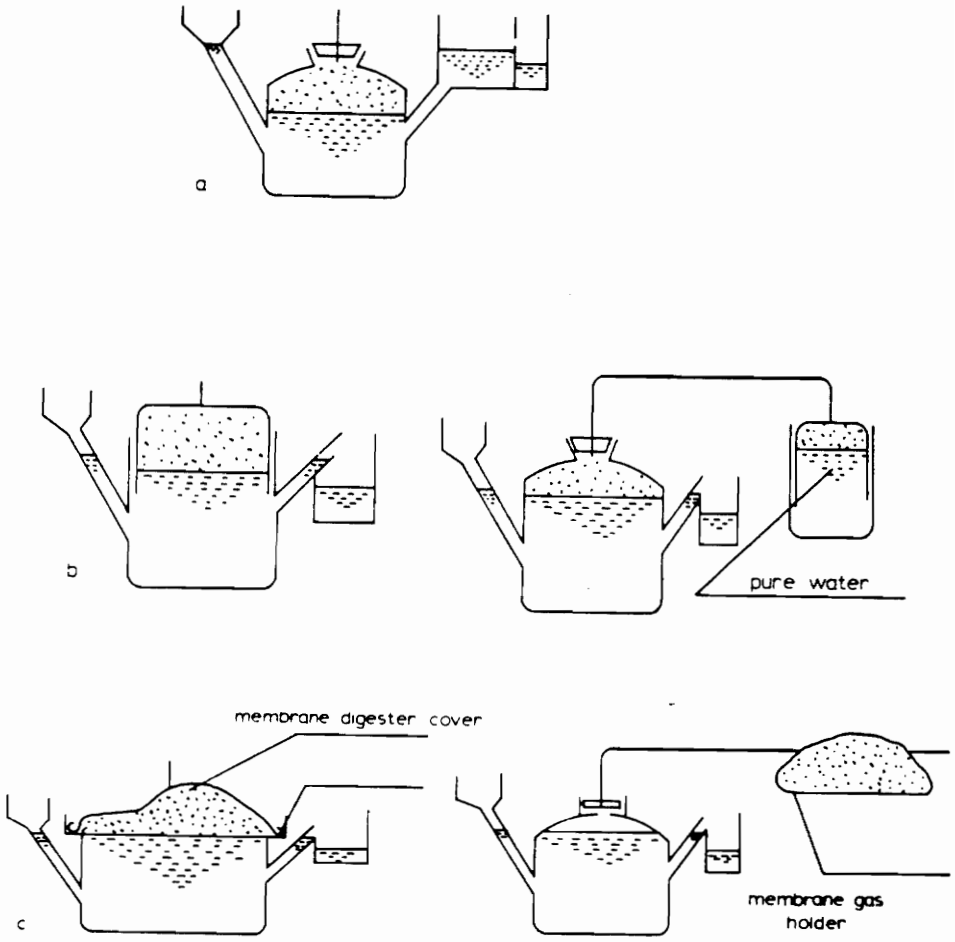

Figure 4. Low pressure gas storage in anaerobic digestion (Ru-Chen, 1982).
a. Fixed dome reactor
b. Floating cover reactor
c. Membrane gas holder reactor

pressure is determined by the force required to lift the cover; namely, the weight of the cover itself. However, additional control of gas pressure can be attained by using a weight and pulley system to increase or decrease the weight of the cover (Stafford *et al.*, 1980). The floating cover type reactor typically stores gas at pressures of 2 to 35 centimeters (cm) (0.8 to 14 in.) of water column pressure (Ru-Chen, 1982). A slight variation of the floating cover is shown in Figure 4b. The reactor is of the fixed dome type. The gas is transported to a separate gas holder that is based on the floating cover type reactor where water takes the place of the reactor contents.

Membrane storage devices. There are two basic types of gas membrane storage devices (Gunnerson and Stuckey, 1986; Ru-Chen, 1982). One employs a flexible and impermeable membrane cover that is attached directly to the top of the reactor as shown in Figure 4c. The other type consists of a storage balloon connected by a gas line to the headspace of a fixed dome type reactor. The membrane is allowed to inflate as gas is produced. Once full, the pressure within the membrane is typically allowed to increase to only 2 to 3 cm (0.8 to 1.2 in.) of water column pressure. The ultimate pressure is controlled using gas pressure relief valves (Ru-Chen, 1982). Operating pressures approaching 40 cm (16 in.) of water column have been used with a Norprene coated nylon fabric bag in Taiwan, China (Gunnerson and Stuckey, 1986).

Medium Pressure Gas Storage

Medium pressure gas storage involves compressing biogas to pressures from 100 to 350 psi in commercially available tanks. Compression of biogas can result in corrosion of compressors due to H_2S, NH_3, and CO_2 as these biogas components react with moisture

in the biogas. Corrosion problems are aggravated with increasing pressures. Therefore, gas scrubbing is recommended prior to compression of the gas to medium range pressures (Hobson *et al.*, 1981). When compressing the gas, the energy requirements of the compression must be considered against the energy value obtainable from the gas itself. Another disadvantage of compression is related to the pressure of gas required by gas burning devices. The pressure of the stored gas must generally be reduced using a pressure reducer/regulator device prior to the point of use. An advantage of compression lies in the ability to store large volumes of gases in relatively small tanks consuming relatively little space.

High Pressure Gas Storage

High pressure gas storage (2,000 psi and up) is almost entirely reserved for very large biogas production facilities and specialized uses (Hobson *et al.*, 1981). The biogas must be scrubbed and dried to produce relatively pure methane gas in order to avoid corrosion problems. Again, as with medium pressure compression, costs of specialized equipment (heavy cylinders, appropriate gas safety devices, pressure gauges, pressure reducing devices, etc.) and handling related costs, along with energy requirements, must all be considered.

High pressure gas storage is most frequently used for special applications which require large volumes of gas in small spaces. An example of this is the use of purified biogas for fueling methane powered vehicles (Lapp *et al.*, 1974). Cylinders with gas compressed to in excess of 2,500 psi are stored on the vehicle and used to power the engine which has been designed or adapted to burn methane gas. The high pressures are

necessary to provide an adequate supply of methane (in a confined space) which will enable reasonable travelling distances between refuelings. High pressure gas cylinders are also sold to specialty gas suppliers who sell and distribute the gas cylinders to laboratories (Hobson *et al.*, 1981).

Liquefaction of the methane component of biogas is not practical for small scale systems. Liquefaction of methane requires a temperature of -82.5°C (181°F) and a pressure of 46 atmospheres (676 psi).

Biogas Utilization

Biogas Handling and Safety Devices

Biogas utilization systems require various devices for safe and efficient operation. Notwithstanding equipment associated with the type of gas storage (low, medium, high pressure) and the extent of gas treatment (removal of H_2S and/or CO_2), all biogas utilization systems should include the following devices where appropriate:

- Condensate trap
- Flame trap (Flame arrester)
- Pressure relief valve
- Pressure regulator
- Check valve

This list is not meant to be all inclusive. Individual systems may require additional gas handling equipment for specific applications. This list does include those devices highly recommended for all biogas utilization systems (Rohlich, 1980; Fredericks and Boll, 1980; Price and Cheremisinoff, 1981; Fry, 1974).

Condensate traps are typically installed at low points in the gas collection and utilization system. Water condenses in gas lines as the biogas cools. Condensate traps allow for the removal of this water enabling the gas to flow freely through the system and preventing ice from forming in colder environments.

Flame arresters are extremely important safety devices. The flame arrester prevents flames from travelling back through gas lines from a point of gas ignition to a point of gas storage. Flame arresters should be installed prior to any point where gas is in contact with and open flame or the possibility of gas ignition exists.

Pressure relief valves are necessary to maintain safe operating pressures within the system. The possible build up of unsafe pressures due to blockages in the gas lines caused by particulate matter, condensate, and/or ice, can be prevented by the strategic placement of pressure relief valves.

Check valves prevent gas from flowing backwards through the gas collection and utilization system to the anaerobic reactor(s). Check valves are particularly important when the gas is pressurized. The check valve acts as a safety device which helps to maintain pressure differences in the gas system should a pump or compressor fail.

Pressure regulators, or pressure reducers, are typically used at the point of gas usage. The regulator maintains a constant delivery pressure required by gas burning devices. This allows for the direct use of gas stored at pressures exceeding the pressure required by the gas burning device.

Additional Safety Precautions

In addition to the safety and control devices described above, additional safety

precautions should be taken prior to and during the operation of a biogas collection and utilization system. At the initial start-up of the anaerobic reactor, the reactor headspace, gas lines, and gas storage equipment will contain air. Methane is explosive when mixed with air in proportions of 5 to 15 % by volume. The range of the explosive limits narrows with increasing amounts of inert gas, such as carbon dioxide and nitrogen as shown in Figure 5 (Zabedakis, 1965). The range increases with increasing pressure and temperature. For this reason, it is recommended that the system be purged of air (Rohlich, 1977; Fry, 1974). This can be accomplished in a variety of ways. The air can be purged from the system by allowing the biogas being generated to displace the air. A sample of gas can then be taken and analyzed to determine if the gas is of sufficient quality to burn. The system can also be flushed with an inert gas (i.e. N_2).

A positive pressure should be maintained in all gas lines to prevent air from infiltrating the system, resulting in an explosive mixture of methane in air (Fry, 1974). The entire system should be checked for leaks prior to operation. This can be accomplished by pressurizing the system with an inert gas such as nitrogen. Soapy water is then applied to areas that may leak. A vigorous bubbling action is evidence of a leak (Auerbach, 1973).

Adequate ventilation around all gas lines and equipment is necessary to prevent the accumulation of gas in the event a leak should occur (Rohlich, 1977; Fry, 1974). Ventilation should be provided at both floor and ceiling level to allow for the ventilation of heavier-than-air and lighter-than-air gases, respectively (Fry, 1974). Gas burning equipment should be located separately from the anaerobic reactor and gas collection

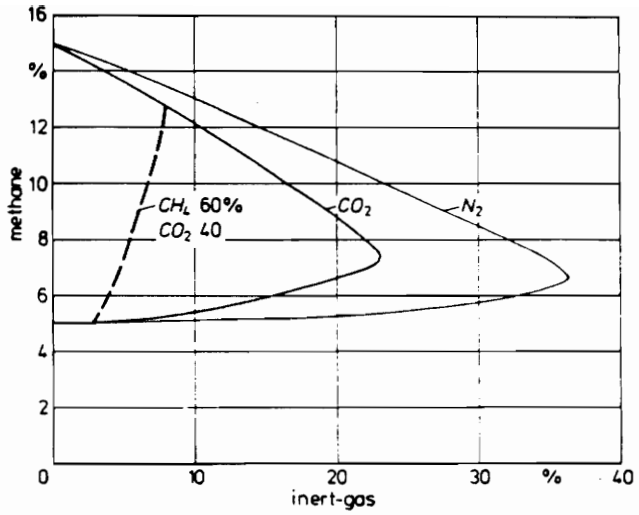

Figure 5. Effect of inert gases on the flammability range of methane/air mixture (Zabedakis, 1965).

equipment to minimize the possibility of a gas build-up near an open flame or other source of ignition (Fredericks and Boll, 1980).

Biogas Utilization Systems

Typical collection and utilization flow diagrams are shown in Figures 6 through 9. These diagrams show the use of the gas handling and control devices discussed above, as well as other gas handling devices found in biogas utilization systems. The system shown in Figure 7 consists of a 270 m^3, glass-fiber, reinforced polyester reactor with a floating gas cover. The system is fed fresh manure from 1700 pigs. The floating cover holds from 50 to 100 m^3 gas at a pressure of 0.015 bar. Gas production is approximately 250 m^3/d. Gas is used to power two 15 kilowatt (kW) generators. The total investment for the system was $84,000 (1979), with an estimated running cost of $2,000 per year (1979). The generators produced 135,000 kilowatt-hours per year (kWh/yr) of electricity, of which 100,000 kWh/yr was used on-site, while 35,000 kWh/yr was sold to a public grid for a total value of $6,300 (1979).

The system shown in Figure 8 consists of two 200 m^3 concrete block reactors with flexible PVC gas covers. The system is fed manure from 150 cows. Each PVC cover holds 120 m^3 gas. Gas production is approximately 300 m^3/d. Electricity is produced from the gas using a modified 40 kW diesel engine and an A/C generator. The total cost of the system was $96,000 (1979) with an estimated running cost of $2,000 per year (1979). The total value of the electricity used and sold (160,000 kWh/yr) was $7,300 per year (1979).

The system shown in Figure 9 consists of two 180 m^3 precast concrete reactors

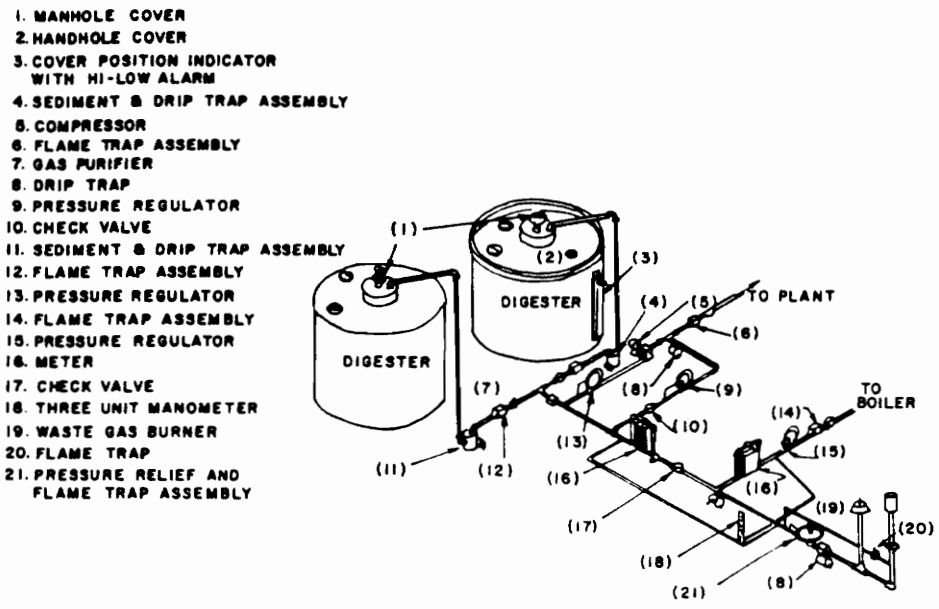

Figure 6. Typical flow and installation diagram (Price and Cheremisinoff, 1981).

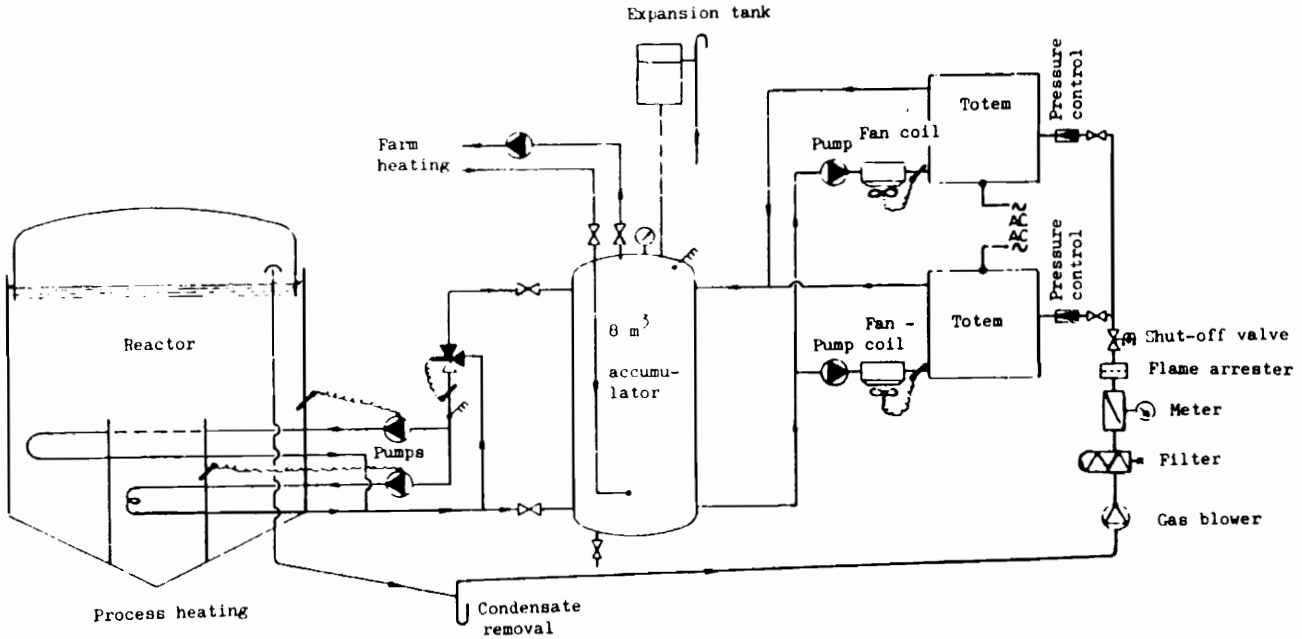

Figure 7. Biogas energy conversion (Gron, 1980).

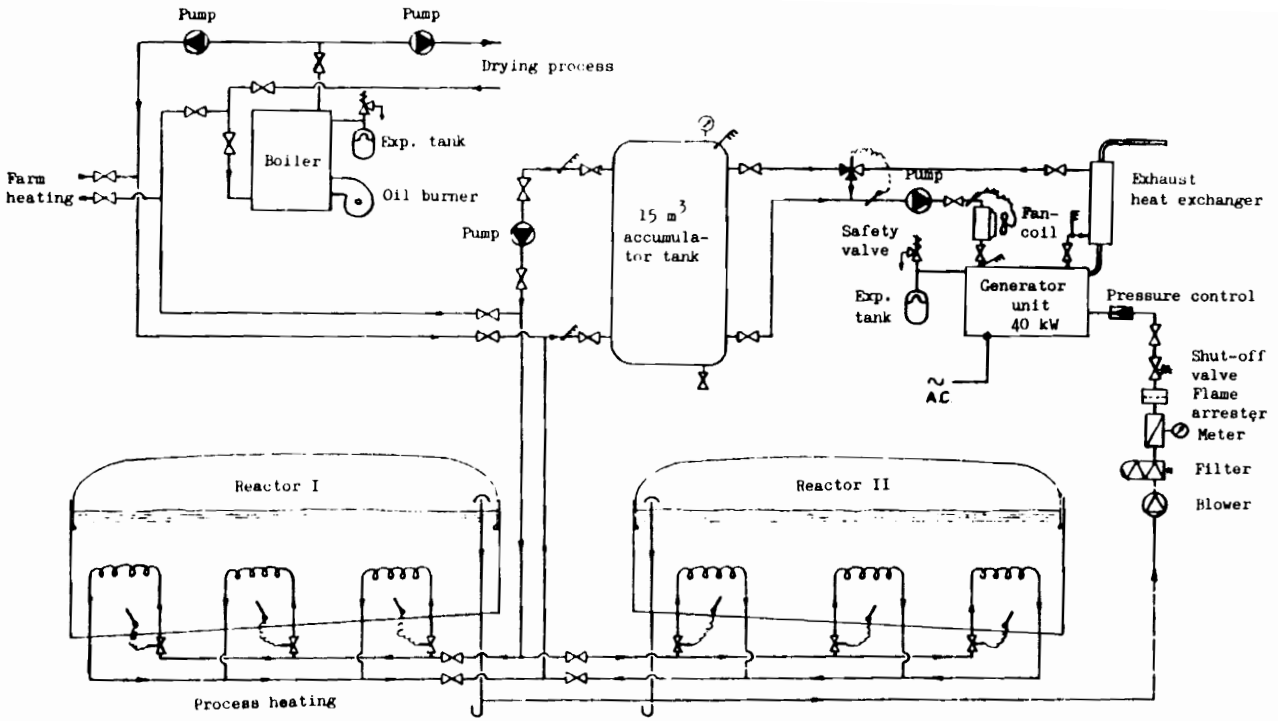

Figure 8. Biogas energy conversion (Gron, 1980).

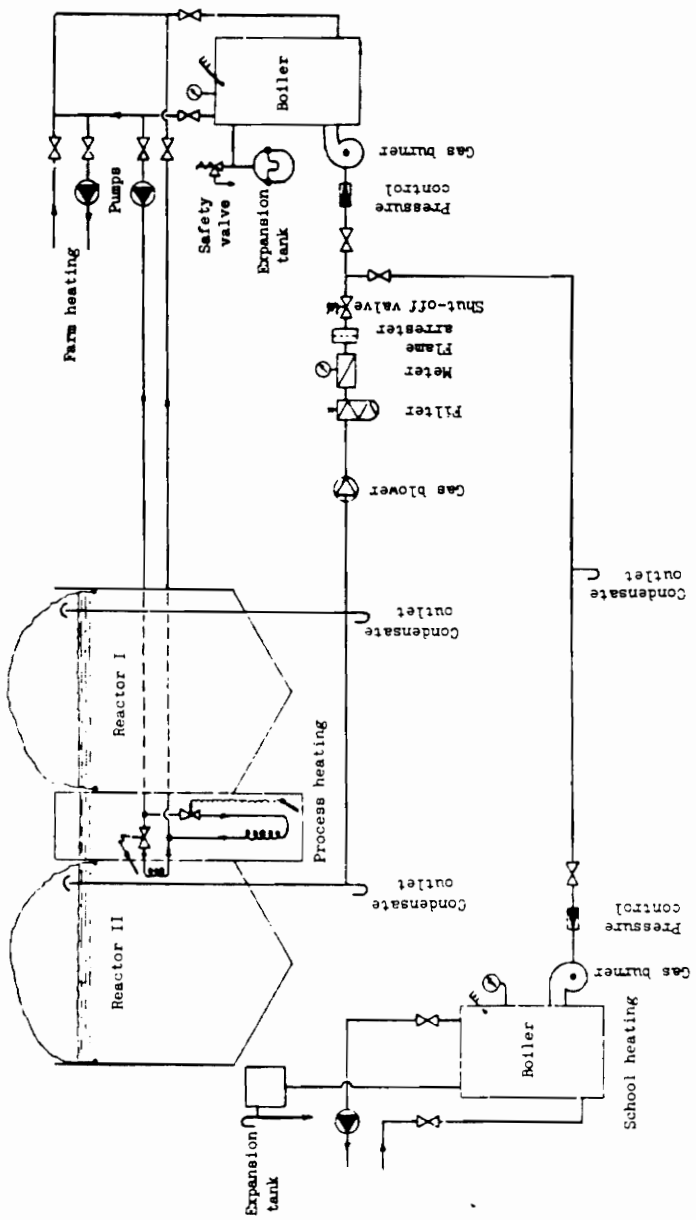

Figure 9. Biogas energy conversion (Gron, 1980).

with flexible PVC gas covers each holding a maximum of 80 m^3. The system is fed fresh manure from 96 cows and 600 pigs. Gas production is approximately 350 m^3/d. Two gas fired boilers are powered by biogas. The total cost of the system was $101,000 (1979) with an estimated yearly operating cost of $2,000 (1979). A total of $15,000 per year was saved by heat generation using biogas instead of oil.

Biogas Combustion

Commercial gas burning devices designed to burn natural gas, propane, etc., normally require minor modifications to combust biogas. Two properties of the biogas make modifications necessary: lower heating value and lower flame velocity than natural gas and propane. Both of these properties are due to the presence of the inert gas, CO_2. Higher concentrations of CO_2 result in lower heating values and flame velocities.

The problems associated with both of these properties can be overcome by increasing the volume of biogas burned per unit time (Fredericks and Boll, 1980; Jiang *et al.*, 1987; Walsh *et al.*, 1988; Orth, 1982) and restricting air intake (Jiang *et al.*, 1987; Walsh *et al.*, 1988). Increasing the volume of biogas available for burning per unit time is accomplished by enlarging the gas orifice or by increasing the biogas delivery pressure. Equations [21] (Jiang *et al.*, 1987) and [22] (Orth, 1982) can be used to calculate required orifice diameter modifications when biogas delivery pressure is unchanged.

$$(d_1/d_2) = [(S_1/S_2)^{0.25}][(H_2/H_1)^{0.5}] \quad [21]$$

d = gas orifice diameter (cm)
S = specific gravity of gas
H = energy value of gas (kJ/m^3)
subscript 1 = biogas
subscript 2 = other gases

$$D_2 = [D_1][W_{01}/W_{02}] \quad [22]$$

D_1 = original orifice diameter
D_2 = modified orifice diameter
W_{01} = Wobbe-Index for original gas
W_{02} = Wobbe-Index for biogas

Equation [22] relies on the Wobbe-Index of the gases involved. The Wobbe-Index is defined as follows:

$$\text{Wobbe-Index} = H/(G)^{0.5} \quad [23]$$

H = heating value of gas
G = specific gravity of gas

The Wobbe-Index ranges from 41.9 to 47.7 MJ/m^3 and 19.8 to 27.2 MJ/m^3 for natural gas and biogas (55-70 % CH_4), respectively. The Wobbe-Index can be used when blending biogas and natural gas or biogas and propane. The objective is to create a fuel mix with a similar Wobbe-Index to that of the original gas used for orifice design (Walsh *et al.*, 1988). This allows for the use of natural gas and propane as back-up fuels.

Alternatively, the gas delivery pressure can be increased, while maintaining the same orifice diameter as shown in equations [24] and [25] (Jiang *et al.*,1987; Orth, 1982).

$$(p_1/p_2) = [(S_1/S_2)][(H_2/H_1)^2] \quad [24]$$

p = gas pressure (mm H_2O)
S = specific gravity of gas
H = energy value of gas (kJ/m^3)
subscript 1 = biogas
subscript 2 = other gases

$$P_2 = [P_1][(W_{01}/W_{02})^2] \quad [25]$$

P_1 = original gas pressure
P_2 = biogas pressure
W_{01} = Wobbe-Index for original gas
W_{02} = Wobbe-Index for biogas

Equation [24] is used to calculate the required gas delivery pressure required to burn biogas in the existing gas orifice. The modification is based on the specific gravities and energy values of the respective gases. Equation [25] is also used to calculate the required gas delivery pressure necessary to burn biogas in the existing gas orifice. The modification, as in equation [23], relies on the Wobbe-Indices of the respective gases.

Table 1 lists orifice diameter multipliers for calculating orifice enlargements when converting from natural gas or propane to biogas. The existing orifice diameter is multiplied by the correct orifice multiplier for the corresponding biogas methane content.

In addition to modification of the main gas orifice, enlargement of the pilot gas orifice will improve pilot flame stability. Some installations have experienced difficulty in maintaining a stable pilot flame. Based on this problem, a separate propane fired pilot may be more effective than a biogas fired pilot. (Walsh *et al.*, 1988)

Table 1. Orifice diameter multipliers for gas appliances (Walsh, 1988).

Percent Methane in Biogas	Orifice Diameter Multipliers	
	Natural Gas (1,050 Btu/ft^3)	Propane (2,500 Btu/ft^3)
70%	1.32	1.63
65%	1.39	1.72
60%	1.46	1.81
55%	1.54	1.92
50%	1.64	2.04

CHAPTER III. METHODS AND MATERIALS

This chapter will focus on the methods and materials used for data collection from laboratory and pilot-scale upflow anaerobic reactors designed for the treatment of crab processing wastewater. Particular attention will be given to a description of the pilot-scale biogas collection, storage, treatment, and utilization system.

Laboratory-Scale Systems

Biogas from two laboratory-scale treatment systems, constructed and operated by a fellow graduate research assistant, was collected, measured, and analyzed. For a complete description of each system, consult "Anaerobic/Aerobic Pretreatment of Crab Cooker Wastewater" (Diz and Boardman, 1994). Each system consisted of two upflow, 4 L anaerobic reactors and an 8 L aeration tank. (Figures 10 and 11) A layer of 240, 0.5 in. foam cubes was added to the first anaerobic reactor of System A to serve as a filter to retain biomass. Both anaerobic reactors of System B were filled with 180 foam pieces (1 x 1 x 0.5 in.) each. Both systems were inoculated with the same concentration of anaerobic sludge on day 0. During the research period, average wastewater flow through each system varied from 0.96 to 2.32 L/d and 0.91 and 2.40 L/d for systems A and B, respectively. Characteristics of the retort waters anaerobically treated in the laboratory-scale systems during this study are provided in Table 2.

Systems A and B were both monitored for a total of 280 days. The first 132 days

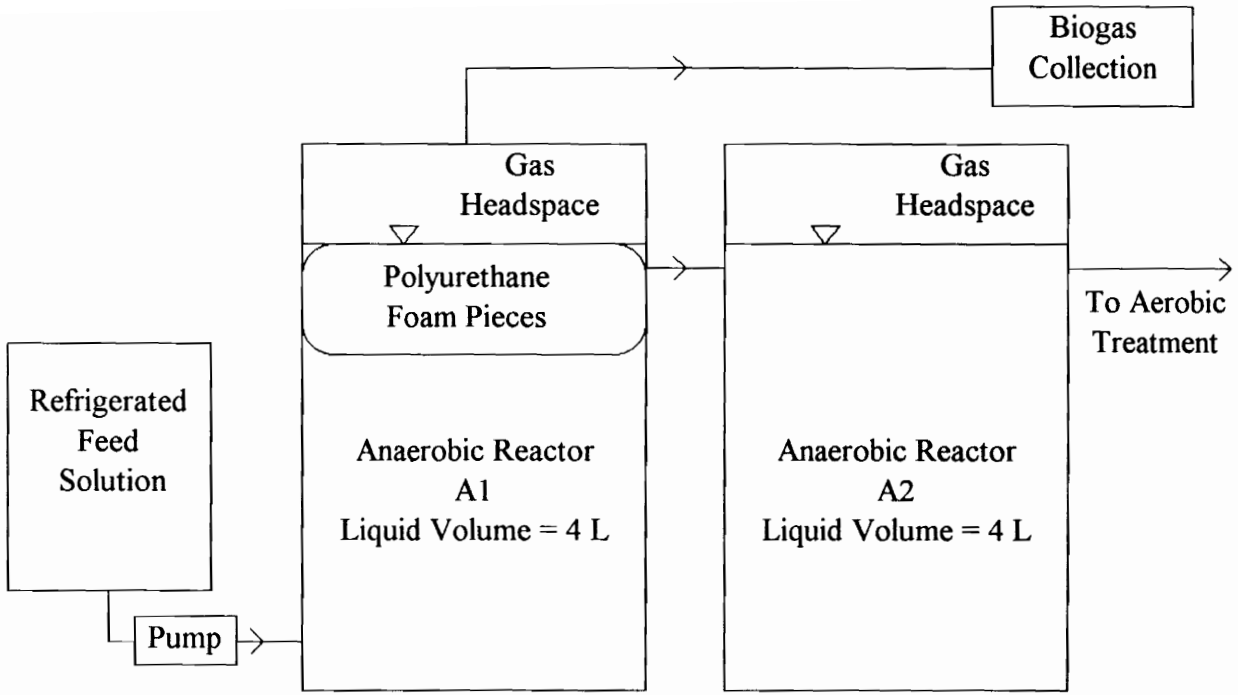

Figure 10. Schematic of System A: Anaerobic/Aerobic treatment system containing 240 0.5 in foam cubes.

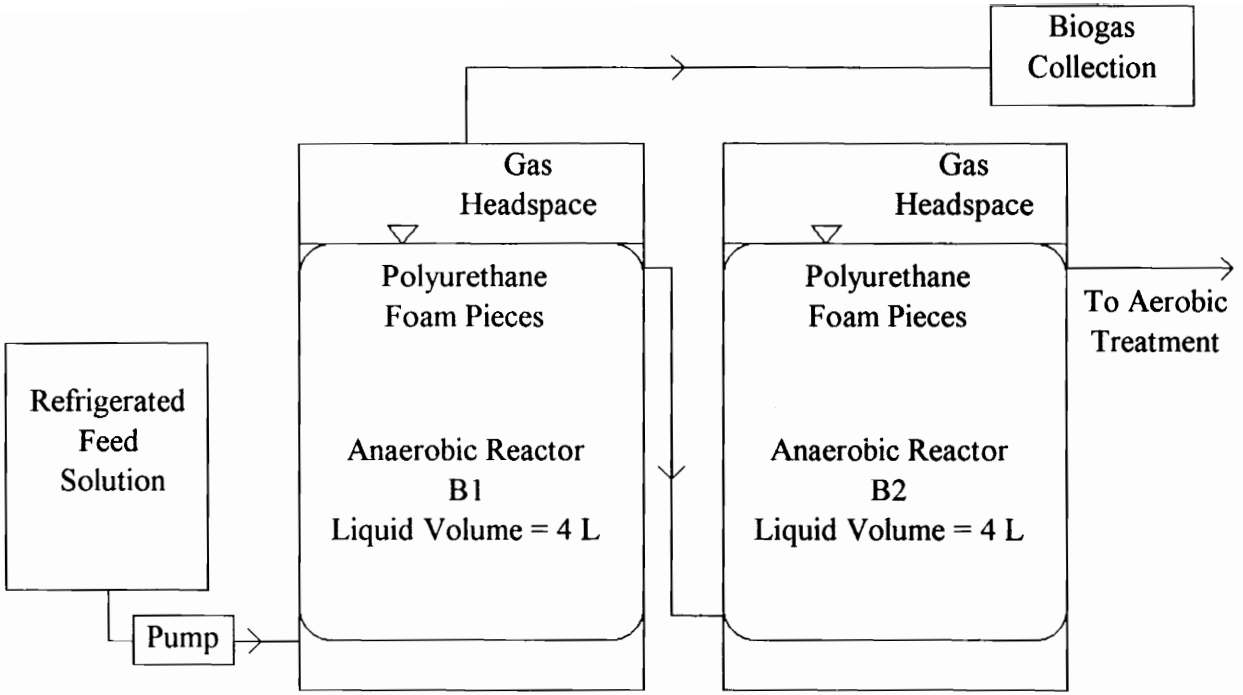

Figure 11. Schematic of System B: Anaerobic/Aerobic treatment system containing 360 foam pieces (1 x 1 x 0.5 in.).

Table 2. Characteristics of Crab Cooker Wastewater (Diz, 1995).

Parameter	Unit	Mean	Min.-Max.
COD[1]	mg/L	18,900	9,300-33,700
BOD_5[1]	mg/L	14,100	12,200-15,500
TSS	mg/L	1,430	530-4,000
VSS	mg/L	1,150	250-2,200
pH	std. unit	7.1	6.8-7.4
NH_3/NH_4-N	mg/L-N	1060	470-1,770
VFA	mg/L-HAc	6,370	3,400-8,900
Alkalinity	mg/L-$CaCO_3$	780	60-2,000
Metals:			
Sodium	mg/L	1,770	890-2,570
Potassium	mg/L	600	340-870
Magnesium	mg/L	230	140-380
Calcium	mg/L	330	200-530
Iron	mg/L	5.6	2.5-8.9
Nickel	µg/L	95	26-150
Cobalt	µg/L	12	1-24
Molybdenum	µg/L	4	3-7
Anions:			
Chloride	mg/L	8,300	3,000-20,000
Nitrite	mg/L-N	12	nd[2]-30
Nitrate	mg/L-N	4	nd-19
Phosphate	mg/L-P	70	14-160
Sulfate	mg/L-S	250	30-460

(1) COD and BOD_5 values were not necessarily obtained for every sample. Therefore, comparison of minimum, maximum, and mean values for these two parameters is not appropriate.
(2) nd = not detected

was designated as the acclimation period during which waste fed to each system was diluted. The degree of dilution was progressively decreased at various times during the 132 day acclimation period. Full strength waste was fed beginning on day 133 and continued until the end of the 148 day study period. Consult "Anaerobic/Aerobic Pretreatment of Crab Cooker Wastewater" for a detailed description of the operation of systems A and B (Diz and Boardman, 1994). The 148 day study period was divided into five "pseudo-steady state" periods based on chemical oxygen demand (COD) loadings.

Gas Collection

Flexible Tygon tubing, initially connected to the top of both anaerobic reactors in each system, connected the reactor headspace to the point of gas collection. During the study period, biogas was collected only from the first anaerobic reactor of each system. Biogas generated by the anaerobic reactors of systems A and B was collected daily in separate Tedlar gas sample valves, each fitted with a septum and polypropylene valve.

The type of gas collection bag used was chosen based on minimizing the reactivity of the compounds of interest with the bag and valve materials, as well as facilitating gas collection and analysis (Parmar, 1991). Twelve and 40 L size bags were used based on the amount of gas being produced by each system during a particular period. The polypropylene valve allowed for direct connection of tubing from reactor headspace to gas bag. The septum was used for withdrawing small samples for analysis using a gas-tight syringe.

Gas Measurement

A 6 foot (ft.) long, 8 in. internal diameter acrylic pipe was adapted for measuring

gas volumes. This size was selected to provide a 60 L of volume for gas measurement; approximately one and one-half the maximum expected daily production from both systems. The acrylic pipe was sealed at both ends and fitted with valves to control the flow of water into and out of the column (Figure 12). Two fittings were placed side by side directly on the top end of the column to allow for gas to enter and exit the column. Two fittings were placed opposite from each other approximately three inches from the bottom end of the column. The column was then filled with water by opening and closing the appropriate valves. The column was graduated using a calibrated Masterflex pump to introduce one liter of air to the column per unit time. The changing water level in the column was marked at appropriate time intervals to correspond to 1 L volume changes.

The modified acrylic column was placed in a 24 x 12 x 6 in. plastic pan. The column was then filled with water using a hose connected to valve (1), with valve (2) open to allow air to escape. Valves (3) and (4) were also left opened until water reached an equilibrium level marked by two 0.5 in. holes drilled approximately 2 in. from the top of the plastic pan. Valves (3) and (4) were then closed to allow the column to fill with water. Valve (1) was closed and a Tedlar gas bag, containing gas to be measured, was attached to valve (2). Valves (3) and (4) were then opened to drain water from the column, forming a vacuum in the column immediately filled by gas from the Tedlar gas bag.

Gas Analysis

Percent by volume of CH_4, CO_2, and H_2S were determined using gas

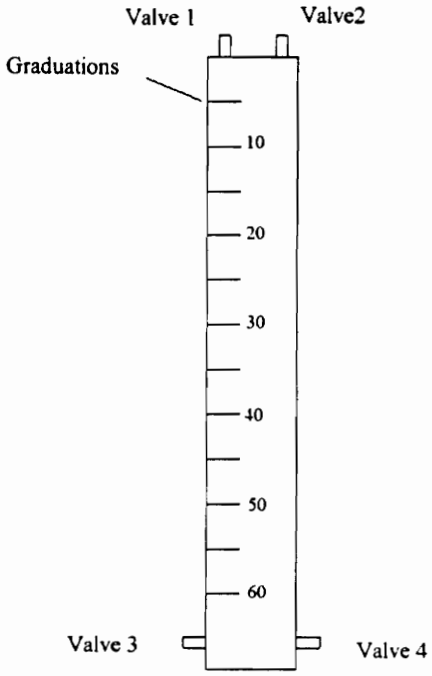

Figure 12. Modified acrylic pipe used for biogas measurement
Dimensions: 6 ft. long, 8 in. internal diameter
Capacity: 60-L

chromatography. Gas samples from systems A and B were analyzed weekly using a Hewlett Packard 5880A Series Gas Chromatograph equipped with a single filament thermal conductivity detector (TCD). A Hamilton 1725, gas tight, 250 microliter (μL) syringe was used for withdrawing 100 μL samples of biogas from Tedlar gas sample bags used for gas collection. The samples were then injected directly into the gas chromatograph injection port. Helium was used as the carrier gas to provide the highest possible sensitivity for detection of the gases of interest (Cowper and DeRose, 1987). Two 6 ft. long, 0.125 in. outside diameter stainless steel columns packed with Porapak Q 80/100 mesh were used. The reference and sample flows were set to 15 milliliters per minute (mL/min). The modulator flow was set to 30 mL/min. Temperatures for oven, injector, and detector were set at 35, 100, and 150°C, respectively.

Duplicate injections of varying amounts of a gas standard with known % by volume composition (+/-2 %) of CH_4, CO_2, and H_2S were made to monitor reproducibility. These were followed by duplicate injections of 50 and 100 μL amounts of pure CH_4 and CO_2 (> 90 %). Together, this data was used to plot a standard curve of peak area versus moles of gas. CH_4, CO_2, and H_2S peak areas generated from 100 μL injections of biogas with unknown composition were then used to calculate relative molar amounts of CH_4, CO_2, and H_2S based on the standard curves.

Reproducibility of the peak areas for CH_4 and CO_2 were determined by making 12 consecutive injections of the same standard and calculating the relative standard deviations (RSD) of the peak areas. The RSD for CH_4 and CO_2 were 1.2 % and 1.3 %, respectively. A similar procedure was used for H_2S, yielding a RSD of 0.27 %.

Biogas from System B was analyzed for NH_3 concentration using Gastec (1-60 ppm) ammonia analyzer tubes. A calibrated Masterflex pump was used in place of a Gastec hand pump for delivery of the samples to the analyzer tubes. The pump was calibrated to deliver the same sample volume (100 mL) as the hand pump over the same sample period (1 minute).

Effluent Collection and Analysis

The volume of effluent treated by each system was collected and recorded daily in graduated 4 L polyethylene containers at the time of gas sample bag replacement. Chemical Oxygen Demand (COD) and Volatile Suspended Solids (VSS) were measured using Methods 5220C and 2540E, respectively, as outlined in Standard Methods for the Analysis of Water and Wastewater (1992).

Pilot-Scale System

Crab Cooker Anaerobic Wastewater Treatment

The pilot-scale anaerobic treatment system was constructed by a fellow graduate research assistant. The system is located at the Virginia Polytechnic Institute and State University Seafood Research and Extension Center in Hampton, Virginia. Only the components of the crab cooker wastewater treatment system pertinent to gas collection will be discussed here.

The treatment system is located approximately 100 yards from a privately owned crab processing facility. The crab processor operates two retorts. All wastewater from

one retort was collected in a 55 gallon drum at the crab processing facility. The wastewater was automatically pumped through 0.75 in. polyvinylchloride (PVC) piping to a 250 gallon holding tank located in a building at the VPI & SU Seafood Research and Extension Center. Wastewater from the other retort emptied directly into the Hampton Creek. Wastewater exceeding the 250 gallon holding tank capacity overflowed into an effluent collection pipe that also emptied into the Hampton Creek.

A Masterflex pump controlled by a pressure switch transferred wastewater from the 250 gallon holding tank into the bottom of the first upflow anaerobic reactor P1 at approximately 30 gpd (Figure 13). Flow was temporarily decreased during periods when a decrease in the quantity of crabs harvested resulted in shortages of wastewater. Effluent flowed from P1 to an anaerobic clarifier, P2, through a line of flexible tubing. P1 and P2 each had a total volume of 190 gallons; approximately 160 gallons of useful liquid volume and 30 gallons of gas headspace volume.

Biogas Collection

Biogas accumulated in the headspace of reactors P1 and P2 up to approximately 3 in. of water column pressure. When this pressure was reached, a pressure switch (G) activated a Masterflex pump (E) and opened a solenoid valve (F) (Figure 13). The gas was then pumped from the reactor headspace, through 0.5 in. PVC piping, until the pressure dropped to approximately 1 in. of water column, at which time the pressure switch cut off the pump and closed the solenoid valve. The solenoid valve served as a check valve to prevent gas from flowing in the reverse direction.

The selection of 1 to 3 in. of water column pressure range was somewhat arbitrary.

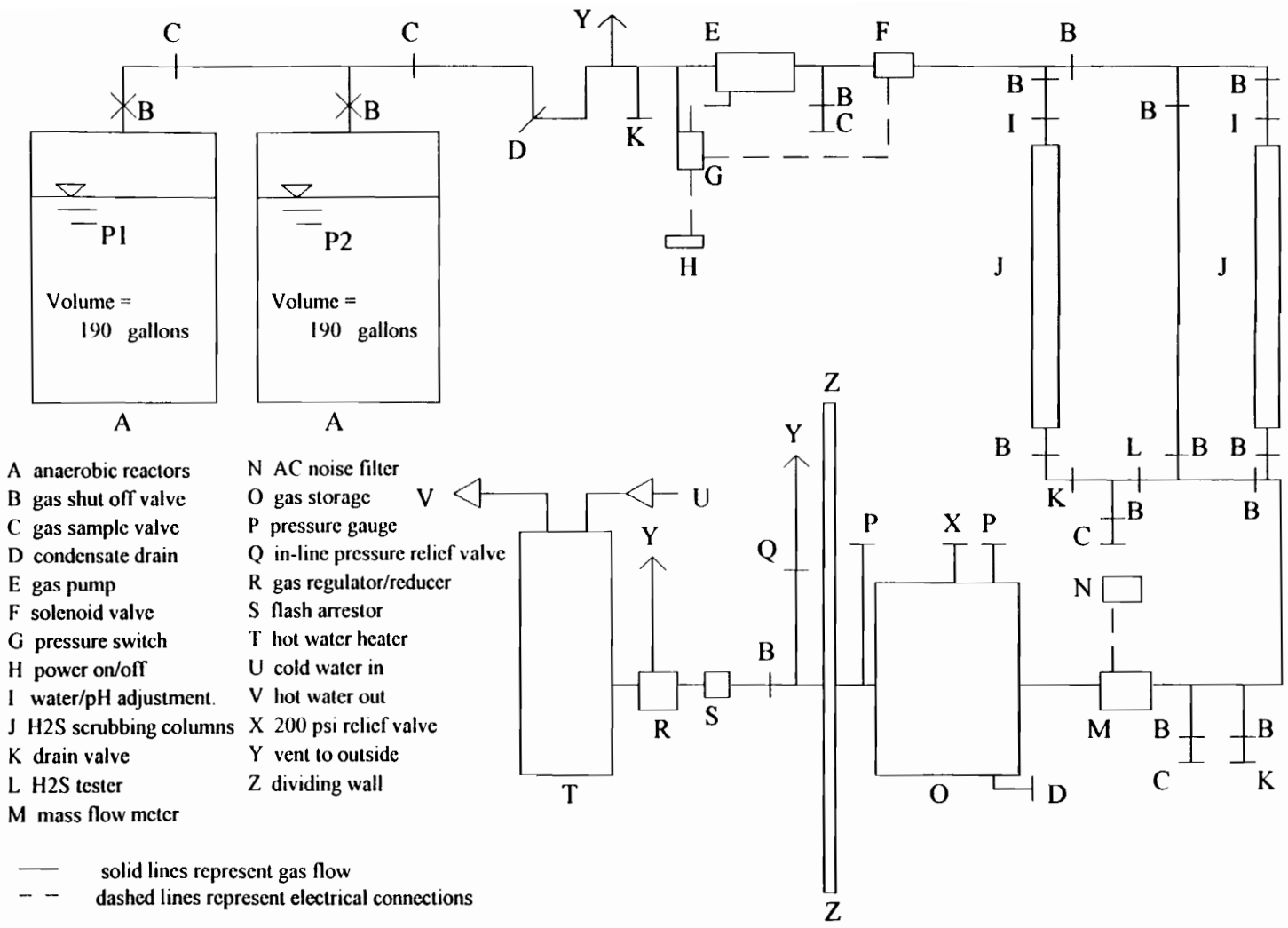

Figure 13. Schematic of pilot-scale gas collection system.

Automatic transfer of biogas from the reactor headspace through H_2S scrubbing columns and into storage at elevated pressure required the use of a pump controlled by a pressure switch. Large pressure changes within the reactors as gas was generated and removed would have resulted in significant changes in liquid levels within the reactors effecting wastewater flow throughout the system. In addition, the pressure range was maintained as low as possible to minimize the potential for gas leaks from the anaerobic reactors.

Gas sample valves were located at various points throughout the gas system for monitoring gas composition. Condensate drains were installed at low points in the system to drain condensate from the gas lines to prevent blockages.

Hydrogen Sulfide Removal

Biogas was pumped through two 3 in. internal diameter, 6 ft. long carbon steel pipes (J) filled with "Iron Sponge". "Iron Sponge" consists of hydrated iron oxide ($Fe_2O_3 \bullet H_2O$) and a sodium carbonate (Na_2CO_3) buffer on a support media of wood chips. Hydrogen sulfide is removed from the gas when the H_2S reacts with the hydrated iron oxide, at a slightly alkaline pH from 8 to 9, to form ferric sulfide (Fe_2S_3). Carbon steel gas lines were required in the immediate area of the hydrogen sulfide scrubbing columns to withstand temperatures, in excess of 38°C, generated by the reaction of H_2S with Fe_2O_3.

A valve (I) was installed at the top of each column for water addition and pH adjustment of the "Iron Sponge". A drain valve (K) was installed at the top of each column to remove excess condensate and water generated upon the removal of H_2S from the biogas. A H_2S tester (L) and a gas sample valve (C) were installed at the base of the

first column in order to monitor the removal of H_2S from the biogas. Gas shut-off valves were located to allow for isolation and removal of a single H_2S scrubbing column without interruption of gas flow.

Biogas Flow Measurement and Control

The methane and carbon dioxide gas mixture then flowed through an Omega mass flow meter (M). The flow meter was used to monitor the cumulative gas produced by the anaerobic reactors. The mass flow meter was followed by a 120 gallon storage tank (O). Varying amounts of gas could be stored depending on the pressure allowed to accumulate in the storage tank. The maximum pressure was limited by the maximum sustained operating pressure (25 psi) of the Masterflex pump (E) used to pump biogas. The actual operating pressure was controlled by venting gas from the drain valve (D) on the storage tank. An in-line pressure relief valve (Q) was installed following gas storage as a safety device. The relief valve was set to automatically release gas if the pressure in the system reached 24 psi.

Biogas Combustion

The stored gas was then burned in a modified 26,000 Btu/hr natural gas hot water heater (T). Modification of the hot water heater consisted of enlarging both the pilot gas orifice and main gas orifice. Based on information presented in the literature review on burner modification, the existing burner orifice (0.094 in.) was enlarged to 0.125 in. (See Appendix B). Prior to burning, the gas pressure was reduced to the 4.5 to 5 in. of water column required by the hot water heater using a pressure reducer/regulator (R). A flash arrestor (S) was installed prior to the hot water heater to prevent a flashback from the

burner assembly to the gas storage tank.

Hydrogen Sulfide Scrubbing Column Design

An estimate of biogas production for the proposed pilot-scale system treating 100 gpd was made based on maximum laboratory-scale system gas production of approximately 30 L of gas per gallon of waste treated. This estimate was set at 3,000 L/d. An estimate of the percent by volume H_2S was set at 1.3 % based on early gas analysis by gas chromatography.

Calculations of required H_2S scrubbing column dimensions were made based on various design parameters. The first design parameter was based on limiting sulfur deposition within the "Iron Sponge" material. It was suggested that sulfur deposition be limited to less than 15 grams of sulfur per square foot of column cross-sectional area per minute (Taylor, 1956b). Based on this limit, and the estimated biogas production (3,000 L/d; 1.3 % H_2S), a minimum column diameter of approximately 2.6 in. would be required.

The second design parameter was based on limiting the rate of gas flow through the column. It was suggested that gas flow through the column be limited to a maximum of 30 ft^3 of gas per hour per cubic foot of sponge material (Connelly GPM, 1994). Based on this limit, and the estimated biogas production (3,000 L/d; 1.3 % H_2S), a minimum volume of 0.15 ft^3 of sponge would be required.

A minimum sponge bed thickness of 10 ft. was recommended to produce a pressure drop sufficient to create a high gas velocity within the sponge material. Pressurizing the gas from one to two pounds per square inch produces this effect, and

therefore, eliminates the need for a 10 ft. deep column. (Taylor, 1956b)

The final H_2S scrubbing column dimensions were based on the calculate 2.6 in. minimum column diameter, the 0.15 ft^3 minimum value of "Iron Sponge", and the available space where the column would be operated. The requirement for ease of removal of the column from the gas system for replacement and regeneration of the sponge material also factored into this decision.

A section of carbon steel pipe, 6 ft. long with a three inch internal diameter was selected. This provided an internal volume of 0.29 ft^3, taking into consideration void space within the column. A second column of equal size was designed into the system to allow for removal of one column without interrupting gas flow. The columns were operated in series during normal operation.

CHAPTER IV. RESULTS AND DISCUSSION

Phase I: Laboratory-Scale Biogas Collection and Characterization

Laboratory results are presented in terms of changes in gas production relative to changes in COD reductions, COD loadings, feed rates, and biomass (expressed as VSS) that occurred during periods designated 1 through 5. The length of each period, and its corresponding mean feed rate and mean COD loading, is given in Tables 3 and 4, respectively. A three day running average was used to smooth out fluctuations among the volumes of effluent collected daily from each system. The values for mean feed rates (3dAVGQ) represent the mean of these three day running average values for each period. The following mean system parameters are also included: COD concentration (mg/L), gas production (L gas/d , L gas/L feed, mL gas/g COD reduced, mL gas/g VSS), COD reduction (mg/d), and methane production (mL CH_4/g COD reduced).

Period 1

The mean COD loadings during the first period, at 33,038 and 33,388 mg/d for systems A and B, respectively, were the second highest loadings of the five periods (Tables 3 and 4). Systems A and B showed the greatest reductions in COD (System A = 26,967 mg/d ; System B = 28,683 mg/d) during period 1. Gas production reached a maximum average of 15.8 L/d for System A. Gas production per amount of COD reduced averaged 587 and 588 mL/g COD for systems A and B, respectively (Figures 14 and 15).

Table 3. Mean system parameters of System A (240, 0.5 in. foam cubes)

Time Period	Time (days)	COD In mg/L	Gas rate L/d	3dAvgQ L/d	L gas/ L feed	COD loading mg/d	COD reduction mg/d	mL gas/ g COD reduced	mL CH4/ g COD reduced	mL gas/ g VSS
1	133-143	14229	15.84	2.32	6.82	33038	26967	587	396	526
2	144-167	10619	15.19	2.29	6.64	24007	13827	1099	742	482
3	173-204	30009	14.65	1.46	10.01	43631	21425	684	462	390
4	205-251	17747	6.32	0.96	6.61	16957	10956	577	389	138
5	252-280	19786	9.06	1.21	7.49	23942	13512	670	452	169

Table 4. Mean system parameters of System B (360, 1 x 1 x 0.5 in. foam pieces)

Time Period	Time (days)	COD In mg/L	Gas rate L/d	3dAvgQ L/d	L gas/ L feed	COD loading mg/d	COD reduction mg/d	mL gas/ g COD reduced	mL CH4/ g COD reduced	mL gas/ g VSS
1	133-143	14229	16.86	2.35	7.18	33388	28683	588	400	216
2	144-167	10619	17.04	2.40	7.11	25303	16856	1011	687	201
3	173-204	30009	19.45	1.64	11.88	48520	27662	703	478	210
4	205-251	17747	7.54	0.91	8.32	16087	11723	644	438	75
5	252-280	19786	10.27	1.19	8.67	23494	14847	692	470	95

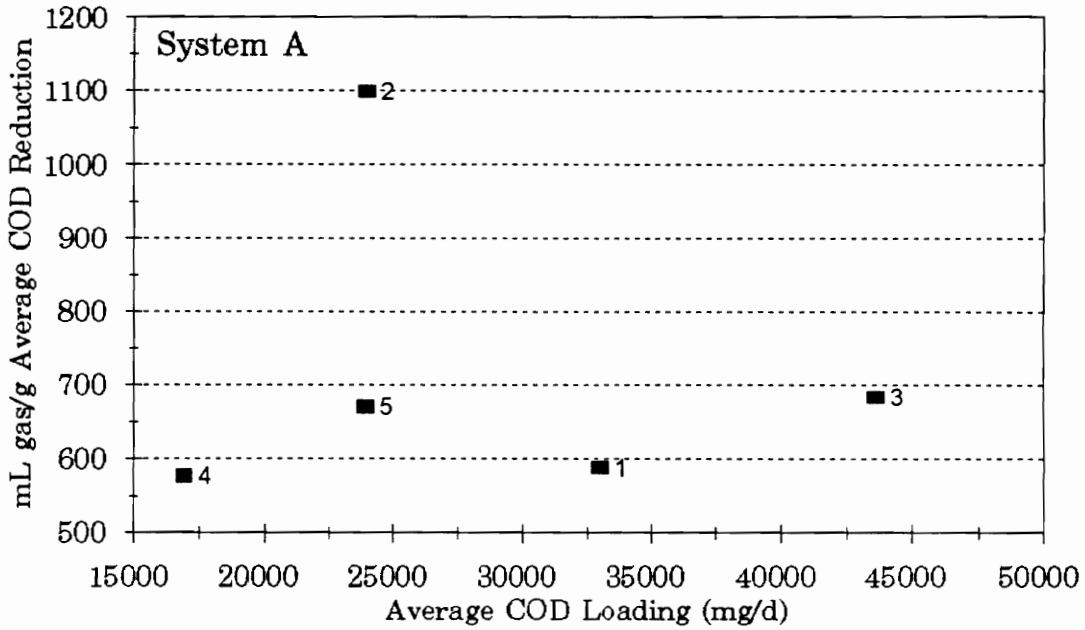

Figure 14. Average gas production per gram of COD reduction versus COD loading for System A; numbers 1-5 represent time periods.

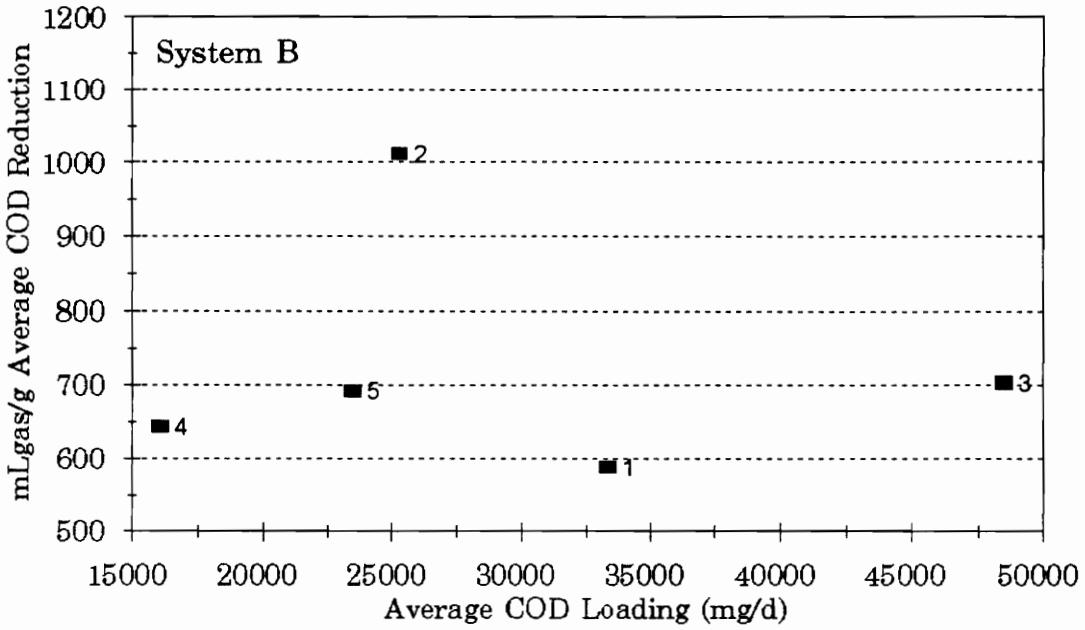

Figure 15. Average gas production per gram of COD reduction versus COD loading for System B; numbers 1-5 represent time periods.

Period 2

The mean COD loading decreased approximately 27 % for System A and 24 % for System B from period 1 to period 2 (Tables 3 and 4). COD reductions decreased 49 % and 41% for systems A and B, respectively. Mean gas production decreased slightly from 15.8 L/d to 15.2 L/d for System A and stayed relatively constant for system B (16.9 L/d to 17.0 L/d). Both systems appeared to have the highest gas production per amount of COD reduced during period 2 at 1,099 and 1,011 mL/g COD reduced in systems A and B, respectively.

Period 3

A five day transition period preceded period 3 during which COD loadings averaged lower than those of either periods 2 or 3. The COD loadings increased significantly from period 2 to period 3 for both systems to the maximum average values for the five periods. The COD loading in System A increased from 24,007 to 43,631 mg/d. The COD loading in System B increased from 25,303 to 48520 mg/d. System A gas production dropped from 15.2 to 14.7 L/d. COD reductions reached the second highest values of the five periods for both systems. System B gas production increased from 17.0 L/d during period 2 to a maximum of 19.5 L/d during period 3. Gas produced per amount of COD reduced decreased to 684 and 703 mL/g COD in systems A and B, respectively, during period 3.

Period 4

The lowest mean COD loadings of the five periods were observed during period 4 for systems A and B, at 16,957 and 16,087 mg/d, respectively. COD reductions also

decreased to the minimum mean values for the five periods of 10,956 and 11,723 mg/d for systems A and B, respectively. System A gas production decreased by 57 % from 14.7 L/d during period 3 to 6.3 L/d. System B gas production decreased by 62 % from 19.5 L/d during period 3 to 7.5 L/d. Gas produced per amount of COD reduced decreased from the previous period to 577 and 644 mL/g COD for systems A and B, respectively.

Period 5

COD loadings increased, relative to period 4, by 41 % and 46 % to 23,942 and 23,494 mg/d for systems A and B, respectively. COD loadings and COD reductions returned to the levels observed during period 2 for System A, while COD loadings and reductions averaged slightly lower during period 5 than period 2 in System B. Gas production increased to 9.1 and 10.3 L/d for systems A and B, respectively. Gas produced per amount of COD reduced increased, relative to period 4, to 670 and 692 mL/g COD in systems A and B, respectively.

Gas Composition

System A. Percent by volume CH_4, CO_2, and H_2S showed little variation throughout the period of analysis at 68, 28, and 1.5 %, respectively, with standard deviations of 4.5, 4.4, and 0.6 %, respectively. Methane ranged from a low of 60 % to a high of 74 %, while CO_2 ranged from 21 % to 37 %. H_2S ranged from 0.5 % to 2.7 % (Figure 16).

System B. System B produced a biogas with an average composition for the period of analysis almost identical to System A of 68, 28, and 1.4 % CH_4, CO_2, and H_2S,

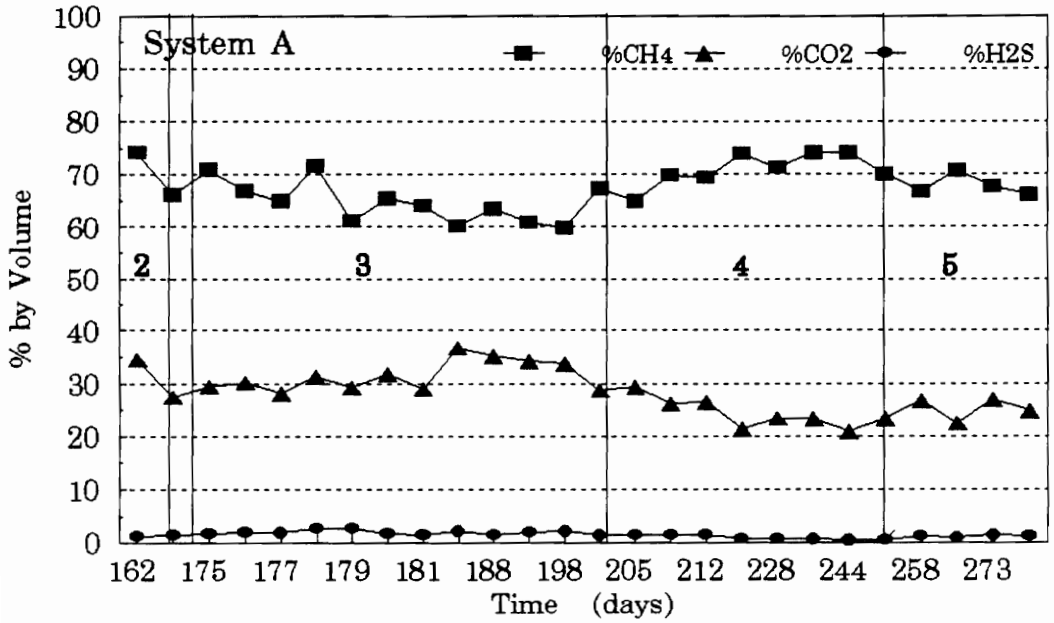

Figure 16. Biogas composition over 120 days during study period for System A; numbers 2-5 represent time periods.

respectively. Methane ranged from 60 % to 76 %; CO_2 ranged from 22 % to 35 %; and H_2S ranged from 0.5 % to 2.6 % (Figure 17). Ammonia (NH_3) was measured and consistently found to be less than 0.5 ppm (part per million; volume basis), with the exception of two measurements at approximately 1ppm.

Biogas versus COD Reduction

System A. Gas produced by System A increased with increasing COD reductions from 6.3 L/d at 10,956 mg/d and 9.1 L/d at 13,512 mg/d, to a maximum of approximately 14 to 16 L/d for COD reductions of 14,000 to 27,000 mg/d (Figure 18) (See Appendices F and G). System A gas production ranged from 577 to 684 mL gas/g COD reduced with the exception of period 2 when gas production was 1,099 mL gas/g COD reduced.

Theoretically, 393 mL of CH_4 is produced for every gram of COD digested at 35°C (McCarty, 1964a) (See discussion in Literature Review). Systems A and B produced biogas with an average percent by volume CH_4 content of 68 %. Therefore, system A produced from 389 to 462 mL CH_4/g COD reduced during the study period, with the exception of period 2, when CH_4 production averaged 742 ml CH_4/g COD reduced (Table 3). The average value of 742 mL CH_4/g COD reduced indicates that CH_4 production was almost twice that which would theoretically be expected. The analysis of the biogas composition during period 2, and subsequent periods, showed that the gas collection bags were not contaminated with air (Figures 16 and 17). A possible explanation for this discrepancy lies in the different frequencies of gas collection versus COD measurement. Gas was collected and measured daily, whereas COD was measured only three times during the second period. Thus, it is possible that the limited number

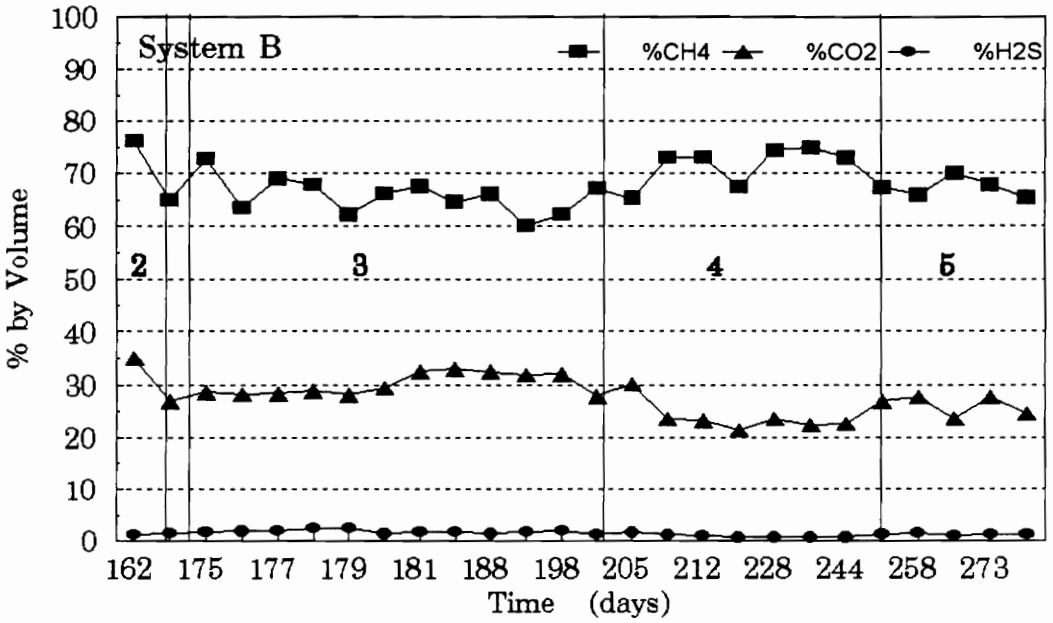

Figure 17. Biogas composition over 120 days during study period for System B; numbers 2-5 represent time periods.

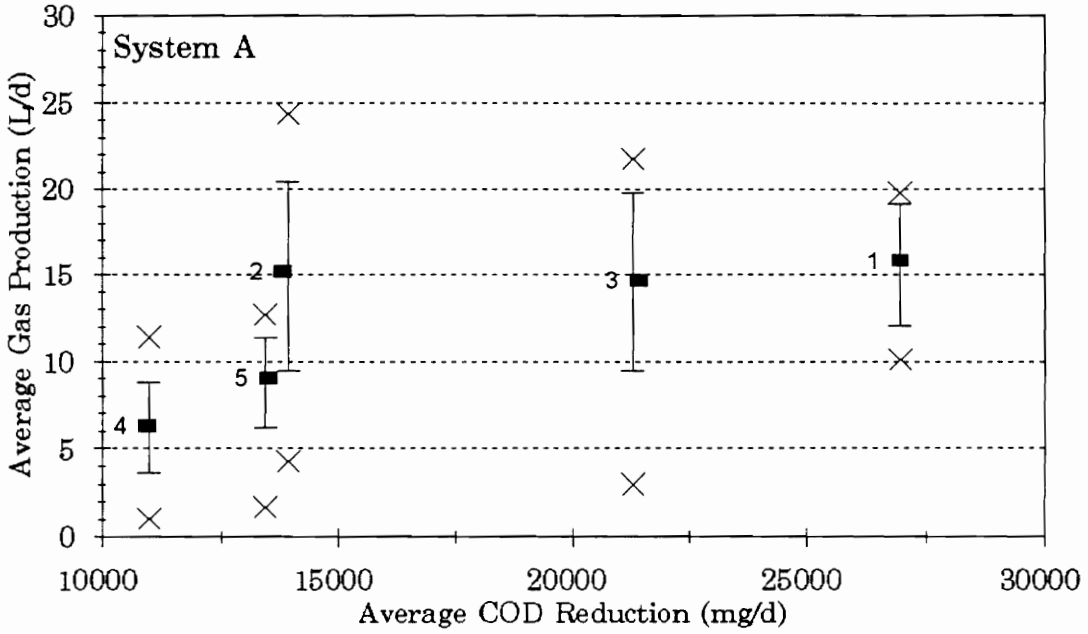

Figure 18. Average gas production versus average COD reduction for System A; numbers 1-5 represent time periods.
Vertical bar represents ± one standard deviation about the mean
■ = mean gas production
× = maximum and minimum values

of COD measurements do not accurately reflect the actual COD reductions during the second period. Actual COD reductions were apparently greater than that measured.

System B. System B gas production increased with increasing reductions in COD from 7.5 L/d at 11,723 mg/d and 10.3 L/d at 14,847 mg/d, to a maximum of approximately 16 to 20 L/d for COD reductions of 17,000 to 29,000 mg/d (Figure 19). System B gas production ranged from 588 to 703 mL gas/g COD reduced with the exception of period 2 when 1011 mL gas/g COD reduced was produced. The average CH_4 content of gas from System B was 68 %. Therefore, System B CH_4 production ranged from 400 to 478 mL CH_4/g COD reduced, excluding period 2's high value of 687 mL CH_4/g COD reduced (Table 4).

Again, the high value of 687 mL CH_4/g COD reduced, which was observed during period 2, is significantly higher than the corresponding values for periods 1, 3, 4, and 5 (Table 4). The same explanation as provided above for System A for the difference between actual and theoretical gas production is offered here.

Biogas versus COD Loading

System A. System A gas production increased with increasing COD loadings from 6.3 L/d at 16,957 mg/d and 9.1 L/d at 23,942 mg/d to a maximum of 14 to 16 L/d at COD loadings of 24,000 to 44,000 mg/d (Figure 20).

System B. System B gas production increased with increasing COD loadings from 7.5 L/d at 16,087 mg/d and 10.3 L/d at 23,494 mg/d to a maximum of 16 to 20 L/d at COD loadings ranging from 25,000 to 50,000 mg/d (Figure 21).

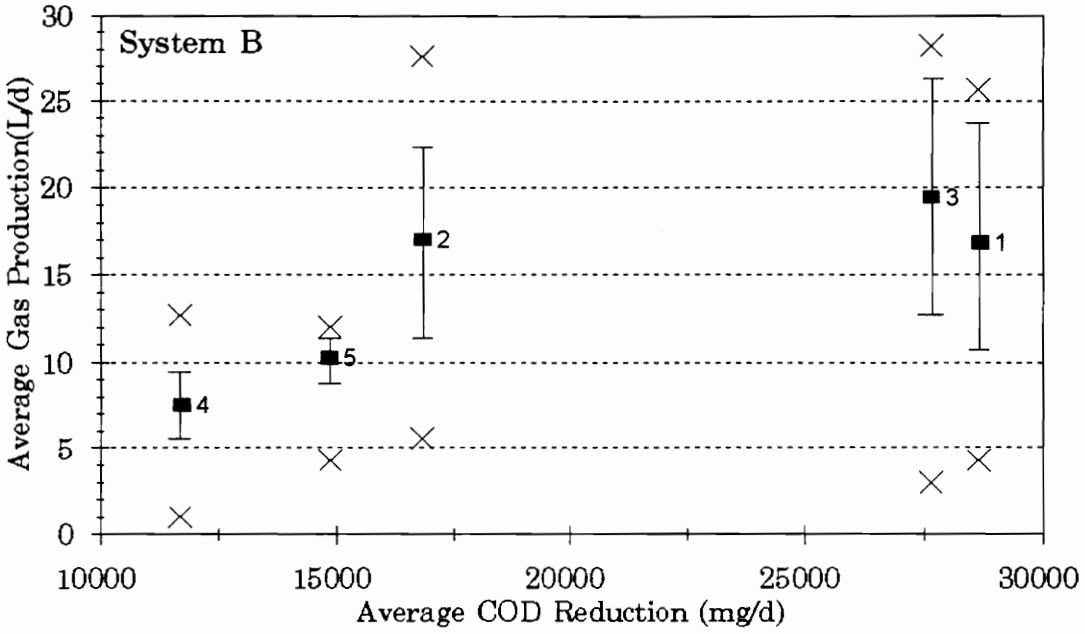

Figure 19. Average gas production versus average COD reduction for System B; numbers represent time periods.
Vertical bar represents ± one standard deviation about the mean
■ = mean gas production
× = maximum and minimum values

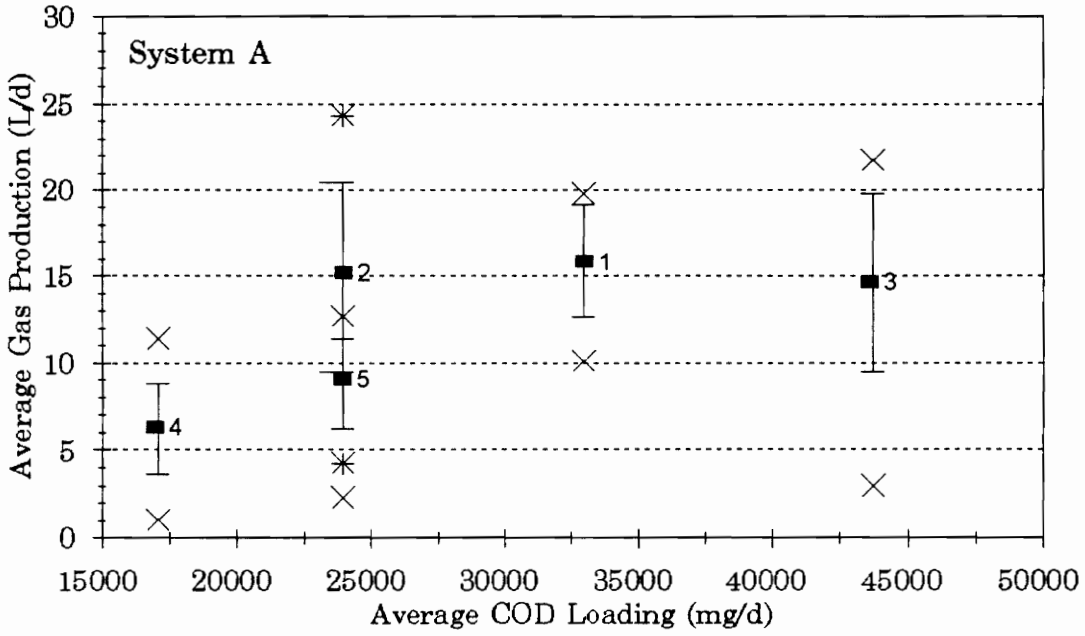

Figure 20. Average gas production versus average COD loading for System A; numbers 1-5 represent time periods.
Vertical bar represents ± one standard deviation about the mean
■ = mean gas production
× = maximum and minimum values
✳ = maximum and minimum values for period 2

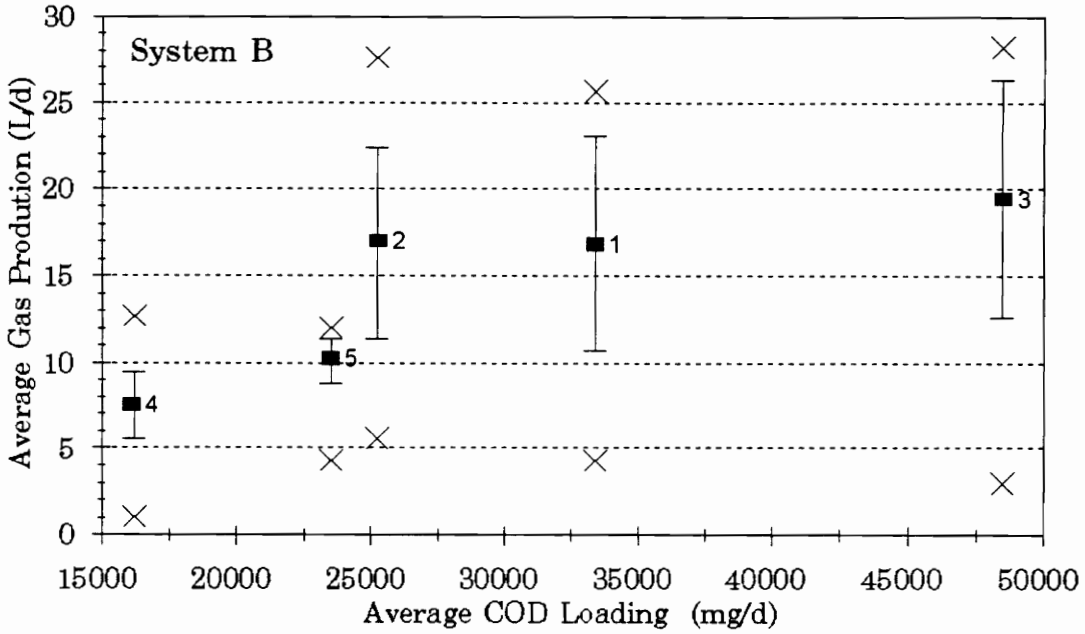

Figure 21. Average gas production versus average COD loading for System B; numbers 1-5 represent time periods.
Vertical bar represents ± one standard deviation about the mean
■ = mean gas production
× = maximum and minimum values

Biogas versus Volume of Feed

System A. System A gas production for periods 1 and 2 averaged 6.6 L gas/L feed. Gas production increased to 10 L gas/ L feed during period 3, corresponding to the maximum average COD loading of 43,631 mg/d. Gas production decreased to an average of 7.1 L gas/L feed during periods 4 and 5. (Table 3)

System B. System B gas production followed the same pattern as System A, but with slightly higher gas productions. Gas production averaged 7.1 L gas/L feed during periods 1 and 2. Gas production reached a maximum of 11.9 L gas/L feed during period 3. During periods 4 and 5, the average was 8.5 L gas/L feed. (Table 4)

Biogas versus Biomass

The volatile suspended solids (VSS) in the first anaerobic reactor of each system was measured on three occasions. The VSS was measured on days 0, 160, and 280. The distribution of suspended solids and solids adhered to the foam pieces is shown in Table 5.

The first reactor of each system was inoculated with 5,500 mg/L VSS on day 0. The solids had increased to 7,900 and 21,700 mg/L VSS in reactors A1 and B1, respectively, by day 160. Solids were measured at 14,100 and 27,800 mg/L VSS in reactors A1 and B1, respectively, on day 280. It was assumed that the bacterial growth followed a linear pattern between measurements as shown in Figure 22.

System B, while having approximately twice the concentration of biomass as System A, did not exhibit significantly higher reductions in COD for the COD loadings observed during the study period. In addition, the total amount of gas produced by both

Table 5. Volatile solids in reactors A1[1] and B1[2] (Diz, 1994).

	Mass (mg)			
	Suspended	On Cubes	Total Solids	VSS Concentration mg/L
Reactor A1				
Day 0	22,000	0	22,000	5,500
Day 160	8,600	23,100	31,700	7,900
Day 280	33,300	23,000	56,300	14,100
Reactor B1				
Day 0	22,000	0	22,000	5,500
Day 160	9,900	76,900	86,800	21,700
Day 280	27,300	83,700	111,000	27,800

(1) A1 = first anaerobic reactor of System A
(2) B1 = first anaerobic reactor of System B

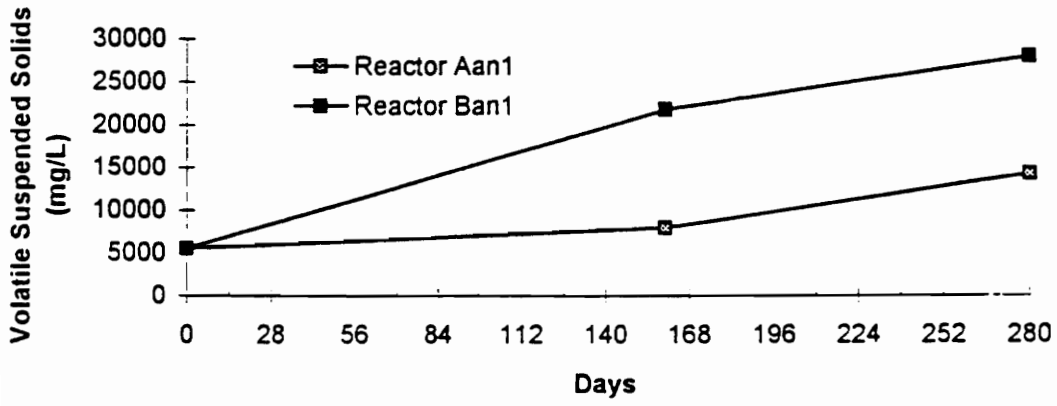

Figure 22. Volatile suspended solids in reactors Aan1[1] and Ban1[2] over the course of the study (Diz, 1994).

(1) Aan1 = A1 = first anaerobic reactor of System A

(2) Ban1 = B1 = first anaerobic reator of System B

systems is not significantly different for the study period. However, gas production per amount of VSS averaged approximately twice as high for System A as for System B (Tables 3 and 4).

System B had three times the volume of foam pieces as System A, while the foam pieces in System A were one-fourth the size of those in System B. The cubes in both reactors became completely filled and covered with biomass. There are various consequences of these conditions that could explain the similar performance of System B, with twice the biomass, to System A in terms of COD reduction and gas production. First, the greater volume of foam pieces in System B would tend to decrease the operating liquid volume of the system, hence decreasing the hydraulic retention time (HRT). Second, the larger individual foam pieces in System B, relative to System A, may have resulted in a lower rate of diffusion of substrate to the microorganisms located within the foam pieces of System B. This may have resulted in a correspondingly lower metabolic rate for those microorganisms located within the foam pieces in System B. Third, the higher sludge age inherent in the larger biomass population of System B, may result in a larger inactive fraction of biomass relative to System A. All three of these factors may have contributed to the similar gas productions and COD reductions observed in systems A and B.

Energy Value

The typical crab processor performs 6 to 20 cooking cycles per day, which yield 400 to 1,000 gallons of crab processing wastewater (Boardman *et al.*, 1993). Gas production in this study ranged from 6.6 to 11.9 L gas/ L feed. A crab processor

producing 400 gallons of waste could, therefore, theoretically produce between 353 and 637 ft^3 of gas per day at 6.6 and 11.9 L gas/L feed, respectively. This corresponds to 212,000 and 382,000 Btu/d for 6.6 and 11.9 L gas/L feed, respectively, for a biogas of 60 % CH_4 (heating value equals 600 Btu/ft^3) (Wheatly, 1980). A crab processor producing 1,000 gallons of waste could theoretically produce between 883 and 1592 ft^3 of gas per day for conversions of 6.6 and 11.9 L gas/L feed, respectively. This corresponds to 530,000 and 955,000 Btu/d, respectively, for a gas of 60 % CH_4.

Sixty percent methane and 6.6 L gas/L feed are the minimum average methane concentration and the minimum average gas production, respectively, observed during this study. These numbers, thereby, provide a conservative estimate of the value of the available biogas; whereas, 11.9 L gas/L feed is the maximum yield of biogas observed which might be used in predicting the most favorable scenario for utilizing the biogas.

Phase II: Pilot-Scale System

System Costs

The major components of the pilot-scale gas collection, treatment, storage, and utilization system are tabulated in Appendix E with the price of each item. The total cost of the major system components was approximately $3,800. This does not include miscellaneous equipment (e.g. shut-off valves, sample valves, piping, etc.) which cost an additional $300 to $400. Therefore, the total cost of the system was approximately $4,200.

CO_2 Removal

As cited in the literature review, the removal of CO_2 from the biogas is generally only economical and necessary when a large quantity of gas is available for sale to a public natural gas line. The estimated cost of caustic scrubbing for CO_2 removal from the biogas produced by the pilot-scale system was calculated assuming an estimated wastewater treatment rate of 100 gpd and gas production of 3,000 L/d (30 % CO_2) (See Appendix A). Carbon dioxide removal would average approximately $5.00 per day ($1,825/yr). This expense was not justified based on the additional equipment and supervision that would be required. The only added benefit of CO_2 removal at the pilot-scale system would have been storage of a higher heating value of gas (1,000 versus 700 Btu/ft^3) in the existing storage tank.

H_2S Removal

The two 6 ft., three inch internal diameter columns filled with "Iron Sponge" successfully removed the hydrogen sulfide from more than 1,200 liters of biogas. Further operation of the gas system will be necessary to determine if water and/or pH adjustment of the "Iron Sponge" material will be necessary. Initial performance suggests that the moisture present in the biogas is sufficient to prevent dehydration of the "Iron Sponge". The "Smyly H_2S tester" located at the base of the first column was used to monitor the removal of H_2S from the biogas. Operation of the tester is based on exposing a paper disk treated with lead acetate to the gas for one minute. The absence of discoloration of the paper disk indicated that there was less than 4 ppm H_2S in the gas leaving the first column. In addition, hydrogen sulfide was not detected in treated gas analyzed using gas

chromatography.

The H_2S scrubbing columns contained a total of 0.60 ft^3 of "Iron Sponge". This material costs $6.50 per bushel (1 bushel = approximately 1 ft^3 installed). The H_2S scrubbing columns costs $180.00 for the carbon steel pipe and fittings. Therefore, the complete H_2S removal system cost less than $190.00 for materials. The life of the "Iron Sponge" material will depend on variations in the H_2S concentration of the biogas and the volume of biogas treated.

System Operation

Prior to operation, the gas system was pressurized with nitrogen to check for leaks. The system was pressurized up to 25 psi. Several leaks were found at pipe connections with threaded fittings. One leak involved an improperly glued PVC fitting. Attempts to repair existing leaks resulted in discovery of additional leaks. It was finally determined that the system was capable of handling pressures up to approximately 12 psi.

The completed gas collection and storage system was operated with virtually no supervision. Daily replacement of gas pump tubing was required. The use of pumps requiring tubing poses a problem in terms of possible breaks which may occur in the tubing, resulting in gas leaks. The pressure gauge indicating gas storage pressure had to be checked daily. This was done to determine if gas had to be vented from storage to prevent pressure from exceeding the predetermined safe level of 12 psi.

Preliminary operation of the pilot-scale system at 30 gpd (December 1994) indicated that the system performed comparably to the laboratory-scale systems. Gas production averaged approximately 10 L gas/L feed. This is comparable to the maximum

observed laboratory-scale gas production of 11.9 L gas/L feed. The flow rate was decreased to approximately 16 gpd on January 27, 1995 due to a decrease in the amount of waste available for treatment.

Biogas Analysis

Biogas generated by the pilot-scale system was analyzed using the procedure outlined previously for gas collected from the laboratory-scale systems. The methane content of the biogas was 73 %.

Biogas Combustion

At the time the hot water heater was initially operated, a sufficient quantity of biogas had not been generated to displace all the nitrogen gas used to leak/pressure test the system. Therefore, the gas in the 120 gallon storage tank was 54 % methane as compared to 70 % methane in the gas being generated by the anaerobic reactors. The pilot gas orifice had to be enlarged slightly to obtain a stable pilot flame. To compensate for the lower methane content of the stored gas, the modified main gas orifice had to be enlarged from 0.125 in to 0.213 in. to obtain a stable flame. The required gas orifice size will decrease significantly (e.g. from 0.213 in. to 0.125 in.) as the methane content in the storage tank approaches 70 %.

Summary of Results

Laboratory-Scale Systems

The biogas generated in this study by the anaerobic treatment of crab processing

wastewater ranged from 60 to 76 % CH_4, 21 to 37 % CO_2, and 0.5 to 2.7 % H_2S.. Laboratory-scale biogas production ranged from 6.6 to 11.9 L gas/L of wastewater. Based on laboratory results, a small crab processor (6 cooks/day) may expect to produce from 212,000 to 382,000 Btu/d for a gas production rate of 6.6 and 11.9 L gas/L feed, respectively, whereas a large crab processor (20 cooks/day) could expect between 530,000 to 955,000 Btu/d. The range of 212,000 to 382,000 Btu/d corresponds to 212 to 382 ft^3/d of natural gas (1000 Btu/ft^3) or a savings of from \$1.19 to \$2.14 per day (\$0.56 per 100 ft^3) (Virginia Natural Gas, 1995). The high range of expected available energy of 530,000 to 955,000 Btu/d corresponds to 530 to 955 ft^3/d of natural gas, or a savings of from \$2.97 to \$5.35 per day.

The crab processor involved in this study used natural gas for boiler operation and for heating during winter months. Records obtained indicated an average monthly natural gas consumption to be approximately 160,000 ft^3 per month. At 70 % methane, biogas has a heating value of approximately 700 Btu/ft^3 (Rohlich, 1977). Therefore, 160,000 ft^3 of natural gas is equivalent to approximately 230,000 ft^3 of biogas. Based on the range of gas productions observed in the laboratory-scale systems (6.6 to 11.9 L gas/L feed), 4,800 to 8,700 gallons of waste would have to be treated daily to produce enough gas to satisfy the crab processors monthly natural gas requirements for boiler operation and heating.

As noted in the literature review, the average large crab processor may produce up to 1,000 gallons of wastewater per day. Under these conditions, the most attractive scenario for the crab processor may be to charge a fee to collect and treat wastewater

from nearby seafood processors. Treatment of the additional wastewater would increase gas production, while the fee charged for wastewater collection and treatment could be used to offset the cost of discharging the treated waste to the municipal sewer and the cost of treatment system operation.

Pilot-Scale System

The pilot-scale biogas system was shown to be capable of collecting, treating, storing, and utilizing biogas generated by the anaerobic treatment of crab processing wastewater, while requiring minimal supervision. Supervision included daily replacement of gas pump tubing and observation of accumulated gas pressure. A tubeless pump would be more appropriate for pumping gas. This would eliminate the need for tubing replacement and the possible danger associated with a break in tubing.

Intermittent pumping of biogas from the reactor headspace using a pump controlled by a pressure switch was an effective means of transferring biogas from the reactors, through the H_2S scrubbing columns, and into the gas storage tank. The maximum pressure allowed to accumulate in the reactor headspace (3 in. of water column pressure) minimized effects of pressure changes on wastewater flow through the waste treatment system.

Pressurization of the biogas demanded that additional time and care be taken in the construction of the gas collection system to insure that all pipe fittings were properly sealed. PVC connections proved to be more reliable than threaded carbon steel and galvanized steel fittings. However, steel components were required near H_2S scrubbing columns due to heat produced by the reaction of H_2S with Fe_2O_3 .

Only a minor modification of the natural gas hot water heater burner assembly was necessary to combust the biogas. Modification consisted of enlarging the existing main gas orifice to accommodate the lower heating value and flame velocity of the treated biogas. The pilot gas orifice was also enlarged slightly to produce a stable pilot flame. The required enlargement of the main gas orifice was larger than that originally calculated (0.213 in. vs. 0.125 in.) due to the presence of nitrogen used to test the system for leaks.

Biogas production from the pilot-scale system (10 L gas/L feed; 73 % CH_4) at a feed rate of 30 gpd was comparable to the maximum average gas production from the laboratory-scale systems (11.9 L gas/L feed). The gas production rate of 10 L gas/L feed corresponds to 1,340 ft^3 of biogas per 1,000 gallons of waste treated; assuming that the crab processor produces and treats 1,000 gallons of wastewater per day. This is equivalent to 936,000 Btu/d or $6.25 in terms of the cost of an equivalent heating value of natural gas.

Pilot-scale gas production estimates were made based on preliminary results obtained during winter months when the crab processor was not receiving crabs on a regular basis. Because of this, the pilot-scale treatment system suffered from shortages in wastewater. The feed rate had to be adjusted accordingly to maintain a constant supply of wastewater to the anaerobic reactors. Further data on gas production under conditions of prolonged system operation (with an ample supply of wastewater) will have to be collected to determine if pilot-scale system gas production is similar to gas production observed in the laboratory-scale systems. Further operation of the pilot-scale system will also be necessary to determine the life of the H_2S scrubbing columns and the possible

difficulties associated with removal and regeneration of the "Iron Sponge".

CHAPTER V. CONCLUSIONS

The following conclusions can be drawn from this research study with crab cooker wastewater:

1. The biogas generated by the anaerobic treatment of the wastewater ranged from 60 to 76 % CH_4, 21 to 37 % CO_2, and 0.5 to 2.7 % H_2S with an approximate heating value of 700 Btu/ft^3.

2. Laboratory-scale biogas production ranged from 6.6 to 11.9 L gas/L of wastewater for COD reductions ranging from 60 to 80 % at loadings of 16,000 to 50,000 mg/d.

3. Based on laboratory-scale biogas production, a crab processor treating 400 gallons of wastewater per day (6 cooks/day) could expect to produce 212,000 to 382,000 Btu/d at a gas production rate of 6.6 to 11.9 L gas/L feed (60 % CH_4), respectively. A crab processor treating 1,000 gallons of wastewater per day (20 cooks/day) could expect to produce 530,000 to 955,000 Btu/d at a gas production rate of 6.6 to 11.9 L gas/L feed (60 % CH_4), respectively.

4. A pilot-scale biogas collection and utilization system was successfully demonstrated. Biogas production was approximately 10 L gas/L feed and the biogas contained 73 % CH_4. COD reductions of approximately 60 % were observed for feed rates ranging from 15 to 30 gpd.

5. Anaerobic treatment of 4,800 to 8,700 gallons of wastewater per day would provide

sufficient quantities of biogas (70 % CH_4) to eliminate the natural gas requirements (160,000 ft^3 per month) of one of the largest crab processors in Virginia. Therefore, collection and utilization of the biogas from an anaerobic system may be a viable option provided that sufficient quantities of wastewater can be collected, a fee can be charged for treating wastewater from other seafood processors, and sufficient space is available for construction of the waste treatment system.

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CHAPTER VII. APPENDICES

Appendix A: Data from laboratory systems A and B.

			System A												
DATE	DAY	COD In mg/l	gas L	effluent (Q) L	3dAvgQ L	AvgCOD load mg/d	gas/AvgCODload mLgas/gCOD	COD A1 mg/l	COD A2 mg/l	COD A3 mg/l	COD In-A1 mg/l	COD A1-A2 mg/l	%removal In to A1	%removal A1 to A2	VSS mg/l
02/21/94	133	**14474**	11.80	2.40	2.13	30757	384								7495
02/22/94	134	14474	12.50	1.85	2.22	32084	390								7510
02/23/94	135	14474	10.10	2.40	2.75	39804	254								7525
02/24/94	136	14474	13.60	4.00	2.80	40527	336								7540
02/25/94	137	14474	19.50	2.00	2.60	37632	518								7555
02/26/94	138	14474	17.10	1.80	1.85	26777	639								7570
02/27/94	139	**13935**	17.60	1.75	2.08	29031	606	2787	2710	1780	11687	77	80.7	2.8	7585
02/28/94	140	13935	16.10	2.70	2.18	30425	529								7600
03/01/94	141	13935	19.50	2.10	2.47	34373	567								7615
03/02/94	142	13935	16.30	2.60	2.23	31122	524								7630
03/03/94	143	13935	20.10	2.00	2.22	30889	651								7645
03/04/94	144	**9302**	4.60	2.05	2.02	18759	245	2456	2605	1786	11556	-149	82.5	-6.1	7660
03/05/94	145	9302	12.60	2.00	2.08	19379	650								7675
03/06/94	146	9302	12.90	2.20	2.53	23565	547								7690
03/07/94	147	9302	5.90	3.40	2.53	23565	250								7705
03/08/94	148	9302	15.00	2.00	2.50	23255	645								7720
03/09/94	149	9302	10.10	2.10	2.20	20464	494								7735
03/10/94	150	9302	11.40	2.50	2.37	22015	518								7750
03/11/94	151	10450	15.10	2.50	2.50	26125	578								7765
03/12/94	152	10450	13.40	2.50	2.57	26822	500								7780
03/13/94	153	10450	18.00	2.70	2.37	24732	728								7795
03/14/94	154	**10450**	10.60	1.90	2.33	24383	435	2520	2320	1940	7143	200	73.9	7.9	7810
03/15/94	155	10450	17.00	2.40	2.10	21945	775								7825
03/16/94	156	10450	14.80	2.00	2.23	23338	634								7840
03/17/94	157	10450	16.00	2.30	2.27	23687	675								7855
03/18/94	158	10450	13.70	2.50	2.43	25428	539								7870
03/19/94	159	10450	19.90	2.50	2.43	25428	783								7885
03/20/94	160	10450	24.10	2.30	2.30	24035	1003								7900
03/21/94	161	10450	13.70	2.10	2.27	23687	578								7952
03/22/94	162	10450	22.40	2.40	2.27	23687	946								8003
03/23/94	163	10450	23.80	2.30	2.47	25777	923								8055
03/24/94	164	10450	23.30	2.70	2.28	23861	976								8107
03/25/94	165	10450	20.10	1.85	2.32	24209	830								8158
03/26/94	166	**16500**	19.40	2.40	1.92	31625	613	5500	4125	3375	4950	1375	47.4	25.0	8210
03/27/94	167	16500	6.80	1.50	1.60	26400	258								8262
03/28/94	168	16500	17.90	0.90	1.12	18425	972								8313
03/29/94	169	16500	14.80	0.95	0.85	14025	1055								8365
03/30/94	170	16500	10.60	0.70	0.85	14025	756								8417
03/31/94	171	16500	10.10	0.90	0.87	14300	706								8468
04/01/94	172	16500	8.50	1.00	1.10	18150	468								8520
04/02/94	173	33700	15.00	1.40	1.20	40440	371								8572
04/03/94	174	33700	10.95	1.20	1.07	35947	305								8623
04/04/94	175	**33700**	16.95	0.60	1.20	40440	419	4400	2800	1900	12100	1600	73.3	36.4	8675
04/05/94	176	33162	19.80	1.80	1.30	43111	459								8727
04/06/94	177	32623	21.55	1.50	1.50	48935	440								8778
04/07/94	178	32085	16.70	1.20	1.27	40641	411								8830
04/08/94	179	31546	16.40	1.10	1.20	37855	433								8882
04/09/94	180	31008	15.50	1.30	1.40	43411	357								8933
04/10/94	181	30469	17.30	1.80	1.60	48750	355								8985
04/11/94	182	29931	16.05	1.70	1.80	53876	298								9037

04/12/94	183	29392	16.60	1.90	1.63	48007	346								9088
04/13/94	184	28854	19.30	1.30	1.60	46166	418								9140
04/14/94	185	28315	19.50		1.30	36810	530								9192
04/15/94	186	27777			1.90	52776									9243
04/16/94	187	27238	15.40	1.90	1.60	43581	353								9295
04/17/94	188	**26700**	12.70	1.30	1.63	43610	291	16600	9900	8300	14310	6700	46.3	40.4	9347
04/18/94	189	26700	17.40	1.70	1.50	40050	434								9398
04/19/94	190	26700	17.05	1.50	1.57	41830	408								9450
04/20/94	191	26700	16.90	1.50	1.58	42275	400								9502
04/21/94	192	26700	17.30	1.75	1.72	45835	377								9553
04/22/94	193	26700	18.90	1.90	1.80	48060	393								9605
04/23/94	194	30600	16.70	1.75	1.85	56610	295								9657
04/24/94	195	30600	18.40	1.90	1.67	51000	361								9708
04/25/94	196	30600	12.10	1.35	1.72	52530	230								9760
04/26/94	197	**30600**	21.50	1.90	1.70	52020	413	13200	12200	9200	14477	1000	52.3	7.6	9812
04/27/94	198	30600	14.90	1.85	1.85	56610	263								9863
04/28/94	199	30600	5.30	1.80	1.50	45900	115								9915
04/29/94	200	30600	10.70	0.85	1.25	38250	280								9967
04/30/94	201	30600	7.20	1.10	1.00	30600	235								10018
05/01/94	202	30600	3.60	1.05	1.07	32640	110								10070
05/02/94	203	30600	3.60	1.05	0.97	29580	122								10122
05/03/94	204	30600	3.00	0.80	0.92	28050	107								10173
05/04/94	205	**19800**	2.50	0.90	0.90	17820	140	12950	11240	6100	17650	1710	57.7	13.2	10225
05/05/94	206	19800	3.25	1.00	0.93	18480	176								10277
05/06/94	207	19800	3.25	0.90	0.87	17160	189								10328
05/07/94	208	19800	3.10	0.70	0.87	17160	181								10380
05/08/94	209	19800	3.80	1.00	0.87	17160	221								10432
05/09/94	210	19800		0.90	1.27	25080									10483
05/10/94	211	19800	4.00	1.90	1.40	27720	144								10535
05/11/94	212	19800	5.40		1.35	26730	202								10587
05/12/94	213	19800	4.90	0.80	0.85	16830	291								10638
05/13/94	214	19800	6.20	0.90	0.77	15180	408								10690
05/14/94	215	19800	5.00	0.60	0.77	15180	329								10742
05/15/94	216	19800	1.50	0.80	0.73	14520	103								10793
05/16/94	217	19800	6.40	0.80	0.80	15840	404								10845
05/17/94	218	**16650**	5.00	0.80	0.78	13043	383	5600	7200	3100	16648	-1600	74.8	-28.6	10897
05/18/94	219	16650		0.75	1.08	18038									10948
05/19/94	220	16650	8.70	1.70	1.23	20396	427								11000
05/20/94	221	16650	2.80		1.25	20813	135								11052
05/21/94	222	16650	2.00	0.80	0.88	14569	137								11103
05/22/94	223	16650	6.60	0.95	0.85	14153	466								11155
05/23/94	224	16650	7.40	0.80	0.88	14708	503								11207
05/24/94	225	16650	7.90	0.90	1.10	18315	431								11258
05/25/94	226	16650	11.50	1.60	1.25	20813	553								11310
05/26/94	227	16650	7.90		1.30	21645	365								11362
05/27/94	228	16650	8.30	1.00	0.95	15818	525								11413
05/28/94	229	16650	2.70	0.90	0.93	15540	174								11465
05/29/94	230	**17400**	7.90	0.90	0.93	16240	486	7900	7200	4800	9312	700	54.1	8.9	11517
05/30/94	231	17400	8.20	1.00	1.00	17400	471								11568
05/31/94	232	17400	7.80	1.10	0.90	15660	498								11620
06/01/94	233	17400	9.00	0.60	0.88	15370	586								11672
06/02/94	234	17400	3.40	0.95	0.82	14210	239								11723
06/03/94	235	17400	9.10	0.90	0.97	16820	541								11775
06/04/94	236	17400	8.80	1.05	0.98	17110	514								11827

06/05/94	237	17400	8.20	1.00	1.08	18850	435								11878
06/06/94	238	**17900**	8.70	1.20	0.97	17303	503	6800	6900	5400	10409	-100	60.5	-1.5	11930
06/07/94	239	17900	1.30	0.70	0.97	17303	75								11982
06/08/94	240	17900	8.60	1.00	0.90	16110	534								12033
06/09/94	241	17900	8.30	1.00	0.87	15513	535								12085
06/10/94	242	17900	8.50	0.60	0.87	15513	548								12137
06/11/94	243	17900	8.70	1.00	0.70	12530	694								12188
06/12/94	244	17900	7.70	0.50	1.03	18497	416								12240
06/13/94	245	**16060**	9.80	1.60	0.97	15525	631	5860	5290	2830	11861	570	66.9	9.7	12292
06/14/94	246	16060	9.20	0.80	1.13	18201	505								12343
06/15/94	247	16060	8.20	1.00	0.83	13383	613								12395
06/16/94	248	16060	9.10	0.70	0.92	14722	618								12447
06/17/94	249	16060	7.00	1.05	0.77	12313	569								12498
06/18/94	250	16060	1.20	0.55	0.80	12848	93								12550
06/19/94	251	16060	5.50		0.80	12848	428								12602
06/20/94	252	**18700**	9.70	1.05	1.03	19168	506	7730	4980	2140	9072	2750	54.0	35.6	12653
06/21/94	253	18700	8.50	1.00	1.22	22752	374								12705
06/22/94	254	18700	9.80	1.60	1.25	23375	419								12757
06/23/94	255	18700	9.20	1.15	1.35	25245	364								12808
06/24/94	256	18700	8.90	1.30	1.28	23998	371								12860
06/25/94	257	18700	8.80	1.40	1.25	23375	376								12912
06/26/94	258	18700	9.70	1.05	1.25	23375	415								12963
06/27/94	259	**21400**		1.30	1.08	23183		9800	10000	3600	8164	-200	45.4	-2.0	13015
06/28/94	260	21400		0.90	1.17	24967									13067
06/29/94	261	21400	9.80	1.30	1.37	29247	335								13118
06/30/94	262	21400	10.30	1.90	1.50	32100	321								13170
07/01/94	263	21400	6.30	1.30	1.47	31387	201								13222
07/02/94	264	21400	10.40	1.20	1.15	24610	423								13273
07/03/94	265	21400	10.30	0.95	1.15	24610	419								13325
07/04/94	266	21400	10.40	1.30	1.03	22113	470								13377
07/05/94	267	**19355**	6.10	0.85	1.18	22903	266	6970	6970	3100	13770	0	66.4	0.0	13428
07/06/94	268	19355	9.80	1.40	1.13	21936	447								13480
07/07/94	269	19355	6.70	1.15	1.32	25484	263								13532
07/08/94	270	19355	11.40	1.40	1.18	22903	498								13583
07/09/94	271	19355	11.30	1.00	1.20	23226	487								13635
07/10/94	272	19355	2.00	1.20	1.27	24516	82								13687
07/11/94	273	**21200**	12.40	1.60	1.20	25440	487	10000	9200	4400	9993	800	50.0	8.0	13738
07/12/94	274	21200	10.50	0.80	1.20	25440	413								13790
07/13/94	275	21200	6.50	1.20	1.07	22613	287								13842
07/14/94	276	21200	9.20	1.20	1.13	24027	383								13893
07/15/94	277	21200	11.00	1.00	1.23	26147	421								13945
07/16/94	278	16520	12.70	1.50	1.10	18172	699								13997
07/17/94	279	16520	2.80	0.80	1.20	19824	141								14048
07/18/94	280	**16520**	10.00	1.30	1.10	18172	550	7870	6880	1380	12782	990	61.9	12.6	14100
				1.20											

			System A												
	Period	COD In mg/l	gas L	effluent (Q) L	3dAvgQ L	AvgCOD load mg/d	gas/AvgCODload mLgas/gCODload	COD A1 mg/l	COD A2 mg/l	COD A3 mg/l	COD In-A1 mg/l	COD A1-A2 mg/l	%removal In to A1	%removal A1 to A2	VSS mg/l
mean	day 133-143	14229	15.84	2.33	2.32	33038	491	2622	2658	1783	11621	-36	81.6	-1.7	7524
mean	day 144-167	10619	15.19	2.30	2.29	24007	630	4010	3223	2658	6046	788	60.6	16.5	7875
mean	day 173-204	30009	14.65	1.46	1.46	43631	333	11788	9035	6375	14634	2753	57.4	24.4	9398
mean	day 205-251	17747	6.32	0.94	0.96	16957	387	6778	6314	3654	11460	464	62.1	4.8	11465

mean	day 252-280	19786	9.06	1.21	1.21	23942	386	8660	8263	3120	11177	398	55.9	4.6	13377

			System B												
DATE	DAY	COD In mg/l	gas L	effluent L	3dAvgQ L	AvgCOD load mg/d	gas/AvgCODload mLgas/gCOD	COD B1 mg/l	COD B2 mg/l	COD B3 mg/l	COD In-B1 mg/l	COD B1-B2 mg/l	%removal In to B1	%removal B1 to B2	VSS mg/l
02/21/94	133	**14474**	8.65	2.80	2.10	30395	285								18966
02/22/94	134	14474	14.30	1.40	2.70	39080	366								19068
02/23/94	135	14474	4.50	3.90	2.95	42698	105								19169
02/24/94	136	14474	13.40	3.55	2.68	38839	345								19270
02/25/94	137	14474	25.00	0.60	2.05	29672	843								19371
02/26/94	138	14474	20.20	2.00	1.45	20987	962								19473
02/27/94	139	**13935**	19.70	1.75	2.50	34838	565	2090	1858	1316	12384	232	85.6	11.1	19574
02/28/94	140	13935	25.50	3.75	2.32	32283	790								19675
03/01/94	141	13935	14.00	1.45	2.67	37160	377								19776
03/02/94	142	13935	17.70	2.80	2.08	29031	610								19878
03/03/94	143	13935	22.50	2.00	2.32	32283	697								19979
03/04/94	144	**9302**	5.10	2.15	2.12	19689	259	1935	2084	1860	12059	-149	86.2	-7.7	20080
03/05/94	145	9302	13.50	2.20	2.23	20774	650								20181
03/06/94	146	9302	14.10	2.35	2.37	22015	640								20283
03/07/94	147	9302	15.00	2.55	2.93	27286	550								20384
03/08/94	148	9302	12.30	3.90	2.48	23100	532								20485
03/09/94	149	9302	12.20	1.00	2.47	22945	532								20586
03/10/94	150	9302	13.00	2.50	2.10	19534	665								20688
03/11/94	151	10450	16.60	2.80	2.57	26822	619								20789
03/12/94	152	10450	14.80	2.40	2.67	27867	531								20890
03/13/94	153	10450	15.40	2.80	2.27	23687	650								20991
03/14/94	154	**10450**	13.20	1.60	2.47	25777	512	2220	2250	1940	7438	-30	77.0	-1.4	21093
03/15/94	155	10450	14.50	3.00	2.43	25428	570								21194
03/16/94	156	10450	14.20	2.70	2.40	25080	566								21295
03/17/94	157	10450	18.60	1.50	2.20	22990	809								21396
03/18/94	158	10450	16.00	2.40	2.33	24383	656								21498
03/19/94	159	10450	23.80	3.10	2.77	28912	823								21599
03/20/94	160	10450	27.80	2.80	2.42	25254	1101								21700
03/21/94	161	10450	22.80	1.35	2.37	24732	922								21751
03/22/94	162	10450	23.70	2.95	2.33	24383	972								21802
03/23/94	163	10450	19.70	2.70	2.68	28041	703								21852
03/24/94	164	10450	24.70	2.40	2.47	25777	958								21903
03/25/94	165	10450	16.00	2.30	2.30	24035	666								21954
03/26/94	166	**16500**	15.90	2.20	2.47	40700	391	3825	3525	2625	6625	300	63.4	7.8	22005
03/27/94	167	16500	26.10	2.90	1.70	28050	930								22056
03/28/94	168	16500	15.90		1.23	20350	781								22107
03/29/94	169	16500	16.10	0.80	0.80	13200	1220								22157
03/30/94	170	16500	12.00	1.60	1.07	17600	682								22208
03/31/94	171	16500	13.00	0.80	1.20	19800	657								22259
04/01/94	172	16500	12.00	1.20	1.13	18700	642								22310
04/02/94	173	33700	15.50	1.40	1.10	37070	418								22361
04/03/94	174	33700	18.63	0.70	0.87	29207	638								22412
04/04/94	175	**33700**	21.60	0.50	1.10	37070	583	4300	2600	1700	12200	1700	73.9	39.5	22462
04/05/94	176	33162	23.25	2.10	1.43	47532	489								22513
04/06/94	177	32623	28.30	1.70	1.75	57090	496								22564
04/07/94	178	32085	20.20	1.45	1.32	42245	478								22615
04/08/94	179	31546	16.30	0.80	1.02	32072	508								22666
04/09/94	180	31008	23.50	0.80	1.50	46512	505								22717
04/10/94	181	30469	16.50	2.90	1.85	56368	293								22767
04/11/94	182	29931			2.35	70338									22818

04/12/94	183	29392	21.25	1.80	1.85	54375	391								22869
04/13/94	184	28854	25.20	1.90	2.07	59632	423								22920
04/14/94	185	28315	23.50	2.50	2.07	58518	402								22971
04/15/94	186	27777	22.40	1.80	2.07	57406	390								23022
04/16/94	187	27238	22.70	1.90	2.07	56292	403								23072
04/17/94	188	**26700**	20.00	2.50	2.03	54290	368	10800	6600	5200	19599	4200	64.5	38.9	23123
04/18/94	189	26700	22.80	1.70	2.03	54290	420								23174
04/19/94	190	26700	22.80	1.90	1.80	48060	474								23225
04/20/94	191	26700	23.10	1.80	1.88	50285	459								23276
04/21/94	192	26700	23.00	1.95	1.95	52065	442								23327
04/22/94	193	26700	25.00	2.10	2.02	53845	464								23377
04/23/94	194	30600	25.20	2.00	2.00	61200	412								23428
04/24/94	195	30600	24.60	1.90	1.93	59160	416								23479
04/25/94	196	30600	23.20	1.90	1.97	60180	386								23530
04/26/94	197	**30600**	26.00	2.10	1.92	58650	443	12600	10600	8300	15080	2000	54.5	15.9	23581
04/27/94	198	30600	17.10	1.75	1.95	59670	287								23632
04/28/94	199	30600	19.50	2.00	1.45	44370	439								23682
04/29/94	200	30600	13.10	0.60	1.23	37740	347								23733
04/30/94	201	30600	7.30	1.10	0.89	27336	267								23784
05/01/94	202	30600	4.20	0.98	1.02	31212	135								23835
05/02/94	203	30600	4.20	0.98	0.97	29682	141								23886
05/03/94	204	30600	3.00	0.95	0.94	28866	104								23937
05/04/94	205	**19800**	3.50	0.90	0.92	18150	193	9900	4950	4570	20700	4950	67.6	50.0	23987
05/05/94	206	19800	4.85	0.90	0.90	17820	272								24038
05/06/94	207	19800	4.85	0.90	0.87	17160	283								24089
05/07/94	208	19800	5.00	0.80	0.80	15840	316								24140
05/08/94	209	19800	6.90	0.70	0.80	15840	436								24191
05/09/94	210	19800	6.40	0.90	0.83	16500	388								24242
05/10/94	211	19800	7.10	0.90	0.90	17820	398								24292
05/11/94	212	19800	7.10	0.90	0.90	17820	398								24343
05/12/94	213	19800	8.30	0.90	0.93	18480	449								24394
05/13/94	214	19800	8.40	1.00	0.90	17820	471								24445
05/14/94	215	19800	6.40	0.80	0.85	16830	380								24496
05/15/94	216	19800	13.00	0.75	0.77	15180	856								24547
05/16/94	217	19800	7.90	0.75	0.87	17160	460								24597
05/17/94	218	**16650**	5.80	1.10	0.92	15263	380	5200	3900	2300	17312	1300	76.9	25.0	24648
05/18/94	219	16650	6.60	0.90	0.90	14985	440								24699
05/19/94	220	16650	6.60	0.70	0.87	14430	457								24750
05/20/94	221	16650	2.90	1.00	0.60	9990	290								24801
05/21/94	222	16650	7.50	0.10	0.72	11933	629								24852
05/22/94	223	16650	7.50	1.05	0.65	10823	693								24903
05/23/94	224	16650	8.50	0.80	0.92	15263	557								24953
05/24/94	225	16650	8.10	0.90	0.80	13320	608								25004
05/25/94	226	16650	11.90	0.70	0.87	14430	825								25055
05/26/94	227	16650	1.80	1.00	0.90	14985	120								25106
05/27/94	228	16650	8.50	1.00	0.97	16095	528								25157
05/28/94	229	16650	8.10	0.90	1.10	18315	442								25208
05/29/94	230	**17400**	6.50	1.40	1.03	17980	362	4600	4600	3100	12787	0	73.5	0.0	25258
05/30/94	231	17400	1.00	0.80	1.10	19140	52								25309
05/31/94	232	17400	8.60	1.10	1.03	17980	478								25360
06/01/94	233	17400	9.10	1.20	1.07	18560	490								25411
06/02/94	234	17400	8.50	0.90	1.17	20300	419								25462
06/03/94	235	17400	7.40	1.40	0.87	15080	491								25513
06/04/94	236	17400	9.20	0.30	1.03	17980	512								25563

06/05/94	237	17400	8.80	1.40	0.90	15660	562									25614
06/06/94	238	**17900**	8.50	1.00	1.07	19093	445	5300	4300	3100	11892	1000	69.2	18.9		25665
06/07/94	239	17900	8.80	0.80	0.93	16707	527									25716
06/08/94	240	17900	8.10	1.00	0.93	16707	485									25767
06/09/94	241	17900	8.20	1.00	0.98	17602	466									25818
06/10/94	242	17900	8.20	0.95	0.95	17005	482									25868
06/11/94	243	17900	8.60	0.90	0.93	16707	515									25919
06/12/94	244	17900	8.40	0.95	0.92	16408	512									25970
06/13/94	245	**16060**	9.60	0.90	0.93	14989	640	5100	4250	570	12592	850	71.2	16.7		26021
06/14/94	246	16060	8.90	0.95	0.93	14989	594									26072
06/15/94	247	16060	9.00	0.95	0.93	14989	600									26123
06/16/94	248	16060	9.60	0.90	0.93	14989	640									26173
06/17/94	249	16060	9.40	0.95	0.85	13651	689									26224
06/18/94	250	16060	6.90	0.70	0.78	12580	548									26275
06/19/94	251	16060	9.80	0.70	0.92	14722	666									26326
06/20/94	252	**18700**	11.80	1.35	1.13	21193	557	6810	5290	1020	10039	1520	59.6	22.3		26377
06/21/94	253	18700	11.00	1.35	1.35	25245	436									26428
06/22/94	254	18700	11.20	1.35	1.28	23998	467									26478
06/23/94	255	18700	9.30	1.15	1.22	22752	409									26529
06/24/94	256	18700	9.80	1.15	1.15	21505	456									26580
06/25/94	257	18700	4.40	1.15	1.15	21505	205									26631
06/26/94	258	18700	10.50	1.15	1.25	23375	449									26682
06/27/94	259	**21400**	10.10	1.45	1.23	26393	383	8500	9000	2800	9425	-500	52.6	-5.9		26733
06/28/94	260	21400	12.10	1.10	1.25	26750	452									26783
06/29/94	261	21400	10.40	1.20	1.17	24967	417									26834
06/30/94	262	21400	10.40	1.20	1.20	25680	405									26885
07/01/94	263	21400	10.90	1.20	1.20	25680	424									26936
07/02/94	264	21400	10.50	1.20	1.18	25323	415									26987
07/03/94	265	21400	10.00	1.15	1.18	25323	395									27038
07/04/94	266	21400	10.80	1.20	1.15	24610	439									27088
07/05/94	267	**19355**	9.70	1.10	1.17	22581	430	7160	6970	1550	13567	190	65.5	2.7		27139
07/06/94	268	19355	9.90	1.20	1.15	22258	445									27190
07/07/94	269	19355	10.50	1.15	1.18	22903	458									27241
07/08/94	270	19355	11.20	1.20	1.38	26774	418									27292
07/09/94	271	19355	9.60	1.80	1.30	25162	382									27343
07/10/94	272	19355	11.20	0.90	1.37	26452	423									27393
07/11/94	273	**21200**	11.50	1.40	1.17	24733	465	8000	8400	3600	12016	-400	60.0	-5.0		27444
07/12/94	274	21200	10.60	1.20	1.20	25440	417									27495
07/13/94	275	21200	8.90	1.00	1.10	23320	382									27546
07/14/94	276	21200	10.90	1.10	1.10	23320	467									27597
07/15/94	277	21200	10.60	1.20	1.18	25087	423									27648
07/16/94	278	16520	11.60	1.25	1.18	19549	593									27698
07/17/94	279	16520	7.70	1.10	0.92	15143	508									27749
07/18/94	280	**16520**	10.80	0.40	0.87	14317	754	5510	5900	1570	15105	-390	73.3	-7.1		27800
				1.10												

			System B												
DATE	DAY	COD In mg/l	gas L	effluent L	3dAvgQ L	AvgCOD load mg/d	gas/AvgCODload mLgas/gCOD	COD B1 mg/l	COD B2 mg/l	COD B3 mg/l	COD In-B1 mg/l	COD B1-B2 mg/l	%removal In to B1	%removal B1 to B2	VSS mg/l
mean	day 133-143	14229	16.86	2.36	2.35	33388	540	2013	1971	1588	12221	42	85.9	1.7	19473
mean	day 144-167	10619	17.04	2.44	2.40	25303	675	3023	2888	2283	7031	135	70.2	3.2	21186
mean	day 173-204	30009	19.45	1.63	1.64	48520	401	9400	6188	4943	16895	3213	65.1	36.1	23149
mean	day 205-251	17747	7.54	0.90	0.91	16087	478	5402	4468	2018	12924	934	70.1	16.6	25157

mean	day 252-280	19786	10.27	1.18	1.19	23494	444	7293	7568	2380	12528	-275	62.8	-3.8	27088

Appendix B: Gas composition data from lab System A

Raw A1

DATE	%CH4	%CO2	%H2S	
03/22/94	74.2	34.5	1.28	
04/03/94	66	27.5	1.5	
04/04/94	70.9	29.5	1.72	
04/05/94	66.8	30.2	1.94	
04/06/94	64.8	28.1	1.87	
04/07/94	71.6	31.3	2.68	
04/08/94	61	29.3	2.7	
04/09/94				
04/10/94	65.4	31.8	1.69	
04/11/94	64	29	1.52	
04/12/94	60.1	36.8	2.13	
04/17/94	63.4	35.2	1.51	
04/26/94	60.9	34.2	2.05	
04/27/94	59.7	33.8	2.11	
05/03/94	67.3	28.8	1.37	
05/04/94	64.9	29.4	1.55	
05/10/94	69.8	26.2	1.44	
05/11/94	69.4	26.4	1.44	
05/21/94	74	21.3	0.8	
05/27/94	71.3	23.4	0.85	*
06/03/94	74.1	23.3	0.74	**
06/12/94	74.1	20.8	0.53	**
06/19/94	70	23.3	0.58	**
06/26/94	66.7	26.7	1.34	**
07/04/94	70.7	22.4	0.89	**
07/11/94	67.6	26.9	1.37	**
07/18/94	66.1	24.8	1.22	**
mean	67.5	28.3	1.5	
minimum	59.7	20.8	0.5	
maximum	74.2	36.8	2.7	

* H2S % based on STD run 5/21/94
** H2S % based on STD run 5/12/94
RSD < 2%

Appendix B cont.: Gas composition data from lab System

Raw B1

DATE	%CH4	%CO2	%H2S	%NH3	
03/22/94	76.1	35.1	1.31		
04/03/94	65	26.9	1.58		
04/04/94	72.8	28.6	1.7		
04/05/94	63.5	28.3	1.86		
04/06/94	69	28.4	1.94		
04/07/94	67.9	28.9	2.45		
04/08/94	62.2	28.1	2.57		
04/09/94	66.2	29.5	1.43		
04/10/94	67.5	32.6	1.72		
04/11/94					
04/12/94	64.6	33	1.74		
04/17/94	66.1	32.5	1.37		
04/26/94	60.1	31.9	1.82		
04/27/94	62.3	32.1	1.96	@1ppm	
05/03/94	67.2	27.9	1.34	<0.5ppm	
05/04/94	65.3	30.2	1.6		
05/10/94	73	23.6	1.11	<0.5ppm	
05/11/94	73	23.3	1.03		
05/21/94	67.4	21.5	0.77	<0.5ppm	
05/27/94	74.3	23.6	0.68	@1ppm	*
06/03/94	74.8	22.5	0.68		**
06/12/94	72.9	22.7	0.62	<0.5ppm	**
06/19/94	67.3	27	1.23	<0.5ppm	**
06/26/94	65.8	27.7	1.54	<0.5ppm	**
07/04/94	70	23.6	0.98	<0.5ppm	**
07/11/94	67.8	27.8	1.23		**
07/18/94	65.3	24.7	1.19		**
mean	68.0	27.8	1.4	0.61	
minimum	60.1	21.5	0.6	0.5	
maximum	76.1	35.1	2.6	1	

* H2S % based on STD run 5/21/94
** H2S % based on STD run 5/12/94
RSD < 2%

Appendix C: Modification of natural gas hot water heater

Modification of the natural gas hot water heater to convert from natural gas to biogas involved enlargement of the main gas orifice.

The following equation was used for estimating the required gas orifice enlargement (Jiang *et al.*, 1987):

$$(d_1/d_2) = [(S_1/S_2)^{0.25}][(H_2/H_1)^{0.5}] \quad [21]$$

d = gas orifice diameter (cm)
S = specific gravity of gas
H = energy value of gas (kJ/m^3)
subscript 1 = biogas
subscript 2 = other gases

A sample of biogas from the pilot-scale system was analyzed to determine CH_4 content (approximately 70 %). The existing gas orifice measured 0.9375 in. The required gas orifice size of 0.126 in. was calculated from the above equation using the following information.

CH_4 content = 70 %
d_2 = 0.9375 in.
S_1 = 0.85
S_2 = 0.55
H_1 = 700 Btu/ft^3
H_2 = 1012 Btu/ft^3

The required gas orifice enlargement was also estimated using the gas orifice multiplier for 70 % CH_4 found in Table 1. The modified gas orifice size of 0.124 in. was calculated using the following information.

Orifice multiplier (Table 1) = 1.32
d_2 = 0.9375 in.
d_1 = (0.9375)(1.32) = 0.124 in.

The actual gas orifice modification was carried out using successive enlargements based on drill bit sizes available. At the time the modified hot water heater was initially operated, a sufficient quantity of biogas had not been generated to displace all the nitrogen gas used to pressurize the system. Therefore, the gas in the 120 gallon storage tank was 54 % methane as compared to 70 % methane gas being generated by the

anaerobic reactors. The pilot gas orifice had to be enlarged slightly to obtain a stable pilot flame. The main gas orifice was then enlarged to 0.213 in. to obtain a stable flame. The required gas orifice size will decrease significantly (e.g. 0.124 in.) as the methane content in the storage tank approaches 70 %.

Appendix D: Cost Analysis of Carbon Dioxide Removal by Absorption into Sodium Hydroxide Solution

The estimated cost of CO_2 removal from the biogas was calculated assuming pilot-scale wastewater treatment of 100 gallons per day (gal./day) and 3000 liters of biogas (30 % CO_2) per day (L gas/day). Gas production was estimated based on initial laboratory-scale system gas production of approximately 30 L gas/1 gal. of wastewater treated.

Removal of CO_2 from biogas by absorption of the CO_2 gas into a caustic solution is controlled by the following reactions:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \qquad K = 10^{-1.5} \text{ at } 25^\circ \text{ C}$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \qquad K = 10^{-2.8}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K = 10^{-6.3}$$

$$HCO_3\text{-} \rightleftharpoons CO_3^{2-} + H^+ \qquad K = 10^{-10.3}$$

With the addition of 2 moles of OH^- per mole of CO_2, (or, in effect, the removal of two moles of H^+ per mole of CO_2) the above reactions are forced to the right. The formation of CO_3^{2-} is favored: the result is the transfer of CO_2 from the gas phase to liquid phase.

The removal of CO_2 from biogas using a NaOH solution occurs based on the following reaction:

$$2NaOH + CO_2 \rightleftharpoons Na_2CO_3 + H_2O$$

Based on stoichiometry, two moles of NaOH would be required for every mole of CO_2. Therefore, approximately 3000 grams of NaOH would be require per day, costing approximately $5.00 per day (based on price quote by Allgood Chemical Co.; January 1995).

Appendix E: Cost of materials used for construction of the pilot scale system

Item description:	Price ($):
Masterflex gas/liquid pump (6-600 rpm, L/S, variable speed) 25 psi continuous/40 psi intermittent	495.00
Pump head (quick load; stainless steel rotor)	140.00
Pump tubing (A60G; size 24; 50 ft.)	85.00
Solenoid valve (ASCO 82638232 brass)	56.58
Pressure switch (ASCO SA42D, 0-12 in w.c.)	253.00
Transducer (ASCO TA40A11, 0-12 in. w.c.)	95.50
Carbon steel pipe (S40 stl pipe for H2S columns)	180.80
H2S tester (Smyly; Connelly GPM)	75.00
Mass flow meter (Omega FMA 869-V; 0-5 SLM; N2)	834.00
Power supply (Omega +/- 15 VDC; 200 mA)	95.00
Batch controller (Omega DPF66-A)	435.00
AC noise filter (Radio Shack 26-1365A)	31.34
Gas storage tank (14355 30 in. x 46 in. vertical air receiver; 200 psi)	425.00
Pressure gauge (2.5 in./0.25 in.; lm 0-60 psi)	35.65
Pressure relief valve (3-50 psi)	19.90
Natural gas regulator (Fisher R522 5-6 in. H2O)	56.20
Flash arrester (Scott M85 #55854)	106.00
Hot water heater (30 gal, natural gas)	195.50
Temperature/Pressure relief valve	4.96
Stainless steel tubing (8 ft. x 0.25 in. internal diameter)	28.76
Iron Sponge (2 bushel bag)	13.04
Nitrogen (2 cylinders)	80.00
Total:	$ 3741.23

Appendix E cont.: Cost of materials used for construction of the pilot scale system

Miscellaneous:	No.:	Unit price ($):	
Gas shut-off valves	14	3.00	42.00
Sample valves	5	15.00	75.00
Drain valves	4	3.00	12.00
In-line shut-off valves	6	4.50	27.00
Water heater insulation	3	15.00	45.00
PVC:			
0.5 in. pipe ($/ft.)	50	1.00	50.00
elbows	26	0.20	5.20
T's	7	0.30	2.10
Carbon steel:			
0.5 in. pipe ($/ft.)	20	0.20	4.00
elbows	6	0.50	3.00
T's	11	0.50	5.50
unions	8	2.00	16.00
		Total:	$ 286.80

Appendix F

Gas Production (L/d)

	System A	System B
Period 1		
Minimum	10.10	4.50
25th Percentile	13.05	13.70
50th Percentile	16.30	17.70
75th Percentile	18.55	21.35
Maximum	20.10	25.50
Period 2		
Minimum	4.60	5.10
25th Percentile	12.30	13.95
50th Percentile	14.90	15.65
75th Percentile	19.53	20.48
Maximum	24.10	27.80
Period 3		
Minimum	3.00	3.00
25th Percentile	12.40	16.80
50th Percentile	16.60	22.40
75th Percentile	17.35	23.38
Maximum	21.55	28.30
Period 4		
Minimum	1.20	1.00
25th Percentile	3.80	6.60
50th Percentile	7.40	8.10
75th Percentile	8.50	8.70
Maximum	11.50	13.00
Period 5		
Minimum	2.00	4.40
25th Percentile	8.65	9.90
50th Percentile	9.80	10.50
75th Percentile	10.40	11.00
Maximum	12.70	12.10

Appendix G: Statistical analysis of daily gas production.

System A

Period 1

Mean	15.8364
Standard Error	1.02401
Median	16.3
Mode	19.5
Standard Deviation	3.39625
Variance	11.5345
Kurtosis	-1.1348
Skewness	-0.3724
Range	10
Minimum	10.1
Maximum	20.1
Sum	174.2
Count	11
Confidence Level(0.950000)	2.00702

Period 2

Mean	15.1917
Standard Error	1.12377
Median	14.9
Mode	13.7
Standard Deviation	5.50533
Variance	30.3086
Kurtosis	-0.5655
Skewness	-0.0933
Range	19.5
Minimum	4.6
Maximum	24.1
Sum	364.6
Count	24
Confidence Level(0.950000)	2.20255

System B

Period 1

Mean	16.8591
Standard Error	1.99892
Median	17.7
Mode	NA
Standard Deviation	6.62966
Variance	43.9524
Kurtosis	-0.4374
Skewness	-0.4604
Range	21
Minimum	4.5
Maximum	25.5
Sum	185.45
Count	11
Confidence Level(0.950000)	3.91781

Period 2

Mean	17.0417
Standard Error	1.09347
Median	15.65
Mode	16
Standard Deviation	5.35691
Variance	28.6964
Kurtosis	0.06497
Skewness	0.33075
Range	22.7
Minimum	5.1
Maximum	27.8
Sum	409
Count	24
Confidence Level(0.950000)	2.14317

Period 3

Mean	14.6532
Standard Error	0.92263
Median	16.5
Mode	3.6
Standard Deviation	5.21918
Variance	27.2398
Kurtosis	0.27033
Skewness	-1.109
Range	21.55
Minimum	3
Maximum	21.55
Sum	454.25
Count	31
Confidence Level(0.950000)	1.83725

Period 3

Mean	19.4494
Standard Error	1.18429
Median	22
Mode	4.2
Standard Deviation	6.69936
Variance	44.8814
Kurtosis	0.78586
Skewness	-1.3239
Range	28.3
Minimum	3
Maximum	28.3
Sum	602.93
Count	31
Confidence Level(0.950000)	2.35831

Period 4

Mean	6.31778
Standard Error	0.3962
Median	7
Mode	7.9
Standard Deviation	2.7162
Variance	7.37774
Kurtosis	-0.9213
Skewness	-0.4687
Range	11.5
Minimum	1.2
Maximum	11.5
Sum	284.3
Count	45
Confidence Level(0.950000)	0.7936

Period 4

Mean	7.54468
Standard Error	0.32783
Median	8.1
Mode	8.5
Standard Deviation	2.24747
Variance	5.05111
Kurtosis	1.81607
Skewness	-0.7942
Range	12
Minimum	1
Maximum	13
Sum	354.6
Count	47
Confidence Level(0.950000)	0.64253

Period 5	
Mean	9.05556
Standard Error	0.47305
Median	9.7
Mode	9.8
Standard Deviation	2.54745
Variance	6.48949
Kurtosis	1.27098
Skewness	-1.3975
Range	12.7
Minimum	2
Maximum	12.7
Sum	244.5
Count	27
Confidence Level(0.950000)	0.96088

Period 5	
Mean	10.2724
Standard Error	0.2695
Median	10.5
Mode	10.5
Standard Deviation	1.45133
Variance	2.10635
Kurtosis	9.24767
Skewness	-2.5871
Range	7.7
Minimum	4.4
Maximum	12.1
Sum	297.9
Count	29
Confidence Level(0.950000)	0.52822

VITA

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