

**TASK 1 FINAL REPORT**  
GTI PROJECT NUMBER 20614

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# Technology Investigation, Assessment, and Analysis

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## Acronyms, Symbols, and Conventions

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### Acronyms and Symbols

The following table provides a selected set of acronyms and symbols that are used within this document.

| Acronym/Symbol      | Definition  |
|---------------------|---|
| A2LA                | American Association for Laboratory Accreditation               |
| AAS                 | Atomic Absorption Spectroscopy                                  |
| AFT                 | Applied Filter Technology                                       |
| AGA                 | American Gas Association  |
| AIO                 | All-in-One System   |
| API                 | American Petroleum Institute                                    |
| Btu                 | British Thermal Unit  |
| Ca                  | Calcium   |
| CCX                 | Chicago Climate Exchange  |
| Cd                  | Cadmium   |
| CH <sub>4</sub>     | Methane   |
| CHP                 | Combined Heat and Power   |
| CNG                 | Compressed Natural Gas  |
| CO                  | Carbon Monoxide   |
| CO <sub>2</sub>     | Carbon Dioxide  |
| COD                 | Chemical Oxygen Demand  |
| Cr                  | Chromium  |
| CSFR                | Compression - Scrubbing - Flash - Recovery                      |
| CSTR                | Continuously Stirred Tank Reactor                               |
| Cu                  | Copper  |
| DEA                 | Diethanol Amine   |
| DGA                 | Diglycolamine   |
| DIPA                | Diisopropanol Amine   |
| DOT                 | Department of Transportation                                    |
| EDL                 | Estimated Detection Limit                                       |
| EGSB                | Expanded Granular Sludge Bed                                    |
| EPA                 | Environmental Protection Agency                                 |
| Fe(OH) <sub>3</sub> | Iron(III) hydroxide or hydrated iron oxide or yellow iron oxide |

|                                |   |
|--------------------------------|---|
| Fe <sub>2</sub> O <sub>3</sub> | Iron(III) oxide or ferric oxide or Hematite                 |
| Fe <sub>3</sub> O <sub>4</sub> | Iron (II,III) oxide or magnetite                            |
| FERC                           | Federal Energy Regulatory Commission                        |
| FID                            | Flame Ionization Detector                                   |
| FPD                            | Flame Photometric Detector                                  |
| H <sub>2</sub>                 | Hydrogen  |
| H <sub>2</sub> S               | Hydrogen Sulfide  |
| HDPE                           | High Density Polyethylene                                   |
| He                             | Helium  |
| Hg                             | Mercury   |
| ICP-OES                        | Inductively Coupled Plasma – Optical Emissions Spectroscopy |
| ISO                            | International Organization for Standardization              |
| kPa                            | Kilopascal  |
| LFG                            | Landfill Biogas   |
| LDC                            | Local Distribution Company                                  |
| LDL                            | Lower Detection Limit                                       |
| LNG                            | Liquefied Natural Gas                                       |
| MDEA                           | Methyl Diethanol Amine                                      |
| MDL                            | Minimum Detection Limit                                     |
| MDPE                           | Medium Density Polyethylene                                 |
| MEA                            | Monoethanol Amine   |
| MIC                            | Microbially Induced Corrosion                               |
| MMscf                          | Million standard cubic feet                                 |
| MMSCFD                         | Million standard cubic feet per day                         |
| Mn                             | Manganese   |
| N <sub>2</sub>                 | Nitrogen  |
| NAPIAP                         | National Pesticide Impact Assessment Program                |
| NESI                           | New Energy Solution Inc.                                    |
| NGLs                           | Natural gas liquids   |
| NH <sub>3</sub>                | Ammonia   |
| Ni                             | Nickel  |
| NMVOC                          | Non-methane volatile organic carbons                        |
| NPK                            | Nitrogen-Phosphorus-Potassium Nutrients                     |
| O <sub>2</sub>                 | Oxygen  |

|       |   |
|-------|---|
| PAH   | Polycyclic Aromatic Hydrocarbon         |
| Pb    | Lead                                    |
| PCB   | Polychlorinated Biphenyls               |
| PFR   | Plug-Flow Reactor                       |
| PLC   | Programmable logic controller           |
| ppb   | Parts per billion ( $10^{-9}$ )         |
| ppm   | Parts per million ( $10^{-6}$ )         |
| PSA   | Pressure swing adsorption               |
| RES   | Renewable Energy System                 |
| RL    | Reporting Limit                         |
| RNG   | Renewable Natural Gas                   |
| RTD   | Resistance Temperature Detector         |
| SCADA | Supervised Control and Data Acquisition |
| Scf   | Standard cubic foot                     |
| SEAD  | Shear Enhanced Anaerobic Digestion      |
| SVOC  | Semi-Volatile Organic Compound          |
| TCD   | Thermal Conductivity Detector           |
| TSA   | Temperature swing adsorption            |
| UASB  | Upflow Anaerobic Sludge Blanket         |
| VOC   | Volatile Organic Compound               |

## Conventions

Throughout this document a set of conventions are observed for footnotes and references. Single or multiple superscripted, bracketed numbers, such as <sup>[3]</sup> or <sup>[4,7]</sup>, refer to a numbered reference(s) in the Bibliography. Single or multiple superscripted, unbracketed numbers, such as <sup>7</sup> or <sup>9,10</sup>, refer to a footnote(s), which will be located at the bottom of the page or, more rarely, at the bottom of the next page if crowding is an issue. On which page a footnote appears is decided entirely by MS Word 2007, which was used in the preparation of this document. From time to time, both a footnote and a reference will be designated, viz: <sup>3,[6]</sup> or <sup>[6],3</sup>.

Footnotes, tables, and figures are numbered consecutively throughout the entire document as opposed to sequentially only within a section.

## 1 Executive Summary

---

This report provides a wide range of introductory information on biogas production, principally focused on biogas derived from the anaerobic digestion of dairy manure. The spectrum of material contained herein covers topics from the status of European efforts at biogas production to sampling methods for testing dairy biogas. A number of digester designs are summarized and categorized into those that appear suitable for dairy manure and those that are not, under the proviso that digester and process modifications may make these categorizations soft. Among those technologies that are considered suitable for processing dairy manure, 98% of them in actual use on farms in the U.S. are comprised of plug flow digesters, completely mixed digesters, and covered lagoon digesters. Numerous companies on the market can provide consulting, sales, and a range of services for the design, construction, and operation of biogas plants.

The demographics in dairy farming in the U.S. during the past 35 years have shifted toward larger herd size, a declining number of farms, and an increase in per cow milk production. The EPA estimates that the number of anaerobic digesters currently (2007) operating at livestock facilities in the U.S. is 111. Because herd size is trending upward, the number of dairy farms, for which a digester plant can become cost-effective, is growing at an average rate of roughly 5.36%/yr. Within the U.S., the manure from the roughly 9 million dairy cattle in the U.S. offers a maximum potential methane production of 1.1% of current (2006) national, natural gas usage. An estimate of the practical, effective methane production yield is roughly 0.25% of national, natural gas usage. In Canada, under similar assumptions, the maximum potential methane production is 0.4% of Canadian national production, and a practical expectation is roughly 0.09%. Circumstances in some parts of the U.S. or Canada may determine higher fractional biomethane productions.

Raw biogas from dairy manure is typically 54-70% methane; the remaining portion is mostly carbon dioxide. Trace, but significant, amounts of hydrogen sulfide and other compounds can also be present, and they could have adverse effects. Raw biogas requires sufficient cleanup to increase its methane content. Doing so improves its quality when compared with natural gas and removes constituents harmful to pipeline infrastructure. A number of various technologies and some example companies that provide those technologies are discussed herein. Based on one simple, two-component model of biogas, the endpoint of the cleanup effort lies in a range from 93-99% methane for interchangeability with “average” U.S. natural gas. This range is indicative of the range of cleanup required in the production of biomethane. Available cleanup equipment can achieve methane fractions in the 97-99% range.

The dairy manure that is primary biomass material destined for the anaerobic digestion process is subject to several potential contaminants sources: bedding material, feed, products used at the farm and products/pharmaceuticals used for animals care. Not much information exists in the literature about how these propagate through the manure, and subsequently how they might be present in dairy-derived biogas. Task 2 of this project will provide much needed information on this subject. Aside from the components known to be corrosive to pipeline infrastructure, hydrogen sulfide and carbon dioxide, little is known about how other trace contaminants might impact some components of the natural gas infrastructure.

Within Europe, several drivers are causing countries to increase biomethane production efforts. Among the most important drivers are EU mandates on the usage of renewable fuels and security against the need to import energy. Among those countries about which GTI has obtained information, Sweden and Germany appear to be leaders in the pursuit of their biogas production efforts. The usage of biogas in Sweden is largely targeted for vehicle use. In Germany, the number of biogas plants has grown by an average rate of roughly 24%/yr during the last 17 years.

## 2 Introduction

---

### 2.1 Project Background

Interest in biomethane as an interchangeable product for natural gas has been noted throughout the country due to environmental, political, and economic drivers. Sources of this increasingly popular fuel include landfill waste, wastewater treatment sludge, agricultural waste, food-processing waste, and dairy farming byproducts. Historically, biogas has been used primarily for on-site electrical power generation or other site specific energy needs; however, operators of distribution and pipeline systems are now frequently approached to purchase and/or take delivery of biomethane. Many wish to take advantage of this opportunity to transport and/or distribute a “green product” or renewable energy source but are somewhat reluctant due to limited experience with it. Currently, gas quality specifications only exist for geologically formed natural gas; therefore, many distribution and pipeline operators lack certainty about the quality, quantity, and possible effects of biomethane. Based on the biomass source material, produced biogas may contain constituents and compounds that pose hazards to human health and the environment. In addition, insufficiently cleaned biogas may contain trace or residual compounds that compromise the integrity and operation of gas utilization equipment or the pipeline system. Trace constituents in biogas must be identified, monitored, and removed, prior to introduction into existing supplies to avoid potential problems.

Local Distribution Companies (LDCs) are actively pursuing opportunities to develop and implement “green” gas opportunities and many efforts are underway nationally to develop and implement renewable energy opportunities, in particular biomass conversion. Numerous processes for converting biomass to fuels, power, and energy products exist. Biomass materials include animal, agricultural, and food wastes, wastewater sludge, and landfill constituents. The raw biogas that is produced from an anaerobic digester contains up to approximately 70% methane gas. The bulk of the remaining 30% or more is carbon dioxide, and small percentages or trace amounts of other constituents comprise the remainder of the raw biogas. Some non-methane components may pose a risk to the public, to end use equipment, or to pipeline infrastructure. Alternative fuels, such as biomethane, introduced into the existing pipeline delivery infrastructure must meet gas quality specifications, consist primarily of methane, and be free from extraneous and potentially harmful substances.

Each biomass source may contain varying but specific constituents that require identification and analysis. For instance dairy waste may contain copper sulfate or residual antibiotics typical in the care of dairy cows; agricultural waste may contain pesticide residue; municipal wastewater may contain heavy organics or heavy metals collected in wastewater sludge; landfills may contain a wide variety of organics and inorganics, which, upon biological digestion, may be released into the biogas. Wide spread, publically available and definitive information regarding components, particularly trace constituents and contaminants that may be present in biogas from possible feedstocks or regarding the effectiveness of cleanup technologies in continuously removing these components, is limited.

The quality of geologically-derived natural gas is specified in gas transportation tariffs, as required by the Federal Energy Regulatory Commission (FERC). These

specifications can vary by region and by individual tariff. Biomethane generated through anaerobic digestion of waste biomass is not sufficiently characterized by these tariff provisions. To ensure the acceptance of biomethane as a viable, renewable energy source suitable for introduction with existing natural gas supplies, examination of biomethane quality and practices is necessary.

## 2.2 Project Objectives and Deliverables

In order to address these gas industry concerns, GTI executed an industry-funded, collaborative project where the ultimate objective was to develop a peer-reviewed Guidance Document specific to the introduction of dairy-waste derived biomethane with existing natural gas supplies. The Guidance Document is not prescriptive. Rather it is intended to provide framework for productive discussions regarding biomethane quality. It provides reference and recommendations for the introduction of biomethane from dairy waste digestion with natural gas in existing gas pipeline networks in North America. The Task 3 Guidance Document incorporates information and data gathered as part of Tasks 1 and 2 of the overall project.

Although different source materials may be anaerobically digested for the purpose of biomethane generation, the focus of this project is biogas derived from the anaerobic digestion of dairy manure. The project, entitled *Pipeline Quality Biomethane: North American Guidance Document for Introduction of Dairy Waste Derived Biomethane into Existing Natural Gas Networks*, has three primary objectives:

- (1) To assess and document available domestic and international information to develop a broader knowledge base related to biogas production, gas treatment, gas quality standards, and gas quality test protocols.
- (2) To develop and execute a laboratory-testing program to evaluate raw (prior to cleanup) biogas and post-cleanup biomethane in order to assess gas quality and comparison of this gas to typical pipeline tariff specifications and specific contract specifications.
- (3) To prepare a peer-reviewed *Guidance Document*, with reference to AGA Report No. 4A, Natural Gas Contract Measurement and Quality Clauses and other gas quality reports.

The Task structure and deliverables of the project mirror the primary objectives (1)-(3):

**Table 1: Project Task Structure and Deliverables.**

| Task # | Task Name  | Deliverables   |
|--------|--|--|
| 1      | Technology Investigation, Assessment, and Analysis | A report compiling the information, assumptions, and conclusions related to objective (1). |
| 2      | Laboratory Testing and Analysis                    | A testing and analysis report.   |
| 3      | Guidance Document                                  | A <i>Guidance Document</i> as per objective (3).   |

## **2.3 Objectives of This Report and Target Audience**

The purpose of this report is to meet the set of goals identified in objective (1) of the section [Project Objectives and Deliverables](#). This report will provide important background information for the target audience to whom it is addressed. The target audience consists of representatives from the sponsoring companies who are concerned with:

- The acceptance into pipeline infrastructure of biogas derived from dairy manure.
- The rudiments of how biogas is produced from dairy manure.
- The basics of the cleanup of biogas to produce biomethane.
- Methods of sampling and testing the constituents of biogas and biomethane.



### 3 Biomethane Interchange in Europe

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#### 3.1 Overview

GTI staff personnel and project consultants visited several European countries during March, 2008 in order to assess the status of biomethane interchange with natural gas supplies. Representatives of the natural gas industry were interviewed, including research organizations, local distribution companies, transmission companies, and natural gas refining operations in the countries of Sweden, Denmark, The Netherlands, France, Germany and Switzerland. Information was gathered through interview and dialog exchange. This information was supplemented with supplied documents and presentation materials, in order to provide an accurate account of current biomethane interchange status.

There is no universally agreed upon international technical standard for biomethane but some countries have developed national standards and procedures for general introduction of biofuels, including landfill gas, syngas, etc.<sup>1</sup> Some of these standards are similar to those used in North America; US tariffs appear to be more detailed in characterization of the gas and specify additional parameter requirements. MARCO-GAZ, the technical association of European Natural Gas Industry has adopted a recommendation concerning technical and gas quality requirement for delivery of non-conventional gases such as “biogas”. However, the application of these recommendations has been limited.

Dialog regarding the introduction of biomethane with existing natural gas supplies should take into account the most common application of natural gas use in Europe. Generally, it is perceived that biomethane can be used for all applications which use natural gas as a fuel. Compared to the US, the use of natural gas throughout the European Union (EU) differs. There are four basic applications of natural gas in Europe: production of heat and steam, electricity production/co-generation, vehicle fuel, and production of chemicals. For some of these applications, cleanup or enrichment is not necessary. It is recognized that some applications require an upgraded biomethane product. These applications include upgrade for fuel use (natural gas vehicles) and for gas grid injection. It is strongly perceived that development of upgraded biomethane will result in improving security of energy supplies. In Europe, dependence of natural gas is increasing, while only two-thirds of European gas consumption is covered by gas originating from the EC. Domestic supplies continue to decrease over time.

The country which is most developed in using biomethane alternatively with natural gas is Sweden. As covered below in the following section, the majority of biomethane produced in Sweden is destined for NGV fuel. Interestingly, natural gas was only introduced to Sweden in 1985 and their limited pipeline network consists exclusively of PVC materials. Sweden does not produce natural gas; it obtains North Sea natural gas from Denmark and distributes it up the coastline to customers and industries. In some communities, gas accounts for 20 to 25 percent of total energy consumption. However, documentation produced in 2006 states that only 55,000

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<sup>1</sup> A tabular summary of standards for non-conventional fuel gases in various European countries is contained in reference [90]. Appendices A and B contain subsets of that information.

customers are connected to the grid in total in Sweden. Most of the biomethane produced is used as fuel and the network of fueling stations for NGV vehicles is growing.

There are a wide variety of opinions regarding the application of biomethane as an interchangeable product with natural gas; there are numerous forces which influence enthusiastic reception of this new fuel. Results of the GTI survey work clearly indicate that the bulk of all biomethane used in Europe is destined for application within the area of vehicle fuel (natural gas vehicles, NGVs) and only in particular countries. Other applications include the interchange of biomethane generated specifically from anaerobic digestion of energy crops, rather than animals waste or other animal bi-products (Germany). In the country which dominated in biomethane use (Sweden), the natural gas network is quite new compared to North America and other EU countries and limited in size. Questions regarding biomethane safety are being pursued through joint research programs (multi-national including natural gas companies, universities, industries and independent researchers). Some European natural gas companies are participating with the GTI Guidance Document work, in order to supplement information gathered from existing projects and to derive consensus with the energy industry in North America.

The key drivers for biomethane interchange in the EU are energy independence and environmental mandates to reduce carbon dioxide emissions. The majority of the countries that participated at the conference of Kyoto have come from the EU and emissions reductions have been set forth for each nation. Transport is the sector where the highest increase in biomethane use is predicted to occur. Using current practices of fossil fuel, the European Commission predicts a 50% increase in the emission of greenhouse gases (GHG) in the sector from 1990 to 2010. In the year 2000, GHG emissions increased almost 25% from the 1990 level. Using current industrial and energy practices in the EU, it is expected that 90% of the increase is attributable to the transportation sector. The application of biomethane as an alternative fuel is expected to help here. A fuel directive (2003/30/EC) from the European Commission set targets for replacement of fossil fuels with biomethane. This was followed by the Directive 2003/55/EC which allowed for interchange of comparable gases within the natural gas network. Following EU mandates and as part of a 20/20 directive, nearly 10% of all natural gas will be replaced with biomethane. In some countries, this number will be substantially higher; the Nordic countries are viewed as leaders in this area of environmental development. At the time of this report preparation, over 60% of all vehicles in Sweden are powered by biomethane. However, there is also a call for support schemes to support the use of alternative fuels. While incentives are available in some countries such as Sweden, much of Europe is lagging in adopting appropriate incentives to encourage the use of alternative renewable fuels such as biomethane.

## 3.2 Sweden

### 3.2.1 Status

According to biogas reports for the Swedish Gas Center (SGC) published in 2007 and interviews with personnel responsible for biomethane interchange for E.ON (Europe's largest privately-owned power company), biomethane has been warmly received as an alternative energy source. However, the application of biomethane as an alternative vehicle fuel has dominated, leaving dependence of fossil fuels behind. The country is substantially ahead of other EU nations in the use of biomethane for vehicle fuel. Biogas is considered a second-generation fuel and Sweden has led the way in interchange of biomethane – beyond the required 20% by 2020. By the year 2005, Sweden had already surpassed a goal of 45% replacement of natural gas for transport, and near-term goals focus on an even higher percentage of replacement. Eventually, Sweden would like to be energy independent, with 100% of gas fuels derived from biomethane or other renewable sources. Swedes enjoy a fuel product which is tax-exempt and filling stations are required to provide a biofuel as an alternative to fossil-fuel based petrol. Local regulations also provide incentives; free parking exists for individuals who own NGVs. The number of NGV models available for consumers is increasing, as is the number of cars which use natural gas/biomethane rather than petrol/diesel. However, the direct interchange of biomethane with existing supplies for residential use, etc, is not as prevalent as expected in North America.

### 3.2.2 Key Parameters

Natural gas has only been available in Sweden since 1985 and only in the south western parts of the country; the customer base is quite limited compared with the situation in North America. The natural gas network is remarkably new and consists of a limited PVC network. Currently, nearly 2 TWh of biogas is produced in Sweden at more than 230 facilities. Contribution by sewage treatment facilities dominates, but co-digestion facilities (organic household waste, food industry waste, manure, and energy crops) accounts for a growing share of the total production. Of the 230 biogas plants in operation, only 35 possess biomethane upgrading units and there are 7 biomethane injection sites, of which 4 are on the E.ON. gas pipeline network. Potential biogas production in Sweden is estimated at a theoretical 14TWh per year or ten times greater than the current production rate. However, in Sweden, co-digestion of waste is typical and it is anticipated that more energy crops will be used to increase biogas yield. As with other countries, biogas yield increases substantially when energy crops are converted to biogas (nearly 3 times the energy potential of manure feedstock). Typical use of biogas in Sweden is: combustion of (raw/partially cleaned) biogas for heat, combustion of (raw/partially cleaned) biogas for combined heat and power and cleaned biomethane for vehicle fuel. The cost for upgrading of biogas is 11-25 €/m<sup>3</sup>, and government incentives for the use of biomethane as an alternative to natural gas in NGVs are encouraging development in the biogas sector. According to recent statistics, in 2006, almost 24 million normal cubic meters of biogas were used as vehicle fuel in Sweden, which is equivalent to 26 million liters of petrol. In 2006, more biogas (54%) was sold as vehicle fuel than natural gas for fueling NGVs. It is reported now that over 60% of all vehicles are powered by biomethane. Biomethane as an interchangeable product with natural gas is also an integral part of Sweden's

aggressive program to reduce GHG emissions, as well as supply biofertilizers for agriculture.

### 3.2.3 Path Forward

Sweden intends on increasing the application of biomethane for vehicle fuel, as a replacement to fossil fuels (natural gas, petrol, diesel, etc.). The production potential for biogas in Sweden is 14 TWh, but a substantial portion of this will be destined for uses which do not require stringent upgrade (suitable for interchange with natural gas supplies.) New biogas production and upgrading facilities are being brought on board, with the purpose of bringing biomethane to areas which have been without natural gas availability. This will further augment the network of fueling stations for NGVs. Sweden is highly confident of the quality of biomethane to meet their energy needs and anticipates a growing market in with this alternative, green fuel, using manure, food-grade industrial waste and wastewater treatment sludge as digester influent materials. Landfill gas has not been considered for interchange in Sweden and will probably not be considered due to safety concerns and due to the high costs involved in upgrading it. However, these attitudes may change as technology upgrades become more cost effective.

## 3.3 Denmark

### 3.3.1 Status

According to biogas reports from the International Energy Agency published for 2008 and interviews with personnel responsible for biomethane interchange for DONG Energy (Denmark's premiere energy company which produces, distributes, develops and trades energy – the Danish government holds 73% interest in the company), biomethane has not been used as an interchangeable fuel with existing supplies. All biogas produced is used for electricity generation, heat, or co-generation. Incentives through the Danish government provide additional premiums based upon electricity produced through biogas use. A premium fixed rate for electricity produced through digestion of waste is negotiated and the price is held for up to a ten year time period, after which the price is revisited. Growth in this area of energy production is expected to increase 3-fold by the year 2020, especially in the area of waste co-digestion. DONG Energy, in particular, is a major producer of natural gas for use throughout the Nordic countries. There are no incentives available in Denmark to encourage the upgrade of biogas to biomethane for interchange; *raw biogas* prices hover similarly with natural gas and low-sulfur/no-sulfur diesel fuel. Therefore, the application of biomethane for replacement of vehicle fuel has been lagging versus Sweden. The cost to upgrade raw biogas to a higher quality biomethane, under this system, is not economical. However, due to pressure from the environmental impact of the transport sector, there has been a movement to increase the availability and accessibility of NGVs in Denmark. With low prices for diesel fuels and natural gas, this interchange may begin slowly, but DONG Energy has invested in the NGV network to the southwest in Sweden. At this time, the production of biogas has been in response to waste management pressures on Danish farmers, rather than a solution to energy needs.

### 3.3.2 Key Parameters

Energy production from the digestion of biomass materials in Denmark falls far short of projected potentials. A vast majority of biomass digested is animal waste (manure), with centralized digester processes (linking waste from various local farms) increasing throughout the country. The incentives to produce biogas primarily benefit the farmers; it is often a matter of income and survival, and societal pressures are great. Currently, much manure is trucked to neighboring countries for digestion. Environmental legislation has mandated GHG reduction and better control on environmental quality and odor reduction. Since 1990, there has been a 5-fold increase of biogas production through anaerobic digestion of manure and incentives for electricity production through the combustion of biogas have encouraged the creation of more centralized plants (4 new plants per year are anticipated until the year 2020). However, at present, only 5% of all farm waste is digested for electricity production and biogas contributes 0.5% of Denmark's electrical energy consumption. There is strong movement to concurrently reduce the consumption of energy in Denmark, so that renewable electricity replaces existing supplies, although realistic projections indicate that only a maximum of approximately 5% of present gross consumption can be replaced through burning of biogas. Because of the prices of natural gas currently available in Denmark, the cost to upgrade raw biogas to an interchangeable biomethane product is prohibitive; raw biogas sent to specific combined heat and power (CHP) systems through designated and separate pipeline systems is up to 35% more expensive than using existing natural gas supplies. Therefore, a more decentralized CHP model is proposed for Denmark, so that local power may provide for local networks.

### 3.3.3 Path Forward

Denmark is encouraging the digestion of farm waste through co-digestion processes. The agricultural and environmental advantages for bio-digestion of manure are a motivating force for farmers and new legislation is in place to assist with the costs for such digestion systems. Mandates from the EU have encouraged reduction in GHG emissions (carbon dioxide and methane); this can be achieved more successfully using programs which include biogas production from farm waste. There exists a goal of 100% exchange of fossil fuels with renewable by the year 2100. However, there is a concurrent program in place to reduce overall consumption of energy. Agriculture incentives dominate in the establishment of new biogas plants in Denmark. The production of biogas is viewed as an inexpensive method of reducing carbon dioxide emission over time, as well as achieving numerous agricultural benefits. There are future goals to completely remove and recycle excess nutrients from the waste and use all residuals products from the digestion process as well as develop and incorporate high energy crops to the co-digestion systems.

## 3.4 The Netherlands

### 3.4.1 Status

According to biogas reports from the International Energy Agency published for 2008 and interviews with personnel responsible for biomethane interchange for Gasunie (The Netherlands' premier natural gas transmission company) and Continuon



(a distribution company which services much of The Netherlands), total production of biogas in The Netherlands is approximately 140 Mm<sup>3</sup>/year. Total injection into the natural gas system is approximately 13 Mm<sup>3</sup>/year, from 6 landfill locations and 1 sewage treatment plant. The biogas is injected into low pressure lines, rather than high pressure transmission networks. However, The Netherlands has lagged behind other EU countries in their advancement of an aggressive renewable energy program and nearly 50% of all small-scale bioenergy projects have ceased or have been placed “on hold” (status – end of year 2007). Biogas facilities which are fully operational total 81 and 9 more have been started. As in Denmark, most biogas has been destined for electricity generation specifically. Biogas combustion has been a steady contributor to electricity production in The Netherlands, but growth in renewable electrical energy has been achieved through an impressive increase in wind and co-incineration projects.

### 3.4.2 Key Parameters

Reports and presentations indicate that the majority of biogas currently produced is derived from landfill gas. Projects being proposed or are in development include biogas production from sewage sludge. There is strong pressure to accommodate biogas as a green fuel; however, worries exist about interchange of this product. Gas composition, capacity of the distribution grid, operational handling issues, liability and responsibility are all issues of concern for gas operation and transmission companies in The Netherlands. However, on-going discussions with all parties have ushered in a unique and robust “Green Gas Certification System” which seeks to insure that, in fact, the gas produced is “green” and that safe and reliable biogas can be increasingly produced.

### 3.4.3 Path Forward

There is strong pressure to develop and use biogas, although there are ongoing discussions regarding conditions for safe injection into the existing pipeline network. It is believed that the potential for biogas production is 1.5 billion cubic feet. In The Netherlands, there is an impressive “Green Gas Certification Program”; this Program is aimed at: 1) determining whether the source is sustainable, 2) the amount of green gas produced, 3) ensuring the quality of the biogas over time, 4) registering the certificates, 5) facilitating the trading of the certificates, and, 5) informing all stakeholders. The Green Gas Certification System provides a checks and balances for all key parameters of biogas production, use and trading. Strict rules will concern gas measurement and the system is paid by participants. This program fits well with the EU developed “Green Electricity” Certification System.

## 3.5 Germany

### 3.5.1 Status

The number of biogas production plants in Germany has grown since 1990 (100) to over 3,750 in 2007. The mechanism for financial incentives for electricity production is based upon a program which adds additional return based upon size of plant, biomass selection, technology selection and CHP selection. Biogas production facilities are designed primarily for a combined energy crop and manure

biomass (83%), followed by energy crop biomass (15%) and manure (2%). The use and development of energy crops for biomethane production is highly advanced in Germany; nearly two-thirds of all biogas plants have more than 50% energy crops as input biomass. As with corn for ethanol production in the US, silage maize has increased in cost due to pressure to use energy crops for biomethane production. A mandate to encourage the injection of biomethane with existing supplies has recently been enacted (March 12, 2008) by the German Federal Cabinet. The aim of the Act is to replace natural gas by 10% by the year 2030. This Act regulates the priority of connections to the grid for biomethane suppliers. Also stipulated is that a considerable part of the costs for gas injection (50%) be paid by grid operators and not by biomethane producers (an obligatory connection). Additionally, the grid operator is responsible for the odorization, enrichment, control of gas quality, and all associated interchange costs.

### 3.5.2 Key Parameters

Germany has a standard for biogas injection (DVGW G262) which has been developed in cooperation with the German Water and Gas Association and the German Biogas Association.<sup>2</sup> The standard is based on the German standard for natural gas, DVGW G260. The German standards allow injection of two types of biogas: biogas for limited injection and biogas for unlimited injection. Unlimited injection of upgraded biomethane is allowed if consistent quality parameters are met. One common quality parameter of consideration is the Wobbe index. Variations in the Wobbe index caused by the injection of biomethane must not lead the mixed gas out of specifications. The maximum shift that is allowed in the G260 document is -5.04 MJ/m<sup>3</sup>. The limit is set in order to preserve the safe operation of end use equipment.<sup>[99]</sup> Considerations of limited and unlimited injection are directly linked to the capabilities of the cleanup system, the monitoring systems, and the injection system. For unlimited injection, the greatest constraints are placed on the cleanup system, so that the gas quality parameters of the final, mixed gas are preserved regardless of the amount of biomethane mixed into the system. For limited injection, the greatest constraints are placed on the injection and monitoring systems. In order to deal with large fluctuations in demand, they must be able very reliably to control the amount of biomethane injected so that the mixed gas retains proper specifications. The German standard also requires the biogas producers to present safety data sheets which describe any health hazards in connection with the handling of the biogas.

### 3.5.3 Path Forward

Germany continues to lead efforts in the production of high quality biomethane from energy crops, combined with manure. Incentives are enhanced for smaller biogas operating facilities, to encourage farmers to prevent or eliminate environmental concerns pertaining to farm waste management. The biogas is most often used to generate electricity; however, interchange with existing grid supplies is increasing yearly. Both smaller production facilities are increasing in number as well as large biogas production facilities, with well-developed gas cleanup systems and technology. The German system of incentives is well developed and encourages combined heat and

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<sup>2</sup> The original G262 document is in German and will not be reproduced herein. However, an extract from G262 will be included in Appendix A.

power use. Incentives also consider “methane slip” (the amount of methane which escapes through the cleanup process to the environment). Some of Europe’s largest production facilities are located in Germany, based solely on energy crop conversion. Energy crop biomass selection is being highly developed. For biogas production with energy crops, up to 60% of negative environmental effects are due to crop production itself (fuel utilization). Therefore, energy crops which yield high biomass per acre are being developed and used.

## **3.6 France**

### **3.6.1 Status**

According to biogas reports from the International Energy Agency published for 2008 and interviews with personnel responsible for biomethane interchange for Gaz de France, France is the fifth largest producer of biogas in Europe. However, most of the biogas is destined for heat and electricity production; NGV-quality biomethane will also be produced soon. There exists a French, electricity feed-in tariff for biogas plants whose power is below 12 MW. The price for electricity is the sum total of three components: base rate, efficiency bonus and digestion plant bonus. These serve as incentives for biogas production and use. Constraints on landfill operations and sewage treatment plants have led to increased use of biogas generated from these biomass sources; currently, production of biogas from food processing wastewater treatment facilities (127), landfills (22), and sewage treatment facilities dominate (70). Plants designed to use solid waste are few (4), but more are scheduled to be built. Plants which are supplied with biomass from agriculture (manure) are increasing in number (< 10 existing, but projected to increase to over 50 in the near future). These facilities will provide CHP to local communities. Described in the EU Directive 2003/55/EC, members states should ensure that biogas and gas from biomass or other types of gas are granted non-discriminatory access to the gas network, provided such access is permanently compatible with relevant technical rules and safety standards. In a June 15, 2004 French Decree, grid operators have to define technical requirements for injection to guarantee technical safety, whereas health risk evaluation is under the responsibility of the Ministry in charge of Energy. To this end, a health study is being carried on by a French government agency and conclusions should have been produced by July, 2008. No injection is allowed prior to the health agreement. Once the agreement has been met, it anticipated that more injection will occur and biomethane will be designed for NGV fuel.

### **3.6.2 Key Parameters**

Gaz de France in 2004 produced a de facto standard for gas injection into their grid system. The standards had more strict limitations on oxygen than other EU standards and considered limits on other constituents outside the normal list considered in natural gas evaluation (heavy metals, halogens, etc.) because these components are likely to be present in biogas (or other unconventional gases) and may cause problems.



### 3.6.3 Path Forward

It is apparent that Gaz de France has investigated biogas from a variety of biomass sources and is committed to expanding biogas interchange if it can be produced safely and in accordance to high quality specifications. To this end, Gaz de France has been very involved with the BONGO (Biologicals On Natural Gas Operations) Collective. This group of natural gas transmission and distribution companies, technology corporations, researchers and university personnel has focused their efforts on the specific characteristics which may affect existing pipeline network and human health and environmental safety.

## 3.7 Switzerland

### 3.7.1 Status

According to biogas reports from the International Energy Agency published for 2008 and interviews with personnel responsible for biomethane interchange for Switzerland, most biogas is derived from the digestion of animal waste, sewage sludge, and other biowaste. No landfill gas can be upgraded for grid injection; bio-degradable food waste from households, etc cannot be landfilled. Upgraded biomethane, mainly from industrial plants and sewage treatments plants, is used routinely for NGV fuel. Biogas from agriculture is directly used in CHP for electricity, as electricity produced from renewables is necessarily accepted into the grid and the producer is compensated for production. However, biogas competes with strong renewable products such as wind, solar, and small hydro. The compensations also have a cap value; other compensation bonuses are realized through use of manure and waste from agricultural operations. Other requirements include the use of renewable for process heat, 50% of gross heat produced to be utilized on top of the process heat used and a requirement for energy efficiency of the CHP. There is tax relief for use of biomethane as a NGV fuel.

### 3.7.2 Key Parameters

Biogas is injected into the natural gas grid at several locations in Switzerland. Two different qualities are allowed in the Swiss regulation (G13): gas for limited injection and gas for unlimited injection.<sup>3</sup> The restrictions for gas for unlimited injection are more stringent than those for limited injection. Just as is the case in the German specifications, the impact that the injected gas has on the quality parameters of the final, mixed gas is the driver for establishing the categories of limited and unlimited injection. Landfill gas cannot be accepted into the grid. Biowaste is primarily digested for NGV fuel production (high quality biomethane).

### 3.7.3 Path Forward

Two action plans have been launched in the areas of renewable energy production and energy efficiency. The focus is on efficiency and the substitution of fossil fuels for heat by renewable. Renewables are expected to increase to 50% from 16.2 to 24% total energy consumption by 2020. To this end, the Swiss have enacted a feed-in tariff

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<sup>3</sup> The G13 document is in German and will not be included herein. However, an extract from the G13 specifications is included in Appendix B.

for biomethane and regionalized biomass strategies. Biomass wastes are grouped and plants devoted to the biomass are built. In addition, the use of natural gas vehicles in Switzerland is increasing yearly and biomethane is augmenting natural gas as a fuel of choice.

## 4 The Anaerobic Digestion Process

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### 4.1 Anaerobic Decomposition of Organic Matter

Anaerobic digestion (AD) is the process of degrading organic material through microbial action in an environment lacking oxygen. The degradation process usually occurs in some form of tank, called a digester or reactor. Organic matter, perhaps pretreated by grinding or mechanical hydrolysis, enters the tank and is held there for a predefined, target duration. For systems that are manure-based, this duration ranges from a few days to a few weeks. For systems that are energy crop based, this residence time can range up to several tens of days. During that period, microbial activity breaks down the organic matter, and the resultant gaseous products will contain a large fraction of methane and carbon dioxide, along with trace fractions of other gases. Eventually, the inputs to the digester will have expended its stay in the reactor and will be replaced by newly entering matter in order to continue the degradation cycle. The new organic matter may replace the entirety of the resident matter in batch, or it may replace it semi-continuously; how this occurs depends on the reactor and on the collection and processing of the input source matter.

In the anaerobic digestion process, complex organic matter (source material) is broken down into simpler constituents, directly through the action of microorganisms and in the absence of oxygen. Figure 1 shows an AD process schematic.<sup>4</sup> The AD process proceeds in 4 stages or subprocesses. In the initial stage, *hydrolysis*, bacteria liquefy and break down organic matter comprised of complex organic polymers and cell structures. The end products of this first stage are organic molecules that consist primarily of sugars, amino acids, peptides, and fatty acids. The second stage of the AD process is *acidogenesis*. In this stage, acid-forming bacteria break down the products yielded from the hydrolytic stage. The resultant compounds formed primarily include volatile organic acids, carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), and ammonia (NH<sub>3</sub>). The penultimate step is *acetogenesis*. Bacteria convert volatile organic acids from the previous step into acetic acid (CH<sub>3</sub>COOH) and acetate, CO<sub>2</sub>, and H<sub>2</sub>. In the final stage of the AD process, methanogenic (methane producing) bacteria transform the end results of the acidogenic and acetogenic stages, i.e. CO<sub>2</sub> and acetic acid, into methane (CH<sub>4</sub>). The resultant gas yield consists primarily of CH<sub>4</sub>, CO<sub>2</sub>, and other trace gases.<sup>5</sup>

[1,2,3]

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<sup>4</sup> Poulsen. This schematic is a simplified version of the original contained in this reference. It has been slightly modified according to the discussion in the Marty (1986) reference.

<sup>5</sup> See Section 6 for more detailed information on the constituent fractions of biogas.

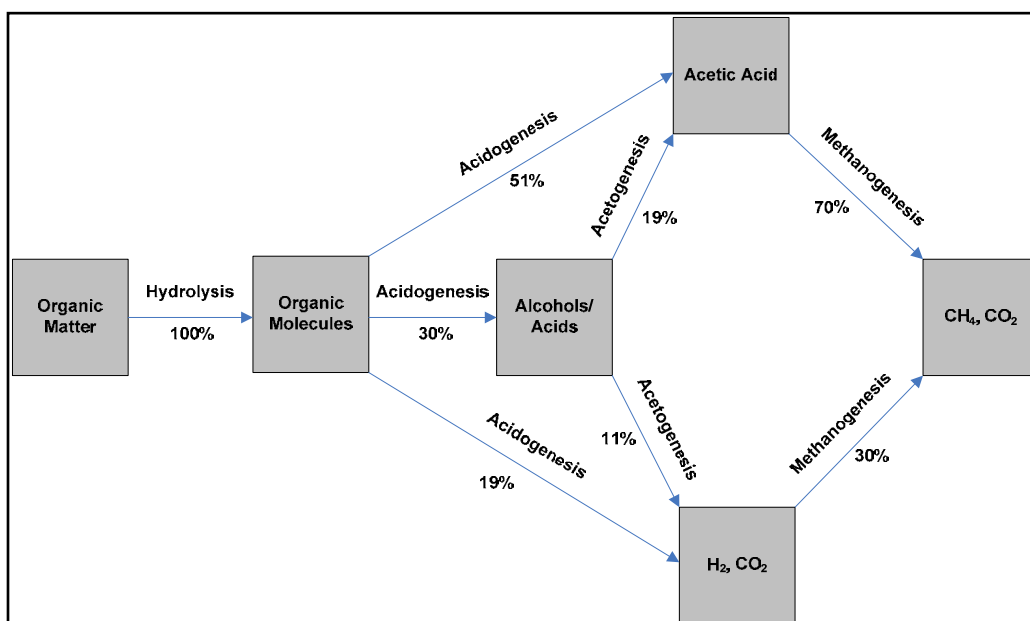


Figure 1: Process Schematic of Anaerobic Digestion. [4,5]

## 4.2 Factors Controlling the Conversion of Waste to Gas

### 4.2.1 Waste Characteristics

As might be expected in a complex system comprised of multiple subprocesses, the efficiency and the rate of anaerobic digestion (AD) are dependent on many variables. Those variables cover the gamut of process parameters necessary for providing the bacterial populations that drive the 4-stage AD process with sufficient source material and for keeping those populations in a hospitable environment. From a typical cow, the rate of manure production is roughly 0.080 lbs(manure)/lb(cow)-day.<sup>6</sup> For a 1400 lb cow, this amounts to roughly 112 lbs/day of manure or, by volume, approximately 13.5 gal/day. The *total solids* (TS) *content* of the manure is the fraction of dry matter contained within this mass. Typically, excreted cow manure is roughly 12.5% total solids content (~14 lb/day from a 1400 lb cow).<sup>7, [1],8,[6]</sup> The total solids content of the manure forms the primary substrate or source material for the AD process. Of the total solids, the *volatile solids* (VS) are the portion of the manure that is available for microbial degradation. The VS *content* usually ranges from 82-85% of the TS content.<sup>[7, 1]</sup> The remaining 15-18% of the total solids are inert. Even among

<sup>6</sup> See: Lorimer. This reference indicates that manure production can range from 0.08 – 0.10 lbs(manure)/lbs(cow)-day.

<sup>7</sup> Published numbers vary slightly on the total solids content. For example, EPA agricultural data (<http://www.epa.gov/oecaagct/ag101/dairymanure.html>) indicate a total solids content for dairy manure of nearly 14%. This amount can also vary seasonally, with the breed of cow, and with the agricultural purpose of the cow (beef vs. dairy). Values of the total solids content can range from 10-15%. See also Lorimer. Lorimer indicates that the distributions of these variables have widths in the neighborhood of  $\pm 30\%$ .

<sup>8</sup> The American Society of Agricultural and Biological Engineers quotes a value of 150 lbs(manure)/cow-day for Holsteins, which comprise 90% of the cow population in U.S. herds. See reference [6].

the VS content, not all constituents are easily degradable. Lignin, a complex chemical polymer that forms part of the intercellular structure of plants, is a substantial component of the VS content of dairy waste, and it is not easily digestible through the AD process.

From a nutrient perspective, the AD process proceeds optimally when the ratios of non-lignin nutrients are in a limited range. The carbon to nitrogen (C:N ratio) optimally falls in the range:  $25 < (C:N) < 32$ .<sup>[8]</sup> Additionally, the ratio of carbon to phosphorus (C:P) should be limited to:  $(C:P) < 187$ .<sup>[1]</sup> Manure, as normally excreted, has a  $(C:N) \sim 10$ .<sup>[1]</sup> In addition, in normal dairy operations, foreign material can also become embedded in the raw manure, and such matter will modify the characteristics of the digestible portion of the source material that eventually gets loaded into a digester. In some instances, materials added (inadvertently or not) will be detrimental as they create an inhospitable environment for the bacterial consortia at work in the digester. In other cases in which sand or silt enters, interrupting the AD process may be required in order to remove obstructions from the digester. In yet other instances, the purposeful addition of alternate source materials to the raw manure can be beneficial. Balancing nutrient ratios and enhancing methane production may result. However, these latter considerations delve into the subject of co-digestion, which is beyond the scope of the present report.

#### 4.2.2 Temperature

The temperature regimes in which anaerobic digester (AD) plants operate are usually divided into 3 categories. The categories are determined by the species of bacteria which operate in each of 3 temperature ranges. *Psychrophilic bacteria* (*psychrophiles*) operate in digesters in a temperature range  $T < 20^{\circ} \text{C}$  ( $68^{\circ} \text{F}$ ). *Mesophilic bacteria* (*mesophiles*) work in digesters in the temperature range of  $20^{\circ} \text{C} < T < 45^{\circ} \text{C}$ ; optimal operation occurs in the range  $35^{\circ} \text{C} < T < 37^{\circ} \text{C}$ .<sup>[1]</sup> Finally, *thermophilic bacteria* (*thermophiles*) live within temperature limits of roughly  $45^{\circ} \text{C} < T < 70^{\circ} \text{C}$ , and their optimal range is  $60^{\circ} \text{C} < T < 63^{\circ} \text{C}$ .<sup>[1]</sup>

The operational characteristics of these digester categories differ and, hence, so do their popularities of usage. Psychrophilic digesters perhaps require the least operational attention. However, because they operate at low temperatures, have the least bacterial activity, and thus offer the least biogas production, they are the least popular category of digester. Mesophilic anaerobic digesters traditionally are the most common. They generally require the least heat to operate, and the exothermic reactions occurring in mesophilic AD processes often allow them to be self-sustaining with heat. Mesophilic digesters tend to operate more stably as the diversity of mesophilic bacteria is larger than that of thermophilic bacteria. Thermophilic digesters offer the advantages of the fastest bacterial growth, the fastest degradation of volatile solids, and, thus, the greatest production rate of biogas. However, because they operate at temperatures quite elevated from ambient temperatures, their parasitic heat requirements can be large. The input energy demand can be especially high during the cold season. Since the water content of the sludge input to the digester is roughly 85%, the large specific heat capacity of water will require much of the energy to bring the digester contents into thermal equilibrium in the thermophilic temperature range.

Digester functioning can be susceptible to ambient temperature conditions. Seasonal and daily temperature changes can affect AD operation. In the case of psychrophilic digesters, outside heat is not usually applied during steady state

operation; however, internal temperatures of these digester can fluctuate with the outdoor temperature. For mesophilic digesters, additional heat may be required in order to maintain their usual operating temperature in the face of external conditions, and for thermophilic digesters, that is certainly true. The rate of bacterial action, the quantity of moisture in the biogas, and the solute fractions of biogas, volatile organics, ammonia, and  $H_2S$  will all depend on the temperature of the contents of the digester.

#### 4.2.3 Acidity vs. Alkalinity (pH)

The description of the AD process in Section 4.1 enumerates four stages or subprocesses. While the description of those subprocesses almost makes them sound as if they operate serially in time, they, in fact, proceed concurrently. While the bacteria transform their food sources, their population densities are changing, and consequently so are the concentrations of their byproducts and food sources. For example, the growth rate of the acidogenic bacteria (acidogens) is greater than that for the methanogenic bacteria (methanogens). Therefore, the concentrations of digestion byproducts change at differing rates. As a result, the system as a whole (bacterial populations, byproducts, and food sources) is a dynamical one, which, in principal, could be modeled via a set of coupled, simultaneous, nonlinear differential equations.<sup>[9,10]</sup>

Thus, for the AD process as a whole to be productive, either the states of the individual subprocesses have to achieve a static equilibrium within themselves and with each other, or they dynamically have to explore a region of stability. In a static equilibrium, favorable conditions for bacterial action remain – ideally – constant. Whether the state of the digester as a whole is able to maintain this equilibrium depends on whether such a state is stable with respect to perturbing influences. Alternatively, if the state of the digester explores a region of stability, the conditions within the digester are changing, but the state of the digester environment evolves in such a way so that it always remains within a favorable range. Outside any region or regions of stability in the digester conditions, one set of bacteria or another finds itself in an inhospitable environment which significantly impacts its effectiveness. A bottleneck to the AD process as a whole usually ensues.

An example of one such variable defining the state of the AD system is the pH of the digester environment. For the cases of the two bacterial populations noted above, each requires different pH environments in order to thrive. Values of  $pH < 6.4$  are toxic to methanogens.<sup>[1]</sup> Their optimal range is:  $6.6 < pH < 7$ .<sup>[2]</sup> The acidogens, on the other hand, have a lower optimal pH range than the methanogens. If acidic compound concentrations increase more rapidly than the methanogens and acetogens can degrade them, then the methanogenic population will find itself in an inhospitable pH environment. The result will be a loss of population and a subsequent reduction in methane production. Thus, a successful AD process requires a balance in production rates between the subprocesses of which it is comprised. Poulsen (2003) quotes, for the AD process, a tolerable operational range of pH values of:  $6 < pH < 8$  and an optimum range of:  $6.7 < pH < 7.4$ .<sup>[4]</sup> Monnet (2003) quotes an operational range of pH as:  $6.4 < pH < 7.2$ , which is largely comparable.<sup>[2]</sup>

#### 4.2.4 Retention Time

Most anaerobic digesters are designed to hold the influent for a defined period of time. The amount of time is called the *hydraulic retention time* (HRT). Usually



measured in units of days, the HRT is the ratio of the volume of the bioreactor tank ( $V_{tank}$  [m<sup>3</sup>]) to the average flow rate ( $Q$  [m<sup>3</sup>/day]) through the tank:

$$HRT = \frac{V_{tank}}{Q} \quad (1)$$

Another, more direct measure of the holding time for the source material in the tank is the *solids retention time* (SRT). It is defined as the ratio of the mass of solids held in the digester to the mass of solids removed per unit time:

$$SRT = \frac{V_{tank}c_d}{Q c_w} = \frac{c_d}{c_w} HRT \quad (2)$$

in which:  $V_{tank}$  = volume of digester tank [m<sup>3</sup>]  
 $c_d$  = solids concentration in digester [kg/m<sup>3</sup>]  
 $Q$  = flow of digester effluent [m<sup>3</sup>/day]  
 $c_w$  = solids concentration in waste effluent [kg/m<sup>3</sup>]

In some types of digesters, the ratio  $c_d/c_w = 1$ , and thus,  $SRT = HRT$ . However, in other digester designs, the concentration of solids in the digester is larger than that in the effluent stream:  $c_d > c_w$ . The result is that  $SRT > HRT$ .

Yet another measure of the time scale on which a digester operates is the *microbial retention time* (MRT). It is defined as the ratio of the microbial mass held in the digester to the microbial mass removed per unit time:

$$MRT = \frac{V_{tank}c_d^m}{Q c_w^m} = \frac{c_d^m}{c_w^m} HRT \quad (3)$$

in which:  $V_{tank}, Q$  = defined as in Equations (1) and (2)  
 $c_d^m$  = microbial mass concentration in digester [kg/m<sup>3</sup>]  
 $c_w^m$  = microbial mass concentration in waste effluent [kg/m<sup>3</sup>].

The values of  $c_d^m$  and  $c_w^m$  are difficult to determine empirically. Since bacteria display a high propensity to adhere to surfaces, it is probably a crude, but reasonable, approximation to assume that a large fraction of the microbes are attached to the surfaces of the solids in the digester. Under such an approximation, if the SRT is increased relative to the HRT, so is the MRT. The MRT tends to follow the changes in the SRT. This provides a rationale for some of the variations in digester system design that incorporate solids feedback and that will be discussed in later sections of this report.

Digester retention times are determining factors in the conversion efficiency of the AD process. The VS content<sup>9</sup> of the input source manure is the substrate that the bacteria convert into biogas. The significance of the retention times, especially the SRT, is that the converted fraction of the VS is a function of SRT. Generally, the longer the retention time, the more bacterial growth that can occur, the more bacterial activity that can occur on the VS content, and the larger the fraction of VS converted to biogas --- *within* a given category of bacteria (psychrophilic, mesophilic, or thermophilic).

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<sup>9</sup> See Section 4.2.1.

Ranging over a variety of bacterial populations, typical periods of growth can span from a fraction of an hour to a day or more. Such growth periods are highly dependent on the environment (pH, temperature, etc.) in which a given bacterial population finds itself. In the complex, dynamic conditions contained within a digester, additional components of the environment also impact bacterial growth. Competition among classes of bacteria, bottlenecks in the availability of food sources, and changes in the digester environment caused by the byproducts of all classes of bacteria found in the tank play a role in slowing the growth rate. The retention times (SRT, HRT, MRT) must, therefore, be matched to the growth rates of the bacteria in the digester tank if maximum solids conversion (production of biogas per unit of solid) is to occur. If the retention time is low compared to the growth time in the digester, then conversion efficiency, and the biogas yield, will suffer. For mesophilic bacteria, these typical retention times are on the order of 15-30 days; for thermophilic bacteria, 12-14 days are characteristic.<sup>[2]</sup>

#### 4.2.5 Loading

Digester loading is a measure of the rate of addition of the concentration of solids contained in the digester tank due to the addition of slurry. The loading ( $L$ ) is typically calculated as:

$$L = \frac{Q c_I}{V_{tank}} = \frac{c_I}{HRT} \quad (4)$$

in which:  $c_I$  = solids concentration of influent to digester [kg/m<sup>3</sup>]  
 $Q, V_{tank}$  = definitions as in Equations (1) and (2).

As is evident from Equation (4),  $L$  has units of [kg/m<sup>3</sup>-day]. Related to the loading rate factor  $L$  are the *organic loading rate* (ORL) and the *volatile solids loading rate* (VSLR). The ORL is a measure of the mass of organic compounds being injected into the digester. ORL is typically determined by measuring the chemical oxygen demand (COD) of the slurry through a standard EPA method;<sup>[11]</sup> it has units of [kg of COD/m<sup>3</sup>-day]. The VSLR is usually measured in [kg/m<sup>3</sup>-day] and is measured by determining the loss of mass (loss of volatiles) when a sample is heated to 550°C.<sup>[12]</sup>

The loading rate is an important control parameter in operating an anaerobic digester. The concentration of food sources for the bacteria in the digester will determine how well the bacterial populations will grow. If a bottleneck slows down the hydrolysis process because input food source concentrations are low, acidogenesis may not proceed as it should. Subsequently, the methanogenic process may also encounter a bottleneck, and biogas production can be decreased or disrupted altogether. On the other hand, overloading may cause hydrolysis and acidogenesis to occur too rapidly. Inhospitable conditions for the methanogenic bacteria may result, and again biogas production can be limited. In addition, overloading can lead to incomplete conversion of solids into biogas, with a concomitant waste of source material for biogas production.

### 4.3 Digester Designs

Utilizing an anaerobic digester for degrading dairy manure entails defining a general set of goals for the reactor plant. On a dairy farm, one purpose is to manage the manure produced from the cows on the farm. Doing so reduces the amount of solid material, reduces odors, and may reduce the pollution issues associated with



large quantities of manure. A second goal is to capture useful liquids and solids from the digester effluent for subsequent use. In going through the digester, the concentration of nutrients (nitrogen, phosphorus, and potassium) in the output solids is slightly increased due to dehydration effects, reduced volume, etc. Either digester effluent is stored for later recycling onto the farmland, or it is processed through a solids-liquids separator. The separated solids are then sold to others who will use them. A third general goal, of course, is to generate energy from the production of the biogas itself. In the U.S., direct use of biogas on-site at a dairy farm often involves producing electrical energy from a generator fueled by biogas. For the production of gas suitable for acceptance into a pipeline, the raw biogas will require, downstream of the digester, additional processing to upgrade it by increasing the methane content and removing unwanted constituents.

In general terms, a digester system contains the components for processing source material in a reactor tank. A given reactor design is a function of the properties of the feedstock that it will be accepting. The mechanical equipment needed for some designs may involve pumps and agitators to stir the digester contents. The specific equipment depends on the properties of the feedstock, particularly its viscosity; the viscosity itself depends on the total solids content, particle size, geometry, and temperature. The design of the digester has to allow the source to flow without becoming clogged. Additionally, the source may contain foreign matter (for example, cow bedding), the presence of which the digester system must be able to address, within some tolerance. Furthermore, when the effluent is emerging from the digester, it contains the soluble products of the AD process, undigested solids, and some portion of the microbial populations contained within the digester. Variations in process design attempt to overcome issues related to the solids retention time (SRT) and the microbial retention time (MRT).

Further process considerations include, of course, the costs of a digester system. The costs include the feedstock costs, system capital costs, and operations costs. In some cases, digester owners may pay for feedstocks that are known to generate high volumes of biogas. If feedstock costs are high, then obtaining the most biogas yield from the source material is probably the paramount issue so that input is not wasted. Such a goal implies longer solids retention times and longer microbial retention times. On the other hand, if feedstock costs are low, then obtaining biogas at a high rate may well be of primary importance. In that case, high loading rates and short HRT are probably the design parameters of focus. These design goals will influence the complexity of the digester design and its attendant system, operational, and maintenance costs. Many designs exist and most are tailored to the farm situation.

While the discussion of AD in previous sections has remained at a general level, the purpose of this document is to provide an understanding of the AD process based on dairy manure as a source material. Toward that end, in the following two sections, digester designs have been categorized into two sets following Burke (2001).<sup>10 [1]</sup> The first set comprises those designs that are not normally appropriate for handling dairy manure; the second contains those designs that usually are. These categorizations, however, are not absolute since myriad variations on reactor and process design are

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<sup>10</sup> Fannon (1987) categorizes reactor design into 3 sets, A-C. The design goal that distinguishes these sets is the relationship between the microbial, solids, and hydraulic retention times. In addition, Fannon breaks down some of his reactor examples, but not comprehensively, by the solids content of the input feed.

possible. A reactor type that may not have usual application to digesting dairy manure may, under a given set of design and/or process modifications, become appropriate for doing so. *Detailed evaluation of production efficiencies, process trade-offs, costs, and overall economics of the following designs, or modifications thereof, are beyond the scope of this report.*

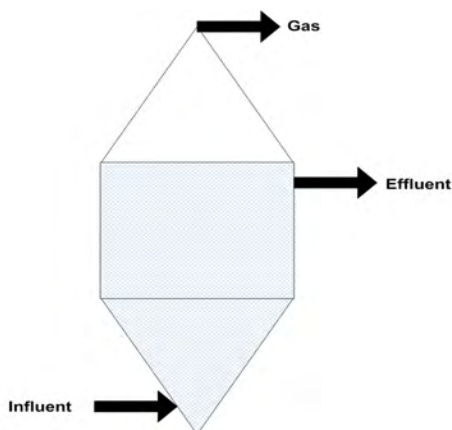
### 4.3.1 Digester Designs Normally Inappropriate for Processing Dairy Manure

#### 4.3.1.1 Fixed Film Reactors<sup>11,12,13</sup>

A fixed film reactor is a modification on a basic digester design. Figure 2 contains a schematic of such a reactor. The influent enters the digester, usually near the bottom of the tank. The tank is filled with a bacterial support medium, which may be comprised of gravel, rocks, charcoal, plastic beads, porous objects, any material which is largely inert to digestion processes and with high surface-to-volume ratio. The media may be oriented in a pattern or randomly. The diluted slurry percolates through the filler medium, emerges near the top of the tank, and the produced gas is available in the headspace of the reactor.

The purpose of providing a support medium of porous surfaces is to enable retention of the operative bacterial populations. A bacterial film accumulates on the media. This preserves the bacteria within the reactor and prevents “washout” in the effluent of this crucial component of the digestion process. Additionally, important bacterial populations tend to separate, with the acidogens near the bottom of the tank and the methanogens farther from the influent. The support medium also helps to separate the solids and produced gases, which can sometimes become attached and trapped by the remaining solids.

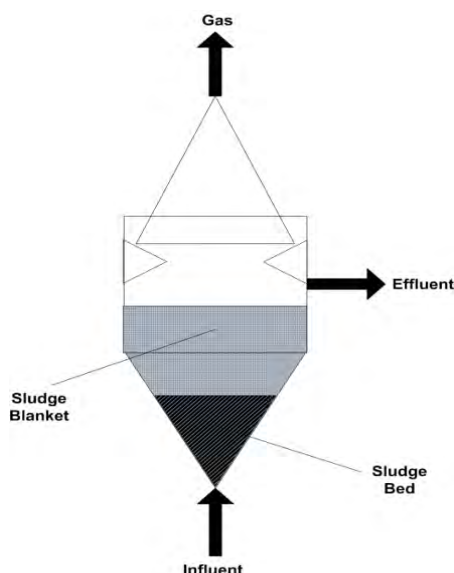
By promoting the accumulation of bacterial films, the fixed film reactor does succeed in increasing the retention time of the microbes. However, it is not suitable for digesting undiluted dairy manure. The typical solids content of dairy manure is rather high for use in such a reactor. The percolation channels can become clogged unless the solids content is diluted substantially. However, this requires additional water to prepare the diluted influent. The fixed film reactor is, however, suitable for transforming the soluble component of any input waste stream. It could, thus, be used to process other input waste streams which are largely in soluble form.



**Figure 2: Schematic of Fixed Film Reactor. The shaded portion of the diagram is the bacterial support medium contained within the reactor.** [Error! Bookmark not defined.]

#### 4.3.1.2 Upflow Anaerobic Sludge Blanket Reactor (UASBR)

The UASBR is a form of stirred reactor. The influent enters the reactor from below and agitates the sludge contained in the tank. This agitation creates 3 zones within the reactor. The bottom zone is the sludge bed. The middle zone, the “sludge blanket”, consists of suspended solid matter. The top zone is the settling or gas-separation zone. The middle zone is continuously stirred by the upward flow of influent through the sludge bed. At the top of the reactor, a gas-solids separator removes the gas trapped within the solids, after which the sludge settles back toward the sludge bed and sludge blanket zones. A process goal of this design is to increase the solids retention time (SRT), the microbe retention time, and to decrease the hydraulic retention time (HRT). This is accomplished with the agitation technique, which allows the fluids to pass through the tank to the effluent while solid matter is retained.



**Figure 3: Schematic of Upflow Anaerobic Sludge Blanket Reactor.** Error! Bookmark not defined.  
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#### 4.3.1.3 Horizontal Baffled Reactor (HBR)<sup>1,11</sup>

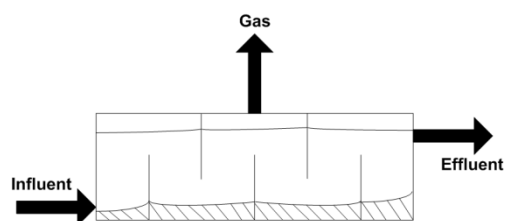
The design of the horizontal baffled reactor is a type of plug flow reactor<sup>12</sup>. Figure 4 contains a schematic. Burke (2001) describes the HBR as a horizontal variation on the UASBR. The digester contains a support medium for bacteria. The support medium, as described for the fixed filter reactor, gives the bacterial population a substrate for attachment. Similarly, the vertical baffles also aid in increasing the microbe retention time; they also improve the solids retention time. In Burke’s version of the digester, the HBR would not be appropriate for wastes, such as dairy manure, that contain a high solids or particulate content. The support medium within the reactor can become clogged with such inputs. It is appropriate for very low solids content or the soluble portion of the source material.

<sup>11</sup> Fannin (1987) calls this reactor a *baffled plug flow reactor*.

<sup>12</sup> See Section 4.3.2.3 for a discussion of plug flow digesters.

On the other hand, in Fannin (1987), the HBR is called a *baffled plug flow reactor*. In Fannin's description, the reactor does not contain a bacterial support medium beyond the baffles themselves. The baffles alone aid in solids and microbial retention. For both variations of reactor described by Burke and Fannin, this is a fairly simple digester. Mechanical mixing is not part of either variation; however, some passive mixing does occur during the production of biogas.

Advantages of this design include its simplicity, and, subsequently, its minimal energy needs. On the other hand, the small energy expenditure implies a lack of control of process parameters. Uniform temperatures inside the reactor will generally be difficult to obtain, especially if cold feedstocks are injected.



**Figure 4: Schematic Diagram of Horizontal Baffled Reactor.** <sup>[Error! Bookmark not defined.]</sup> The cross-hatched portion depicted in the bottom of the tank is a sludge bed within the reactor. The vertical lines represent the baffles within the tank.

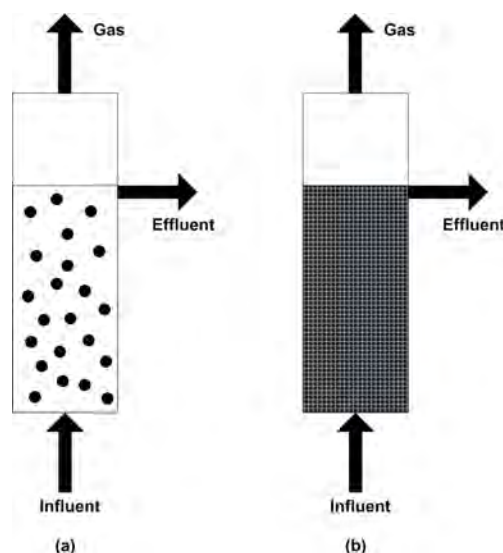
#### 4.3.1.4 Fluidized and Expanded Bed Reactors (FBR, EBR)<sup>13</sup>

The fluidized and expanded bed reactors are variations on each other and variations on the UASB reactor and the fixed film reactor. Their schematics are depicted in Figure 5 (a) and Figure 5 (b). Each contains a support medium of high surface-to-volume ratio to promote the growth of bacterial films, the purpose of which is to increase the microbial retention time with respect to the hydraulic retention time. In the FBR, the support medium itself is not fixed to the structure of the reactor, and the inflowing source material agitates it into suspension in the tank's fluid. In the EBR, the combination of variable medium and/or slower flow velocities of the influent cause the bed to expand but not become suspended. The expansion allows the influent to percolate through the bed. In either case, as the influent flows upward into the reactor, it passes through the support medium. The medium itself may consist of inert material such as sand, or it may consist of reactive material such as carbon.

Any design choices entail trade-offs and benefits. Compared to a fixed film reactor, the surface areas for bacterial attachment can generally be greater. This drives up the microbial retention time. The ability of the support medium to move generally allows this design to process influents of higher solids concentration than the fixed film reactor, as some solid matter will be able to pass through the medium along with the soluble matter and liquids. Still, Fannin (1987) qualifies this reactor as suitable for low solids content (< 5% solids), highly biodegradable feedstock **Error! Bookmark not defined..** Fannin (1987) notes that the disadvantages of this reactor design include its

<sup>13</sup> Fannin (1987). Neither of these reactor types is directly described in Burke (2001).

energy needs to agitate the bed, the lack of separation it provides the acidogenic and methanogenic phases, the washout of support material that can occur, the subsequent maintenance costs due to lost material and to potential pump damage and the potential requirement of a gas-solids separator.

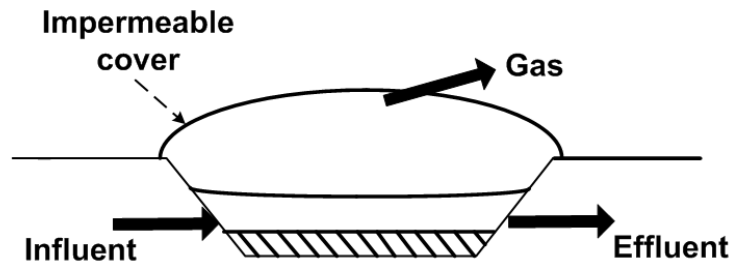


**Figure 5: Schematic diagram of (a) Fluidized Bed Reactor, (b) Expanded Bed Reactor. In diagram (a), the black dots represent the fluidized support medium that is suspended by the upflow of influent.**

## 4.3.2 Digester Designs Appropriate for Processing Dairy Manure

### 4.3.2.1 Covered Anaerobic Lagoons

A covered anaerobic lagoon is perhaps the simplest and least expensive of all digester forms. It is comprised of an earthen pond topped by an impermeable cover that traps biogas as it is produced. In Figure 6, the lagoon is portrayed as an in-ground container with settled solids at the bottom, and a cover over the top for collecting the biogas. Temperature is unregulated, so the contents will be subject to seasonal temperature changes and to the temperature of the influent. The lower temperatures to which this digester equilibrates translate into poorer bacterial growth rates and subsequently diminished rates of production of raw biogas. Usually, explicit mechanical mixing of the contents of the lagoon is not included in its operation. The solids content of the input is typically  $< 2\%$ ,<sup>[13]</sup> so some mixing is naturally caused by the flow of influent and by the rise of biogas to the headspace over the lagoon's contents. Under the assumption that the lagoon is already constructed but has not been covered, the chief advantage of the anaerobic lagoon is its low cost. The attending disadvantage is its low rate of energy production, primarily because process control is nonexistent.



**Figure 6: Schematic Diagram of an Anaerobic Lagoon.** The cross-hatched portion at the bottom of the lagoon represents the settled solids.<sup>[1]</sup>

#### 4.3.2.2 Completely Mixed Digesters (CMD)<sup>14,[1]</sup>

A completely mixed digester is a very common form of reactor. Besides being found on farms, it is found frequently in sewage treatment facilities and in industrial treatment plants. It typically can operate on influents with solids content < 10%<sup>[13]</sup>. Operation of this digester typically occurs in the following sequence:

- input source material
- hold, mix, digest concurrently
- output digester byproducts

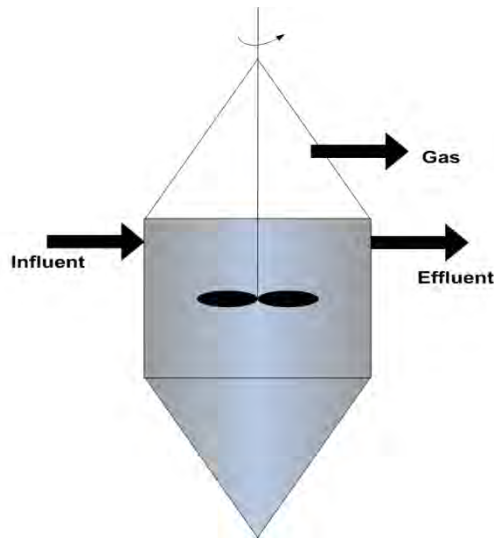
This flow sequence implies that the hydraulic residence time is the same as the solids residence time and the same as the microbial residence time:  $HRT = SRT = MRT$ . If the HRT is less than the bacterial growth period under the conditions within the digester, then conversion efficiency will decrease and the digester may become unstable because bacteria are being washed out too frequently. This requires that fresh influent be utilized for producing more bacteria rather than for converting VS. The production rate declines accordingly.

Process control can be exerted on two fronts: mechanical mixing is explicitly performed, and the contents of the digester are heated. Mixing can be accomplished using pumps to recycle input slurry, stirring (as depicted in Figure 7), or gas recycling. Mechanical stirring is the most efficient in terms of required power per gallon of digester contents.<sup>[1]</sup> Heating of the source material often occurs with a spiral flow heat exchanger, which supplies hot water in thermal contact with the influent.<sup>[1]</sup> Most CMDs operate in the mesophilic temperature range, but Burke (2001) does indicate that some do operate in the thermophilic range.<sup>[1]</sup>

The constant mixing and heating accomplish several design objectives. A more uniform substrate distribution in the tank is obtained. This condition increases the contact between the microbes and the substrate itself. Both the mixing and the heating contribute to uniform temperature conditions within the tank. The mixing itself also minimizes the development of adverse conditions within any region of the reactor. And finally, the mixing inhibits plugging and the trapping of gas within the solids.

<sup>14</sup> Fannin (1987). Fannin calls this digester type a *completely stirred tank reactor (CSTR)*.





**Figure 7: Schematic Diagram of a Completely Mixed Digester.** The schematic depicts a propeller to indicate mixing, but the actual mechanism for achieving mixing may be one of several options.  
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#### 4.3.2.3 Plug Flow Digesters (PFD)<sup>15,[1]</sup>

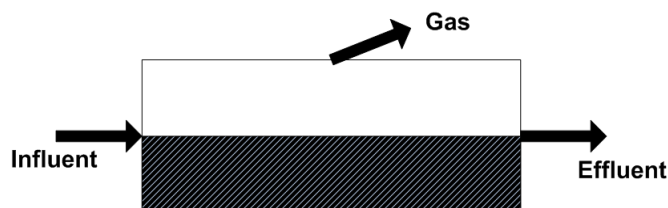
Of similar simplicity to the anaerobic lagoon is the plug flow digester. It consists primarily of a horizontal or vertical tank. As with nearly all digesters, influent enters the tank at one end and effluent emerges elsewhere after a defined retention time; typically,  $15 < \text{HRT} < 20$  days.<sup>[13]</sup> Biogas is drawn from the headspace above the digester contents. As regards process control, explicit, mechanical mixing is typically not employed. However, some small, natural, vertical mixing does occur during gas production and solids settling. Heating of the influent or of the contents of the reactor generally occurs but in isolated cases, it may not be utilized.

The origin of the term “plug flow” is that material enters at one end of the digester and flows through as an unmixed plug, as if it were contained in a pipe. This primarily occurs because the typical solids content of the influent can be 11-14%, which is a normal solids content of cow manure, as excreted.<sup>[13]</sup> This makes the influent viscous and inhibits horizontal mixing during the inflow of source material.

The simplicity of this digester type offers both attendant advantages and disadvantages. It is simple to operate, and its energy needs are smaller than other designs. Its parasitic electrical demand is less than other options, but its heating needs are similar. This makes it attractive for farm use. On the other hand, the lack of vigorous mixing inhibits uniform substrate conditions within the digester. Stratification problems can occur within the reactor tank. Sand will settle to the bottom of the digester and buoyant organic matter will form a floating crust. Unless provision for cleanup is made in the design of the reactor tank, it will need to have sediments removed periodically, or the influent will need to be thoroughly screened to prevent the accumulation of sediment and other foreign material. The disadvantage of such pre-conditioning of the influent is that it complicates the process. It also

<sup>15</sup> Fannin (1987). Fannon calls this a *plug flow reactor*.

inadvertently diminishes the energy production capability by removing source material for conversion to biogas.



**Figure 8: Schematic of a Plug Flow Digester.**

#### 4.3.2.4 Contact Digesters<sup>16,[1]</sup>

The contact digester is a variation on previous digester design themes. The design goal of such a reactor is to preserve solids and bacterial mass within the digester. In other words, an explicit attempt is made, by incorporating process feedback, to increase the solids (and, therefore, the microbial) retention time over the hydraulic retention time. The enhanced retention times are targeted to match the growth periods of the more slowly growing methanogenic population. A design which accomplishes this will be able to increase its loading rate and process source material at a larger rate for a given reactor volume. An increased rate of solids conversion results, of course, in an increased rate of biogas production. All these goals are achieved if the solids and microbial retention times are enhanced relative to the hydraulic retention time.

Figure 9 depicts one example of the processing involved with a contact digester system. The system incorporates a front-end reactor that receives the influent. The digestion process itself occurs in the reactor tank, after which effluent from the reactor flows into a separator. Solids are removed from the reactor effluent and fed back to the digester. This returns microbial mass and unconverted solids to the reactor tank. The front end reactor in Figure 9 is a completely mixed digester; however, this is merely an example. Nearly any digester type could incorporate this feedback mechanism in order to enhance solids and microbial retention times over the hydraulic retention time. Additionally, the reactor could be run under either mesophilic or thermophilic temperature conditions.

The separation of the solids occurs in the unit downstream of the reactor. If the waste is relatively dilute (< 2.5% solids) or if the reactor is a CMD, then gravity settling in a tank will perform reasonably well within a period of a few days.<sup>[1]</sup> A more active separation technique involves screening of the solids content from the reactor tank effluent. As the manure is placed onto a screen, free liquids fall through, and the saturated solids are moved toward the end of the screen for collection. Screens can be stationary, rotating, or vibrating. Even yet more active separation can be deployed through the use of belt presses and centrifugal separators. On a belt press, both gravity drainage and compression are used to remove liquids from solid matter. In a centrifuge, the differing densities of the liquid and solid components of the reactor effluent separate them within the interior holder of the centrifuge itself. The liquid can

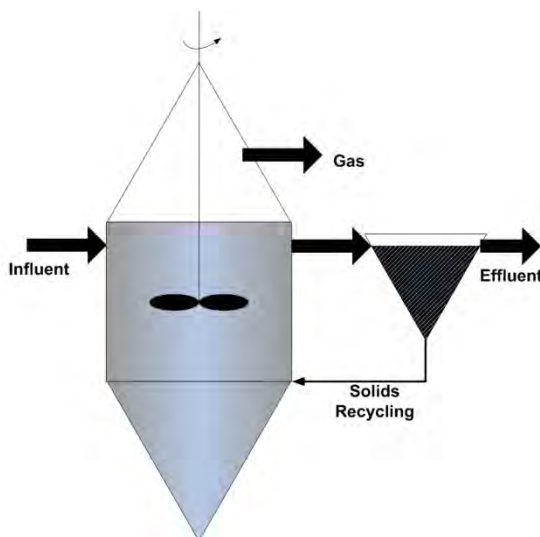
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<sup>16</sup> Fannin (1987). Fannin gives an example of this general digestion scheme and calls it a *completely stirred tank reactor with solids recycling*.



then be extracted by pumping it away from the concentrated solids. The solids are then removed from the holder.

As previously discussed, the additional elements of this process design offer both benefits and challenges. One challenge includes the additional capital, operating, and maintenance costs for the recycler system: the separator equipment and the feedback pump. A second involves the physical attributes of the reactor effluent. Those attributes will, in part, determine the selection of separation equipment. The solids content of the influent and the content of inert, foreign matter normally expected in the influent will determine how much tolerance the separator has to have in handling the reactor output. Another challenge to consider is the impact of any given separation technique on the bacterial populations. Vigorous separation techniques can inhibit bacteria. Since the explicit goal of the feedback of solids into the reactor is to increase the solids and microbial retention times, the separation technique must be selected and operated so that it is not counterproductive of this goal. A final consideration is the additional complexity of the feedback process since additional equipment and additional effluent streams must be controlled.



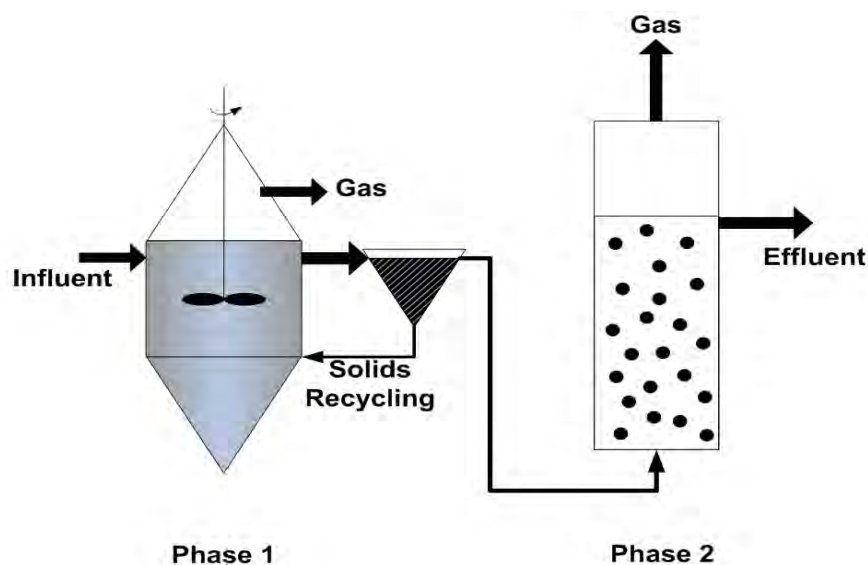
**Figure 9: Example Schematic of a Contact Digester.** This figure depicts a completely mixed digester (CMD) as the input and reactor tank; however, other digester types may also be utilized in this role. [Error! Bookmark not defined.]

#### 4.3.2.5 Phased Digesters

As in the section on contact digesters, phased digestion is a variation on reactor themes previously presented. The overarching concept in a phased digester system is separation of bacterial populations into different reactors that are linked together serially. Figure 10 depicts an example of a two-phased system, after Fannin (1987). The effluent from the first reactor tank (or part of it), becomes the influent to a second reactor tank. The division into distinct reactors may be either “acid-phased” or “temperature-phased”.<sup>[1]</sup> In acid-phased digestion, phase 1 entails the hydrolytic and acidogenic stages of digestion. Phase 2 involves the acetogenic and methanogenic stages that produce CH<sub>4</sub>. In temperature-phased digestion, phase 1 is comprised of a thermophilic stage; phase 2 is a mesophilic stage.

Several benefits are obtainable by performing acid-phased digestion. The parameters that this design attempts to exploit are the differing growth rates of the bacterial populations involved in the digestion process. The methanogens have a longer growth period than the other populations. Retention times set to accommodate the acidogens are too short for the growth period of methanogens. Thus, isolating the methanogens prevents their being washed out from the faster-paced acidogenic phase. Retention times set to accommodate the methanogens will allow acid-buildup, which will inhibit the methanogens themselves. In this case, separating the populations allows more precise control of the environmental conditions (particularly the pH) most hospitable for the differing sets of bacteria. The influent to the phase 2 tank only needs to contain the necessary, soluble byproducts from phase 1 for producing CH<sub>4</sub>. This improves the size efficiency of both tanks. Finally, the CO<sub>2</sub> produced in the first reactor tank can be removed independently of the methanogenic stage. This will result in a higher CH<sub>4</sub> concentration in the biogas output from the second reactor.<sup>[14]</sup> While the benefits of acid-phased digestion are apparent, application to dairy manure processing has been limited.<sup>[15]</sup> However, pilot programs for waste water treatment have been executed, and actual water treatment facilities have been operating with this technology for more than a decade (as of 2008).<sup>[16]</sup> Additionally, successful testing of the acid-phased approach has been conducted on swine manure.<sup>14</sup>

Alternatively, the temperature-phased approach entails a different separation of bacterial populations. In this system, the phase 1 digester operates at thermophilic temperatures, and the phase 2 reactor operates in the mesophilic range. One of the chief advantages of this form of dividing the digestion system is that pathogens are killed in the thermophilic phase. Temperature-phased digestion has been studied for treatment of dairy wastewater,<sup>[17]</sup> installed in actual farm operations,<sup>[18]</sup> and has been employed in the processing of municipal sludge.



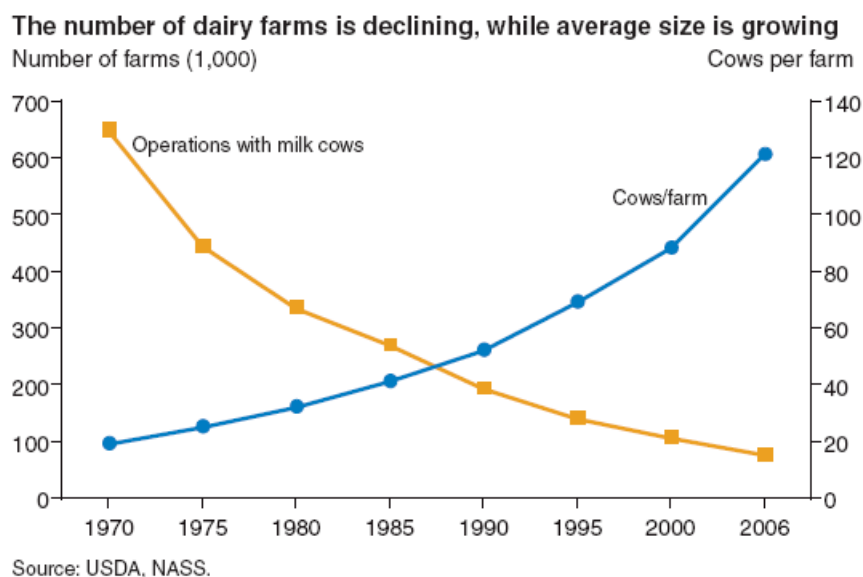
**Figure 10: Example Schematic of a Phased Digester System.** In this example, phase 1 is comprised of a contact digester system involving solids recuperation, and phase 2 is a fluidized bed reactor.<sup>[Error! Bookmark not defined.]</sup> Combinations of other reactor types could be employed in such a system.

## 5 Dairy Farm Practices and Biogas Production Potential

### 5.1 Background and Introduction to Dairy Farm Production in the U.S.

As is the case today, in the mid-nineteenth century, the dairy industry in the U.S. was centered on the family-owned farm. Whatever cows a farmer owned were almost exclusively used for the residents of the farm --- the farmer, his family, and perhaps farm workers, if they were utilized. Advances in the late 19<sup>th</sup> century and early 20<sup>th</sup> century began to transform the dairy industry. During this period, bacteriology was beginning to mature, Pasteur conducted his fundamental work and developed the pasteurization process, the Land Grant Act of 1862 led to state schools of agriculture throughout the U.S. in which a scientific outlook was systematically applied to farming practices, mechanical technology allowed for better separation and manufacturing processes, and the development and application of proper testing began to prevent the spread of tuberculosis via milk.

During the first part of the 20<sup>th</sup> century, the Great Lakes region of the U.S. contained the greatest numbers of dairy cows and herds. This region of the country is well-suited for both the cow and for production of her feed. It was also relatively close to many population centers at a time when refrigeration was not universally available and concerns over spoilage of milk were high. Improvements in transportation infrastructure, vehicles, methods of feeding, caring for, and managing herds, and the improved ability to raise cattle feed using irrigation, all contributed to geographical and demographic shifts in dairy production within the U.S. Not only did new sources of milk production geographically shift to western states in the U.S., but production process improvements led to fewer dairy cows and increased production per cow. As is evident from Figure 11, the number of dairy farms has decreased by roughly a factor of 10 in the 36 years from 1970-2006. Concurrently, average herd size has risen by a factor of about 6. Per cow milk production during that period has nearly doubled.<sup>[19]</sup>



**Figure 11: Numbers of U.S. Dairy Farms and Per Farm Average Herd Size vs. Time.<sup>[20]</sup>**

The main “engine” of dairy production is, of course, the cow. Within the U.S., the cow population is dominated almost completely by the Holstein breed. They comprise 90% of the dairy cow population.<sup>[21]</sup> Their approximate weight at maturity is 1500 lbs. The Jersey cow is the 2<sup>nd</sup> largest segment of the dairy cow population; it comprises 7% of the U.S. dairy herd.<sup>[21]</sup> The Jersey cow is a smaller cow, at approximately 1000 lbs., but the composition of its milk is a bit different from that of the Holstein, and it, thus, offers some advantages for ice cream and cheese production. The remainder of the U.S. dairy cow population is comprised of a variety of breeds: Ayshires, Brown Swiss, Guerneys, and Milking Shorthorns. Each of these latter breeds has pros and cons, ranging from the composition of its milk to their adaptability in particular climates to its reproductive capabilities.

The lifecycle of cows in the dairy herd is controlled to optimize each cow for milk productivity. A calf is usually removed from her mother within a day after birth. Heifers (female calves) will receive milk or a milk substitute until weaning at roughly 7 weeks of age. Once she reaches a target breeding weight, usually around 800 lbs, she is bred. If the breeding takes place, she will have her first calf at about 24 months of age. After birth, lactation will begin and will last for about 305 days. Production will then terminate for a period of about 2 months, prior to the next calving. Breeding occurs during the early part of the lactation cycle with the goal of obtaining a yearly calving per lactating cow. The cow will reach full maturity of size at approximately 4 years of age. While the average cow will undergo 2.5 lactation cycles, the tail of the distribution of lactations is longer, and a substantial portion are productive for more cycles. Cows eventually are culled from the dairy herd after their productive lifetime. Among the reasons requiring a cow to be removed from the herd are low production, infertility, mastitis,<sup>17</sup> and lameness.<sup>[21]</sup>

## **5.2 Understanding Production Potential and Dairy Manure**

Section 4 of this report discussed the basic process of anaerobic digestion, some of its governing parameters, and the designs of digesters. Although most of that discussion remained general and often referred to “source material”, “influent”, and “effluent” in broad terms, one purpose of this document is to provide an understanding of anaerobic digestion based on dairy manure as a digester influent for the production of biogas. Accomplishing that objective entails two components: (1) understanding the production potential for biogas that dairy farms possess, and (2) understanding dairy farm practices and how some of those practices influence manure production and composition.

## **5.3 Biogas Production Potential: An Indication of the Scale**

Section 4 describes general characteristics of dairy manure pertaining to its use as an influent to an anaerobic digester. Among those characteristics is the important one of *volatile solids (VS) content* of the manure. The VS comprises about 83% of the total solids in the manure, and they contain those components which are most amenable to digestion in typical retention times of 15-30 days. An important metric regarding the production of biogas is the yield of biogas per unit of VS content, usually measured in [m<sup>3</sup>/kg VS] or [ft<sup>3</sup>/lb VS]. The theoretical maximum methane production from the

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<sup>17</sup> Mastitis is an infection and inflammation of the udder.

destruction of VS is 5.62 ft<sup>3</sup> CH<sub>4</sub>/lb VS consumed.<sup>[1]</sup> Methane fractions typically range from 54-70% of the content of raw biogas.<sup>[18]</sup> Thus, the total volume of raw biogas ranges from approximately 8.03-10.41 ft<sup>3</sup> raw biogas/lb VS consumed.

Based on these raw production numbers, setting a scale for the biogas production potential throughout the United States is possible. North America has over 10 million cattle in dairy farms, 9 million of which are on the 65,000 dairy farms of the United States.<sup>[22]</sup> In approximate terms, this number of U.S. dairy cattle will produce roughly 1 x 10<sup>9</sup> lbs of manure/day.<sup>[19]</sup> This amounts to 1.1 x 10<sup>8</sup> lbs of VS/day, based on a total solids content of manure of 12.5% and VS content of 83% of solids. The production potentials of this source material are 2.18 x 10<sup>11</sup> ft<sup>3</sup>/yr (0.218 Tcf/yr) of CH<sub>4</sub>. For comparison with recent natural gas usage, in 2006 the consumption of natural gas in the United States amounted to 19.2 Tcf/yr.<sup>[23]</sup> Thus, averaged throughout all of North America, the production potential of methane from anaerobically digested dairy manure alone is roughly 1.1% of current natural gas usage in the United States. Local and regional variations of potential CH<sub>4</sub> production via AD will exist and may be higher than this figure. These potential values are, however, maxima when considering the U.S. as a whole. Their validity rests on assuming 100% efficiency in usage of all dairy cattle, 100% efficiency in manure collection and its timeliness (so that VS content is not substantially reduced through evaporation and degradation), a 100% conversion of VS content, and a 100% duty factor in operation of digester facilities. Because conditions of such high efficiency are almost surely impossible to obtain, these potential values represent a snapshot of an absolute maximum biomethane production from dairy manure alone.

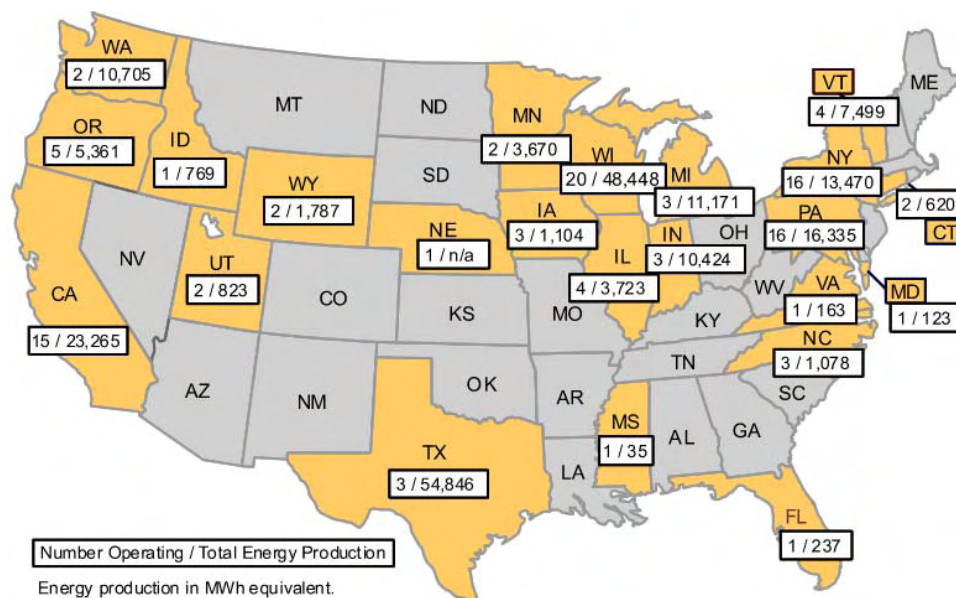
The U.S. Environmental Protection Agency (EPA) has developed a guide to actual market opportunities for the operation of biogas recovery systems.<sup>[24]</sup> The guide examines a number of perspectives related to the environmental benefits, the identification of profitability, and the energy production potential of biogas digester systems. EPA estimates that, as of 2005, approximately 100 systems were in operation or under construction within the U.S. Another 80 systems were in the planning stages. As of 2007, EPA estimates that roughly 111 anaerobic digesters are operating at commercial livestock facilities in the U.S.<sup>[25]</sup> The distribution of these digesters across the United States is displayed in Figure 12. As is evident from the figure, the majority of operating digesters are located on the West Coast, in the Midwest, and in the Northeast of the country. Taken at face value, the numbers of anaerobic digesters operating at such commercial facilities has increased at a rate of roughly 5.36%/yr on average over the past two years.

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<sup>18</sup> See Section 6.

<sup>19</sup> Based on a manure production of 0.08 lb(manure)/lb(cow)-day or 114 lb(manure)/cow-day for a 1400 lb animal. See Section 4.





**Figure 12: Number and Energy Production from Operating Manure Digesters by State.** <sup>[25]</sup>

Beyond the current numbers of systems in operation or planning, EPA has determined that technical feasibility for biogas exists at approximately 2600 dairy operations in the United States. Their assessment is based on several factors: (1) the size of the operation in number of cattle, (2) the method by which manure is managed at the operation, and (3) local energy costs. Because unit costs for construction decrease as the size of a biogas system increases, dairy operations with greater than 500 head of cattle appear to have potential viability. This represents a general guideline. This lower cutoff value is dependent on local factors and costs that may allow operations with smaller herds to economically employ a biogas system. Similarly, simply exceeding 500 head of cattle will not alone ensure economic viability of such a system.

Manure management practice and local energy costs are the remaining parameters in EPA's assessment of the operational and economic viability of a digester system for the production of biogas. Discussion later in this section will focus on manure management issues. Energy costs represent potential economic benefit to the operator of a dairy farm. Dairy farms have typically only used the biogas produced from AD for on-site energy needs: to generate electrical power, to fuel boilers, and to produce hot water. The benefit obtained is in supplanting the need for purchasing some fraction of external energy for farm operations. Additionally, the sale of excess electricity, if it is produced, to local utilities can provide another revenue stream.<sup>20</sup> And finally, greenhouse gas markets for commerce in carbon credits are emerging as another potential revenue stream. The production and usage of biogas reduces methane emissions from dairy manure, which alone contributes a significant fraction (several percent) to U.S. methane emissions. Since methane is a factor of 21 times more potent as a greenhouse gas than carbon dioxide, reduction of the entire methane

<sup>20</sup> Excess power is sold to the grid at most sites that generate electrical power. Curt Gooch, P.E., Senior Extension Associate, Department of Biological and Environmental Engineering, Cornell University, personal communication, 25 August 2008.

emissions fraction from dairy operations is equivalent to 10's of percent reduction in CO<sub>2</sub> emissions.

Realistic production potentials, methane emissions reductions, and numbers of candidate farms for economic viability were estimated using EPA's greenhouse gas (GHG) inventory methodology.<sup>[24]</sup> The estimates are listed by state in Table 2 below. The table contains the top 10 states for potential biogas production and an agglomerated estimate for the remaining 40 states. Only farms with herd sizes exceeding 500 head and with flushed or scraped freestall barns and drylots are included in the table.<sup>21 [24]</sup> The protocol for calculating the biogas production potential used an average methane production rate of 38.5 ft<sup>3</sup>/cow-day as determined from two studies which examined mesophilic, plug-flow digesters with HRT = 20 days.<sup>22 [24,26,27]</sup> Therefore, the protocol intrinsically accounts for efficiency losses in several categories, including incomplete conversion of VS content. As can be seen from the table, California has the potential to produce roughly 18 x 10<sup>9</sup> ft<sup>3</sup>/yr (18 Bcf/yr) of methane.<sup>23</sup> The combined, effective, methane production potential from dairy manure in the United States is in the neighborhood 48.2 x 10<sup>9</sup> ft<sup>3</sup>/yr (48.2 Bcf/yr). This amounts to approximately 0.25% of the usage of natural gas in the United States in 2006.<sup>24</sup> While this represents a small fraction of overall natural gas usage, this estimate incorporates only the potential methane production from dairy manure alone. It is known that methane yield can be significantly enhanced by adding organic biomass, generated either on or off the farm, to the dairy manure. Detailed examination of such issues of other source materials, co-digestion, and their potentials for energy production relative to manure alone are beyond the scope of this report. Additionally, the manure-based production potential of 48.2 Bcf/yr is averaged over the entire U.S. While the production is small on the scale of the entire country, regional production potentials may comprise a larger fraction of regional natural gas usage. Only a direct, regional assessment of biogas production potential could determine whether that is true.

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<sup>21</sup> ....flushed or scraped freestall barns and drylots define manure management and animal housing practices. See later in this section of the report for more details.

<sup>22</sup> Recall that HRT = *Hydraulic Retention Time*. See Section 4.2.4.

<sup>23</sup> A different production potential of 14.6 Bcf CH<sub>4</sub>/yr is stated for California in: Krich, Ken, Augenstein, Don, et al., *Biomethane from Dairy Waste, A Sourcebook for the Production and Use of Renewable Natural Gas in California*, July 2005, prepared for the Western United Dairymen. The production rate in Krich (2005) is based on an overall, average production rate of 23 ft<sup>3</sup>/cow-day, which is smaller than that used in the *Market Opportunities (2006)* reference. In addition, Krich (2005) also differs from the *Market Opportunities (2006)* reference in sample selection; no cut on herd size is applied to require a minimum ≥ 500 head. So one factor drives the Krich (2005) estimate down from, the other up toward, the estimate in *Market Opportunities (2006)*. The net result lies a bit below the 18.1 Bcf CH<sub>4</sub>/yr estimate of *Market Opportunities (2006)*.

<sup>24</sup> The *Market Opportunities (2006)* document, from which the information in Table 2 is extracted, utilizes a conversion factor for the volume of CH<sub>4</sub> produced per pound of volatile solids different from that used earlier in this section. *Market Opportunities (2006)* performs its calculations with a conversion factor, which is termed B<sub>0</sub>, of 3.84 ft<sup>3</sup>/lb-VS. The corresponding conversion factor, used to calculate the maximum production potential of 0.21 Tcf/yr earlier in this section, is 5.62 ft<sup>3</sup>/lb-VS, after *Burke (2001)*. Putting the *Market Opportunities (2006)* production potential on par with the earlier calculation requires multiplying it by the ratio 5.62/3.84 = 1.46. This would transform the production potential from 48.2 Bcf/yr to 70.3 Bcf/yr or 0.37% of annual natural gas usage in the U.S. in 2006.



**Table 2: Potential for Biogas Production and Methane Emission Reduction.**  
**\*Candidate Farms require >500 cows, and Flushed or Scraped Freestall Barns and Drylots.<sup>[24]</sup>**

| <b>U.S. State</b>   | <b>Number of Candidate Farms*</b> | <b>Methane Emissions Reduction (kton/y)</b> | <b>Methane Production Potential (Bcf/y)</b> |
|---------------------|-----------------------------------|---|---|
| California          | 963                               | 263   | 18.1  |
| Idaho               | 185                               | 61  | 4.0   |
| New Mexico          | 123                               | 62  | 3.9   |
| Texas               | 149                               | 32  | 2.3   |
| Wisconsin           | 175                               | 8   | 2.1   |
| New York            | 157                               | 6   | 2.0   |
| Arizona             | 73                                | 35  | 1.9   |
| Washington          | 122                               | 22  | 1.9   |
| Michigan            | 72                                | 6   | 1.9   |
| Minnesota           | 60                                | 3   | 0.7   |
| Remaining 40 States | 544                               | 75  | 9.4   |
| <b>Total</b>        | <b>2,623</b>                      | <b>573</b>                                  | <b>48.2</b>                                 |

\*Candidate Farms require >500 cows, and Flushed or Scraped Freestall Barns and Drylots.

Obtaining a similar understanding of the scale of potential biogas production in Canada requires examining the distribution of dairy farms and dairy cows within that country. An additional one million dairy cows are located on the 14,660 dairy farms of Canada<sup>[28]</sup>. The distribution of farms throughout the Canadian provinces in 2003-2004 is depicted in Figure 13. Farms are concentrated overwhelmingly in Ontario and Quebec, each province containing, respectively, 33.2% and 47.5% of all Canadian dairy farms. The number of dairy cows by Canadian Province (in 2007) is listed in Table 3. Ontario and Quebec dominate this distribution as well.

Under the same assumptions of biomethane production potential that were applied to U.S. dairy populations, the maximum Canadian methane production potential is 0.024 Tcf/yr; this represents a mere scaling of the U.S. maximum production potential. Compared to the Canadian natural gas production rate of roughly 17 Bcf/day or 6.2 Tcf/yr,<sup>[29]</sup> the maximum methane production potential of dairy manure alone, relative to current natural gas production, is approximately 0.4%. Recall that this value represents a maximum and is based on 100% production efficiencies and duty factors in every phase of the conversion of dairy manure to biogas. Assuming the same scale down factor from ideal to reality of (0.25%/1.1%), as in the U.S. situation, a more realistic production rate of methane from the conversion of dairy manure amounts to roughly 0.005 Tcf/yr or 0.09% of annual Canadian natural gas production.



Figure 13: Number of Dairy Farms and Plants by Canadian Province, 2003-2004. The total number of dairy farms during this period was 16,970, but it has since declined to 14,660 according to the recently published statistics.<sup>[30]</sup>

Table 3: Number of Dairy Cows by Canadian Province, 2007.<sup>[28]</sup>

| Province         | Number of Dairy Cows (Thousands) |
|------------------|----------------------------------|
| British Columbia | 70.0                             |
| Alberta          | 83.5                             |
| Saskatchewan     | 29.0                             |
| Manitoba         | 44.0                             |
| Ontario          | 325.0                            |
| Quebec           | 375.0                            |
| New Brunswick    | 18.8                             |
| Nova Scotia      | 23.5                             |
| Pierre           | 13.0                             |
| Newfoundland     | 6.7                              |
| Total            | 988.5                            |

### 5.3.1 Influences of Dairy Farm Practices on the Composition of Biogas Source Material

The second major influence on biogas production from dairy manure is the quality and quantity of the source material. The quality and contents of the manure have an influence on its capacity for producing biomethane. Operational practices in the dairy farm industry can impact both of these items. How the herd is housed and bedded, what the contents of the cow's diet are, what constituents enter the manure, and how the management of that manure is executed are all practices that potentially affect the manure itself and subsequently may influence the biogas produced from it.

### 5.3.1.1 Dairy Cattle Housing and Bedding

Cow comfort is an important issue affecting the health and well-being of the cow and subsequently her productivity. A comfortable environment helps the cow to maximize its lying time. Increased lying time reduces stress on the animal, reduces the chance of injury, and improves blood flow across the mammary glands. All these factors contribute to maximizing product quality and productivity of the dairy animal.<sup>[31]</sup> Dairy housing design and bedding selection both impact comfort.

Dairy cow housing is also a parameter that will affect the viability for producing biomethane. As will be discussed in a later section, farmstead layout influences the manure management practices. A survey was conducted for the National Agriculture Pesticide Impact Assessment Program (NAPIAP) in 1997 with major farms in New York State.<sup>[32]</sup> One of the survey objectives was to determine how farms house their cattle.

Table 4 through Table 6 show the results of the survey for calves, heifers, and cows, respectively.<sup>25</sup> The survey revealed that calves are typically housed in individual, indoor pens, that heifers are raised in a combination of pasture, indoor pens, and feed barns, and that cows are stored in stanchions. Stanchions are upright bars that restrict cow movement within the stall. From an AD standpoint, indoor pens are desirable because the manure is in a fixed area; manure is easily collected and conveyed by pumps or gravity to a treatment area or to storage. Manure treatment options prior to digestion include solid-liquid separation to remove course manure solids and in some limited cases to remove sand bedding.

The bedding utilized within the housing is important, not only from the viewpoint of cow comfort, but also from the viewpoint of biomethane production. During manure collection, stall bedding material will inevitably be captured with the manure and make its way to the digester. Many different materials are used for bedding. Table 7 shows the results of one survey, based on data from the New York state, under the National Pesticide Impact Assessment Program (NAPIAP). The survey found that the most common bedding materials, from greatest to least common, are straw, hay, wood shavings, and sawdust. The NAPIAP survey bears some similarities to a survey completed a decade earlier in 1987 in the state of Pennsylvania. In that survey, the leading bedding materials were identified as straw (57.2%), sawdust (9.8%), hay (4%), corn stover (1.2%), and combinations of these (27.8%).<sup>[33]</sup> However, farther west in the U.S., sand appears to have a greater incidence of use.<sup>26 [34]</sup>

Sand offers several benefits to the cow as a bedding material. It easily conforms to the cow's contour, it drains well, and being inorganic helps it to reduce the incidence of udder diseases such as mastitis. Larger dairy operations appear to utilize more sand for bedding; one report on a survey in Ohio determined that 22.7% of Grade-A herds with less than 500 head of cattle used sand, 75% of those with greater than 500 head, and 100% of those with greater than 700 head.<sup>[35]</sup>

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<sup>25</sup> *Calves* are, of course, the offspring of cows and between the ages of 0 and 1 year. *Heifers* are cows that are older than 1 year and that have not yet produced any offspring. *Cows* are mature female bovines.

<sup>26</sup> This reference indicates the following fractions of usage of bedding materials in South Dakota: straw – 89.4%, sand – 6.7%, wood chips – 4.7%, shredded paper – 1.6%, corn fodder – 1.6%, none – 1.6%.

**Table 4: Animal Housing for Calves in the State of New York.** <sup>[32]</sup>

| <b>Calf Housing</b> | <b># of Responses</b> | <b>% of All Records (167)</b> |
|---------------------|-----------------------|-------------------------------|
| Indoor Pen          | 104                   | 62.3%                         |
| Combination         | 33                    | 19.8%                         |
| Outdoor Hutch       | 15                    | 9.0%                          |
| Not Applicable      | 7                     | 4.2%                          |
| Indoor Stalls       | 4                     | 2.4%                          |
| Indoor Tie Stalls   | 1                     | 0.6%                          |
| Pasture             | 1                     | 0.6%                          |
| Stalls              | 1                     | 0.6%                          |
| Stanchion           | 1                     | 0.6%                          |
| <b>Total:</b>       | <b>167</b>            |                               |

**Table 5: Animal Housing for Heifers in the State of New York.** <sup>[32]</sup>

| <b>Heifer Housing</b>             | <b># of Responses</b> | <b>% of All Records (167)</b> |
|-----------------------------------|-----------------------|-------------------------------|
| Combination                       | 102                   | 61.1%                         |
| Feed Barns with access to pasture | 22                    | 13.2%                         |
| Indoor Pen                        | 21                    | 12.6%                         |
| Pasture                           | 9                     | 5.4%                          |
| Not Applicable                    | 6                     | 3.6%                          |
| Feed Barns                        | 1                     | 0.6%                          |
| Indoor Stalls                     | 2                     | 1.2%                          |
| Stalls                            | 1                     | 0.6%                          |
| Stanchion                         | 2                     | 1.2%                          |
| Tie-Stalls and Stanchions         | 1                     | 0.6%                          |
| <b>Total:</b>                     | <b>167</b>            |                               |

**Table 6: Animal Housing for Cows in the state of New York.** <sup>[32]</sup>

| <b>Cow Housing</b>                | <b># of Responses</b> | <b>% of All Records (167)</b> |
|-----------------------------------|-----------------------|-------------------------------|
| Stanchion                         | 76                    | 45.5%                         |
| Free-Stall                        | 43                    | 25.7%                         |
| Combination                       | 37                    | 22.2%                         |
| Feed Barns with access to pasture | 3                     | 1.8%                          |
| Not Applicable                    | 4                     | 2.4%                          |
| Tie-Stalls                        | 4                     | 2.4%                          |
| <b>Total:</b>                     | <b>167</b>            |                               |

**Table 7: Bedding Used for Calves in the State of New York.** <sup>[32]</sup>

| Type of Bedding   | # of Responses | % of All Records (167) |
|-------------------|----------------|------------------------|
| Hay               | 51             | 30.5%                  |
| Newspaper         | 1              | 0.6%                   |
| None              | 5              | 3.0%                   |
| Old Hay           | 5              | 3.0%                   |
| Paper             | 7              | 4.2%                   |
| Paper Sludge      | 1              | 0.6%                   |
| Sand              | 3              | 1.8%                   |
| Sawdust           | 28             | 16.8%                  |
| Sawdust plus lime | 1              | 0.6%                   |
| Shredded Paper    | 2              | 1.2%                   |
| Straw             | 74             | 44.3%                  |
| Wood Shavings     | 50             | 29.9%                  |
| <b>Total:</b>     | <b>228</b>     |                        |

### 5.3.1.2 Dairy Cattle Diet and Dietary Supplements

Another essential factor affecting manure composition is the cattle's diet. Cows are herbivores and ruminant animals. They have a complex digestive tract with a stomach partitioned into four sections. The first and largest of these is the *rumen*. In part of the cow's digestion process, it *ruminates* on its food: the cow regurgitates a portion of it from the rumen so that it can be chewed again. This process aids the digestion of fibrous materials, which are mechanically and chemically broken down as the cow grinds its regurgitant. Additionally, the rumen contains micro-organisms, which live symbiotically within the cow. In fact, some of the functionality of the rumen directly parallels the AD process.<sup>27</sup> Just as in that process, micro-organisms break down the cow's feed into volatile fatty acids, which it can directly absorb and utilize as energy.

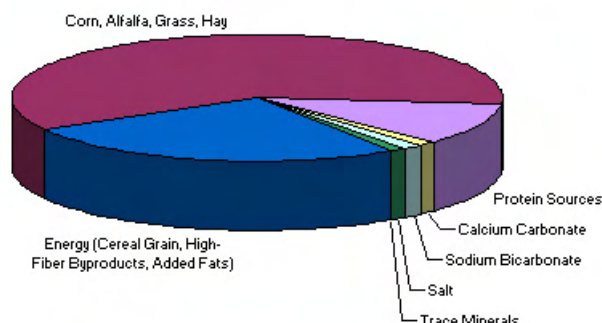
The composition of dairy cattle diet is determined by the functions that the cow performs: reproduction and lactation. Targeted feed composition depends on the cow's state: dry, prepartum, post-partum, targeted milk production levels. It also depends on forage quality and on the cost for purchased feed ingredients. Determining the composition of its diet has reached a stage of high process control so that the maturation of young animals and the milk production of adult animals can be optimized. In fact, modeling of the digestive process has been performed,<sup>[36]</sup> and feed design has been computer-automated.<sup>[37]</sup>

Typical components of cattle diet include forages, cereal grains, high-fiber feeds, fats, protein, and minerals. Forages include, by majority, hay and silage, and in some cases farms also ensile other crops like early cut barley.<sup>28</sup> The typical diet

<sup>27</sup> See Section 4.

<sup>28</sup> *Forage* refers to hay, silage, and crop residues. *Hay* is grasses or legumes that have been cut, dried, and stored for feed. *Silage* is crop matter that has been packed and stored while it is still moist so that it will ferment under anaerobic conditions in, for example, a silo.

for cattle is 25-35 lbs dry matter (DM) per day of forages, 7-12 lbs DM per day of cereal grains, 1-5 lbs DM per day of high-fiber byproduct feeds, 0-1 lb of DM per day of added fats, 4-7 lbs DM per day of protein, 1 lb per day of calcium carbonate (e.g. limestone), 0.75 lb per day of sodium bicarbonate, 0.5 lb of salt per day, and trace amounts of other mineral ingredients. These components amount to 39-62 lbs/day of ingested DM. Given that approximately 14 lbs/day of total solids is excreted in the manure from a 1400 lb cow, some 23-35% of the solid matter is either undigested or only partially digested by the cow. Figure 1 illustrates the distribution of the typical components of cattle's diet.



**Figure 14: Dairy Cattle Daily Feed Composition.**<sup>[37]</sup>

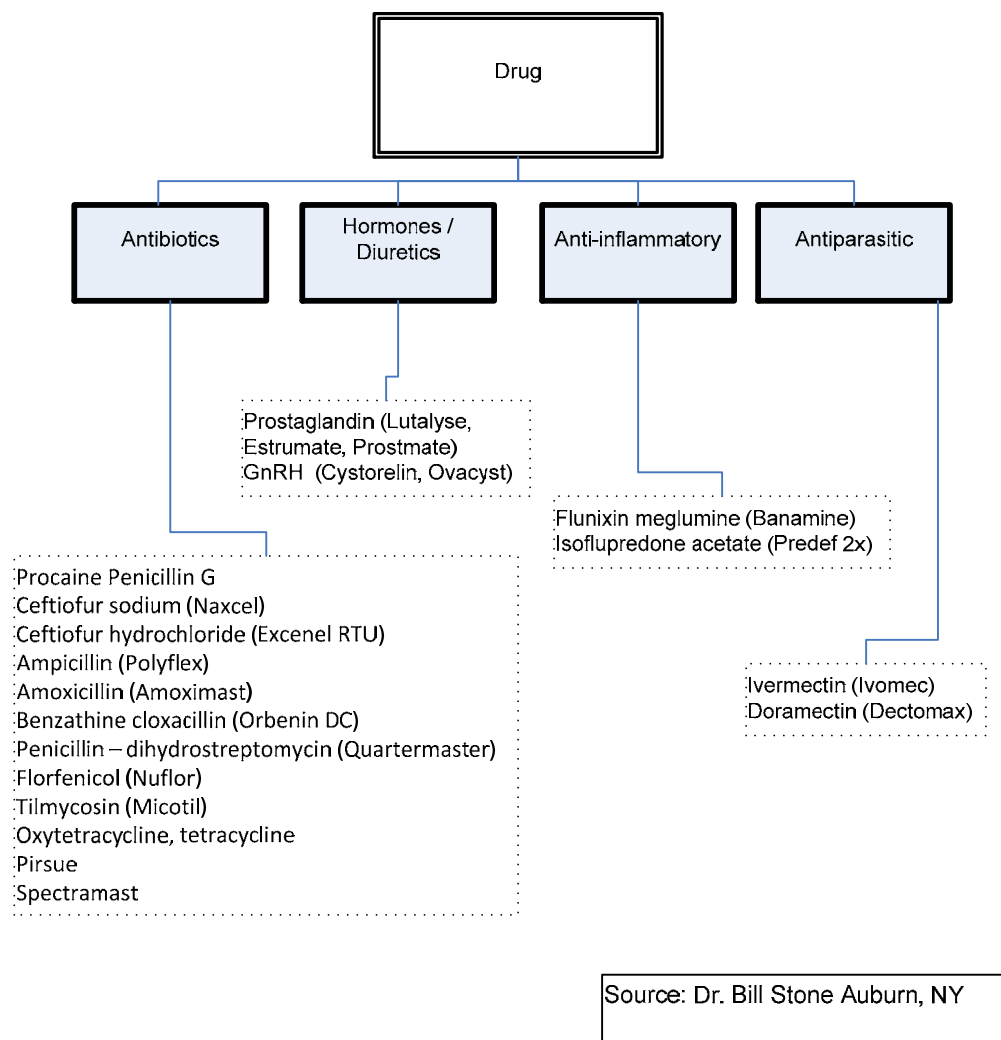
Managing a dairy herd requires ensuring and restoring, if necessary, the health of the cows it contains. Farmers, of course, make substantial effort to prevent disease in their animals; however, the herd is, indeed, impacted throughout its life cycle by disease. A list of common disorders experienced by dairy cattle appears in Table 8. To set a scale for the incidence of disease, a report from the *Journal of Dairy Science* identified that 13.4% of dairy cows suffer from mastitis, 11.6% from infertility, 10.5% from lameness, and 3.4% from chronic diarrhea.<sup>[38]</sup> Many of the conditions listed in the table are either painful or life threatening. Beyond a range of infections, surgical procedures are another means in which pain could be induced to the animal during its care. Procedures such as dehorning, castration, tail docking (shortening), C-section, and suturing wounds are among common surgeries that are performed on dairy cattle.

**Table 8: Table of Common Dairy Cow Disorders.** <sup>[21]</sup>

| Animal  | Disease         | Explanation   |
|---------|-----------------|---|
| Calf    | Dystocia        | Birth difficulties.   |
|         | Scours          | Diarrhea.   |
|         | Pneumonia       |   |
| Heifers | Bloat           | A form of indigestion in which excess gas production in the rumen cannot be expelled.           |
|         | Injury          |   |
|         | Pneumonia       |   |
| Cows    | Mastitis        | Bacterial infection of the udder and teats.   |
|         | Lameness        |   |
|         | Milk fever      | Hypocalcemia or low blood calcium levels.   |
|         | Ketosis         | Metabolic disorder that leads to a chemical imbalance in the bloodstream.                       |
|         | Metritis        | Postpartum infection of the uterus.   |
|         | RFM             | Retention of fetal membranes after birthing a calf.   |
|         | Johne's disease | Bacterial infection indicated by chronic diarrhea, weight loss, and diminished milk production. |
|         | Infertility     |   |

Since milk production is a function of cow comfort, alleviating these disorders directly, or their symptoms, improves the cow's productivity. Cows will be administered medications or supplements that accomplish this goal. These supplements include antibiotics, hormones/diuretics, anti-inflammatory drugs, and antiparasitic drugs. Antibiotics, for example, will be administered therapeutically in order to treat specific conditions and subtherapeutically to prevent the onset of infection and to improve growth rate. Such subtherapeutic applications of antibiotics have been in practice for 50 years.<sup>[39]</sup> Figure 15 shows a breakdown of these categories of supplements that are used in dairy farm operations.





**Figure 15: Drugs used to treat dairy cattle.**<sup>[40]</sup>

In addition to medicinal additives which are purposely given to cows, other compounds can also enter the diet of cattle, after which they may enter the cow's manure if they are not metabolized in some way. Volatile metals and heavy metals may get into the soil and/or into the cattle feed and may be inadvertently ingested. Metals may enter the production process of the dairy industry through a couple of channels: (1) deposition through the atmosphere, (2) application of compounds to the soil. Inorganic fertilizers, biosolids, agrochemicals, and animal manures may all contribute through the latter channel. In Figure 16 is a summary of a preliminary, unpublished study performed at the University of Minnesota. The figure contains a list of the metals which were found in surveying dairy farms in the state of Minnesota. The survey was conducted by taking biopsies from the livers of cattle and by the analysis of soil. In addition to Pb, Cd, Cr, and Ni, it is also known that Cu, Ca, and Mn are present both in dairy cattle diet and in soil.<sup>[41]</sup> In a different, published study of dairy

feeds, the study focused on heavy metal concentrations in feeds used in Wisconsin dairy operations. One component of the study was concerned with the accumulation of heavy metals in soils to which manure is applied. <sup>[42]</sup>

**Table 1. Concentrations of some non-nutritional mineral elements in the liver of dairy cows from dairy herds surveyed in Minnesota<sup>1</sup>.**

| Mineral element | No. of cows | Minimum | Maximum | Mean | SD <sup>2</sup> | Mean + (3*SD) |
|-----------------|-------------|---------|---------|------|-----------------|---------------|
| Al              | 440         | 2.2     | 94.5    | 11.3 | 10.0            | 41.5          |
| B               | 440         | 1.4     | 22.3    | 5.0  | 2.8             | 13.2          |
| Cd <sup>3</sup> | 440         | 0.1     | 3.1     | 0.4  | 0.3             | 1.2           |
| Cr <sup>4</sup> | 440         | 0.2     | 21.2    | 1.2  | 1.5             | 5.5           |
| Ni <sup>5</sup> | 440         | 0.6     | 12.5    | 1.7  | 1.6             | 6.5           |
| Pb <sup>6</sup> | 440         | 1.5     | 23.4    | 4.5  | 2.9             | 13.3          |

<sup>1</sup> Concentrations in parts per million.

<sup>2</sup> Standard deviation.

<sup>3</sup> Concentrations were below the detection limit in 27 cows.

<sup>4</sup> Concentrations were below the detection limit in 52 cows.

<sup>5</sup> Detectable levels in only 165 cows.

<sup>6</sup> Detectable levels in only 76 cows.

**Table 2. Concentrations of some heavy metals in native soils with no manure application and soils receiving manure for crop fertilization on the surveyed dairy farms.**

| Mineral | Soil type | No. of samples <sup>1</sup> with detectable levels | Concentration, ppm (DM basis) <sup>2</sup> |         |      |                 |
|---------|-----------|--|--|---------|------|-----------------|
|         |           |  | Minimum                                    | Maximum | Mean | SD <sup>3</sup> |
| Cd      | Manured   | 24   | 0.03                                       | 0.23    | 0.12 | 0.05            |
|         | Native    | 24   | 0.04                                       | 0.34    | 0.13 | 0.08            |
| Cr      | Manured   | 6  | 0.02                                       | 0.06    | 0.03 | 0.02            |
|         | Native    | 7  | 0.02                                       | 0.06    | 0.03 | 0.02            |
| Ni      | Manured   | 24   | 0.22                                       | 4.53    | 1.94 | 0.93            |
|         | Native    | 24   | 0.14                                       | 3.88    | 1.95 | 0.97            |
| Pb      | Manured   | 24   | 0.37                                       | 2.79    | 1.54 | 0.74            |
|         | Native    | 24   | 0.36                                       | 6.09    | 1.76 | 1.27            |

<sup>1</sup> A sample of native soil and one of manure-fertilized soil was taken from each of twenty-four farms (N = 24). In several samples, mineral concentrations were below limits of detection.

<sup>2</sup> Concentrations in parts per million. Statistics computer-based on number of samples with detectable levels for each mineral.

<sup>3</sup> Standard deviation.

**Figure 16: Concentrations of minerals in the liver of dairy cows surveyed in Minnesota. <sup>[41]</sup>**

### 5.3.1.3 Pesticides and Their Application

Another set of contaminants that may also enter dairy manure are pesticides. Because the infesting insects vary with the season, pests are an ongoing issue for dairy farms, and they must be combated with pesticides so that the infestation does not rise to a level detrimental to dairy productivity. In a survey of South Dakota and regional farms, flies, lice, worms, mange are among the dominant pests. <sup>[34]</sup> The order of prevalence depends on whether the focus is on South Dakota alone or on the wider north-central region of the U.S. The survey identified the top 10 ingredients used in dairy animals in the north-central region and in South Dakota. The pesticides are applied either through pour-ons and sprays, ear tags which allow slow release, or through area sprays. Some are also directly injected or used as feed additives.

**Table 9: Top 10 active ingredients used for dairy animals in the north central region of the U.S. and in South Dakota.** <sup>[34]</sup>

| <b>Active Ingredient</b> | <b>% of Dairy Animals (Region)</b> | <b>% of Dairy Animals (South Dakota)</b> | <b>Class of Chemical</b> |
|--------------------------|------------------------------------|--|--------------------------|
| permethrin               | 16.6                               | 37.2                                     | Pyrethroid               |
| eprinomectin             | 10.2                               | 16.8                                     | Avermectin               |
| pyrethrins               | 6.8                                | 0.5                                      | Pyrethroid               |
| coumaphos                | 6.7                                | 9.1                                      | Organophosphate          |
| cyfluthrin               | 6.7                                | 3.9                                      | Pyrethroid               |
| ivermectin               | 6.6                                | 7.1                                      | Avermectin               |
| morantel tartrate        | 2.4                                | Not reported                             | Acetocholine mimics      |
| stirophos                | 2.2                                | Not reported                             | Organophosphate          |
| dichlorvos               | 1.4                                | 12.8                                     | Organophosphate          |
| doramectin <sup>2</sup>  | 1.2                                | Not reported                             | Avermectin               |

The Northeast Area Pesticide Impact Assessment Program did an extensive study on how dairy farmers in New York state apply pesticides, and what compounds are used for various needs. Table 10 lists the application equipment. The leading methods are sprayers, dust bags, and foggers. Directly pouring on, back rubbers, high-pressure sprayers, and mist blower were the next most prevalent means of application. Table 11 -- Table 13 list the insecticides used for fly control in the barn, fly control on cattle in pasture, and lice/mite control, as indicated in the survey. While most treatments appear to be applied directly to the animal or to a general containment area, West Virginia University reported that a small fraction (6%) of respondents to their survey treat the manure itself directly to control flies in the barn.<sup>[43]</sup>

**Table 10: Application Equipment Used by Dairy Producers.** <sup>[32]</sup>

| <b>Equipment</b>              | <b>Number of Responses</b> | <b>Percent of All Records (167)</b> |
|-------------------------------|----------------------------|-------------------------------------|
| Aerosol can                   | 7                          | 4.2%                                |
| Backpack or hand-pump sprayer | 66                         | 39.5%                               |
| Backrubbers                   | 13                         | 7.8%                                |
| Dish-soap bottle              | 1                          | 0.6%                                |
| Dust bags                     | 47                         | 28.1%                               |
| Fogger                        | 44                         | 26.3%                               |
| Hand duster                   | 4                          | 2.4%                                |
| High-pressure sprayer         | 9                          | 5.4%                                |
| Jar                           | 1                          | 0.6%                                |
| Liquid duster                 | 1                          | 0.6%                                |
| Mist blower                   | 7                          | 4.2%                                |
| NA                            | 4                          | 2.4%                                |
| Pour-on                       | 15                         | 9.0%                                |
| Pour-on applicator            | 1                          | 0.6%                                |
| Spray bottle                  | 1                          | 0.6%                                |
| <b>Total:</b>                 | <b>221</b>                 |                                     |

Table 11: Insecticides used for Fly Control in the Barn. <sup>[32]</sup>

| Method of Application    | Insecticide  | Number of Responses | Percent of Records (167) |
|--------------------------|--|---------------------|--------------------------|
| <b>Baits</b>             | Apache, Golden Malrin (or other methomyl bait)     | 75                  | 44.9%                    |
| <b>Manure treating</b>   | Cygon (or other dimethoate formulations)           | 1                   | 0.6%                     |
|                          | Rabon (or other tetrachlorvinphos formulations)    | 5                   | 3.0%                     |
|                          | Orkin Pest Control                                 | 1                   | 0.6%                     |
| <b>Milk room</b>         | Pyrethrins plus synergist                          | 43                  | 25.7%                    |
|                          | IND Food Handling Spray                            | 1                   | 0.6%                     |
|                          | Orkin Pest Control                                 | 1                   | 0.6%                     |
| <b>Oral formulations</b> | Rabon Oral Larvicide (or other tetrachlorvinphos)  | 6                   | 3.6%                     |
|                          | Orkin Pest Control                                 | 1                   | .6%                      |
| <b>Residual sprays</b>   | Atroban, Ectiban, Permethrin (or other permethrin) | 14                  | 8.4%                     |
|                          | Cygon (or other dimethoate formulations)           | 6                   | 3.6%                     |
|                          | Rabon (or other tetrachlorvinphos formulations)    | 6                   | 3.6%                     |
|                          | Tempo (or other cyfluthrin formulations)           | 7                   | 4.2%                     |
|                          | 3-M Spray  | 1                   | 0.6%                     |
|                          | Orkin Pest Control                                 | 6                   | 3.6%                     |
|                          | Sodium hypochlorite                                | 1                   | 0.6%                     |
| <b>Space sprays</b>      | Atroban, Ectiban, Permethrin (or other permethrin) | 25                  | 15.0%                    |
|                          | Pyrethrins plus synergist                          | 22                  | 13.2%                    |
|                          | Vapona, Cionap (or other dichlorvos formulations)  | 2                   | 1.2%                     |
|                          | C-EM-DIE   | 1                   | 0.6%                     |
|                          | Orkin Pest Control                                 | 4                   | 2.4%                     |
|                          | Sodium hypochlorite                                | 1                   | 0.6%                     |
|                          | Sure Kill  | 1                   | 0.6%                     |

**Table 12: Insecticides Used for Fly Control on Cattle in Pasture.**<sup>[32]</sup>

| <b>Method of Application</b> | <b>Insecticide</b>                                     | <b>Number of Responses</b> | <b>Percent of Records (167)</b> |
|------------------------------|--|----------------------------|---------------------------------|
| <b>Animal sprays</b>         | Atroban, Ectiban, Permethrin (or other permethrin)     | 45                         | 26.9%                           |
|                              | Ciodrin (or other crotoxphos formulations)             | 2                          | 1.2%                            |
|                              | Malathion  | 6                          | 3.6%                            |
|                              | Pyrethrins plus synergist                              | 7                          | 4.2%                            |
|                              | Vapona, Ciovap (or other dichlorvos formulations)      | 6                          | 3.6%                            |
|                              | C-EM-DIE   | 1                          | 0.6%                            |
|                              | Eprinomectin   | 1                          | 0.6%                            |
|                              | Orkin Pest Control                                     | 3                          | 1.8%                            |
|                              | pyrenone   | 1                          | 0.6%                            |
|                              | Sure Kill  | 1                          | 0.6%                            |
|                              |  |                            |                                 |
| <b>Backrubbers</b>           | Ciodrin (or other crotoxphos formulations)             | 2                          | 1.2%                            |
|                              | Co-Ral (or other coumaphos formulations)               | 8                          | 4.8%                            |
|                              | Ectiban, Permethrin (or other permethrin formulations) | 13                         | 7.8%                            |
|                              | Malathion  | 2                          | 1.2%                            |
|                              | Methoxychlor   | 1                          | 0.6%                            |
|                              | Vapona, Ciovap (or other dichlorvos formulations)      | 2                          | 1.2%                            |
|                              | D furl Ten Count Back Rub                              | 1                          | 0.6%                            |
|                              | Eprinomectin   | 1                          | 0.6%                            |
|                              | Orkin Pest Control                                     | 1                          | 0.6%                            |
| <b>Dust Bags</b>             | Ciodrin (or other crotoxphos formulations)             | 1                          | 0.6%                            |
|                              | Permethrin (or other permethrin formulations)          | 18                         | 10.8%                           |
|                              | Rabon (or other tetrachlorvinphos formuatioms)         | 7                          | 4.2%                            |
|                              | Coumaphos  | 3                          | 1.8%                            |
|                              | IBA  | 1                          | 0.6%                            |
| <b>Ear tags</b>              | Atroban, Ectiban, Permethrin (or other permethrin)     | 2                          | 1.2%                            |
|                              | Ectrin (fenvalerate)                                   | 5                          | 3.0%                            |
| <b>Hand dusting</b>          | Ciodrin (or other crotoxphos formulations)             | 1                          | 0.6%                            |
|                              | Permethrin (or other permethrin formulations)          | 7                          | 4.2%                            |
|                              | Rabon (or other tetrachlorvinphos formulations)        | 10                         | 6.0%                            |
|                              | Coumaphos  | 3                          | 1.8%                            |
|                              | Eprinomectin   | 1                          | 0.6%                            |
| <b>Oral formulations</b>     | Rabon Oral Larvicide (or other tetrachlorvinphos)      | 6                          | 3.6%                            |
|                              | Vigilante (diflubenzuron)                              | 1                          | 0.6%                            |
|                              | Orkin Pest Control                                     | 1                          | 0.6%                            |

**Table 13: Insecticides Used for Lice or Mite Control.** <sup>[32]</sup>

| Method of Application | Insecticide  | Number of Responses | Percent of Records (167) |
|-----------------------|--|---------------------|--------------------------|
| <b>Animal sprays</b>  | Atroban, Ectiban, Permethrin (or other permethrin) | 41                  | 24.6%                    |
|                       | Ciodrin (or other crotoxphos formulations)         | 1                   | 0.6%                     |
|                       | Co-Ral (or other coumaphos formulations)           | 10                  | 6.0%                     |
|                       | Pyrethrins plus synergist                          | 1                   | 0.6%                     |
|                       | Taktic (amitraz)                                   | 13                  | 7.8%                     |
|                       | Vapona, Ciovap (or other dichlorvos formulations)  | 1                   | 0.6%                     |
|                       | Boss   | 3                   | 1.8%                     |
|                       | Dectomax   | 1                   | 0.6%                     |
|                       | DeLice Pour-on                                     | 2                   | 1.2%                     |
|                       | Difuel Injectable                                  | 1                   | 0.6%                     |
|                       | Durasect   | 1                   | 0.6%                     |
|                       | Eprinomectin                                       | 9                   | 5.4%                     |
|                       | Ivermectin   | 4                   | 2.4%                     |
|                       | Lysoff   | 2                   | 1.2%                     |
|                       | Pyrenone (or other pyrethrin plus synergist)       | 1                   | 0.6%                     |
|                       | Used oil   | 1                   | 0.6%                     |
| <b>Dusts</b>          | Ciodrin (or other crotoxphos formulations)         | 4                   | 2.4%                     |
|                       | Co-Ral (or other coumaphos formulations)           | 25                  | 15.0%                    |
|                       | Permethrin (or other permethrin formulations)      | 11                  | 6.6%                     |
|                       | Rabon (or other tetrachlorvinphos formulations)    | 5                   | 3.0%                     |
|                       | DeLice Pour-on                                     | 1                   | 0.6%                     |
|                       | IBA  | 1                   | 0.6%                     |

A survey from the United States Department of Agriculture (USDA) also examined pesticide application methods throughout 21 states included in the survey. The data showed that the most common form of application is pour-on directly on the dairy cattle, followed by sprays, dust bags, injection, ear tags, rubbing, shots and pills.<sup>[44]</sup> These have the potential of being flushed into the manure, or already existing in the manure. Their retention times in the manure are based on their half-life, the amount of time it takes for the compound to decompose to half of its original concentration. The results of the survey are shown in Table 14.



**Table 14: Insecticide Application Methods.\***

| <b>Application Method</b> | <b>Percentage</b> |
|---------------------------|-------------------|
| Pour-On                   | 59                |
| Spray                     | 20                |
| Dust Bag                  | 8                 |
| Injection                 | 4                 |
| Ear Tags                  | 4                 |
| Rubbing                   | 3                 |
| Pills/Shots               | 2                 |

\* Survey results from 21 states: CA,CO,FL,ID,IL,IN,IA,KY,MI,MN,MO,NM,NY,OH,PA,TN,TX,VT,VA,WA,& WI.

The USDA conducted yet another survey to find out the gross amount of insecticide that was used for dairy cattle and their facilities. Table 15 and Table 16 show how much insecticide was used in 2006 from the 17 participating US states.<sup>[45]</sup> The primary concerns for pesticides are risk to the infrastructure and end use equipment (e.g. toxic combustion products). Generally, they are applied in the spring months when the bugs are beginning to thrive. However, they are implemented periodically year round.

**Table 15: Amount of Insecticide Used on Dairy Cattle in 2006.**

| <b>State</b> | <b>Amount Applied<br/>(Thousand lbs)</b> |
|--------------|--|
| WI           | 24.9                                     |
| VT           | 20.1                                     |
| TX           | 19.7                                     |
| PA           | 14.8                                     |
| MN           | 10.8                                     |
| VA           | 10.8                                     |
| CA           | 10.0                                     |
| NM           | 9.1                                      |
| WA           | 8.8                                      |
| IN           | 8.8                                      |
| NY           | 7.9                                      |
| ID           | 6.7                                      |
| IA           | 5.3                                      |
| OH           | 5.2                                      |
| MI           | 4.9                                      |
| MO           | 3.9                                      |
| KY           | 2.2                                      |
| <b>TOTAL</b> | <b>174.0</b>                             |

**Table 16: Amount of Insecticide Used in Dairy Cattle Facilities in 2006.**

| <b>State</b> | <b>Amount Applied<br/>(Thousand lbs)</b> |
|--------------|--|
| TX           | 34.8                                     |
| WI           | 20.5                                     |
| PA           | 16.0                                     |
| IA           | 14.8                                     |
| MN           | 12.5                                     |
| NY           | 10.2                                     |
| ID           | 8.1                                      |
| IN           | 7.8                                      |
| CA           | 7.4                                      |
| MO           | 7.0                                      |
| MI           | 2.9                                      |
| WA           | 1.9                                      |
| OH           | 1.6                                      |
| KY           | 1.3                                      |
| VT           | 1.0                                      |
| VA           | 1.0                                      |
| NM           | 0.3                                      |
| <b>TOTAL</b> | <b>149.1</b>                             |

These numbers reflect the total amount of insecticide used in 2006. The actual compounds tested are listed in the sampling methods section, and in the Task 2 report. Official studies have not been done on how pesticides may affect digestion, nor have studies been performed on permutations of source material content.

#### 5.3.1.4 Manure Management

Dairy farms generally must collect manure as a routine part of their operations. Removal decreases the insect population from the barn, and the farmer often uses it in a spreader to distribute it onto crop fields. Collected manure is either directly recycled to the land base, or it is stored short-term or long-term. Alternatively, it may be treated before recycling or storage. Table 17 lists the types of cleaning systems used by dairy farmers in the state of New York. The two most common cleaning systems are scraping and flushing. Scraping entails mechanical removal of the manure, generally with automatic alley scrapers, with a skid-steer, or with a tractor-mounted implement. Flushing involves removal of barn manure by washing it out with large volumes of water. The manure is conveyed to storage or to treatment equipment. As is evident from the table, scraping completely dominates the survey responses, with ‘scraping and flushing’ and ‘hosing’ running a distance second and third, respectively. Scraping essentially maintains the solids content in the manure. In contrast, flushing operations are typically used when a lower solids content is desired. For the purposes of biogas production, diluting the manure could certainly be one step in pre-

processing it, if that were desirable. Slush cleaning is typically used in warm climates where anaerobic lagoons are used to treat flushwater laden with manure. In South Dakota dairies, a similar dominance of scraping is apparent in Table 18, but use of automated barn cleaners is more common than in New York and comprises 13.6% of survey respondents. A barn cleaner is a mechanical, automated set of paddles that aggregates and conveys excreted into barn alleys.

The frequency with which the manure is removed is also an important consideration. The biogas yield from stale manure is reduced if volatile solids are diminished due to premature fermentation. In New York, survey has indicated that manure/bedding removal frequencies differ between calves and heifers, on one hand, and cows, on the other. For calves, manure and bedding are removed on a daily basis by about 65.3% of farms; for heifers, daily removal occurs in about 61.1% of the cases. Weekly removal is the second most frequent in each case at 17.4% and 20.4% for calves and heifers, respectively. For cows, in contrast, daily removal comprises 95.2% of cases.<sup>[32]</sup> In a similar survey of flush removal of manure in South Dakota, 88.8% and 11.1% of respondents indicated that they flush their barns 2 times/day and 3 times/day, respectively, with no other responses that identified either more frequent or less frequent flushing than these.<sup>[34],<sup>29</sup></sup>

**Table 17: Manure Collection Methods in New York State Dairies.**<sup>[32]</sup>

| <b>System</b>         | <b># of Responses</b> | <b>% of All Records (167)</b> |
|-----------------------|-----------------------|-------------------------------|
| Barn Cleaner          | 2                     | 1.2%                          |
| Hosing                | 5                     | 3.0%                          |
| Not Applicable        | 1                     | 0.6%                          |
| Scraping              | 140                   | 83.8%                         |
| Scraping and flushing | 6                     | 3.6%                          |
| Scraping and liming   | 1                     | 0.6%                          |
| Slatted Floors        | 2                     | 1.2%                          |
| Sweeping              | 2                     | 1.2%                          |
| <b>Total:</b>         | <b>159</b>            |                               |

When collecting the manure to clean the barn area, it is inevitable that additional material present in that area will be captured along with the manure itself. Bedding material, leftover cattle feed, drug residuals, and pesticides that are used for pest control are all candidate components. This all contributes to the source material that could enter an anaerobic digester.

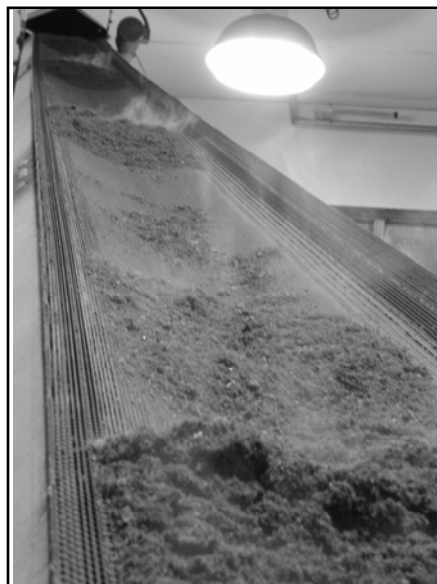
Solid-liquid separators can generally be designed to take out bedding material so that it may not hinder anaerobic digestion. Thus, sand and sawdust are generally separated on a conveyer before the manure reaches the lagoon or other holding point. This bedding material is dried, and can be reused. Figure 17 shows separated bedding sand passing along a conveyer belt, and Figure 18 shows its collection at a retrieval

<sup>29</sup> All reported survey data on flushing frequency summed to 99.9%. This is most likely a roundoff error in data reporting.

point. Additional discussion of separation techniques is contained in the section on Contact Digesters.

**Table 18: Usage of Manure Collection Systems in South Dakota Dairies.** <sup>[34]</sup>

| <b>System</b>                                    | <b>% of Dairies Utilizing</b> |
|--|-------------------------------|
| Manual/equipment scraping of barn                | 80.3                          |
| Automated barn cleaner with daily manure hauling | 7.5                           |
| Automated barn cleaner with manure stockpiled    | 6.1                           |
| Floor flushing system                            | 3.5                           |
| Manual/equipment scraping, then flushing         | 2.6                           |



**Figure 17: Separated bedding sand going to retrieval point on a conveyor belt. Photograph taken during visit to Sheland Farms in New York State, 26 March 2008.** <sup>[46]</sup>



**Figure 18: Bedding sand collected at retrieval point. Photograph taken during visit to Sheland Farms in New York State, 26 March 2008.<sup>[47]</sup>**

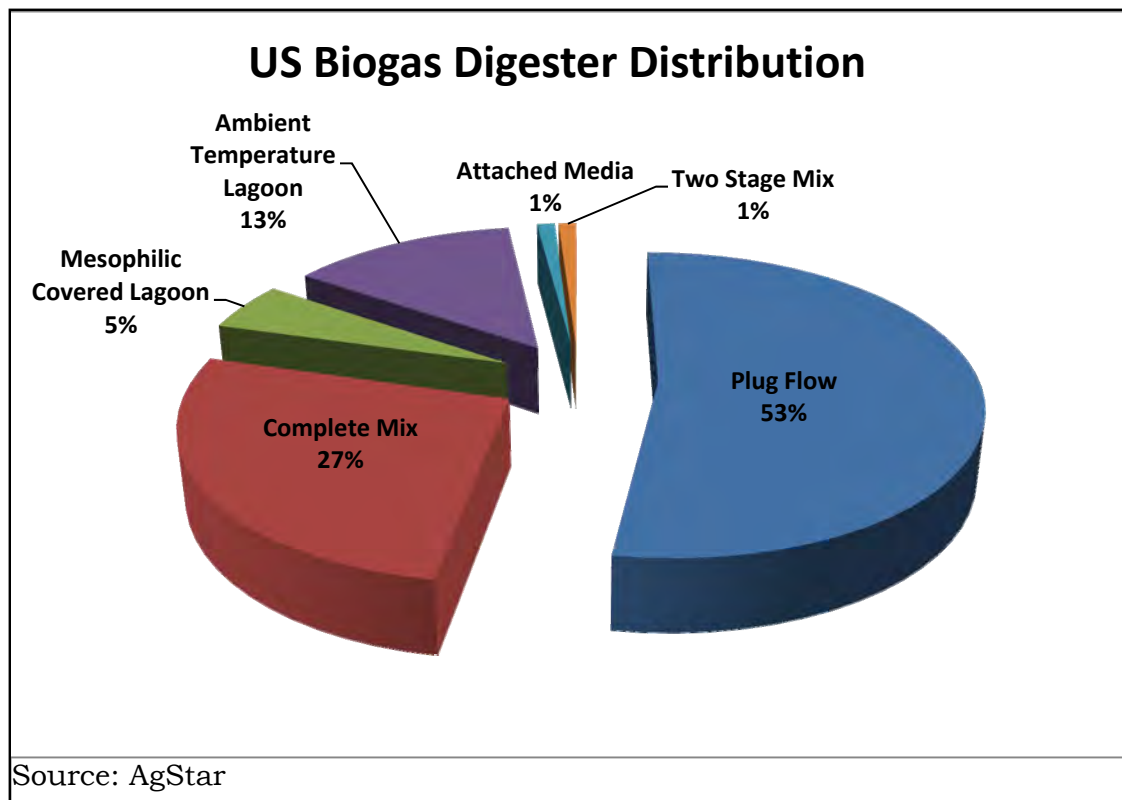
#### **5.4 Farm-based Biogas Recovery Systems Used in the U.S.**

Historically, the primary reason farms have chosen AD is odor reduction of post-digested manure that is to be stored long term. However, for the farmer, several advantages are possible by producing biogas. One advantage is the opportunity of utilizing a combined heat and power (CHP) source for the farm. The farmer can also sell any net energy produced to the electrical grid (although often at rates lower than retail value) or as renewable natural gas (RNG). The liquid effluent that is drained from the digester is a rich, organic fertilizer that is suitable for land application. The undigested portion of the solids may be recycled as stall bedding for the animals or, if economical to do so, the solids may be sold for other farms to use. In addition, the farm can claim carbon credits that can be saved and sold on the Chicago Climate Exchange (CCX) or the European carbon market.

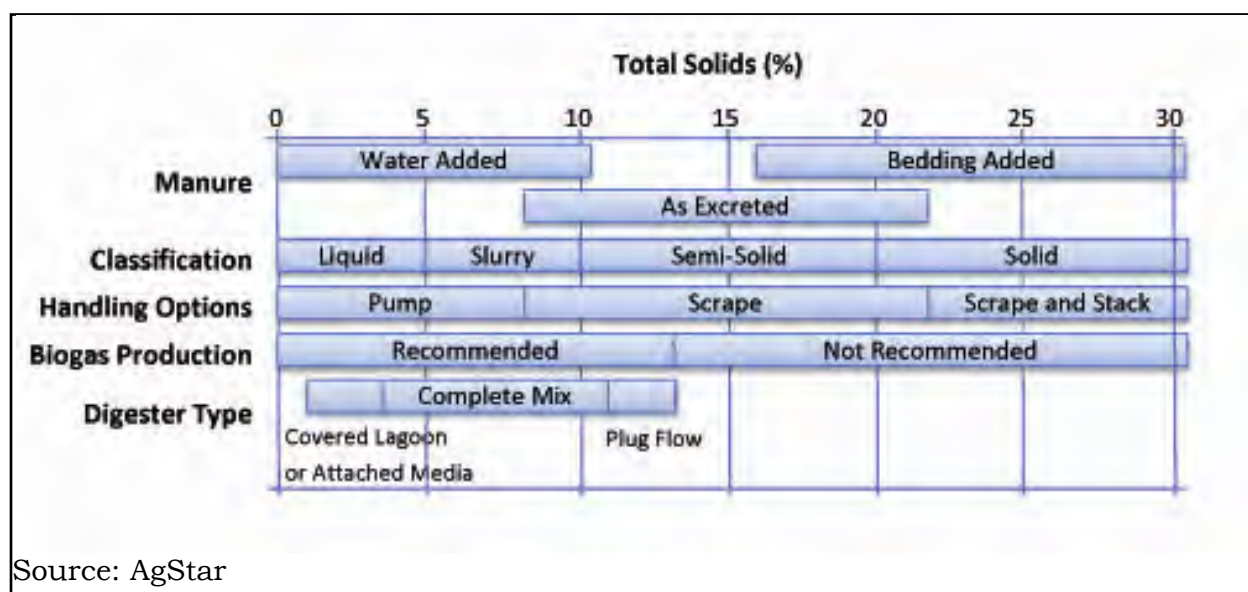
A major disadvantage of this technology for the farmer is the extensive investment required for both the digester and clean-up equipment. The farm, in addition, must also be considered as an industrial site, which means the farm is subjected to full air and water regulations.<sup>[48]</sup> Finally, if clean biogas is produced for injection to the natural gas infrastructure, the issue of transporting the gas to the interconnect site exists. More will be discussed about this issue in Section 8.

For the farmer to produce biomethane, one important aspect of achieving a high biomethane conversion is choosing the best biogas production technology for the specific type of manure at a dairy farm. The most commonly used biogas production systems on farms are the plug flow digester and the complete mix digester. Covered lagoons are also a significant portion. Figure 19 displays the percentage of biogas recovery systems used in the US, with 53% of them being plug flow reactors. Figure

20 is a chart obtained from AgStar that demonstrates which technologies work best based on the solids content of the manure. Liquid manure (Solids Content < 5%) is generally pumped into a covered lagoon for digestion. Slurry manure (5% < Solids Content < 10%) is usually pumped, or scraped, into a complete mix digester. Semi-solid manure (10% < Solids Content < 20%) is typically scraped, or flushed, into a plug flow digester. Semi-solid manure with over 20% solid content is not recommended for anaerobic digestion unless the system is designed to handle high total solids concentrations.



**Figure 19: Biogas Recovery Systems in the U.S. Includes digesters in start-up and construction phases.**



**Figure 20: Manure Management Options Based on Percentage of Solids.**<sup>[49]</sup>

### 5.4.1 Example Companies that Manufacture Digester systems

This subsection and the next provide an overview of a handful of companies that offer digester system design, construction, installation, consulting, and operation. Not all companies specialize in digester applications for dairy farms. *The list is not exhaustive, and no attempt is made to be comprehensive either internationally, nationally, or regionally.* However, this set of companies does display a range of possible options, and it offers a sense of competitive market conditions. Many other companies exist that are outside this list and that offer these services or a subset of them.

#### 5.4.1.1 Andigen

Andigen is located in Logan, Utah. The founder is a faculty member at Utah State University, who has 20 years of experience in studying agricultural development and in developing digester systems. The company markets its Induced Blanket Reactor (IBR), which is a modification of an Upflow Anaerobic Sludge Blanket (UASB). Andigen offers installation of entire pre-engineered systems including, the digester, heat exchangers, sensors, and electronic monitoring equipment. The company will also help with obtaining and installing building infrastructure, holding and mixing tanks, gas storage units, and electrical generation.

Andigen's IBR system handles waste streams from cattle operations of greater than 250 head of cattle or so, and it handles waste from other animal operations. The HRT of the digester is 5 days, which is shorter than nominal retention times in most digester designs. The low HRT reduces the front-end storage volume required for manure since only enough volume for 5 days and some safety buffer is required. The solids content that the system will accept is in the range of 2-10%.

The system can be designed for above or below ground usage. Systems are configured into small cells, which allow them to be scaled up and to have improved reliability. The system is housed in a temperature controlled building. In addition to the design and installation of such systems, Andigen also offers a remote monitoring



and control services for its plants. This service operates by using network software over the internet to manage process temperatures and flows.

#### 5.4.1.2 Microgy

Microgy, a subsidiary of Environmental Power Corporation, is located in Tarrytown, NY. It holds an exclusive license from Xergi, a Danish company, for their co-digestion and thermophilic digester technology. This technology has operated at facilities in the United States and in Europe over the past 15 years.

Microgy manure management and biogas clean-up systems are outfitted with monitoring and controlling devices that the Microgy operating team manages. This can be done either on-site or remotely so that necessary adjustments can be made. The Microgy anaerobic digester uses dairy manure to produce raw biogas with roughly 65% methane content. About 1 cows yield an energy production rate of 1 kW. Pretreatment of the substrate dilutes it to 8-10% solids by making a slurry. The end-use of the biogas is direct combustion, electrical generation, and pipeline grade gas. Direct combustion entails using the biogas to fire boilers on-site. Microgy also sells biogas to the local utility for on-site electric generation that is owned by the power company. Microgy can also treat the biogas to meet the specifications of the customer utility company. The treatment involves an absorption process and/or a pressure swing head.

In the facilities that they have operated, produced biogas is often sold to the local utility that owns and operates the on-site electric power generator. The utilities are rewarded with green credits and will often pay a premium on the biogas to generate “green” energy. Microgy works with the state in order to obtain permits and with local utilities for regulatory approval. Microgy does not work with public agencies in any mode that would sacrifice their proprietary information. Their sources of revenue derive from the energy sold either as pipeline quality gas or as electric power.

The European company from which Microgy licenses its technology has about 28-30 digesters in operation in Europe. It does not upgrade to pipeline quality gas, but it does upgrade for end-use in villages, where no access to natural gas is available and where the biogas is distributed for residential purposes.

#### 5.4.1.3 Bigadan

Bigadan A/S is a privately held company, headquartered in Skanderborg, Denmark. It has more than 20 years of experience. It has many projects in 5 different countries and pending projects in the U.S. as well. Bigadan focuses its business on large biogas plants with over 100 tons/day of source material input. Its technologies use a variety of feed such as liquid manure, industrial organic wastes, and sewage sludge. Bigadan’s biogas plants typically accept feed from local food processing industries, from municipalities, and from dairy and swine farms. To comply with European Union (EU) legal standards set in October 2002, Bigadan pre-treats source materials at thermophilic temperatures to pasteurize the waste from animal byproducts, thereby, reducing pathogens. In this process, the influent is heated to 70°C for 1-hour.

Bigadan employs thermal hydrolysis, the incorporation of water and heat, to enhance the breakdown of organic material in the digester. Thermal hydrolysis breaks

down cells and cell clusters, which makes them more easily digestible. Because dissolved organic solids are more readily digestible than suspended solids, maximum degradability is not achieved without this pre-processing. In addition, mechanical mixing is utilized to aid digestion by physically breaking down solids and creating larger substrate surface areas. The addition of heat provides conditions for cell polymers to hydrolyze into sugars and amino acids. Both groups become more acidic, in turn yielding high concentrations of volatile fatty acids, which are more easily digestible. Degradation of these materials becomes more efficient with thermal hydrolysis, and therefore, optimizes the availability of nutrients for the bacteria. Consequently, the production rate of biogas improves. Efficiency of solids destruction is increased by 15-30%. Bigadan typically operates with retention times in the range: 12 days < HRT < 25 days.

After completion of the digestion, raw biogas is transferred to storage tanks that are equipped with a gas proof membrane to contain the biogas. Depending on the usage of the effluents, the biogas plant may involve other mechanical steps such as a treatment through a solids-liquids separator. Biogas is typically used on-site to operate combined heat and power, from which net energy is then sold to the grid. The heat generated is used as district heating for nearby energy needs.

Bigadan uses countercurrent heat exchangers that are available in modules of 6 m each. A high surface area of the heat exchanger and a low fluid flow rate create a high heat transfer coefficient. The heat exchangers are insulated with 200mm of mineral wool and covered by Plastisol coated steel plates after installation. Typically installed as 12 serially connected elements, the heat exchangers heat to 70°C, exchanging about 70-80% of their heat.

Bigadan's gas cleanup system can remove more than 90% of the H<sub>2</sub>S content using bioscrubbers. The bioscrubbers are located in a 10-foot sea-container. The use of sulfur reducing bacteria, thiobacillus thiooxidans, and small amounts of liquid nutrients encourage bacterial growth. The bacteria use CO<sub>2</sub> as a carbon source and the H<sub>2</sub>S as an energy source. The byproducts are sulfate and sulfur, products that can be spread onto farmland.

#### 5.4.1.4 Schmack

Schmack Biogas A/G is located in Schwandorf, Germany. Schmack provides a wide array of services for constructing and operating on-farm digester facilities. The company provides digester technology, consulting services in the production of biogas, site assessments, laboratory analysis of feedstocks, construction project planning and management, actual plant construction, operational and technical support, and a variety of financing or co-ownership options.

PASCO is Schmack's feeding technology. Because bacteria require a hospitable environment to maximize production, it is imperative that consistent conditions are kept. PASCO provides a balanced feeding schedule with biological monitoring to ensure that the bacteria are fed in an energy-efficient manner. This technology has been tested to comply with the requirements needed for the digester system. PASCO is connected to BIOWATCH, a program that allows for the control, automation, and process management of the unit. The feeding technology provides reliable and

simplified plant operation. The storage containers for feeding material can range between 20 m<sup>3</sup> to 80 m<sup>3</sup>, allowing for customization that is suitable for most farms.

EUCO Titan is Schmack's Plug-Flow Digester. It is a long, horizontal, above-ground concrete digester that is constructed to provide optimal mixing and even heating distribution. Like other Schmack technologies, it is also equipped with monitoring and control equipment to maintain the quality of the production process.

The EUCO TS is a horizontal-axis paddle stirring mechanism that ensures low-power requirements as low as 2.2kW to keep parasitic power usage minimal. It provides a gentle way of homogenizing the substrate with slow revolutions of 0.75 rpm but can handle a loading torque of 30,000 ft. lbs. The location and position of the stirrer causes a controlled direction of flow; this prevents the formation of sinking and floating layers. The EUCO TS stirring mechanism is centrally heated so that heat is evenly distributed throughout the digester to provide a uniform environment for bacterial populations.

For low energy density feedstock, such as liquid cow or pig manure, Schmack offers the COCCUS Titan Standardized Plant system. It consists of a traditional pit storage fermenter and can be used with low dry-matter feedstock. In addition, this system remains flexible and can be easily upgraded to add the EUCO Titan Plug-Flow Fermenter or to integrate Schmack's All-In-One cogeneration system. The COCCUS TS stirring mechanism, REMEX, is suitable for feedstock with little dry substance. It is a modified version of the EUCO TS to handle larger volumes (1,200 m<sup>3</sup> to 2,400 m<sup>3</sup>). It uses two stirrer paddles on opposite sides of the fermenter that are positioned at different heights to guarantee mixing throughout the large space.

Schmack provides an All-In-One (AIO) Biogas cogeneration system that offers a compact construction. An advantage of this is the reduction of construction and installation times. This also allows for more immediate operation and production of electricity and heat. The unit is available for electrical power outputs ranging from 185 kW to 640 kW. The AIO pumping system is centrally controlled. It uses a number of suction and pressure lines to provide complete mixing. The AIO is equipped with a range of sensors to provide reliable operation.

The AIO container also comes with unique software, called BIOWATCH, which allows for the control, automation and process management of the unit. Similarly, the software BIOWATCH XL provides system status and monitoring. In the event of failure, the control unit reports important information about the problem via email or call forwarding.

Typically biogas is used in cogeneration (CHP) to provide electrical power for an extensive transport network. The Schmack plant efficiency can greatly increase depending on the use of the waste heat recycled throughout the biogas plant by increasing efficiency from roughly 30% without the use of waste heat to approximately 68.5% with recycling all of the waste heat generated. The idea of feeding the upgraded biogas (biomethane) into the natural gas grid expands the usage of the biogas into a myriad of sources. This provides more opportunity to deliver the biomethane because the plant is not limited to customers within close proximity to the biogas plant.

Schmack provides technology that is suitable for upgrading biogas to pipeline quality. Schmack owns Carbotech, a gas cleanup company, and used Carbotech equipment for that purpose. Purifying the biogas and improving its methane content to

roughly 96% is important for pipeline injection. First, the biogas must undergo the removal of carbon dioxide, sulfur, and water. This removal process must meet the criteria and regulations set forth by the German Waterworks Association. The removal method preferred by Schmack is the pressure swing adsorption process. Following cleanup, the purified biogas is fed to the grid. Part of the biogas is used in a CHP unit to cover the electrical and thermal demand of the plant. Excess electricity generated is fed to the public grid.

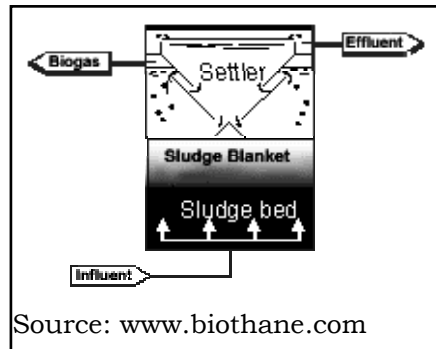
Compared to existing electricity generation, feeding the purified natural gas into the existing natural gas grid is more efficient. Typically, the cleanup of biogas accounts for about 15% of the potential electricity generated. About 5% is lost through processing, leaving an 80% net efficiency level. This can be transferred to the natural gas grid for heating facilities, CHP units, and outside the gas grid as a fuel for vehicles.

Schmack's Biomethane plant in Plienig, Germany is the first of its kind to upgrade to pipeline quality biomethane on an industrial scale. In cooperation with Renewable Energy Systems (RES) and Aufwind SchmackBetriebs GmbH & Co. KG, biogas was fed directly into the natural gas grid. The biomethane is transported in the gas pipelines to a location 10 miles away from the biogas plant.

#### 5.4.1.5 Biothane

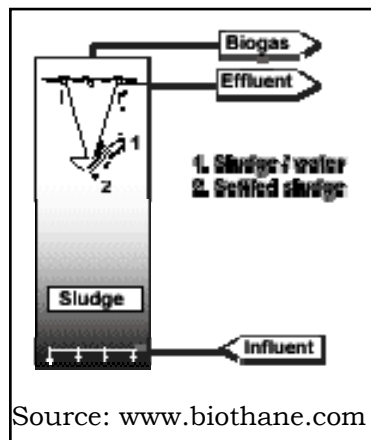
Biothane has offices in 6 countries, including the United States, in Camden, NJ. Its headquarters is located in Delft, The Netherlands. It has been in the biological treatment technology business since the early 1970s and has actively participated in more than 500 non-farms based installations in 40 countries and in a variety of industrial sectors.

Biothane offers four different anaerobic digestion systems. The Biothane Upflow Anaerobic Sludge Blanket (UASB) is used to treat industrial wastewater and has been in full-scale operation for over 25 years. An advantage of the UASB is its loading rate of 10-15 kg COD/m<sup>3</sup>-day, which yields a short hydraulic retention time of less than 48 hours.



**Figure 21: Biothane Upflow Anaerobic Sludge Blanket (UASB).**

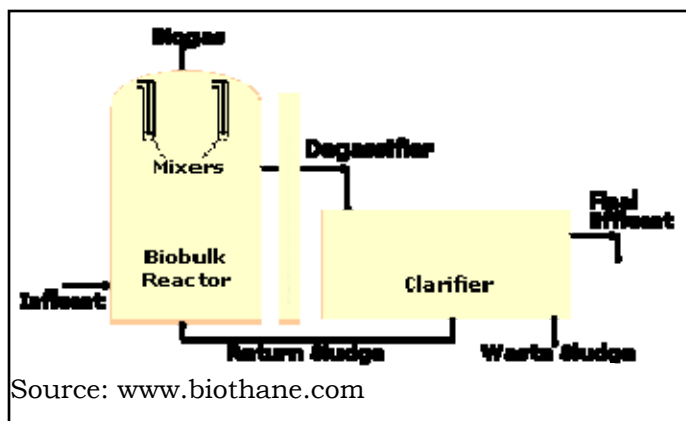
The Biobed Expanded Granular Sludge Bed (EGSB) operates at an organic loading capacity of 15-35 kg COD/m<sup>3</sup>-day. This technology incorporates the UASB technology and consists of two major components: the double baffle plated settler at the top of the tank and the feed distribution at the bottom of the tank. The feed distribution system increases wastewater to sludge contact via several feed inlet points. This multi-feed inlet aids in preventing channeling of the influent through the sludge.



**Figure 22: Biobed Expanded Granular Sludge Bed.**

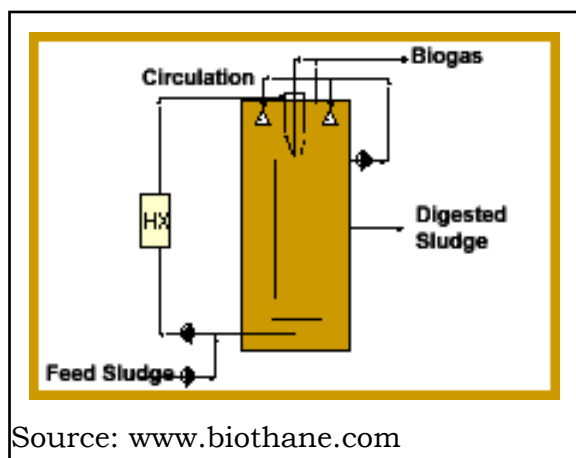
The Biobulk Completely Stirred Tank Reactor (CSTR) is an example of a Contact Digester.<sup>30</sup> It is a medium rate system with loadings of 1.5 – 5 kg COD/m<sup>3</sup>-day, and hydraulic retention times within the reactor on the order of 5-7 days. The biomass is injected in the bottom of the reactor and mixed in the reactor using high injection jet nozzles located at the top of the reactor. This mixing promotes passive degassing of the solids. Effluent from the reactor flows to an external clarifier or solids separator. A recycling loop returns the biomass to the reactor vessel after this mass separation step.

<sup>30</sup> See Section 4.3.2.4.



**Figure 23: Biobulk Completely Stirred Tank Reactor.**

The Shear Enhanced Anaerobic Digestion (SEAD) process is designed for the digestion of sludge and other solid waste and slurries. It is a completely mixed anaerobic digestion process that has a short hydraulic retention time. Mixing is created by a large flow of influent on the bottom of the reactor and by one or more of the high-shear nozzles on the top of the vessel. The nozzles break up the biomass and substrate solids and accelerate mass transfer within the reactor by inducing circulation.



**Figure 24: Shear Enhanced Anaerobic Digestion.**

Biothane's cleaning technology for the removal of  $H_2S$  is Biopuric. This process involves a chemical scrubber coupled with a biological trickling filter. Sulfur oxidizing microorganisms metabolize the  $H_2S$  into elemental sulfur and sulfuric acid. This technology effectively treats biogas with concentrations ranging from 1,000 ppmv to 15,000 ppmv and is capable of removing 90-98% of the  $H_2S$ .





**Figure 25: Biopuric Plant in Northeast U.S.**

#### 5.4.1.6 RCM

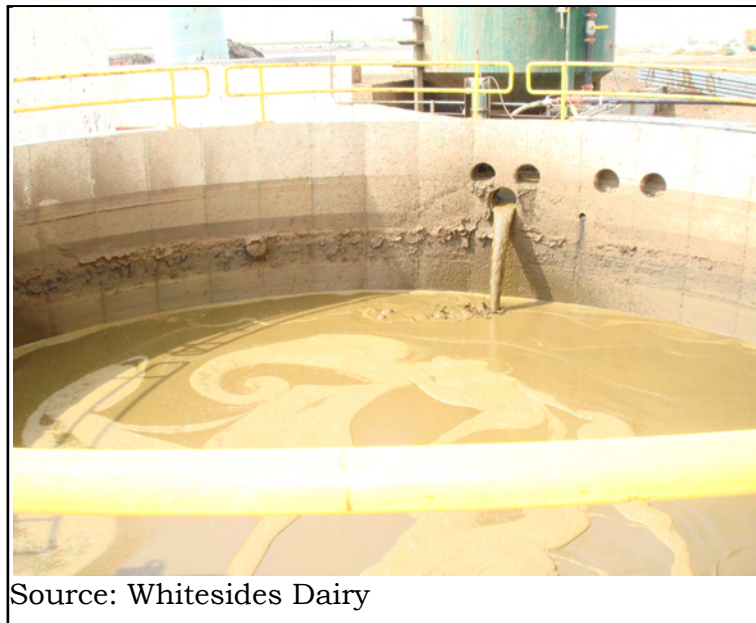
RCM Digesters is located in Berkeley, CA. Since 1982, RCM has built and designed over 40 manure-based anaerobic digesters that are in operation throughout the USA and abroad, including Armenia, Belize, the Philippines, China, Italy, Spain, among others. RCM has four technologies for different agricultural and industrial waste: Plug Flow, Complete Mix, Covered Lagoon, and Heated, Mixed Covered Lagoons. The Plug Flow digester is designed for dairy farms. It is an unmixed heated rectangular tank that digests raw manure with 11-13% solids. The digested solids can be separated and sold. The Complete Mix digester is designed for pig manure or for dairy manure blended with other substrates. The Complete Mix reactors are mixed to optimize bacterial activity and to preclude settling if dilute influents are used. The Covered Lagoon is designed for flushed pig or dairy wastes. This design operates at ambient conditions, which causes variation in the biogas yields with changing seasonal temperatures. For this reason, the Covered Lagoon design is usually implemented in regions with warmer climates and is limited to odor reduction in colder areas. The Heated, Mixed Covered Lagoon is used primarily for odor reduction, not energy production, and consequently is relatively inexpensive to build and operate. The specifications of each digester are dependent on the site and on the amount of waste available. Typically RCM works with dairy farms of about 1,000 - 2,000 cows, but it has projects with farms of up to 28,000 cows.

### 5.4.2 Example Companies that Provide Digester Consulting and Engineering Services

#### 5.4.2.1 Intrepid

Intrepid is a company located in Idaho that uses Andigen, LC (Logan, Utah) as its technology provider. Intrepid systems can be customized to fit smaller or larger farms or processing plants. The size of the anaerobic digester depends on the size of the farm or amount of waste produced. Figure 6 below depicts an example of a manure tank at Whitesides Dairy in Idaho.





**Figure 26: 70,000-Gallon Manure Storage Tank on Whitesides Dairy Facility.**

When used on a dairy farm, the manure is collected daily and is pretreated into a slurry of 8-10% solids. Typically, substrate with 3% solids content requires larger tanks with larger footprints. One gallon of dairy waste with 8.5% solids yields 3.5 ft<sup>3</sup> of biogas containing 65% methane, 6% H<sub>2</sub>O and 29% CO<sub>2</sub>, with about 800ppmv of H<sub>2</sub>S. Because manure has a high calcium carbonate (CaCO<sub>3</sub>) content, it acts as an excellent buffering substrate for acidic material that may enter the digester.<sup>[50]</sup> The digester breaks down 30-50% of the 8-10% total solids in the influent.

The solid and liquid effluent goes through a solids separator manufactured by Accent. This separator has a stainless steel frame, is designed for turn-key installation, and uses a pumped flow to separate some of the liquids from the solids. The solids are then dewatered to create a high quality fiber material that is on the market as competition to peat moss. This revenue stream makes up 40% of Intrepid's income. Separated liquid is stored in a lagoon and is subsequently used for irrigation. Carbon credits sold through the Chicago Climate Exchange makes another 10% of Intrepid's revenue stream.

The output from the reactors consist of methane gas, water that is suitable for irrigation or flushing, and solids for use as soil fertilizer or conditioner (mentioned above). Gas upgrading is performed by an designed gas cleanup unit, including a unique system of sulfur removal. The resulting biomethane has been verified as meeting the quality requirements for the receiving gas utility.

A concern with digesters that operate in the western U.S., or in other regions where sand is used as bedding, is accumulation of that sand, bedding, other inorganics, or non-digestible organics within the digester. This issue can be a cause of digester failure and reduced duty factor. To address this problem, Intrepid has modified its tank design. At the bottom of the tank is a cone, where settled sand is forced out the bottom by the hydraulic head.

#### 5.4.2.2 Ros Roca

Ros Roca is a multinational company headquartered in Tarrega, Spain. The office which focuses on their digester plant business is located in Germany. Since the early 1990s, Ros Roca has focused on mechanical-biological waste treatment systems combining sorting, digestion and composting systems. Ros Roca works mainly as general contractors of turnkey systems throughout Europe.

Ros Roca uses a wet technology to treat various organic materials such as municipal solid waste, agricultural waste, food waste, household waste, and sewage. The first step is the wet pre-treatment step where water is mixed in with the organic waste in a turbomixer and a suspension with solid concentration of up to 15% is produced. The suspension passes through a screen and an aerated sand trap to remove larger particles such as glass and stones and then goes through a crusher to ensure that particle size is below 12 mm before passing to the sanitation process.

The sanitation process occurs for at least 1 hour at 70°C and is performed prior to digestion. The design of the sanitation process allows any suspension that was not sufficiently sanitized to enter a suspension buffer tank and be passed through the sanitation step again. The sanitized suspension flows into the anaerobic digester that contains no moving parts. The mixer is powered by compressed biogas. The digestion process requires little electricity and produces high amounts of biogas. After digestion, the suspension is dewatered by centrifuge. The solids and liquids are ready to use or sold for agricultural uses. The biogas is then upgraded to natural gas quality and is utilized as fuel for buses.

#### 5.4.2.3 Valley Air Solutions

Valley Air Solutions is located in Stockton, CA. It provides dairy farmers with a range of services related to operating their farms. Its services include consulting, filing permits, providing solutions such as anaerobic digestion, project design and execution, and monitoring equipment. Valley Air offers extended warranty, on-site service repairs, and overhauls. They provide service agreements for up to three years and perform all routine scheduled maintenance.

The digester technology offered by Valley Air Solutions consists of anaerobic lagoons. This technology works with either flush or scrape dairy farms, or other agricultural facilities. Coarse solids are removed and the separated liquid enters the digester, which is a lagoon covered with a gas-tight, high-strength plastic (HDPE). The HRT is about 40-60 days. Biogas is removed from the headspace of the covered lagoon. Residual solids are dried or composted and used as fertilizer or bedding. The digested liquid effluent is used as liquid fertilizer and is enriched in nitrogen, phosphorous, and potassium.

The resulting biogas has not been “cleaned” to pipeline standards. Rather, it is destined for use in engines and microturbines. The conditioning system removes select contaminants, including H<sub>2</sub>S, sulfur, and moisture. Sensors monitor the gas treatment process to prevent problems with the engines. Cogeneration of electricity and heat is incorporated into the system. An engine or microturbine is used to produce mainly electricity, but waste heat from the engine may also be captured and can be used for food processing, water heating, and steam production, among other uses. The electrical generator is interconnected to the grid, and allows the farm to sell net generated electricity to the utility. Valley Air Solutions will work with the local utility

company to determine the best equipment needed for the electrical interconnection system and the best scheme for the dairy farm to sell any net electrical energy.

Upgrading to pipeline quality specifications is also available. After conditioning of the gas to remove H<sub>2</sub>S, further purification is required and compressing to meet pipeline gas specifications. These cleanup systems come in standard and customizable sizes and can be retrofitted to existing digesters. This too can also be sold and injected to gas utility pipelines.

#### 5.4.2.4 Agri-Waste Energy

Agri-Waste Energy, Inc. is located in St. Paul, MN. It is operates as a developer, a consultant, a project manager for digester systems installation, and an operations manager. The company's principal focus is the conversion of livestock manure into energy, fertilizer, and bedding materials. In producing fuel, it prepares fully conditioned biomethane, compresses it, and injects it into the natural gas grid. Agri-Waste works with an array of partners in gas conditioning, sales, building design, and pipeline engineering. It can provide a span of digester types and attendant cleanup units. In their role, Agri-Waste conducts feasibility studies, understands zoning issues and environmental rules, and ascertains proximity to natural gas infrastructure. After the digester and a biogas cleanup systems are installed, Agri-Waste provides operational startup, and supports owners in marketing the output products from the operations.

### 5.4.3 Summary of Example Digester Companies

Table 19 and Table 20 summarize parameters of the biogas technology and service providers listed in the previous subsections. *Parameters are listed either as they were reported or as they are found in company literature or on websites. Not all parameters are available. GTI has not independently verified the available data on parameter values.*

**Table 19: Summary of Example Digester Companies.**  
N/A indicates an attribute that is not available to report.

| Attribute                       | Example Digester Company   |   |   |                             |   |  |                                    |   |
|---------------------------------|--|---|---|-----------------------------|---|--|------------------------------------|---|
|                                 | Intrepid   | Microgy   | Bigadan   | Schmack                     | Biothane  | RCM                                    | Ros Roca                           | Valley Air Solutions  |
| <b>Substrate(s)</b>             | dairy farm manure, agricultural wastes   | dairy farm manure   | liquid manure, industrial organic wastes, and sewage sludge             | energy crops                | waste water   | animal waste, food waste               | biowaste, industrial organic waste | dairy farm manure, agricultural wastes  |
| <b>Biogas Yield</b>             | dairy waste: 3.5 ft <sup>3</sup> biogas/gal<br>cheese whey: 7 ft <sup>3</sup> biogas/gal       | 0.3-1 kW/cow  | N/A   | N/A                         | N/A   | 65-80 cu. ft/day (1-2,000 cows)        | N/A                                | N/A   |
| <b>Biogas Content</b>           | 65% CH <sub>4</sub> ; 29% CO <sub>2</sub> ; 6%H <sub>2</sub> O; 800ppmv H <sub>2</sub> S       | 65% CH <sub>4</sub>   | N/A   | N/A                         | N/A   | 60-70% CH <sub>4</sub>                 | N/A                                | 60-80+% CH <sub>4</sub> †   |
| <b>Hydraulic Retention Time</b> | 5 days   | N/A   | 12-25 days  | N/A                         | 2 - 7 days  | 20+ days                               | N/A                                | 40-60 days  |
| <b>Upgrading</b>                | 3 <sup>rd</sup> party company provides upgrading to pipeline quality standards with 7-15% loss | Direct burn, fire boilers, electric generation, pipeline natural gas as specified by customer utility company | Remove more than 90% of the H <sub>2</sub> S content using bioscrubbers | Upgrade to pipeline quality | 90-98% H <sub>2</sub> S removal (1,000-15,000 ppmv) | H <sub>2</sub> S filter in development | N/A                                | Biogas to Electricity projects. Removal of H <sub>2</sub> S sulfur, moisture, CO <sub>2</sub> |
| <b>Storage</b>                  | Processed quickly to pipeline quality, compressed into tube-tank trucks                        | Not on-site   | Storage tanks with gas-proof membrane roof                              | N/A                         | N/A   | N/A                                    | N/A                                | N/A   |

†A content of 80% CH<sub>4</sub> for biogas production from an anaerobic lagoon, the technology employed by Valley Air Solutions, seems to be a rather high value.

**Table 20: Continued Summary of Example Digester Companies.**  
N/A indicates an attribute that is not available to report.

| Attribute                       | Example Digester Company |  |
|---------------------------------|--------------------------|--|
|                                 | Andigen                  | Agri-Waste                                     |
| <b>Substrate(s)</b>             | Cattle manure            | Livestock manure                               |
| <b>Biogas Yield</b>             | N/A                      | N/A  |
| <b>Biogas Content</b>           | N/A                      | N/A  |
| <b>Hydraulic Retention Time</b> | 5 days                   | Various, depending on digester type.           |
| <b>Upgrading</b>                | N/A                      | N/A  |
| <b>Storage</b>                  | N/A                      | Compressed biomethane, then injection to grid. |

## 5.5 Processes to Improve Biogas Quality

According to the “Biomethane from Dairy Waste” report prepared for the Western United Dairymen<sup>[52]</sup>, there are a number of measures that could have the potential to either increase the production or improve the quality of produced biogas. Several pretreatment techniques used at landfill and water treatment facilities were discussed but applicability to dairy waste is not well known. The addition of certain substances to the digester has demonstrated positive effects on biogas produced specifically from dairy manure. While detailed discussion of co-digestion is outside the scope of this report, the topic is addressed briefly in the subsection on digester additives.

### 5.5.1 Pretreatment

Thermal pretreatment was performed separately on water hyacinth and slaughterhouse waste. In each case, the material was heated for a particular period of time at a specific temperature. Pretreatment of the slaughterhouse waste resulted in increased methane yields although experiments with water hyacinth showed no benefit.

Increased biogas production was observed after pre-treating sewage sludge with low-frequency ultrasound. Ultrasonic pretreatment promotes breakdown of the organic matter. Increased destruction of volatile solids results in improved digester performance and increased biogas production.

Methane production from municipal solid waste has benefited from impact grinding as a pretreatment method. Impact grinding has been shown to help disintegrate the organic portion of the waste resulting in faster methane production and a more stable digestion process.

### 5.5.2 Digester Additives

Bench-scale tests using commercial products, Aquasan® and Terasan® with cow manure have shown encouraging results although commercial scale effectiveness has not been validated. The two products activate microbes within the manure and are

able to accelerate digestion and restrict odor emissions. Gas production increased 55% and 34.8% when adding 15ppm of Aquasan® to cow manure and 10ppm Terasan® to cow manure and kitchen waste, respectively.<sup>[51]</sup>

While the purpose of this report is not to delve deeply into issues of co-digestion, it must be mentioned as a method for improving biogas quality and production. Co-digestion of cattle manure with other waste types is a better understood technique than those mentioned above. Multiple advantages to the owner/operator can be realized when manure is mixed with sewage sludge or slaughterhouse, industrial, or food wastes, etc., at appropriate proportions. A better balance of organic compounds creates good fertilizer and a stable digestion process. The owner/operator can increase earnings through tipping fees for waste disposal, but of most interest to this project is the significant increase in biogas production. After reviewing the operations at three Swedish biogas plants, Krich and co-authors (2005) concluded that co-digesting slaughterhouse waste with manure on a dairy farm should be limited to no more than 33% slaughterhouse waste based on the amount of monitoring and control required by biogas plants that use higher percentages. They also recommended the co-digestion to be performed in a complete-mix digester rather than in plug flow or covered-lagoon designs.<sup>[52]</sup>

Additional digester additive methods were reviewed in a master's thesis by Zicari.<sup>[53]</sup> The addition of iron phosphates into the digester causes an increase in pH whereby the emission of sulfide gas is reduced and soluble sulfide concentrations increased. Sulfide emissions were reportedly reduced by 96.6% to 100ppm using this method. A 95.8% reduction down to 100 ppm was reported when insoluble iron phosphate was added to the digester. Allegedly, hydrogen sulfide reductions of 80 – 99%, ranging from 20 – 100ppm, were realized when less than 5% of air by volume was added to the digester.<sup>[53]</sup>



## 6 Gas Composition

### 6.1 Raw Biogas Composition

The composition of raw biogas can vary widely depending on the materials being digested. Landfill biogas, for instance, can contain significant amounts of hydrogen sulfide, H<sub>2</sub>S, as well as trace amounts of ammonia, mercury, chlorine, fluorine, siloxanes, and volatile metallic compounds.<sup>[54, 55]</sup> The composition of dairy manure produced biogas tends to be more consistent with less “surprise” elements. The typical compounds and their reported concentration ranges are shown in Table 21. Methane concentration is shown as high as 74% but is generally reported as being around 60%. The addition of food wastes into a manure-based digester seems to improve biogas production and may increase methane concentration. Carbon Dioxide is often measured at 40%. Nitrogen, hydrogen, oxygen, and hydrogen sulfide are found in smaller quantities. Hydrogen sulfide measured from gas samples taken at five dairy farms in New York State are reported to range from 600 ppm to more than 7000 ppm. Addition of other organic material into the digester, environmental aspects, and sulfur concentration in the water supply are thought to account for the wide variation.<sup>[56]</sup>

**Table 21: Biogas Composition.**

|                  | Compound   | Concentration                 |
|------------------|--|-------------------------------|
| CH <sub>4</sub>  | Methane  | 54-70%                        |
| CO <sub>2</sub>  | Carbon Dioxide   | 27-45%                        |
| N <sub>2</sub>   | Nitrogen   | 0.5-3%                        |
| H <sub>2</sub>   | Hydrogen   | 1-10%                         |
| CO               | Carbon Monoxide  | 0-0.1%                        |
| O <sub>2</sub>   | Oxygen   | 0-0.1%                        |
| H <sub>2</sub> S | Hydrogen Sulfide   | 600-7000+ ppm <sup>[56]</sup> |
|                  | Trace elements, amines, sulfur compounds, non-methane volatile organic carbons (NMVOC) <sup>[56]</sup> , Halocarbons <sup>[56]</sup> |                               |

Adapted from: "3-Cubic Meter Biogas Plant A Construction Manual." Wisconsin Chapter of the American Society of Farm Managers and Rural Appraisers. 1980. VITA. 24 Jan 2008 <sup>[57]</sup>

### 6.2 Raw Natural Gas Composition

As biogas composition varies by digester influent composition, raw natural gas composition varies by the well from which it is produced. Raw natural gas can be classified into three categories. Raw natural gas that is extracted from oil wells is called “associated” or casing head gas. Gas well gas is removed from natural gas wells. The third type of raw natural gas is mixed with liquid hydrocarbons, found in



condensate wells, and is known as condensate well gas.<sup>[58]</sup> Typical compositions of the three types of raw natural gas are shown in Table 22 where each component is shown by percentage.

**Table 22: Raw Natural Gas Composition.**

| <b>Compound</b>  | <b>Casing head<br/>(Wet) Gas<br/>Mol%</b> | <b>Gas Well<br/>(Dry) Gas<br/>Mol%</b> | <b>Condensate<br/>Well Gas<br/>Mol%</b> |
|------------------|---|--|---|
| Carbon Dioxide   | 0.63                                      | -                                      | -                                       |
| Nitrogen         | 3.73                                      | 1.25                                   | 0.53                                    |
| Hydrogen Sulfide | 0.57                                      | -                                      | -                                       |
| Methane          | 64.48                                     | 91.01                                  | 94.87                                   |
| Ethane           | 11.98                                     | 4.88                                   | 2.89                                    |
| Propane          | 8.75                                      | 1.69                                   | 0.92                                    |
| Iso-Butane       | 0.93                                      | 0.14                                   | 0.31                                    |
| n-Butane         | 2.91                                      | 0.52                                   | 0.22                                    |
| Iso-Pentane      | 0.54                                      | 0.09                                   | 0.09                                    |
| n-Pentane        | 0.80                                      | 0.18                                   | 0.06                                    |
| Hexanes          | 0.37                                      | 0.13                                   | 0.05                                    |
| Heptanes plus    | 0.31                                      | 0.11                                   | 0.06                                    |
| Total            | 100                                       | 100                                    | 100                                     |

Source: Foss, Michelle Michot. Interstate Natural Gas - Quality Specifications & Interchangeability. Sugarland, TX: Center for Energy Economics, 2004.<sup>[59]</sup>

### **6.3 FERC Tariffs and Quality**

The Federal Energy Regulatory Commission (FERC) who regulates the interstate transmission of electricity, natural gas, and oil requires natural gas transmission companies to file tariffs. Although FERC has no generic quality policy,<sup>[60]</sup> it has the authority under section 5 of the Natural Gas Act to require a pipeline company to include “just and reasonable gas quality and interchangeability standards” in their tariffs.<sup>[61]</sup>

### **6.4 Typical Tariff Quality**

In Report No. 4A, the American Gas Association’s Transmission Measurement Committee reported on variations in pipeline tariffs. Table 23 shows their findings of the threshold and typical values of gas properties specified in tariffs.

**Table 23: Pipeline Quality Composition.**

| <b>Gas Property</b>                                    | <b>Contract Limits</b>                             | <b>Typical Values</b>                    |
|--|--|--|
| Water Content  | 7lb./MMscf, Maximum                                | 2 – 7 lb./MMscf                          |
| Heat Content (dry)                                     | 967 – 1120 Btu/scf                                 | 1010 – 1060 Btu/scf                      |
| Temperature  | 32 – 120 °F  | 40 – 60°F                                |
| Hydrocarbon Dew Point - °F                             | 15°F Maximum at Pipeline Pressures                 | 0 – 15°F at 550 psig                     |
| Sulfur Compounds – Hydrogen Sulfide (H <sub>2</sub> S) | ¼ – 0.3 grains per 100 scf, Maximum <sup>(5)</sup> | 0 – 1/8 grains per 100 scf               |
| Mercaptans (RSH)                                       | No Specification                                   | Highly Variable 0 – 40ppm <sup>(1)</sup> |
| Total Sulfur Compounds, as sulfur                      | 5 – 20 grains per 100 scf – Maximum                | 0 – 1 grains per 100 scf                 |
| Diluent Gases Total                                    | 4 – 5% Maximum                                     | 0.5 – 3%                                 |
| Oxygen (O <sub>2</sub> )                               | 0.2% Maximum <sup>(6)</sup><br>0.001% Desirable    | 0 – 0.001%                               |
| Helium (He)  | 0.2% Maximum                                       | 0 – 0.1%                                 |
| Nitrogen (N <sub>2</sub> ) <sup>(2)</sup>              | 3% Maximum <sup>(4)</sup>                          | 0 – 2%                                   |
| Carbon Dioxide (CO <sub>2</sub> )                      | 2 – 3% Maximum <sup>(4)</sup>                      | 0 – 2%                                   |
| Mercury (Hg)   | No Specification                                   | 0 – 1ppb <sup>(3)</sup>                  |
| Solid Particles  | 3 – 15 microns, Maximum                            | 3 – 15 microns                           |

(1) Parts per million (10<sup>-6</sup>), molar basis

(2) This is free, gaseous nitrogen, nitrogen compounds are not known to occur in most gas.

(3) Parts per billion (10<sup>-9</sup>), molar basis

(4) The carbon dioxide and nitrogen are sometimes limited to combined maximum content of 3%.

(5) NFPA 54-1999, ANSI Z223.1, Natural Fuel Gas Code, section 2.6 lists pipe material restrictions if more than 0.3 gr. H<sub>2</sub>S/100 scf. Where H<sub>2</sub>S cannot be limited to 0.3 gr. /100 scf or less, notify end-users, LDCs, and/or state agencies, which can affect the use of appropriate pipe materials for high H<sub>2</sub>S gas.

(6) To limit pipeline corrosion effects, the desirable O<sub>2</sub> contract limit is 0.001% but the maximum contract limit may be specified up to 0.2% in dry or processed gas with no H<sub>2</sub>O present in liquid form.

Source: American Gas Association. Transmission Measurement Committee. AGA Report No. 4A, Natural Gas Contract Measurement and Quality Clauses. Washington, DC: American Gas Association, 2001. <sup>[62]</sup>

Gas property values extracted from company FERC tariffs were analyzed. GTI created ranges for each property and determined the number of companies that specified a value in that range. Properties and the percentage of companies requiring a value which fell in a particular range are shown in Table 24.

Using maximum heating value as an example, GTI determined the minimum and maximum posted values and created bins within those extremes, 900 and 1100 Btu/scf. The ranges used were  $\leq 900$ , 901-925, 926-950, 951-1000, 1001-1050, 1051-1099, and  $\geq 1100$ . Of the 170 posted values, 2 were equal to 900 and counted in the  $\leq 900$  bin resulting in 1.18%. The largest group was the 951-1000 bin with 101 companies, 59.41%, specifying a minimum heating value in this range. Zero companies reported minimum heating values between 901 and 925 or 1001 and 1099 and therefore are not shown.

**Table 24: FERC Tariff Survey Values.**

| Gas Property                    | Value       | % Respondents |
|---------------------------------|-------------|---------------|
| Water Content (lb./MMscf)       | =3          | 0.64%         |
|                                 | =4          | 13.03%        |
|                                 | =5          | 15.38%        |
|                                 | =6          | 3.21%         |
|                                 | =7          | 64.10%        |
| Maximum Heating Value (Btu/scf) | $\leq 1018$ | 3.30%         |
|                                 | 1051-1150   | 73.74%        |
|                                 | 1151-1250   | 21.21%        |
|                                 | $\geq 1600$ | 1.01%         |
| Minimum Heating Value (Btu/scf) | $\leq 900$  | 1.18%         |
|                                 | 926-950     | 38.82%        |
|                                 | 951-1000    | 59.41%        |
|                                 | $\geq 1100$ | 0.59%         |
| Maximum Temperature (°F)        | $\leq 80$   | 0.68%         |
|                                 | 100-119     | 10.14%        |
|                                 | 120-128     | 87.84%        |
|                                 | $\geq 129$  | 1.35%         |
| Minimum Temperature (°F)        | $\leq 20$   | 15.79%        |
|                                 | 26-35       | 10.53%        |
|                                 | 36-50       | 69.74%        |
|                                 | $\geq 65$   | 2.63%         |

|  |              |        |
|--|--------------|--------|
| Hydrogen Sulfide-H <sub>2</sub> S (grains / 100 scf) | 0.01-0.09    | 0.57%  |
|  | 0.20-0.25    | 66.67% |
|  | 0.26-0.50    | 8.05%  |
|  | 0.75-1.0     | 22.99% |
|  | ≥1.1         | 1.68%  |
| Total Sulfur Compounds, as sulfur (grains / 100 scf) | ≤1           | 7.6%   |
|  | 1.1-5.0      | 25.73% |
|  | 5.1-10       | 14.04% |
|  | ≥20          | 52.05% |
| Hydrogen (%)   | 0.01-0.05    | 90.91% |
|  | 0.051-0.1    | 9.09%  |
| Oxygen - O <sub>2</sub> (%)                          | 0.0001-0.001 | 17.76% |
|  | 0.0011-0.005 | 5.26%  |
|  | 0.011-0.1    | 7.24%  |
|  | 0.11-0.2     | 40.79% |
|  | 0.21-0.5     | 15.13% |
|  | 0.51-1.0     | 13.82% |
| Nitrogen - N <sub>2</sub> (%)                        | ≤1.0         | 1.85%  |
|  | 1.0-1.9      | 3.70%  |
|  | 2.0-2.9      | 12.96% |
|  | 3.0-3.9      | 72.22% |
|  | ≥4.0         | 9.26%  |
| Carbon Dioxide - CO <sub>2</sub> (%)                 | .001-.0019   | 0.70%  |
|  | 1.0-1.9      | 9.86%  |
|  | 2.0-2.9      | 50.70% |
|  | 3.0-3.9      | 38.03% |
|  | ≥4.0         | 0.7%   |

In some scenarios, the energy contained in the methane portion of biogas can be harnessed without any cleanup processes. However, in introducing biogas into a natural gas pipeline, the biogas will need to be cleaned and upgraded to meet quality requirements of the end user. Table 25 demonstrates the quantity of components in raw biogas and representative pipeline quality natural gas. The quantity of methane in biogas will need to increase substantially by decreasing the carbon dioxide content. A very crucial part of the upgrade will be the removal of hydrogen, oxygen, and hydrogen sulfide. Nitrogen and carbon monoxide levels may be acceptable.

**Table 25: Composition of Raw Biogas vs. Pipeline Quality Gas.**

|                  | <b>Compound</b>   | <b>Biogas<sup>[57]</sup></b>                              | <b>Representative Pipeline Quality Natural Gas<sup>[59]</sup></b> |
|------------------|---|---|---|
| CH <sub>4</sub>  | Methane   | 54 - 70%  | 75% +   |
| CO <sub>2</sub>  | Carbon Dioxide  | 27 - 45%  | 3 – 4%  |
| N <sub>2</sub>   | Nitrogen  | 0.5 - 3%  | 3 – 4%  |
| H <sub>2</sub>   | Hydrogen  | 1 - 10%   | 0   |
| CO               | Carbon Monoxide   | 0 – 0.1%  | Not specified   |
| O <sub>2</sub>   | Oxygen  | 0 - 0.1%<br>0 – 1000 ppm                                  | 0.2 - 1.0 ppmv  |
| H <sub>2</sub> S | Hydrogen Sulfide  | 600 - 7000+ ppm <sup>[56]</sup><br>37.5 – 437.5 gr/100scf | 0.25 - 1.0<br>gr/100scf   |
|                  | Total Sulfur  | Not specified   | 5 - 20 gr/100scf  |
|                  | Trace elements, amines, non-methane volatile organic carbons (NMVOC)[56], Halocarbons[56] | Trace amounts   | Not Specified   |

## 7 Gas Cleanup

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### 7.1 Introduction

Natural gas produced from traditional wells requires processing in order to be suitable for transport to end users. Some processing, oil and condensate removal, can take place at the well head but gas is typically piped through low pressure gathering lines to a processing facility for removal of natural gas liquids (NGLs), hydrogen sulfide, and carbon dioxide. Most NGLs are removed by absorption or cryogenic expansion. Amine processes account for more than 95% of U.S. hydrogen sulfide removal operations. <sup>[63]</sup>

In order for biogas from dairy manure to be suitable for natural gas pipelines, it will need to go through one or more cleanup processes to remove high levels of unwanted components, thereby enriching the gas. Once the gas is sufficiently cleaned up, it can be referred to as biomethane. Some level of quality control needs to be in effect to prevent uncleaned biogas or less than pipeline quality biomethane from entering the natural gas pipeline.

There are a plethora of methods and processes that can be used to remove contaminants in gas streams. Figure 27 demonstrates a nearly exhaustive, color-coded organizational chart of processes to remove hydrogen sulfide and/or carbon dioxide and water. Included are named examples of products and processes. A number of them are well established while others are not as developed. Some are appropriate for use on farms and others are only economical at gas flows measured in Million Standard Cubic Feet per Day (MMSCFD) and where sulfur removal rates are measured in tons per day. The ability of a process to remove unwanted compounds is highly dependent on a number of factors and assessment of the true practicality of the method for a given application requires careful evaluation.

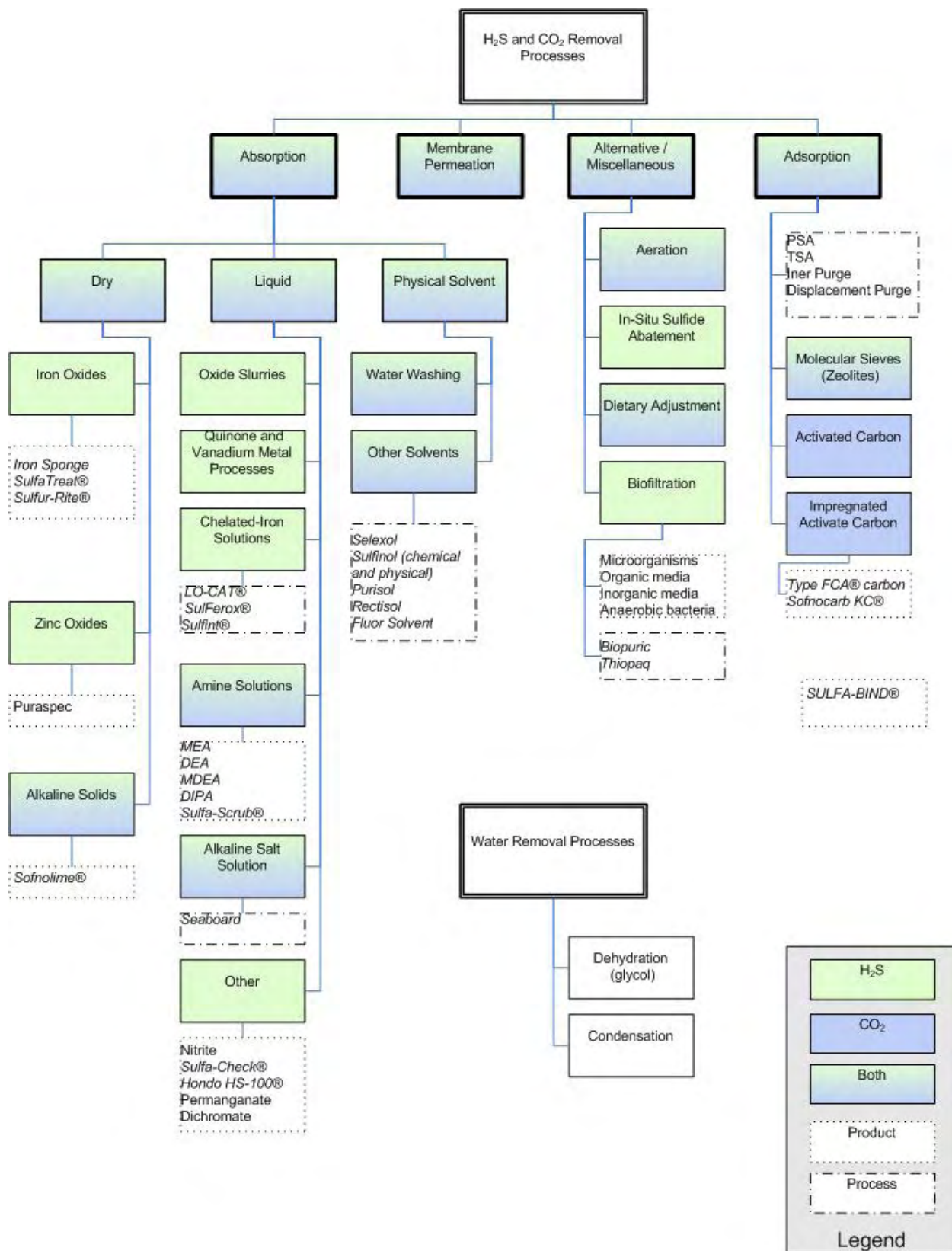


Figure 27: Gas Cleanup Methods.



In terms of the large number of processes and the current state of the art, some of the under-developed and non-applicable technologies shown in Figure 27 will not be discussed in any detail in this report. Better suited and more applicable processes will be explained in greater length than applications less suited for farm operations.

## 7.2 Major Categories of Physico-Chemical Removal

Because many of the hydrogen sulfide removal methods can also be used for carbon dioxide removal, they are not separated in the organizational chart in Figure 27. The methods were instead divided into four main divisions that include absorption, membrane permeation, alternative or miscellaneous, and adsorption. Absorption is further divided into three major categories and contains the largest number of processes and products. The boxes containing categories of processes are color coded for ease of reading. Solid green boxes are processes used to remove hydrogen sulfide only. Solid blue boxes represent processes used only for carbon dioxide removal. Boxes with a green to blue color gradient correspond to methods that can be utilized for carbon dioxide and hydrogen sulfide removal. To decipher between commercially available products and named processes, dotted line and dot-dashed line boxes were used, respectively. Where a commercial product is used to name the process, the name is shown in italics.

### 7.2.1 Absorption

#### 7.2.1.1 Oxides

Commercially available iron oxide products used for removal of sulfur typically consist of iron oxide compounds distributed within or over a separate material. An iron oxide product is placed in a reaction bed through which the gas is passed. Sulfur compounds react with the iron oxides and form insoluble iron sulfides. Some iron oxide processes are regenerable with air, meaning they can be used repeatedly without a chemical change out.

The conventional iron oxide product is known as “iron sponge” which originally consisted of steel wool coated with rust. It has evolved to iron impregnated wood chips which provide a better surface to volume ratio and can be purchased from multiple commercial outfitters. A typical setup is to place two beds in series with a down-flow of gas at 140kPa and an empty bed residence time greater than 60 seconds. Residence time is the amount of time the gas is in contact with the bed of media and is determined by the flow rate, cross-sectional area of the bed, and the depth of the media. A reduction from 3600 ppm to less than 1 ppm has been reported using “iron sponge.” <sup>[53]</sup>

“Iron sponge” has a number of drawbacks. Special care must be taken during regeneration to prevent ignition of the sponge from heat buildup. Each regeneration of the media reduces the effectiveness by 33% creating the need to change out old media which results in waste material that must be disposed. A complication of the amount of spent product is that it is considered hazardous in some instances and should not be put into a landfill without remediation. The change out process can be labor intensive and the overall use of “iron sponge” can create high operating costs. <sup>[53]</sup>

In addition to “iron sponge” a number of other iron oxide products are available. Information from company literature and the Zicari report are compiled in Table 26 which is meant to compare four iron oxide products. SULFA-BIND® is considered an adsorption process but is included here because it is an iron oxide removal product.

**Table 26: Iron Oxide Products.**

|   | Iron Sponge   | SulfaTreat®   | Sulfur-Rite®     | SULFA-BIND®                             |
|---|---|---|------------------|---|
| Substrate containing iron oxide material              | Wood chips  | Proprietary granules  | Ceramic base     | Calcinated, inorganic, natural material |
| Coated or Impregnated                                 | Impregnated   | Coated  | Impregnated      | Coated                                  |
| Primary Constituent                                   | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> | Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>     | Not known        | Fe(OH) <sub>3</sub>                     |
| Regenerable?  | Y, up to 3x   | N   | N                | Y, up to 15x                            |
| Pyrophoric?   | Y   | N   | N                | N                                       |
| H <sub>2</sub> S Removed per Kilogram of Product      | 2.5 kg H <sub>2</sub> S / kg Fe <sub>2</sub> O <sub>3</sub>     | 0.55 – 0.72 kg H <sub>2</sub> S / kg Fe <sub>2</sub> O <sub>3</sub> | Not known        | 0.5 kg H <sub>2</sub> S / kg media      |
| Spent Media Hazardous?                                | Y   | N   | N                | N                                       |
| Reduction of H <sub>2</sub> S                         | 3600 ppm to < 1ppm  | Not known   | Down to < 1 ppm  | 60 - 100 ppm to < 0.2 ppm               |
| Cost per removed kg of H <sub>2</sub> S               | \$0.35 – 1.55   | \$4.85 – 5.00   | \$7.95 – 8.50    | \$2.90 – 3.00                           |
| Annual Product Cost? (100 ppm – 400 ppm loading) [53] | \$250 – 4,300   | \$3,400 – 13,500  | \$5,560 – 23,840 | \$2,050 - \$8,290                       |

Iron oxides are not as selective as zinc oxides which are more favorable for removing only trace amounts of hydrogen sulfide. Zinc oxides remove hydrogen sulfide from gas streams by a reaction that forms insoluble zinc sulfide. A potentially major drawback of zinc oxides for biogas cleanup is that the temperature requirement for effective performance is around 200°C. <sup>[53]</sup>

#### 7.2.1.2 Chelated-Iron Solutions

The two major chelated-iron processes are LO-CAT® trademarked by Gas Technology Products and Sulferox® service marked by Shell Oil Company. Both marketed processes operate on reduction/oxidation (redox) reactions. During a redox

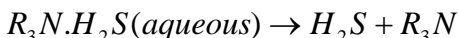
reaction, oxidation numbers are changed. In both processes, the iron oxidation number is reduced and hydrogen sulfide is separated into elemental sulfur by an increase of its oxidation number. Regeneration is possible with both processes and is accomplished by an oxidation reaction. Sulferox® is recommended for use with gas flows less than 10 MM m<sup>3</sup>/day that contain between 100 kg and 5 ton of sulfur per day. LO-CAT® has a typical range of 150 lbs to 20 long tons (22.4 tons) of sulfur per day at flow rates up to 10,000 SCFM. Sulferox® claims removal of hydrogen sulfide to less than 1ppmv. LO-CAT® asserts their units can be designed to achieve better than 99.9% hydrogen sulfide removal efficiency. Gas Technology Products also offers MINI-CAT™ units which use the same catalyst as LO-CAT® but are designed to remove 100 – 1,000 kg sulfur per day. MINI-CAT™ units are prefabricated, skid-mounted, and have a smaller footprint than the LO-CAT® units.<sup>[64,65]</sup>

### 7.2.1.3 Amine Solutions

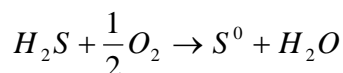
Large scale cleanup of natural gas is typically done by the ‘amine process’ which can also be called the Girdler process. Amine processing units can be designed for high removal rates of hydrogen sulfide and carbon dioxide or hydrogen sulfide only. In the amine process, sour gas is passed through a column containing the amine which absorbs the undesirable components. The reaction is depicted in the following equation where the amine is R<sub>3</sub>N.



Once the reaction has taken place, the amine can be regenerated by dropping the pressure and increasing the temperature. The regeneration reaction is shown below.

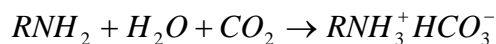


At this point, the hydrogen sulfide is in a concentrated form which is either flared or converted to elemental sulfur using air in a sulfur recovery unit (SRU) represented by the following equation.



[63,66]

Amine solvents have also been used for carbon dioxide removal from power plant flue gases. Scaled down versions have been successfully applied for landfill applications. Regeneration of the amine is done by the same method above, consisting of a drop in pressure and an increase in temperature. The equations corresponding to carbon dioxide removal and amine regeneration are shown below.



[52]

Drawbacks of amine processes on a small scale include high energy needs for regeneration, stringent safety measures regarding concentrated hydrogen sulfide gas streams, complicated flows, and foaming issues associated with liquid absorption procedures.<sup>[53]</sup> Removal of carbon dioxide via amines has disadvantages that include

corrosion, breakdown of the amine, and buildup of contaminants. <sup>[52]</sup> Table 27 lists commonly used amines. Table 28 lists proprietary amine processes and their descriptions.

**Table 27: Generic Amines.**

| Common Name | Name                   |
|-------------|------------------------|
| MEA         | Monoethanol Amine      |
| DEA         | Diethanol Amine        |
| MDEA        | Methyl Diethanol Amine |
| DIPA        | Diisopropanol Amine    |
| DGA         | Diglycolamine          |

**Table 28: Proprietary Amines.**

| Process Name                                 | Description   |
|--|---|
| Sulfa-Scrub®<br>(Quaker Chemical)            | Hexahydrotriazine   |
| Sulfinol-X<br>(Shell)                        | A mixture of two or more alkanolamines – generally a base amine such as MDEA or Sulfinol-X (diisopropanolamine) and an accelerator. |
| ADIP-X<br>(Shell)                            | A mixture of two or more alkanolamines – generally a base amine such as MDEA and an accelerator.                                    |
| The ELIMINATOR™<br>(Gas Technology Products) | A high molecular weight hexahydrotriazine-based chemical  |
| COOAB™<br>(Cirmac)                           | Special amine composition   |

#### 7.2.1.4 Water and Solvent Scrubbing

Water scrubbing is a cheap and simple method for cleanup and is most appropriate for an operation where water is easily accessible, such as a water treatment facility. One advantage of water scrubbing is the simultaneous removal of hydrogen sulfide and carbon dioxide. Biogas cleaning by water scrubbing loses about 2% methane during processing but results in a gas that contains roughly 95% methane.

Water scrubbing is accomplished by pressurizing the biogas and injecting it into the bottom of a packed column containing water flowing from the top. The water

dissolves the carbon dioxide and passes out of the bottom of the column. The “cleaned” gas leaves the top of the column. The water can be circulated into an air column for regeneration, i.e. CO<sub>2</sub> removal, and then passed back into the column. However, regeneration is not recommended for gas streams containing large amounts of hydrogen sulfide.

Solvents, including amines, can replace water in the packed column to improve the scrubbing process. Solvent scrubbing is more efficient than water washing since carbon dioxide and hydrogen sulfide are more soluble in solvent than water. This results in lower solvent and pumping requirements. Solvents also have the ability to upgrade the methane content to above 95%. The most well known solvent is Selexol, which is licensed by UOP, and can be used to selectively remove hydrogen sulfide or carbon dioxide individually. Sour gas feeds composed from 5 – 60% carbon dioxide and hydrogen sulfide can be cleaned to ppmv or percent volume as applicable. Regeneration of the solvent is done through steam stripping.

Table 29 lists a number of processes used for solvent scrubbing as well as the process owner / licensor and the solvent used. Sulfinol is listed here as it is a physical absorption process although it also enlists amine agents to improve acid gas (H<sub>2</sub>S) removal.

**Table 29: Scrubbing Solvents.**

| Process Name   | Owner             | Solvent                               |
|----------------|-------------------|---------------------------------------|
| Selexol        | UOP               | Dimethyl ether of polyethylene glycol |
| Sulfinol       | Shell             | Sulfolane, DIPA or MDEA and water     |
| Purisol        | Lurgi AG          | Normal methyl pyrrolidone             |
| Rectisol       | Lurgi AG          | Methanol                              |
| Fluor Solvent™ | Fluor Corporation | Propylene carbonate                   |

### 7.2.2 Membrane Permeation

Membrane separation processes, which are primarily used for carbon dioxide removal, are accomplished by utilizing pressure and a membrane which is selective to a particular gas. Pressurized gas is passed along one side of the membrane which, utilizing the pressure differential, allows specific molecules to permeate to the other side. Gas streams containing high levels of hydrogen sulfide can degrade the membrane and shorten its useful life. To extend membrane life, cleanup units can be employed to pre-clean the gas before entering the membrane process. Membranes can be highly selective or highly permeable but rarely both. The process efficiency is therefore less than ideal as multiple passes are needed and gas is lost. However, membranes are highly reliable, easy to operate, and can be used for gas dehydration.

Air Products manufactures PRISM® membranes which offer separation of carbon dioxide, hydrogen sulfide, and nitrogen as well as air drying and gas dehydration. <sup>[67]</sup> According to Freemantle, odor removal studies conducted at Imperial College London using a specialized membrane indicate that low hydrogen sulfide levels can be

removed from nitrogen gas streams effectively and economically. Other attempts to remove hydrogen sulfide using membranes include the use of a liquid adsorbent on the exit side of the membrane. This method has a lower pressure requirement than the membrane process above but is far less developed. Positive results have been realized using sodium hydroxide or a coral solution as the liquid sorbent. <sup>[68, 53]</sup>

### 7.2.3 Adsorption Processes

Sour gas is passed through a bed of adsorbate which likely exhibits a high surface area to unit weight ratio. The adsorbent is typically a microporous solid that attracts and holds onto selective components (adsorbate) from the gas stream. The force which binds the gas components to the solid is quite weak making regeneration easily attainable by decreasing gas pressure, increasing temperature, and gas purges. Regeneration of adsorbents can be accomplished through one of the four following cycles: Temperature Swing Adsorption, Inert Purge Adsorption, Displacement Purge Adsorption, or Pressure Swing Adsorption. <sup>[69]</sup>

#### 7.2.3.1 Temperature Swing Adsorption (TSA)

TSA is used primarily for dehydration and removal of small concentrations of impurities. The gas is passed through the adsorbent but at a low temperature. Once the bed becomes saturated, the temperature is raised and the gas continues to pass through the bed until saturation occurs at the raised temperature. Adsorption and regeneration is accomplished through a heating and cooling cycle which is both time and energy intensive. <sup>[69]</sup>

#### 7.2.3.2 Inert Purge Adsorption Cycle

Gas is passed through the adsorbent bed until saturation at partial pressure occurs. A non-adsorbing gas is then fed through the bed causing desorption by reducing the partial pressure of the adsorbate. It is the heat of adsorption that causes the temperature difference. There is an increase during adsorption and a decrease during desorption eliminating the need for externally created heating and cooling as with TSA. The Inert Purge Adsorption Cycle occurs quickly but is limited to low concentration changes and is usually employed for hydrocarbon separation. <sup>[69]</sup>

#### 7.2.3.3 Displacement Purge Adsorption Cycle

The Displacement Purge Cycle is similar to the Inert Purge cycle. The major difference occurs in the desorption approach. In Displacement Purge, a purge gas which is more strongly adsorbed than the removed component is passed through the bed. Though Displacement Purge and Inert Purge have short cycle times and are used for hydrocarbon separation, Displacement Purge can realize greater removal amounts. The major drawback of Displacement Purge is the necessity of the separation of the purge gas from the purge stream and from the adsorbent. <sup>[69]</sup>

#### 7.2.3.4 Pressure Swing Adsorption (PSA) Cycle

Rapid cycling is also possible with PSA. This cycle relies on pressure changes to adsorb contaminants from the gas stream. Desorption occurs by lowering the pressure. Application of PSA to biogas has been performed in the United States and Europe. Pretreatment is recommended prior to employing this process for carbon



dioxide adsorption. This includes reducing hydrogen sulfide levels and dehydrating the gas.

A typical PSA configuration includes four pressurized vessels, each containing the adsorbent. The gas is fed through one vessel and the methane rich, cleaned gas exits the top. When the adsorbent in this vessel becomes saturated, raw gas is sent to another vessel. Regeneration of the first vessel is accomplished through depressurization. The gas released in this step is recycled back to the inlet for methane recovery. The vessel is then evacuated using a vacuum and is ready to absorb more carbon dioxide. The use of four vessels allows energy savings from the need for less gas compression and depressurization between the vessels. The operation is continuous in a similar manner to a four cylinder engine in which each piston is in a different position in the cycle and will fire in sequence. <sup>[69][70]</sup>

#### 7.2.4 Adsorbents

Although Pressure Swing Adsorption, Temperature Swing Adsorption, Inert Purge, and Displacement Purge cycles make regeneration of adsorbents possible, not all adsorbents are economically regenerable. There are a number of options for cleanup using adsorbents. Silica or alumina based adsorbents are preferred for gas dehydration operations. Gas cleanup adsorption methods would employ molecular sieves or carbon-based adsorbents. Carbon-based adsorbents can be activated making them capable of organic vapor adsorption. Molecular sieves are unique in that they are capable of dehydration and selective adsorption. <sup>[69]</sup>

##### 7.2.4.1 Molecular Sieves

Molecular sieves used as adsorbents occur in nature but the most commonly used sieves are synthetic. They are commonly referred to as zeolites. Molecular sieves are capable of adsorbing or excluding a molecule based on size. High adsorption capacity at low concentrations, as well as possessing a high affinity for polar compounds (H<sub>2</sub>S, H<sub>2</sub>O, NH<sub>3</sub>, etc), make it an attractive product for gas purification. The four most widely used are type 3A, 4A, 5A, and 13X. The type name refers to the size of molecules it will absorb. For instance, type 4A will not absorb any molecule larger than 4 Ångströms (1 Ångström = 1×10<sup>-10</sup> meters). Type 13X has a pore size of 10 Ångströms.

In regard to gas processing, pore size limitations of 4A and 5A sieves can only adsorb light mercaptans making a 13X a preferred adsorbent for complete sulfur removal. With size 13X, preferential adsorption of polar compounds allows for selective removal of water and hydrogen sulfide over carbon dioxide. <sup>[69]</sup>

##### 7.2.4.2 Activated Carbon

Carbon-based materials with the ability to adsorb have been dubbed ‘active carbon’ or ‘activated carbon’. A significant number of source materials have been used to produce them including wood, nutshells, rice hulls, bones, petroleum coke, and coal to name a few. In order to ‘activate’ the carbon material, source materials are ground, mixed with a binder, extruded, and heated. Additional steps like adding chemicals or using oxidizing gases can increase adsorption properties. Active carbons are preferred adsorbents for removal and recovery of volatile organic compounds and odor abatement as a form of air pollution control. <sup>[69]</sup>



#### 7.2.4.3 Impregnated Activated Carbon

To adapt active carbons to remove hydrogen sulfide, they can be impregnated. Carbons impregnated with compounds like sodium hydroxide or sodium carbonate can attract and keep sulfur compounds through an acid-base reaction. This has been shown to increase hydrogen sulfide and methyl mercaptan adsorption by 40 – 60 times that of the original carbon. Metal oxide impregnated carbons contain sulfur as metal sulfates or sulfides. <sup>[69]</sup>

### 7.3 Summary of Hydrogen Sulfide Removal Processes in Farm Operations

| Table 5.3: Summary of H <sub>2</sub> S Removal Process Characteristics  |   |                            |                                    |                                 |                          |   |                                   |
|---|---|----------------------------|------------------------------------|---------------------------------|--------------------------|---|-----------------------------------|
| Removal Technique   | Applicability for farm biogas<br>(+ = high) | Capital Costs<br>(+ = low) | Operating/Media Costs<br>(+ = low) | Ease of operation<br>(+ = easy) | Regenerable<br>(+ = yes) | H <sub>2</sub> S < 250 ppm<br>(+ = yes) | Environmental impact<br>(+ = low) |
| Iron Oxides   | +   | +                          | +/-                                | +/-                             | +/-                      | +                                       | -                                 |
| Zinc Oxides   | -   | +                          | -                                  | +/-                             | -                        | +                                       | -                                 |
| Alkaline Solids   | -   | +                          | -                                  | +/-                             | -                        | +                                       | -                                 |
| Impregnated Activated Carbons   | +   | +                          | +/-                                | +/-                             | -                        | +                                       | -                                 |
| Molecular Sieves  | +/-   | +/-                        | -                                  | -                               | +                        | +                                       | -                                 |
| Chelated Iron Solutions   | +/-   | -                          | -                                  | -                               | +/-                      | +                                       | +/-                               |
| Nitrite Solutions   | +/-   | +                          | -                                  | +                               | -                        | +                                       | -                                 |
| Alkaline Salt Solutions   | -   | -                          | -                                  | -                               | -                        | +                                       | -                                 |
| Amine Solutions   | -   | -                          | -                                  | -                               | +                        | +                                       | -                                 |
| Water Scrubbing   | +/-   | +/-                        | +/-                                | +/-                             | +                        | +/-                                     | -                                 |
| Physical Solvent Scrubbing  | +/-   | +/-                        | +/-                                | +/-                             | +                        | +/-                                     | -                                 |
| Membrane: Low Pressure  | +/-   | -                          | -                                  | -                               | +/-                      | +/-                                     | +/-                               |
| Membrane: High Pressure   | -   | -                          | -                                  | +/-                             | n/a                      | +/-                                     | +                                 |
| Digester pH Control   | +/-   | +                          | +/-                                | +/-                             | n/a                      | -                                       | +/-                               |
| Digester Iron Addition  | +   | +                          | +                                  | +                               | n/a                      | -                                       | +/-                               |
| Dietary Adjustment  | +/-   | +                          | +                                  | +/-                             | n/a                      | -                                       | +                                 |
| Air Dosing to Biogas  | +   | +                          | +                                  | +                               | n/a                      | +/-                                     | +                                 |
| Commercial Biological Processes   | +/-   | -                          | +/-                                | +/-                             | +/-                      | +                                       | +                                 |
| Estimate Cow-Manure Compost Processes   | +   | +                          | +                                  | +                               | n/a                      | +                                       | +                                 |
| <div> <div>n/a = not applicable</div> <div>+/- = neutral</div> <div>desirable</div> <div>- = undesirable</div> </div> |   |                            |                                    |                                 |                          |   |                                   |

Source: Zicari, Stephen McKinsey. 2003. Removal of Hydrogen Sulfide from Biogas Using Cow-Manure Compost. Master's Thesis, Cornell

Figure 28: Rating of H<sub>2</sub>S Removal Processes as Applied to Farm Operations.

### 7.4 Biogas Clean Up Systems

This section provides an overview of a handful of companies offering gas cleanup technologies. The list of companies is not exhaustive but is used to illustrate available options and market competitiveness for processing biogas. Most of the companies

listed here offer the full range of services for gas cleanup. Outfits exist outside of this list that provide any and all services for biogas cleanup be it design, construction, operation, or maintenance. Overall, the options are nearly endless for anyone wishing to upgrade biogas. Systems can be built on-site or pre-fabricated and delivered on a skid. They can be purchased or leased. Systems can be designed for a large range of flow rates. Additional filters can be implemented for biogas with higher acid gas content. Off-gases can be upgraded and sold or simply flared. Controls and operation can be automated.

## 7.4.1 Example Companies that Manufacture Biogas Cleanup Systems

### 7.4.1.1 CarboTech Engineering GmbH

CarboTech, a subsidiary of Schmack Biogas AG, and located in Germany offers a complete biogas upgrading service through their Mobile Adsorber Rental Systems (MAMS). CarboTech also transports, replaces, and reactivates spent carbon materials. The MAMS-G, which is used for gas applications, utilizes carbon molecular sieves and a pressure swing adsorption process. In short, the cleanup process steps are

1. Compression of the gas
2. Water removal by cooling
3. Desulphurization by activated carbon
4. Impurity removal by PSA using carbon molecular sieves

**Table 30: Cleaned Gas Content – CarboTech.**

| Compound         | Cleaned                            |
|------------------|------------------------------------|
| CH <sub>4</sub>  | Up to 99%                          |
| H <sub>2</sub> S | < 3.59 ppm (<5 mg/m <sup>3</sup> ) |

Advantages include a programmable logic controller (PLC) for fully automatic operation, no process water, no wastewater handling, no chemicals, no corrosion issues, low energy requirements, low operation and maintenance requirements, and a compact and safe design. The CarboTech process also offers the ZETECH4® system as an option, which prevents methane and hydrogen sulfide emissions. <sup>[71]</sup>

### 7.4.1.2 Purac

Lackeby Water Group, which operates on three continents and in 70 countries is an independent, privately owned Swedish group. Its expertise in water treatment and biogas production lies with its contracting group Purac. Purac supplies, builds, and commissions plants specially designed to meet client needs. A specially composed amine called Cooab is the absorption liquid employed to remove carbon dioxide from the biogas and is considered the core segment of the cleanup process, which as a whole is called the LP Cooab process. The upgrading process is accomplished by:

1. Optional - H<sub>2</sub>S removal by caustic scrubber and bioreactor system (for H<sub>2</sub>S concentrations >500ppm)
2. H<sub>2</sub>S removal by activated carbon (Air added at inlet, if needed)
3. CO<sub>2</sub> removal by amine scrubbing
4. Drying of upgraded gas by PSA or TSA
5. Gas quality analysis (gas not to specification is reprocessed)
6. Addition of odorant

**Table 31: Cleaned Gas Content – Purac.**

| Compound         | Cleaned            |
|------------------|--------------------|
| CH <sub>4</sub>  | > 99%              |
| H <sub>2</sub> S | Typically <0.5 ppm |

Company literature lists the following benefits: less than 0.1% methane lost to the atmosphere, operational costs that are proportional to the actual capacity, high purity CO<sub>2</sub> that can be re-used and output gas, which is of pipeline quality.<sup>[72]</sup>

#### 7.4.1.3 NESI

Located in Massachusetts, USA, New Energy Solutions, Inc., NESI has been in green energy for 5 years. NESI's technical team supports the design and operation of the BioGas Clean-Up Unit which serves as the base unit for the NEO-Hydrogen™ and NEO-Gas™ plant. The unit cleans via two adsorption beds. The bed media is supplied and changed out by US Filter. The NEO-Gas™ plant cleanup process is as follows:

1. Removal of moisture, particulates, H<sub>2</sub>S, and siloxanes by adsorption
2. Compression of the gas
3. Further cleanup and drying of the gas by PSA

**Table 32: Cleaned Gas Content – NESI.**

| Compound         | Cleaned |
|------------------|---------|
| CH <sub>4</sub>  | ≥ 98.5% |
| H <sub>2</sub> S | 2-6 ppm |
| Siloxanes        | 2-6 ppm |

The NEO-Gas™ plant is capable of producing 1,200 scfh of pipeline quality gas. The system comes with a fully automated control feature. It uses the Allen Bradley SLC 500 series PLC. This is used to feed information to the Human Machine Interface (HMI), which is a laptop style datalogger. The HMI provides information regarding the operation of the unit, including details about inputs and outputs on a flow diagram and any error or warning messages. <sup>[73,74]</sup>

#### 7.4.1.4 Applied Filter Technology

Since early 1996 Applied Filter Technology (AFT) has been a leader in removal of siloxanes from gas streams and has developed many technologies that are in use in 80 different countries. Most recently they have developed the SWOP process that has efficiently removed siloxanes, volatile organic compounds, organosilicons, and sulfur compounds from landfill biogas. The most recent technological advancement of AFT is their SWOP™ Process with SAG™ Final Polishing. The SWOP™ process involves:

1. Removal siloxanes and VOCs in the concentrator vessel
2. “Polishing” of the gas in 1 or 2 SAG™ vessels
3. Cleaned gas used by power generation equipment

**Table 33: Cleaned Gas Content – AFT.**

| Compound         | Cleaned       |
|------------------|---------------|
| CH <sub>4</sub>  | Not Specified |
| H <sub>2</sub> S | Not Specified |
| Siloxanes        | Not Specified |

Regeneration of the SWOP™ process is continuous and self supported. The SWOP™ process operates using treated gas, which is about 0.5-1.0% of the total gas flow. The entire system draws about 8kW of electricity. <sup>[75]</sup>

#### 7.4.1.5 Guild

For over 5 years, Guild has fabricated and installed over 2-dozen biogas upgrading systems, and services various markets. Guild provides an easy-to-use system that is reliable, requires little attention and is environmentally friendly.

1. Compression of the gas to 60-100 psig
2. Removal of H<sub>2</sub>O, CO<sub>2</sub>, and H<sub>2</sub>S by PSA

**Table 34: Cleaned Gas Content – Guild.**

| Compound         | Cleaned                         |
|------------------|---------------------------------|
| CH <sub>4</sub>  | As required by pipeline company |
| H <sub>2</sub> S | Typically to 4ppm               |
| CO <sub>2</sub>  | Typically to 1-3%               |
| Water            | >7 lbs per MMSCF                |

The raw biogas is first compressed to 60-100 psig before entering the biogas upgrading system. Guild uses a PSA adsorption system for the removal of water, CO<sub>2</sub>, and H<sub>2</sub>S in a single step. This system is customized to meet the specification of pipeline quality as defined by its customer. Afterwards, the adsorbent vessel is regenerated by the removal of water, CO<sub>2</sub>, and H<sub>2</sub>S by depressurization and desorbing through a vacuum pump. The contaminants and a small feed of methane leave the vessel as a form of tail gas that can be flared or used as a local fuel.

Cleaned biogas is cleaned under the specifications outlined by the local distribution or pipeline company. However, typically Guild removes water to less than 7lbs per MMCSF, H<sub>2</sub>S to 4ppm, and CO<sub>2</sub> to 1-3%.<sup>[76]</sup>

#### 7.4.1.6 QuestAir Technologies Inc.

Founded in 1996 and based in Burnaby, British Columbia, QuestAir develops, manufactures, and supplies gas purification systems for hydrogen recovery, hydrogen purification, helium purification, and methane recovery from biogas. QuestAir offers skid mounted PSA systems, M-3100 and M-3200 for gas purification. Varying the adsorbent material and valve design, the systems can be reconfigured to clean different gases.

1. Removal of contaminants by an integrated fast-cycle PSA using proprietary structured adsorbent material

**Table 35: Cleaned Gas Content – QuestAir.**

| Compound         | Cleaned       |
|------------------|---------------|
| CH <sub>4</sub>  | Up to 99%     |
| H <sub>2</sub> S | Not Specified |

The M-3100 and M-3200 can remove CO<sub>2</sub> and H<sub>2</sub>O as well as other trace gases to meet pipeline specification. This is accomplished by using a specially structured adsorbent material that reduces the amount of adsorbent needed and allows higher cycle speeds than traditional PSA systems. QuestAir also employs a proprietary rotary valve, which is more compact than typical PSA systems and reduces capital and installation costs.<sup>[77]</sup>

## 7.4.2 Example Companies that Provide Biogas Cleanup Equipment and Services

### 7.4.2.1 Flotech

Based in New Zealand, Flotech is known internationally as an industrial equipment supplier, providing solutions in heat exchange, gas compression, and gas purification. Flotech offers modular pre-engineered plants as well as custom solutions. Biogas cleanup is accomplished via Greenlane™, Flotech's "Compression – Scrubbing – Flash – Recovery" system. The system operates on an advanced water scrubbing technique which employs the use of a regenerating water system. The process in a basic form is:

1. Removal of moisture and particulates
2. 2 stage compression of the gas
3. H<sub>2</sub>S and CO<sub>2</sub> removal by a specially design water scrubber
4. Drying of the gas by PSA/TSA
5. Gas quality analysis (gas not to specification is reprocessed)
6. Recovery of CH<sub>4</sub> from process water in a flashing tank
7. Stripping of CO<sub>2</sub> from process water for re-use

**Table 36: Cleaned Gas Content – Flotech.**

| Compound         | Cleaned       |
|------------------|---------------|
| CH <sub>4</sub>  | ≈ 97%         |
| H <sub>2</sub> S | Not Specified |

The Greenlane™ process removes almost all siloxanes. This is more critical in non-dairy manure derived biogas as dairy manure derived biogas typically does not contain siloxanes. The process is optimized to control methane losses to about 0.1%. In order to maintain the efficiency of the system, Flotech offers an automatic washing solution for Greenlane™ plants that removes biological debris that accumulates throughout the system. GE Ro-Flo compressors were selected for the system because they are capable of standing up to H<sub>2</sub>S concentrations of 90%.<sup>[78]</sup>

### 7.4.2.2 SouthTex Treaters

SouthTex has been providing contract gas treating services and equipment since 1986. Their more than 70 employees work in four states and services include design, construction, and start-up of plants to process gas. Processing options include acid gas removal, amine treatment, gas dehydration, NGL recovery, and landfill gas treatment. SouthTex designed and constructed their first manure to methane plant in 2006. Specific information of their cleanup processes were not readily available. The plants that they currently operate employ the following clean up processes:



1. Amine Treatment
2. Sulfinol
3. Physical Solvent
4. Dehydration

**Table 37: Cleaned Gas Content – SouthTex Treaters.**

| Compound         | Cleaned         |
|------------------|-----------------|
| CH <sub>4</sub>  | 950-970 BTU/scf |
| H <sub>2</sub> S | < 4 ppm         |
| Siloxanes        | Not Specified   |

Since 2001 SouthTex Treaters has been treating landfill gas in Kansas City. The plant treats about 3850 scfm and cleans the gas to pipeline specifications. The maximum CO<sub>2</sub> content of the treated gas is 2%. Water content is less than 7 Lb/MMSCF and O<sub>2</sub> is less than 50 ppm. Since the treated gas is being piped to and used by residential customers, shutdowns have been installed for each quality constraint.<sup>[79]</sup>

### 7.4.3 Other Companies Providing Upgrading Services

**Table 38: Additional Biogas Processing Companies.**

| Company                      | Location                   | Website   |
|------------------------------|----------------------------|---|
| Cirmac International bv      | Apeldoorn, The Netherlands | <a href="http://www.cirmac.nl/?url=products_biogas.php">http://www.cirmac.nl/?url=products_biogas.php</a>         |
| FirmGreen®                   | Newport Beach, CA          | <a href="http://www.firmgreen.com">http://www.firmgreen.com</a>   |
| HAASE Energietechnik AG      | Neumuenster, Germany       | <a href="http://www.haase-energietechnik.de/en/Home/">http://www.haase-energietechnik.de/en/Home/</a>             |
| Malmberg                     | Åhus, Sweden               | <a href="http://www.malmberg.se/module.asp?XModuleId=14136">http://www.malmberg.se/module.asp?XModuleId=14136</a> |
| Phase 3 Renewables           | Cincinnati, OH             | <a href="http://phase3dev.com">http://phase3dev.com</a>   |
| R.C. Costello & Assoc., Inc. | Redondo Beach, CA          | <a href="http://www.rccostello.com/naturalgas.html">http://www.rccostello.com/naturalgas.html</a>                 |
| Unison Solutions             | Dubuque, IA                | <a href="http://www.unisonsolutions.com">http://www.unisonsolutions.com</a>                                       |

**Table 39: Summary of Biogas Upgrading Technologies.**

|   | <b>CarboTech</b>  | <b>Purac</b>                           | <b>Flotech</b>                                   | <b>NESI</b>   | <b>AFT</b>   | <b>Guild</b>  | <b>SouthTex</b>                                | <b>QuestAir</b>   |
|---|---|--|--|---|--|---|--|---|
| <b>Source(s)</b>                        | Digester gas  | Wastewater                             | Wastewater sludge with food and organic waste    | Digester gas  | Landfill gas, digester gas   | Digester gas  | Landfill gas                                   | Landfill gas, digester gas                              |
| <b>Processes</b>                        | Adsorption, PSA   | Activated carbon, Amine scrubbing, PSA | Water scrubbing, PSA/TSA (CSFR system)           | Adsorption, PSA   | Adsorption   | PSA   | Amine, sulfinol, or physical solvent scrubbing | PSA   |
| <b>Typical Raw Biogas Content</b>       | 55-70% CH <sub>4</sub><br>30-45% CO <sub>2</sub><br><2% nitrogen<br><0.5% oxygen<br><500 ppmv H <sub>2</sub> S<br>water saturated | Not Specified                          | 55-65% CH <sub>4</sub><br>45-36% CO <sub>2</sub> | 55-60% CH <sub>4</sub><br>40-45% CO <sub>2</sub> ,<br>Up to 4000ppm of H <sub>2</sub> S and siloxanes | 46-48% CH <sub>4</sub><br>36-38% CO <sub>2</sub><br>10-12% nitrogen<br>1.5-1.8% oxygen<br>624 ppmv VOCs<br>3.17 ppmv organosilicon | 60 % CH <sub>4</sub><br>40% CO <sub>2</sub><br>3-4,000 H <sub>2</sub> S water saturated | Not Specified                                  | 25-90 % CH <sub>4</sub>                                 |
| <b>Cleaned Methane Content</b>          | Up to 99%   | > 99%                                  | ≈ 97%  | ≥ 98.5%   | Not Specified  | As required by pipeline company   | Not Specified                                  | Up to 99%   |
| <b>Cleaned Hydrogen Sulfide Content</b> | < 3.59 ppm  | Typically <0.5 ppm                     | Not Specified                                    | 2-6 ppm   | Not Specified  | Typically to 4 ppm  | < 4 ppm  | Not Specified   |
| <b>Utilization</b>                      | Natural gas substitute<br>Vehicle fuel  | Natural gas network<br>Vehicle fuel    | Vehicle fuel                                     | CNG vehicle fuel<br>Electrical use  | Power generation   | Natural gas network   | Natural gas network                            | Natural gas network<br>Vehicle fuel<br>Power Generation |

## 8 Transfer to Natural Gas Infrastructure

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### 8.1 Means of Transfer

Section 5.4 contained a discussion of some of the issues with which the dairy farmer must be concerned in producing biogas. One of those issues is how any net energy production of cleaned gas from the biogas plant will be transferred to another user or acceptor. If the biogas plant is conveniently located near a distribution network or a transmission line, then perhaps a direct connection can be made and gas may be injected directly into the network. This almost certainly will require construction of some length of pipeline between the biogas plant and the network injection point. However, if a dairy farm is isolated from any major transmission or distribution lines, the gas has to be transported either as compressed gas using bulk transportation vehicles (i.e. “tube trailers”) or as liquefied gas, using LNG tankers. By either of these means, the gas is transported to a facility at which the gas is injected into the pipeline network. In the case of LNG, Figure 29 and Figure 30 show typical trailers used for compressed natural gas (CNG) and liquefied natural gas (LNG) transport, respectively. One clear advantage of LNG is that some infrastructure is already in place to accept it. Since LNG is mostly imported from outside the country, in-state production of liquefied biomethane (LBM) may have an economic advantage over imported LNG with respect to transportation costs and trade tariffs.

An alternative to injecting biogas into the transmission or distribution systems would be to inject it directly into natural gas storage wells. If a set of dairy farms were located in reasonable proximity to a storage well, the farms could transfer their biogas to the storage well. Perhaps biogas could even be transferred to a clean-up facility near the well, which would jointly cleanup raw biogas from all nearby farms. Given a critical density of dairy farms, a central cleanup facility may benefit from economies of scale. From the utility company’s point of view, an automated measurement system could be set up directly after the clean-up unit to monitor the important parameters of the biogas. Thus, the utility would minimize the number of monitoring stations required and may only need to monitor a single station as opposed to a larger set of transmission and distribution interconnect site.

Capital cost and operational comparisons of direct injection to infrastructure, of compressed gas transport, of liquefied gas transport, and of injection to storage wells through centralized cleanup units are highly case dependent. Detailed considerations of the economics and operational cost-benefits are beyond the scope of this report.



**Figure 29: Side View of CNG Transporting Trailer.**<sup>31</sup>



**Figure 30: Side View of LNG Tanker.**<sup>32</sup>

### 8.1.1 Examples of biomethane transfer

Information regarding introduction of cleaned biomethane into the existing pipeline network throughout North America is limited. Since there are only a few utilities that are injecting biomethane derived from dairy waste into their infrastructures, or *are planning to do so*, this section will be based on two case-study examples: Northern Natural Gas, and Pacific Gas and Electric (PG&E). Note that of

<sup>31</sup> Picture provided by Agri-Waste Energy, Inc.

<sup>32</sup> Picture provided by FIBA Canning, Inc.

these examples, GTI was only able to collect samples from the biomethane supplier (Agri-Waste Energy) providing biomethane to the Northern Natural System.

Northern Natural Gas is injecting dairy-manure-based biogas into its natural gas grid in Baldwin, WI with the help of Agri-Waste Energy. The biogas is generated at Emerald Dairy in Emerald, WI. The dairy has a digester that receives manure from 4000 cows. Downstream of the digester, the system cleans up the gas to DOT Class 2, Division 2.1 specification, suitable for CNG transport. After filling the tube trailer, excess biogas is used by the farm in a hot water boiler. A picture of the high pressure storage tanks is in Figure 31.



**Figure 31: Emerald Dairy Farm High-Pressure Storage Tanks in Emerald, WI.**

After the gas is collected in the cylinders on the tube trailer, it is transported to the local northern natural gas transmission facility. Figure 32 and Figure 33 show the entrance to the RNG (“renewable natural gas”) transfer station. At this point, gas can be injected either to the transmission line or the distribution line. The condition required for injecting the biomethane into the distribution line is that the flow in the line at that time is very high. Because biogas cools at roughly 7°F for every 100 psi drop, frost starts to build on the line once it reaches 32°F unless sufficiently high flow conditions exist to remove the cooled gas. The transmission line is at a fairly constant pressure of approximately 700 psi, so the temperature cooling in this case is about 120°F. This is why frost accumulates very quickly, but as the pressure of the cylinders equilibrates to the pressure of the transmission line the temperature drop decreases. The injection port into the transmission line is shown in Figure 34.





**Figure 32: Agri-Waste RNG Transfer Station Entrance in Emerald, WI.**



**Figure 33: Agri-Waste RNG Transfer Station with Tube Trailer in Emerald, WI.**



**Figure 34: Biogas injection port into the transmission line at Northern Natural Gas facility in Baldwin, WI.**

The biogas content and flow is continuously monitored for conformance to pipeline tariff specifications. American Petroleum Institute (API) specifications are followed, and an in-line gas chromatograph and mass flow meter are used to make sure the gas meets those specifications. The gas analyzer must be calibrated periodically.<sup>[80]</sup> If the biogas does not meet even one of the requirements, the automatic check valve shuts off flow to the transmission line. A mass flow meter is generally inserted by Agri-Waste on the biogas supply side of the interconnect to verify Northern Natural Gas flow measurements.

In the next interconnect example, Vintage Dairy is planning to supply biomethane directly into a PG&E transmission line. Information provided here was supplied by PG&E and has not been verified by GTI. Since Vintage is so close to the transmission line, it was convenient to install pipe going out of the clean-up unit from their biogas facility and tap right into PG&E's transmission line. A compressor will step up the biomethane to the required transmission pressure.

Automated, in-line monitoring of gas properties related to standard requirements will occur. H<sub>2</sub>O vapor and O<sub>2</sub> will be monitored, and filters will remove particulates and microbials.<sup>[81]</sup> A SCADA system will integrate flow for a Btu measurement basis. A continuous sampler system, designed by Welker Engineering, will also be installed to bottle gas in a summa canister of approximately 6L in volume. These measurements will be taken on a periodic basis and will be compared with the automated measurement system. Again, if any of the parameters were to fall out of specification, an automatic check valve would close immediately.



## 8.2 Interconnection Standards and Requirements

In general, each gas utility has a process which a potential fuel provider must follow in order to gain permission to inject into the natural gas grid. This process is similar to interconnecting into the electrical grid, but the rates vary depending on the amount of gas being injected, the frequency of injection, and the source (e.g. LNG, biogas).

Since it is the responsibility of the utility to control its gas metering, each utility has to have its own procedure in place for interconnection into its system. It has been noted that the typical workflow summary for an interconnect project is similar to the following for distributed energy systems <sup>[82]</sup>:

1. Contact utility for necessary information, and submit an application for interconnection.
2. Application is reviewed by utility. If it passes initial review, they schedule a brief consultation period about the interconnection process.
3. An interconnection study is performed, which entails analyzing parameters of the interconnect system.
4. A formal interconnect and operating agreement is established.
5. Utilities provide design and construction to the grid, and the cost is paid by the company/person(s) providing the gas.
6. The project is inspected, tested and approved.
7. Ongoing maintenance operations and sampling is performed by the utility.

Methods of transfer based on trucking have direct impact on the required purity of the gas. The first important parameter is the methane purity. Depending on the utility, typical pipeline tariffs require a heating value of 990 Btu/scf on a dry basis. However, DOT requires 98% methane content when transporting via tube trailers.<sup>[83]</sup> In addition, Table 40 shows the difference in requirements between a typical pipeline tariff and CNG bulk transportation specification for water vapor, hydrogen sulfide, total sulfur, oxygen, and carbon dioxide. As is noted in the table, when CNG is transported via tube trailer, its water vapor concentration has to be 10 times less than the concentration for pipeline quality. In addition, the H<sub>2</sub>S has to be less than half of the pipeline quality and total sulfur must be less than 200 times pipeline quality depending on the utility.

Another issue to be sorted out in trucking bioethane is the rental or ownership of a tube trailer. The trailers are required to have DOT-3AAX seamless steel cylinders. The pressure must not exceed the rating of the cylinders, which is generally around 2400-3600 psig. Lastly, all hazardous materials designations must be clearly marked because CNG is considered a Class 2 division 2.1 hazardous material by DOT.

Similarly, LNG tankers are also a large investment. They require a double-walled insulated steel tank approved by DOT. Since the LNG is stored as a cryogenic liquid at a temperature of -260°F (-162°C), it is stored at relatively low pressures (e.g. 20 – 150 psi). It requires special handling, and requires all of the same designations as CNG tube trailers.

**Table 40: Pipeline Tariffs vs. CNG Bulk Transportation Specifications.**

| <b>Component</b> | <b>Pipeline Tariff<sup>1</sup></b> | <b>CNG Bulk Transportation Specification<sup>2</sup></b> |
|------------------|------------------------------------|--|
| Water Vapor      | < 6 lbs/mmcf                       | < 0.5 lbs/mmcf   |
| Hydrogen Sulfide | ≤ 0.25 grains/Ccf                  | ≤ 0.10 grains/Ccf  |
| Total Sulfur     | ≤ 20 grains/Ccf                    | ≤ 0.1 grains/Ccf   |
| Oxygen           | ≤ 0.2% <sup>3</sup>                | < 1.0%   |
| Carbon Dioxide   | ≤ 2.0%                             | < 3.0%   |

<sup>1</sup> Northern Natural Gas Company FERC Tariff – 4<sup>th</sup> revised sheet, issued 1 MAY 2003.

<sup>2</sup> DOT regulations DOT-E-8009 13<sup>th</sup> revision.

<sup>3</sup> All percent values listed are by volume.

## 8.3 Issues and Concerns Related to Injecting Dairy-Derived Biomethane

### 8.3.1 Concerns for the Infrastructure

A requirement of transportation of natural gas by pipelines is that the gas must be free of liquid and solid particulate matter. The basis of the requirement is to minimize problems with operation and maintenance. Water, including vapor form, is the liquid most likely to be found in biogas. If not removed, water vapor can condense to water causing hydrate and ice formation, which can threaten safety if equipment failures result. Temperature drops of 6-7°F occur in gas through a regulator for about every 100 psi of gas pressure. This drop can be enough to cause ice and hydrate formation that clog the regulator or piping if the gas contains an excessive amount of water.<sup>[84]</sup> Natural gas liquids have been reported to have the potential to be a breeding ground for microbiologically induced corrosion (MIC).<sup>[62]</sup> Hydrogen sulfide and carbon dioxide also need to be removed from natural gas because of the threats they pose. Hydrogen sulfide is toxic and, when mixed with water, becomes sulfuric acid, which is highly corrosive. Additionally, it can potentially cause sulfide stress cracking in steel. Carbon dioxide can create carbonic acid if it mixes with water. Carbon dioxide is also undesirable because it takes up volume without possessing any energy content.<sup>[85]</sup>

In regards to traditional natural gas operations, increases in liquids and liquefiables result in increases in downtime, operation efforts, and maintenance. Currently, these considerations apply more to production areas, where liquids are more common, although downstream compressor stations and measurement and regulation facilities could also realize operational problems<sup>[59]</sup>. For the direct injection of biogas into the distribution system, the risks associated with liquids and liquefiables normally found in production areas become risks in distribution areas if quality standards for the biogas are not met.

The U.S. distribution system has more than 1,214,342 miles of main and 63,534,950 services<sup>[86]</sup>. As seen in Figure 35, approximately 52% of mains are metallic and therefore susceptible to corrosion. Figure 36 shows that approximately 39% of services are non-plastic and therefore are at risk for corrosion.<sup>[86]</sup> In addition to piping, joints, valves, and regulators are also at risk to contaminants. Beyond the metal components of valves and regulators, diaphragms, gaskets, o-rings, flange seals, quad seals, and valve seats can consist of thermoplastics, elastomers, natural rubbers, and synthetic rubbers which may be sensitive to gas impurities. Polyethylene has been shown by the Plastics Pipe Institute to be resistant to 90 percent sulfuric acid and microbial attack by sewage bacteria.<sup>[87]</sup>

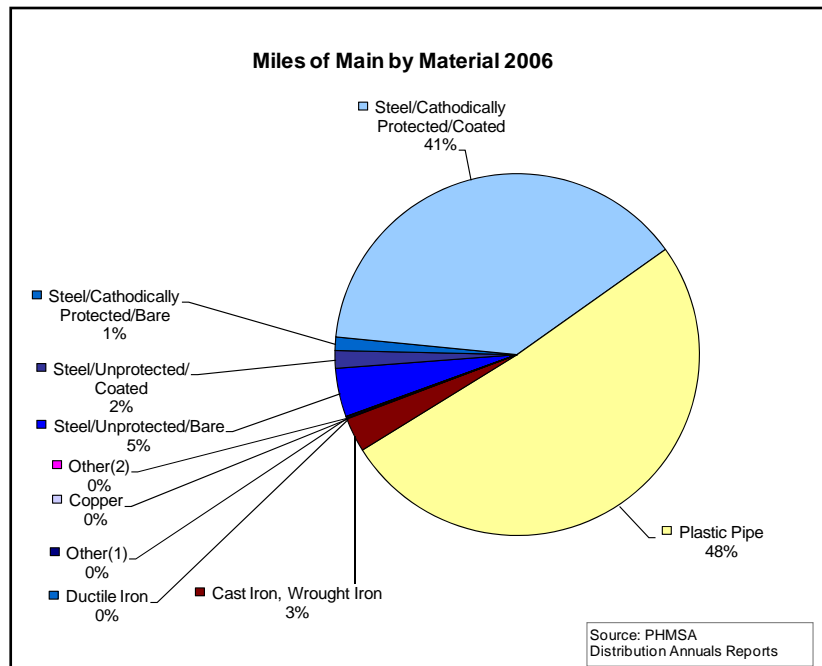


Figure 35: Miles of U.S. Mains Services by Material.<sup>[86]</sup>

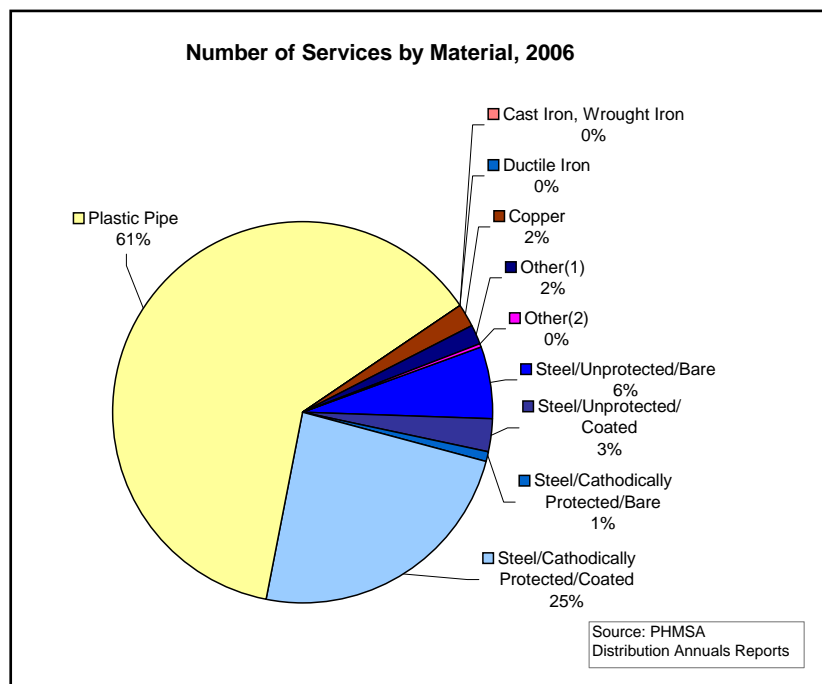


Figure 36: Number of U.S. Gas Services by Material.<sup>[86]</sup>

### 8.3.2 Concerns for Human Health

Risks to human health by transmission of disease through biogas have been addressed by the Swedish Institute of Infectious Diseases, the National Veterinary

Institute and the Swedish University of Agricultural Science. Condensate water from gas pipes and gas from biogas upgrading systems were sampled and cultured for microbes. Some of the microorganisms identified were fungi and spore- and non-spore forming bacteria. Digesters used on dairies that employ thermophilic heat treatment for 1 hour at 70 °C could potentially destroy non-spore forming pathogens. Generally, it was shown that most microorganisms were not transported by the gas but instead remained in the digested residue. Reduction in the number of microorganisms could be accomplished by passing compressed gas through a 1µm particle filter.

Natural gas was also sampled as part of the study. *Although the study was not exhaustive and the results are preliminary, it showed the densities of microorganisms found in biomethane were in a similar range as those found in natural gas.* Specific pathogen identification was not performed. It is assumed that biologicals would be completely destroyed through burning of the gas. Otherwise, inhalation of trace quantities of biomethane through end use would only occur in small volumes. Due to these factors, it was suggested that the risk of spreading disease through the use of cleaned biogas is very low.<sup>[88]</sup> However, further study in this area is most likely necessary to draw specific conclusions regarding a specific biomethane source. The group with the highest health risk by pathogens would be plant personnel, though nearly all the systems are closed. In the event that workers did inhale the unprocessed gas, hydrogen sulfide and ammonia exposure would be of much higher consequence. Levels of hydrogen sulfide concentrations and their consequences are shown in Table 41.

**Table 41: Summary of Hydrogen Sulfide Toxicity.<sup>[89]</sup>**

| <b>Exposure Concentration<br/>[mg/m<sup>3</sup>]</b> | <b>Effect on Health</b>                      |
|--|--|
| 2.8  | Bronchial constriction in asthmatics.        |
| 5-29   | Increased eye complaints and eye irritation. |
| > 140  | Paralysis of olfactory nerve.                |
| > 560  | Respiratory distress.                        |
| > 700  | Death.                                       |

The dangers associated with exposure of work personnel to unclean biomethane are potential risks to end users if proper measures are not taken to prevent accidental injection to the grid. Accidental injection would also impact system integrity and appliance operation. The concerns of injection of improperly cleaned biomethane into the distribution system have been summarized in

Table 42 and are categorized by human health, system integrity, and appliance operation.<sup>[90]</sup>

**Table 42: Summary of Injection Concerns per Area.**

| <b>Area</b>         | <b>Concern</b>   | <b>Contributing Component</b>  |
|---------------------|--|--|
| Human Health        | <ul style="list-style-type: none"> <li>▪ Direct toxicity from a confined environment leak</li> <li>▪ Indirect toxicity from combustion</li> <li>▪ Water pollution from storage injection</li> <li>▪ Air pollution</li> </ul> | <ul style="list-style-type: none"> <li>▪ Hydrogen Sulfide</li> <li>▪ Ammonia</li> <li>▪ Carbon Monoxide</li> <li>▪ Trace Constituents</li> </ul>                       |
| System Integrity    | <ul style="list-style-type: none"> <li>▪ Corrosion</li> <li>▪ Clogged pipes and valves</li> <li>▪ Odorant fade/masking</li> </ul>  | <ul style="list-style-type: none"> <li>▪ Hydrogen Sulfide</li> <li>▪ Hydrogen</li> <li>▪ Ammonia</li> <li>▪ Water/water vapor</li> <li>▪ Trace Constituents</li> </ul> |
| Appliance Operation | <ul style="list-style-type: none"> <li>▪ Change in combustion properties</li> <li>▪ Appliance performance</li> </ul>   | <ul style="list-style-type: none"> <li>▪ Hydrogen</li> <li>▪ Siloxanes</li> <li>▪ Trace Constituents</li> </ul>  |

### 8.3.3 Concerns for End Use Equipment

The concerns for the operation of end-use equipment when utilizing a replacement gas in the pipeline delivery system have long historical roots. For the case of utilizing biomethane alone within a pipeline delivery system or mixing biomethane with natural gas, the central issue is interchangeability of fuel gases. That concern has existed at least since the 1930s and 1940s when natural gas began competing with manufactured gas in many markets. Recent interest in the subject of interchangeability is driven from a need to understand the impact of liquefied natural gas (LNG) on the U.S. market. Currently, LNG represents a small portion of the overall U.S. natural gas usage, ~1% as of 2003. However, imports of LNG are expected to grow, and it is expected to reach a level of ~25% of the U.S. market by 2025.<sup>[91]</sup>

The long history of study over the last 80 years, coupled with the recent strong interest, means that an extensive amount of literature exists on the subject of interchangeability. Discussion of only a miniscule fraction of that literature falls within the scope of this report. Within that context, two objectives are possible: (1) a short summary of interchangeability issues, in which particular implications for the end-use of biomethane are noted, and (2) an indication of what literature is available to explore the general issue of interchangeability in more detail.

From an end-use perspective, part of the basic answer to the question of interchangeability lies in whether one fuel gas can replace another without

significantly impacting combustion performance. The Natural Gas Council + Interchangeability Task Group (NGC+) has defined it as follows:

*The ability to substitute one gaseous fuel for another in a combustion application without materially decreasing operational reliability, efficiency or performance while maintaining air pollutant emissions within regulatory limits. Interchangeability is described in terms of technically based quantitative measure, such as indices, that have demonstrated broad application to end users and that can be applied without discrimination of either end users or individual suppliers.<sup>[92]</sup>*

The metrics for combustion performance in the natural gas industry are related to the heat and flame characteristics at the burner, which can become modified when one fuel gas is substituted for another. Output heat flux, the amount that the flame lifts off the burner, the potential for flashback of the flame into the burner, the production of soot during combustion (called yellow-tipping), and the composition of the emissions from combustion are indicators of the relative interchangeability of two fuel gases.

The American Gas Association (AGA) has contributed for decades to the understanding of gas interchange issues. As early as 1932, the AGA had completed extensive research on 250 manufactured and mixed gases of 800 Btu/scf or less. In 1946, as natural gas was emerging in competition with manufactured gases, impetus existed to re-examine the issue of interchangeability, particularly since natural gases contain a higher energy density than the 800 Btu/scf that was previously examined in AGA's 1932 report. AGA's research with gases of higher heating value lead to a selection of indices that indicated whether one fuel gas may be substituted for another: (1) a lifting index, (2) a flash-back index, and (3) a yellow-tipping index.<sup>[93]</sup> The indices are figures of merit giving the performance of a potential substitute gas relative to gas representative of the particular region of the country in which an LDC is located. In 1951, E.R. Weaver at the U.S. Bureau of Mines extended the number of indices to account for: (4) output heat flux, (5) air supply, and (6) incomplete combustion.<sup>[94]</sup>

The output heat flux from a burner is one of the most important interchangeability parameters. If the orifice of the burner has cross sectional area  $A$  and if a pressure differential of  $\Delta p$  is driving the fuel of density  $\rho$  through the burner, the output heat flux is:

$$\mathcal{H} = A \sqrt{\frac{2 \Delta p}{\rho}} HV$$

$HV$  is the heating value of the fuel [Btu/scf or MJ/m<sup>3</sup>], the energy release per unit volume when combusted.<sup>33</sup> The expression for  $\mathcal{H}$  is derived from Bernoulli's equation under the assumption of incompressible gas flow through the orifice. That assumption should be valid under small pressure differentials  $\Delta p$ . In comparing the use of two fuel gases on a fixed burner of cross sectional area  $A$  and at a fixed pressure differential  $\Delta p$ , the only remaining parameters to consider are the heating values ( $HV$ ) and the densities ( $\rho$ ). Thus, the minimal comparative figures of merit for two gases, labeled  $a$  and  $b$ , are:

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<sup>33</sup> This is normally the higher heating value or gross heating value. The differences between the higher and lower heating values are not the focus of this discussion.



$$W_{a,b} = \frac{HV_{a,b}}{\sqrt{\rho_{a,b}}}$$

Rather than the absolute gas density  $\rho$ , the specific gravity with respect to air under given conditions is usually specified. This entails merely scaling the above ratio by a constant. When that density normalization is taken into account,  $W_{a,b}$  is called the *Wobbe index* for gas a (or b). The value of  $W$  has units of [Btu/scf] or other comparable units of energy density. However, the units are often taken for granted, and just the value alone is often quoted. Within the U.S.  $HV$  is usually the higher heating value for natural gas. Throughout the U.S. the higher heating value has a mean of 1033 Btu/scf with a range covering -6% to +9% around that value.<sup>[95]</sup> The Wobbe index itself has a mean within the U.S. of 1336 (Btu/scf) with a range from -10% to +6% around that value.<sup>[95]</sup>

The output heat flux, as embodied in the Wobbe Index, is the single most important parameter for interchangeability because nearly every other index is related to it. The concerns for flame flash-back and lift are related to the change in flame speed incurred in using a substitute fuel gas. The flame speed itself is related to the flame temperature, which is related to the air:fuel mixing ratio, the so called equivalence ratio. But the equivalence ratio is directly related to the Wobbe index, since the air:fuel ratio determines the amount of fuel combusted and subsequently the amount of heat release. Incomplete combustion, or the formation of carbon monoxide (CO), is essentially a function of the air:fuel ratio, which again is related to the Wobbe index. At a constant Wobbe index, CO formation is influenced only a small amount by the gas fuel composition.<sup>[96]</sup>

While the Wobbe index merits a place of prominence in interchangeability considerations, it does not describe all phenomena. Yellow-tipping, or soot production during combustion, is the only attribute that is not, to first order, largely specified by the Wobbe index. A decrease in the air:fuel ratio (a decrease in the Wobbe index) tends to increase the probability of soot formation, but fuel composition also plays a role. The propensity of sooting from each of the alkanes is different. Because the constituents of the fuel are a determining factor, the Wobbe index does not fully describe yellow-tipping.<sup>[96]</sup> However, the indices developed by the AGA and Weaver do offer figures of merit for it.

Additionally, the set of Weaver indices is linked to the Wobbe index and to the heating value of the gas. In a 2-dimensional plot of Wobbe index against heating value, the criteria of the Weaver indices provide curves of constraint. A region of acceptability that meets the Weaver criteria can thus be established via limits on the Wobbe index and the heating value.<sup>[96]</sup>

Given that the Wobbe index is the leading indicator of interchangeability, an examination of the Wobbe index is appropriate for obtaining some understanding of the conditions of biogas/biomethane interchangeability with natural gas. One of the Weaver metrics for comparing two fuel gases is the ratio of the Wobbe indices for the two:

$$\frac{W_{BG}}{W_{NG}} = \frac{HV_{BG}}{HV_{NG}} \sqrt{\frac{\rho_{NG}}{\rho_{BG}}}$$

In the above expression,  $BG$  = biogas,  $NG$  = natural gas. In the U.S., the average  $HV_{NG}$  = 1033 Btu/scf (higher heating value). Dairy-derived biogas is essentially comprised of  $CH_4$  and  $CO_2$ . The  $HV_{BG}$  will be calculated using a model in which only the  $CH_4$  component of the biogas combusts. In that case,  $HV_{BG} = f_{CH_4} * HV_{CH_4}$ , in which  $HV_{CH_4}$  = 1067 Btu/scf is the higher heating value of methane and  $f_{CH_4}$  is the fractional content of methane in the biogas.<sup>[95]</sup> From the ideal gas law, the relative density of the two gases, presuming the same temperature and pressure conditions, is their relative molecular weights:

$$\sqrt{\frac{\rho_{NG}}{\rho_{BG}}} = \sqrt{\frac{\mathcal{M}_{NG}}{\mathcal{M}_{BG}}}$$

The mean molecular weight of natural gas in the U.S. is  $\mathcal{M}_{NG}$  = 17.3 grams/mole.<sup>[95]</sup> The mean molecular weight of biogas comprised of methane and carbon dioxide is:

$$\mathcal{M}_{BG} = f_{CH_4}\mathcal{M}_{CH_4} + (1 - f_{CH_4})\mathcal{M}_{CO_2} = \mathcal{M}_{CO_2} - f_{CH_4}(\mathcal{M}_{CO_2} - \mathcal{M}_{CH_4}).$$

Substituting the expressions above into the expression for the ratio of the Wobbe indices yields:

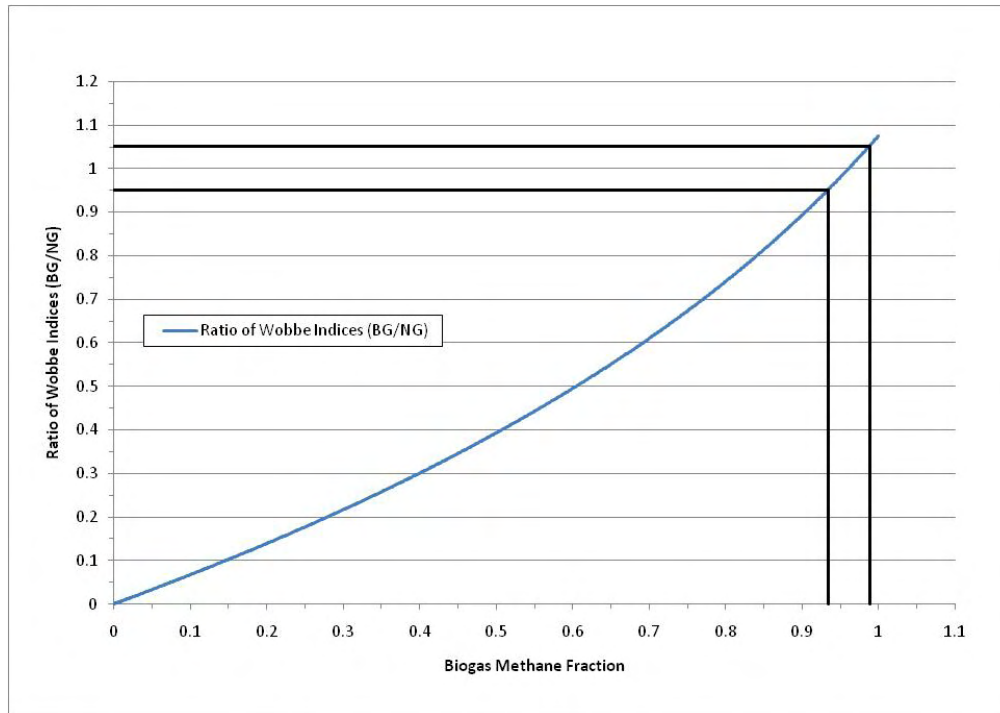
$$\frac{W_{BG}}{W_{NG}} = \frac{f_{CH_4} HV_{CH_4}}{HV_{NG}} \sqrt{\frac{\mathcal{M}_{NG}}{\mathcal{M}_{CO_2}(1 - f_{CH_4}(1 - \frac{\mathcal{M}_{CH_4}}{\mathcal{M}_{CO_2}}))}} = \frac{HV_{CH_4}}{HV_{NG}} \sqrt{\frac{\mathcal{M}_{NG}}{\mathcal{M}_{CO_2}}} \frac{f_{CH_4}}{\sqrt{1 - f_{CH_4}(1 - \frac{\mathcal{M}_{CH_4}}{\mathcal{M}_{CO_2}})}}$$

Aside from the variable  $f_{CH_4}$ , the remainder of the expression involves ratios of known quantities. Inserting the known molecular weights and heating values makes the ratio of Wobbe indices:

$$\frac{W_{BG}}{W_{NG}} = \frac{0.6477 f_{CH_4}}{\sqrt{1 - \frac{7}{11} f_{CH_4}}}$$

The only remaining variable is the fractional methane content of the biogas,  $f_{CH_4}$ . A plot of the ratio of Wobbe indices as a function of  $f_{CH_4}$  appears in Figure 37. For raw, dairy-derived biogas, the methane content is in the range from  $54\% < f_{CH_4} < 70\%$ . This range of methane content maps onto a range in the Wobbe index ratio of  $0.43 < \frac{W_{BG}}{W_{NG}} < 0.61$ . In the U.S., the typical acceptable range for interchangeability lies within 4-5% of  $\frac{W_{BG}}{W_{NG}} = 1$ , although this is regionally and company dependent.<sup>[97,95]</sup> As will be noted in Figure 37, under the assumptions of the model specified above, the range of methane content that achieves this ratio of Wobbe indices is roughly  $93\% < f_{CH_4} < 99\%$ .<sup>34</sup> In Europe, the acceptable range of Wobbe indices lies within 5-10% of the nominal, regional value, depending on the country.<sup>[96]</sup>

<sup>34</sup> It must be remembered that this is a comparison of the mean U.S. natural gas to a model of biogas/biomethane that includes only the two constituents, methane and carbon dioxide. More detailed consideration of the trace compounds in biogas, of regional circumstances, and of gas company policies may dictate a different range of suitability. This range of methane content is meant to be indicative only.



**Figure 37: Ratio of Wobbe Indices for Biomethane and the Mean U.S. Natural Gas as a Function of Biogas Methane Fraction. The black lines indicate the range of methane fractions in which the ratio of Wobbe Indices is  $1.0 \pm 5\%$ .**

The end-use equipment for which fuel combustion characteristics must be maintained include appliances, industrial/commercial burners, turbines, stationary engines, and transportation uses such as natural gas vehicles. As mentioned above, the Wobbe index will be largely indicative of the interchangeability of fuel gases for this equipment. However, it may not be as descriptive of relative quality in cases involving lean, pre-mixed burners, which appear in modern appliances and which are purposely designed to operate with excess air to optimize pollutant emissions.<sup>[96]</sup> The Wobbe index may not offer a good picture of gas interchange in another area: modern burners with oxygen sensors and emissions feedback; this equipment is designed to respond optimally to a range of input air:fuel ratios. Light-duty natural gas vehicles have such controls, which mitigate any changes in the input gas composition.<sup>[95]</sup>

## 9 Sampling and Testing Methods and Standards

### 9.1 Testing For Compounds Not Normally Found In Natural Gas

Unlike testing of natural gas or of synthetic gas, biogas/biomethane potentially contains components that are not normally examined with the analytic methods usually employed for gas testing. Based on the origin of the source material, microbials, pesticides, herbicides, and pharmaceuticals are, in principle, all potential components that might be found either in raw or cleaned biogas. A comprehensive summary of all of the testing methods employed by GTI and detailed in Task 2 of this project, including those compounds that are not normally found in natural gas, is contained in Table 43. These are tests selected by GTI for the purposes of this study and may not be representative of all testing needs for a specific project.

**Table 43: Summary of Sampling Methods by GTI in Task 2.**

| Analysis              | Method Reference(s) | Sampling Container  | Instrument/ Analysis Method |
|-----------------------|---------------------|---|-----------------------------|
| Major Components      | GTI Procedure       | 5 L Tedlar bag <sup>1</sup> or Inerted stainless steel cylinder | ASTM D1945/D1946            |
| Extended Hydrocarbons | GTI Procedure       | 5 L Tedlar bag <sup>1</sup> or Inerted stainless steel cylinder | GC/FID                      |
| Sulfur                | GTI Procedure       | 5 L Tedlar bag <sup>1</sup> or Inerted stainless steel cylinder | ASTM 6228                   |
| Halocarbons           | GTI Procedure       | 5 L Tedlar bag <sup>1</sup> or Inerted stainless steel cylinder | ELCD/EPA TO-14              |
| Siloxanes             | GTI Procedure       | 5 L Tedlar bag <sup>1</sup> or Inerted stainless steel cylinder | GC-AED                      |

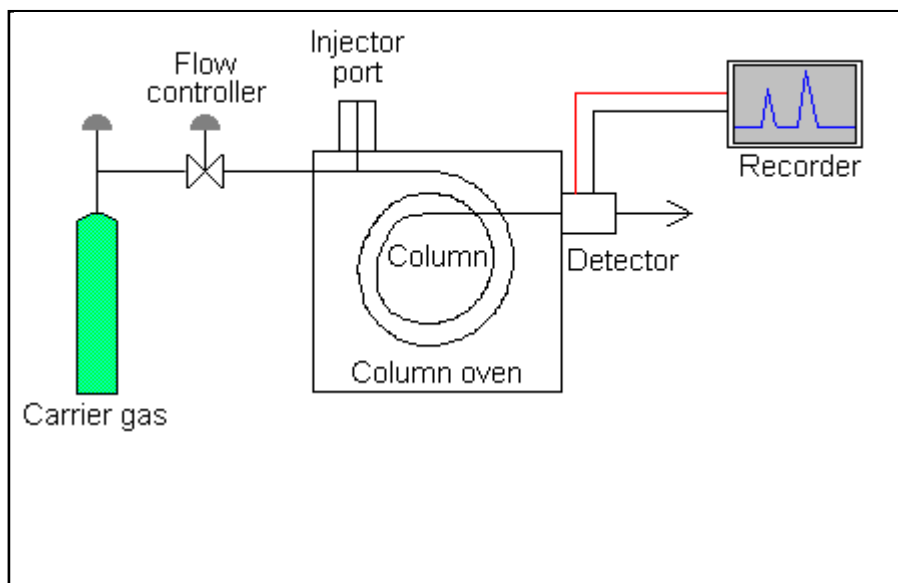
|                                       |                        |                                     |                                    |
|---------------------------------------|------------------------|-------------------------------------|------------------------------------|
| SVOCs/PAHs                            | Mod NIOSH 5515         | XAD-2 resin <sup>2</sup>            | GC/MS/<br>EPA Method 8270C         |
| PCBs                                  | Mod NIOSH 5503         |                                     | GC/ECD or GC/MS/<br>EPA Method 680 |
| Pesticides                            | Mod NIOSH 5600/5601    |                                     | GC/ECD, HPLC/UV                    |
| Exploratory analyses                  | NA                     |                                     | GC/MS                              |
| Pharmaceuticals/ Animal care products | TBD                    | Porapak-R                           | LC/MS                              |
| Mercury                               | ASTM D5954             | Gold plated borosilicate beads      | AAS                                |
| Volatile Metals                       | EPA Method 29 modified | Acid and peroxide aqueous solutions | ICP/<br>EPA Method 29              |

<sup>1</sup> NMOC, VOCs, expanded VOCs and siloxanes may be collected in the same sampling container.

<sup>2</sup> SVOCs, PCBs, pesticides, herbicides, and some exploratory analyses may be collected with the same sorbent tube (XAD-2).

All of the analyses in Table 43, with the exception of pharmaceuticals, mercury and volatile metals, are performed by gas chromatography (GC). Figure 38 depicts a schematic of a gas chromatograph. All of these methods of analysis require a small amount of analyte gas volume inserted at the injector port into the head of the chromatographic column. The GC column is a long tube, which may have different, selected lengths, radii, and internal material properties to tailor the GC analysis for the compounds of interest. An inert gas, called the carrier gas or mobile phase, is required to pull the analyte gas through the column. Then as this mixture is pulled through the column oven, the constituent compounds within the analyte gas flow at different rates. The internal material, called the stationary phase, of the chromatographic column separates the various components by a variety of mechanisms, both physical and chemical. Routine gas chromatography separates components by volatility, or boiling point, by raising the temperature of the chromatographic column in the oven. Eventually each component of the gas will elute from the column and reach the detector, some earlier, some later. The GC detector registers eluent as it emerges. Compounds are identified by their retention times, the time it takes for the compound to elute through the column.

Liquid Chromatography (LC) and High Performance Liquid Chromatography (HPLC) are similar to GC, but the retention time in the column depends on the polarity of the molecules rather than their volatility. An example of a HPLC unit is shown in Figure 39, which shows the HPLC pump (far left), steel-reinforced column (middle), and a spectrometer for measuring absorbance (far right).



**Figure 38: Simplified Diagram of a Gas Chromatography Unit.**



**Figure 39: A High Performance Liquid Chromatography Unit. From left to right: HPLC pump, steel-reinforced column, apparatus for measuring absorbance.**

Mercury measurement is performed by Cold Vapor Atomic Absorption Spectroscopy (CVAAS). For analysis, the sample is collected on a gilded silica sorbent. It is heated to evolve mercury, which is then swept into a fixed path length AA cell. The atoms in the AA cell are illuminated by, and absorb energy from, a mercury cathode lamp. This technique utilizes Beer's law of absorption. Beer's law states that  $A = \epsilon l c$ , in which  $A$  = absorbance,  $\epsilon$  = molar absorptivity (a constant dependant on the element or compound to be analyzed),  $l$  = path length = the length of sample over which the



absorption occurs, and  $c$  = sample concentration. Thus, the amount of absorption observed in the sample is an indicator of the concentration of mercury within it.

The volatile metals are analyzed with inductively coupled plasma - optical emission spectroscopy (ICP-OES). This measures the concentration of inorganic elements by aspirating a liquid into an Argon plasma to atomize the sample. Emission spectroscopy is used to examine the wavelength emitted by the elements. The observed intensity of the emitted light is proportional to the concentration.

## 9.2 Examples of Automated Sampling Technology

While there are no official standards for automated sampling and concurrent analysis of biogas or biomethane in particular, there are examples of on-line solutions from Rockwell Automation, Emerson gas chromatographs, and MSA North America. Allen-Bradley, a part of Rockwell Automation, produces condition sensing switches and control systems. The Allen-Bradley condition sensing offers control for automatic operation of machines and processes. As the link in an electrical circuit, condition sensors supply control intelligence at important values and either communicate information to automatically sequence equipment or provide a signal to operators for manual operation. With standard percent uncertainties of  $\pm 1\%$  for most of their processes, their panel view control system is regarded as one of the industry's best.

Emerson Process Management has made several advances in automated gas analysis. The Rosemount Analytical Model 700 micro-flame ionized gas chromatograph allows measurement of trace hydrocarbons in a variety of samples at parts per billion (ppb) concentrations. The micro-FID fits inside the explosion-proof housing. Typical applications include measuring trace impurities in gases and light hydrocarbons, as well as ambient air monitoring. Figure 40 shows an example of an Emerson chromatograph, using its line of Rosemount Analytical products.



Figure 40: Emerson Gas Chromatograph at Emerald Dairy in Emerald, WI.



MSA North America focuses on monitoring gas quality and safety. Its Ultima X Series Gas Monitors are microprocessor-based transmitters, and they can be custom engineered for biomethane monitoring. The latest mechanical and electrical technologies offer a state-of-the-art design for any gas detection need. Advanced sensing technologies monitor against the threat of combustible and toxic gases and for oxygen deficiency, with a  $\pm 1\%$  percent uncertainty for  $H_2S$ , and with a 2 parts per million (ppm) lower detection limit.

Mass flow meters are also automated to measure the mass of the gas stream in real time. While there are many types of flow meters available for use in the natural industry, this discussion will mention two technologies because GTI has witnessed them in use at a biogas plant based at a dairy farm. The first is the thermal mass flow meter. Thermal mass flow meters are a common choice for flow metering devices in the commercial and industrial metering markets. A typical sensor element for use in thermal meters is a resistance temperature detector (RTD), the resistance of which is related to the temperature of the element itself.

Another class of mass measuring flow meters is based on the Coriolis Effect. Coriolis flow meters are direct mass measuring flow meters. They detect the twist or bending caused by the Coriolis force when fluid is flowing through a vibrating tube or set of tubes. There are two basic configurations: curved tube and straight tube. The curved tube varieties are generally more sensitive to mass measurement than straight tube models because the straight tube is not as good at accounting for temperature changes in the process stream, due to its rigidity. The Coriolis mass flow meter facilitates a higher degree of precision, since it directly measures the mass flow rate. Figure 41 below shows a picture of a thermal mass flow meter and Coriolis mass flow meter in operation at Emerald Dairy in Emerald, WI.



**Figure 41: Mass Flow Meters at Emerald Dairy in Emerald, WI. From left to right: Coriolis mass flow meter, thermal mass flow meter.**

### 9.3 Manual Sampling Methods

During Task 2 of this project, many manual sampling and analysis methods were used by GTI. Most of them are associated with ASTM standards, but some of them are methods developed by GTI. The table below lists all of these methods, their detection limits, and the technology used for the analysis.

**Table 44: Manual Sampling Methods Used in Task 2.**

| Method                                     | Detection Limit | Technology                                   |
|--|-----------------|--|
| Extended Hydrocarbon (GTI Method)          | 1 ppm           | GC   |
| Volatile Metals (GTI Method)               | *               | ICP-OES                                      |
| Trace Ammonia (ASTM in development by GTI) | 1 ppm           | GC w/ NCD <sup>a</sup>                       |
| Volatile Hydrocarbons (EPA TO-14A)         | 0.1 ppm         | GC w/ PID <sup>b</sup> and ELCD <sup>c</sup> |
| Sulfur (ASTM D6228)                        | 0.05 ppm        | GC   |
| Major Components (ASTM D1946)              | *               | GC w/ TCD <sup>d</sup> and FID <sup>e</sup>  |
| Mercury (ASTM D5954)                       | 0.4 ng          | AAS <sup>f</sup>                             |

\* Detection Limit depends on analyte and volume of sample.

<sup>a</sup> NCD = Nitrogen Chemiluminescence Detection. A means of detecting nitrogen compounds from the emissions spectra they produce.

<sup>b</sup> PID = Photo-ionization detector. Utilization of ultra-violet radiation to ionize selected compounds and thereby detect their presence.

<sup>c</sup> ELCD = Electrolyte Conductivity Detection.

<sup>d</sup> TCD = Thermal Conductivity Detection. Means of measuring the presence of an analyte by a change in thermal conductivity of the column effluent.

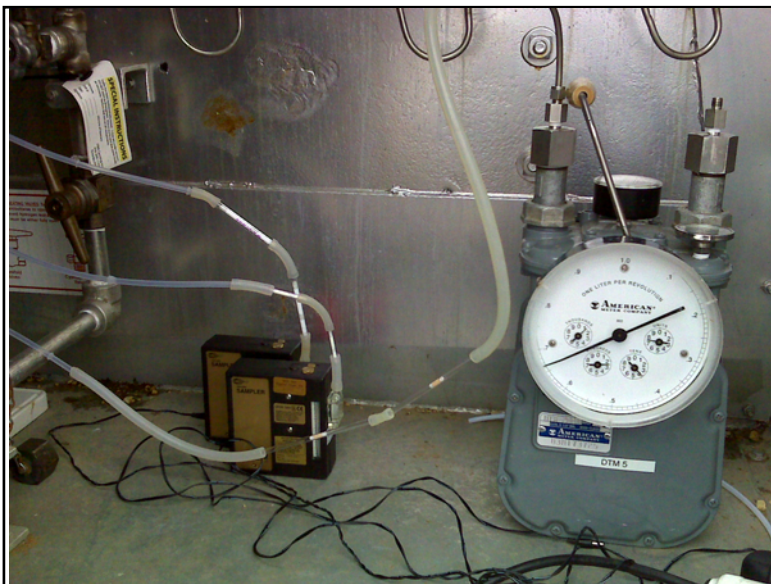
<sup>e</sup> FID = Flame Ionization Detection. Operation of a flame to ionize effluent compounds from the GC column in order to measure the presence of an analyte.

<sup>f</sup> AAS = Atomic Absorption Spectroscopy. Detection of the presence of an analyte by the frequencies of electromagnetic radiation that it absorbs.

The analyses for major components, trace ammonia, volatile hydrocarbons, sulfur, and extended hydrocarbons require a 5-L tedlar bag filled with sample for GC analysis. All that is required for this is enough pressure in the line to push through the septum of the bag. In the event that the line pressure is too low, a SKC Vac-U-Chamber™ connected to a pump downstream is used to create a negative pressure to draw the sample. Use of a minimal amount of tubing is critical as to ensure none of the sample gets caught in the tubing. Silicone or Teflon tubing works well as inert materials. An alternative technique to use for clean samples from a high pressure line is to use inerted stainless steel cylinders that are rated to 1800 psia. The preferred technique for raw sample or partially cleaned samples is the Tedlar bag due to the high H<sub>2</sub>S levels present.

Mercury gets captured by using gold-plated silica beads. These beads are placed in a tube, with a dimple downstream to ensure that the entire sample is collected. A

calibrated, dry test meter is placed at the end of the assembly to monitor the sample volume. Figure 42 shows the mercury sample assembly below.



**Figure 42: Mercury Sample Assembly. In foreground with large dry test meter (DTM-5) on the right.**

A slightly-modified EPA Method 29 is used in sampling for volatile metals. Based on previous experience, the sampling train will consist of two 250-ml liquid spargers (“bubblers”) in series each fitted with a coarse frit. Each sparger contains 100-ml of a 5% HNO<sub>3</sub> / 10% H<sub>2</sub>O<sub>2</sub> solution. This mixture allows the capture of many volatile metals by absorbing them into the solution. A third empty sparger serves as a spray trap. The detection limits for the metal compounds will be dependent on the volume of gas sampled. A 4-hour sampling period should result in a detection limit of 1.0 µg/m<sup>3</sup>. Prior to use, each sparger should be cleaned by soaking in dilute nitric acid and by rinsing several times using pure nitric acid and double-deionized water. Similarly, a dry test meter is placed at the end of the assembly to monitor the sample volume. Figure 43 below shows the bubbler sequence.



**Figure 43: Impinger Train of  $\text{HNO}_3/\text{H}_2\text{O}_2$  Solution.**

### 9.3.1 Precision

All manual sampling methods that were used for major components, expanded hydrocarbons, and sulfur compounds at GTI have percent uncertainties associated with them. This data was all obtained experimentally by a working analytical laboratory using the control chart method from A2LA (American Association for Lab Accreditation), using control samples of similar composition.

Analysis in the gas phase was by gas chromatography using flame ionization detectors (FID), thermal conductivity detectors (TCD), and flame photometric detectors (FPD). Volatile metals were analyzed using inductively coupled plasma optical emissions spectroscopy (ICP-OES) on a hydrogen peroxide-nitric acid mixture after the subject gas has bubbled through for the appropriate volume. Uncertainties will vary depending on the analyte concentration, mostly due to variability in the ability of the instruments to perform an adequate baseline separation of closely eluting compounds, or due to the inherent lability of certain analytes such as sulfur. Hexane analysis has its own built-in bias if the analysis is performed by a back-flush technique, which tends to broaden the peak. The table below shows the percent uncertainty associated with their respective compound.

**Table 45: Percent Uncertainty of Analytes Analyzed by GTI.**

| Analyte                     | Uncertainty (%) |
|-----------------------------|-----------------|
| CO <sub>2</sub>             | 2.4             |
| Ethane                      | 2.5             |
| Nitrogen                    | 1.9             |
| Methane                     | 0.2             |
| Hexane                      | 4.6             |
| Propane                     | 2.0             |
| i-Butane                    | 2.3             |
| n-Butane                    | 3.0             |
| neo-pent                    | 3.0             |
| i-Pentane                   | 2.8             |
| n-Pentane                   | 3.0             |
| O <sub>2</sub>              | 2.2             |
| CO                          | 2.2             |
| H <sub>2</sub> S (1% level) | 3.8             |
| H <sub>2</sub> S (ppmv)     | 5.6             |
| COS                         | 4.4             |
| DMS                         | 3.9             |
| Hg                          | 3.0             |
| Inorganics via ICP-OES      | 4.0             |

#### 9.4 MIC Agent, Pesticide, Herbicide, and Pharmaceutical Testing

All of the analysis of the MIC (microbially induced corrosion), pesticide, herbicide, and pharmaceutical testing was performed by META Environmental, Inc. in Massachusetts. Samples were collected at each site with both XAD-2 resin tubes and Porapak-R resin tubes. The XAD-2 resin tubes collect SVOCs/PAHs, PCBs, pesticides and herbicides. Porapak-R resin tubes are able to contain the pharmaceuticals, and other animal care products that may be used on the cows.

GTI has constructed sampling methods for both MIC and XAD-2 resin tubes and Porapak-R resin tubes. These will be included in the Task 2 report.

Table 46 below shows the pesticides analyzed by META labs. Since there are many compounds besides pesticides that are analyzed, the percent uncertainty depends on the sample. The lower detection limit is based on the reporting limit (RL) of the sample (generally 50% of the RL), which is equivalent to the lowest linear calibration concentration.

**Table 46: Pesticides Analyzed by Meta Labs.**



| <b>Pesticides</b>   |
|---------------------|
| BHC (a-d)           |
| Heptachlor          |
| Aldrin              |
| Heptachlor Epoxide  |
| Chlordane (a and g) |
| Endosulfan I and II |
| Endosulfan Sulfate  |
| Endrin              |
| Endrin Aldehyde     |
| Endrin Keytone      |
| 4-4'-DDE            |
| 4-4'-DDT            |
| Dieldrin            |

**Table 47: Pharmaceuticals Analyzed by Meta Labs.**

| <b>Pharmaceuticals</b>          |
|---------------------------------|
| Ampicillin<br>Trihydrate        |
| Amoxicillin<br>Trihydrate       |
| Oxytocin                        |
| Florfenicol                     |
| Tripelennamine<br>hydrochloride |
| Ceftiofur                       |
| Tilmicosin                      |
| Furosemide                      |
| Flunixin meglumine              |
| Fenbendazol                     |
| Doramectin                      |

## 10 Appendix A: Extract of German Standards for Biomethane Injection<sup>35</sup>

The German standards for natural gas (G260) and biogas (biomethane) (G262) are contained in the documents:

- DVGW Arbeitsblatt G260 Gasbeschaffheiten.
- DVGW Merkblatt G262 Nutzung von Deponie-, Klär- und Biogasen.

Both documents are in German, but excerpts of the standards that they communicate are included in references [98, 99], which are written in English. The main specifications for natural gas are contained in Table 48.

**Table 48: German Specifications for Natural Gas According to the G260 Standards Document.**

| Property             | Specification  |
|----------------------|--|
| Wobbe Index (higher) | 12.8-15.7 kWh/m <sup>3</sup> (n) (H-gas)<br>10.5-13 kWh/m <sup>3</sup> (n) (L-gases)                 |
| Water dew point      | < ground temperature   |
| H <sub>2</sub> S     | < 5mg/Nm <sup>3</sup><br>< 10mg/Nm <sup>3</sup> in exceptional cases                                 |
| Sulfur (total)       | < 30 mg S/Nm <sup>3</sup> during normal operation<br>< 150 mg S/Nm <sup>3</sup> in exceptional cases |
| CO                   | < 1% (when mixing with gases of 1 <sup>st</sup> gas family)  |
| CO <sub>2</sub>      | -  |
| H <sub>2</sub>       | < 12% (when mixing with gases of 1 <sup>st</sup> gas family)   |
| O <sub>2</sub>       | < 3% (in dry grids)<br>< 0.5% (in wet grids)   |
| Dust                 | < 5mg/N m <sup>3</sup>   |

Normal pressure and temperature conditions for European natural gas are (1.01 bar, 0<sup>o</sup> C).[99] Using these conditions, European gas volumes are shifted upward by about 5% (excluding compressibility considerations) and energy densities are shifted downward when comparisons are made to U.S. specifications (1.01 bar, 15<sup>o</sup> C). This will mean that 1 kWh/m<sup>3</sup> will translate to approximately 101 Btu/ft<sup>3</sup>. For biogas, in

<sup>35</sup> Reference [90] contains a summary table of the standards for the injection of nonconventional gaseous fuels for several European countries.



addition to the parameters listed in Table 48, three additional requirements are specified in document DVGW 262:<sup>[99]</sup>

- $\text{CO}_2 < 6\%$
- $\text{H}_2 < 5\%$  (vol.)
- A safety data sheet must be provided with the biogas (biomethane).

## 11 Appendix B: Extract of Swiss Standards for Biomethane Injection<sup>36</sup>

The Swiss G13 document specifying biogas (biomethane) injection standards is written in German, but references [98,99] contain summaries of the specifications for limited and unlimited gas injection. Table 49 and Table 50 list the standards for unlimited and limited injection, respectively, of biogas into the Swiss grid.

**Table 49: Specifications for Unlimited Injection of Biomethane into the Swiss Natural Gas Grid.**

| Property                              | Symbol           | Specification                     | Units              |
|---------------------------------------|------------------|-----------------------------------|--------------------|
| Methane content                       | CH <sub>4</sub>  | > 96                              | Vol%               |
| Relative humidity at grid temperature | φ                | < 60                              |                    |
| Dust                                  |                  | Technically free                  |                    |
| Odourisation                          |                  | According to Swiss regulation G11 | Vol%               |
| Oxygen                                | O <sub>2</sub>   | < 0.5                             | Vol%               |
| Carbon dioxide                        | CO <sub>2</sub>  | < 6                               | Vol%               |
| Hydrogen                              | H <sub>2</sub>   | < 5                               | Vol%               |
| Hydrogen sulfide                      | H <sub>2</sub> S | < 5                               | mg/Nm <sup>3</sup> |
| Total Sulphur                         | S                | < 30                              | mg/Nm <sup>3</sup> |

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<sup>36</sup> Reference [90] contains a summary table of the standards for the injection of nonconventional gaseous fuels for several European countries.

**Table 50: Specifications for Limited Injection into the Swiss Natural Gas Grid.**

| Property                              | Symbol           | Specification                     | Units              |
|---------------------------------------|------------------|-----------------------------------|--------------------|
| Methane content                       | CH <sub>4</sub>  | > 50                              | Vol%               |
| Relative humidity at grid temperature | φ                | < 60                              |                    |
| Dust                                  |                  | Technically free                  |                    |
| Odourisation                          |                  | According to Swiss regulation G11 | Vol%               |
| Oxygen                                | O <sub>2</sub>   | < 0.5                             | Vol%               |
| Carbon dioxide                        | CO <sub>2</sub>  | < 6                               | Vol%               |
| Hydrogen                              | H <sub>2</sub>   | < 5                               | Vol%               |
| Hydrogen sulfide                      | H <sub>2</sub> S | < 5                               | mg/Nm <sup>3</sup> |
| Total Sulphur                         | S                | < 30                              | mg/Nm <sup>3</sup> |

## 12 Glossary

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### **Absorption**

The process by which a substance is taken up by another substance with which it is in contact.

### **Acetogenesis**

A step in the anaerobic digestion of matter in which bacteria convert volatile organic acids into acetic acid.

### **Acidogenesis**

A stage in the anaerobic digestion of organic matter in which the byproducts of hydrolysis are broken down by acid-forming bacteria.

### **Activated Carbon**

Carbon based materials capable of adsorption.

### **AD**

Anaerobic Digestion.

### **Adsorption**

The adhesion of molecules to the surfaces of solid bodies or liquids with which they are in contact.

### **Ammonia**

Chemical compound with chemical formula,  $\text{NH}_3$ , and consisting of a single nitrogen atom bound to three hydrogen atoms.

### **Anaerobic Digester**

The reactor tank in which anaerobic digestion occurs.

### **Anaerobic Digestion**

The process in which complex organic matter is broken down into simpler constituents, directly through the action of microorganisms and in the absence of oxygen.

### **Anaerobic Lagoon**

A shallow manure pond of slurry (with low solids content), in which anaerobic digestion occurs. Suitable for dilute wastewater streams such as those generated by flush dairy facilities.

### **Bcf**

Billion Cubic Feet.

### **Biogas**

Gas produced by the anaerobic digestion of organic feedstocks such as manure, food waste, etc. Usually, this refers to the resultant gas prior to cleanup. Alternatively, and for emphasis, called *raw biogas* when it is intended to refer only to the gas prior to cleanup or treatment.

## **Biologically Degradable Solids**

The portion of the volatile solids that are biodegradable.

## **Biomethane**

Either (1) methane (CH<sub>4</sub>) produced by the biological breakdown of organic matter, or (2) depending on context, upgraded biogas, which will largely be methane (~95%) after it emerges from the cleanup unit. The second meaning is also conveyed by the phrase *cleaned biogas* or *upgraded biogas*.

## **Biomethanation**

The formation of methane by microbial activity to degrade organic matter..

## **Check Valve**

Type of valve that will shut off the flow of gas if the gas stream does not meet one or more required specifications.

## **Chromatography**

An analytical technique in chemistry used to identify and quantify organic compounds by separating them from other compounds with which they are mixed.

## **Co-digestion**

The concurrent digestion of 2 or more source materials within a digester tank, usually in order to boost the quality and methane content of the output raw biogas.

## **Completely Mixed Digester**

A type of anaerobic digester that has a mechanical mixing system, in which solids are kept in suspension and which is normally used to co-digest manure with other biomasses.

## **Drylot**

Type of housing<sup>99</sup> that allows cows to be penned if they are in a pasture, typically a straw yard.

## **Fixed Solids (FS)**

The portion of the total solids that remains after subjecting a sample to a high temperature heating process for a specific time period.  $FS = TS - VS$ .

## **Forage**

Bulky food, typically grass, hay, or corn silage for cattle.

## **Freestall Barn**

Type of cow housing system that allows cows to choose between resting, eating, or watering in designated areas of a large pen; this housing system is utilized by dairy farms that could operate an anaerobic digester.

## **HRT**

Hydraulic Retention Time.

**Hydraulic Retention Time**

Typical time scale on which influent to an anaerobic digester is retained within the tank.

**Hydrolysis**

Initial stage of anaerobic digestion in which bacteria liquefy organic polymers and cells.

**Interconnect**

An injection point of natural gas into the grid.

**Iron Sponge**

A conventional iron oxide product, originally consisting of steel wool coated with rust, used to remove hydrogen sulfide from raw biogas.

**Landfill Biogas**

Biogas generated from decomposing materials in landfills.

**Loading**

A measure of the rate of change of the concentration of solids contain in the digester tank due to the explicit addition of source material. Units are usually [kg/m<sup>3</sup>- day].

**Mesophilic**

A type of bacteria that thrive in temperature environments between 20-45 °C.

**Methane**

Chemical compound with chemical formula, CH<sub>4</sub>, consisting of a single carbon atom bound to 4 hydrogen atoms and containing the useable energy component of biogas or biomethane.

**Microbial Retention Time**

Typical time scale on which microbial matter is retained within an anaerobic digester.

**Molecular Sieve**

Adsorbent materials, artificial or naturally occurring, which can adsorb or exclude a molecule based on size.

**MRT**

Microbial Retention Time.

**Natural Gas Liquids**

Hydrocarbons of higher molecular weight than methane found in raw natural gas once they have been processed. Examples: ethane, propane, normal butane, isobutene, pentanes.

**NPK**

**N**itrogen, **P**hosphorus, **P**otassium (chemical symbol = **K**). Usually refers to the mineral contents of the solid matter extracted from a digester.



**pH**

A measure of the concentration of hydrogen ions in solution. A measure of alkalinity or acidity:  $\text{pH} < 7$  refers to acidic solutions,  $\text{pH} > 7$  to basic solutions, and  $\text{pH}=7$  to neutral solutions.

**Plug Flow Digester**

A type of anaerobic digester that does not use mechanical agitation and is suitable for influent total solids concentrations ranging from 10-13% solids content and in which the retention time is a function of digester length for a fixed influent flow rate.

**Raw Biogas**

Biogas in its original, unconditioned, unpurified state upon production within an anaerobic digester.

**Raw Natural Gas**

Natural gas which has not been processed.

**Redox reaction**

A reaction during which a change in oxidation numbers occurs

**Solids Retention Time**

Typical time scale on which the solid matter portion of the influent to an anaerobic digester is retained with the tank.

**Spectroscopy**

An analytical technique used to determine quantities of compounds by means of their emission or absorption of electromagnetic radiation of varying wavelengths.

**SRT**

Solids Retention Time.

**Stanchion**

A traditional cow stall design that uses hardware to restrain a cow in an individual stall where she rests, consumes feed and water, and is milked.

**Substrate**

Solids within the input source material of the digester that act as the food source for the microbial degradation that occurs within an anaerobic digester.

**Tcf**

Trillion Cubic Feet.

**Thermal Hydrolysis**

The breakdown of organic compounds by means of heat.

**Thermophilic**

A type of bacteria that thrive in high temperature environments in the range of 45-70 °C.

**Total Solids**

The fraction of dry matter contained within manure.

**TS**

Total Solids.

**Tube Trailer**

A trailer that carries multiple pressurized cylinders containing compressed natural gas.

**Volatile Solids**

Solid materials that are readily decomposable at relatively low temperatures. The portion of the TS that does not remain after subjecting a sample to a high temperature heating process for specific time period.  $VS = TS - FS$ .

**VS**

Volatile Solids.

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