Guidance Document for Introduction of Dairy Waste Biomethane

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1.0 Executive Summary – Task 3

The Gas Technology Institute (GTI) has constructed a Guidance Document (Task 3) as part of a larger project: Pipeline Quality Biomethane: North American Guidance Document for Introduction of Dairy Waste Derived Biomethane into Existing Natural Gas Networks. This Guidance Document is not prescriptive; it is intended to provide framework for productive discussions regarding biomethane quality. It provides reference and recommendations for the introduction of biomethane, a renewable natural gas (RNG), from dairy waste digestion with natural gas in existing gas pipeline networks in North America. The Guidance Document incorporates information and data gathered as part of Tasks 1 and 2 of the overall, larger project. The purpose of this Task 3 Document is to enable useful dialog between suppliers of biomethane and companies who will be receiving the RNG. Representative processes of biomethane production are captured in the Report resulting from Task 1 work; the results of a biogas/biomethane sampling and analytical testing program are compiled in the Report from Task 2 work. Task 3 of the project is the so-called “Guidance Document” which compiles constituents and parameters which may need to be considered for introduction of biomethane to pipeline networks. While specific gas quality tariffs may vary, many common basic quality parameters exist. Overview of the basic gas quality parameters for biomethane, analytical ranges typical to pipeline tariffs for the parameters and representative analytical tests are included. Additionally, an example Verification Testing Program and schedule for gas quality monitoring has been presented. Through the total work effort of this specific project executed by GTI and based upon the criteria against which the biomethane samples (two sources) were evaluated, it can be concluded and demonstrated that dairy waste- based biomethane of high quality may be produced within agreed-upon tolerance specifications for introduction with natural gas supplies. Biogas needs to be conditioned, cleaned and/or filtered depending on the specifics of the on-farm digester, the biomass digested, and the specific requirements of the natural gas pipeline network into which the biomethane is to be injected. The degree to which the biomethane is conditioned, etc. may be company specific. Specific tariff requirements for individual gas companies must be considered for the purpose of constructing a suitable contract for biomethane.

2.0 Purpose and Scope

The purpose of the Guidance Document (Task 3) of the project Pipeline Quality Biomethane: North American Guidance Document for Delivery of Dairy Waste Derived Biomethane into Existing Natural Gas Networks is to establish a common framework for the introduction of a RNG fuel, biomethane, into existing natural gas supply networks. Biomethane introduction with natural gas supplies is relatively new to the natural gas
industry in North America; there is a need to understand the quality and potential impacts of introduced gases to the pipeline network. This Document does not provide specific “cleanup standards” for biomethane. Rather, it may serve as industry-wide reference covering basic biomethane quality/characteristics and measurement techniques that can be used in contracts or new tariffs. This Document explains analytical parameters in biomethane (cleaned biogas) which may be of importance, referenced by way of the range of typical natural gas tariffs in North America. The intent of this Document is to create common understanding of the product between all stakeholders: natural gas companies, farmers, anaerobic digester technology providers and providers of biogas cleanup technologies.

The Guidance Document is organized as follows: each parameter has an overview, a range of values for contract consideration and representative analytical tests suitable for testing of the parameter. This Document also provides an example Program for Biomethane Quality Verification / Test Schedule; the purpose of the Verification Testing Program is to offer a model test scheme if independent corroboration of gas quality is desired. Such a Test scheme helps to assure the gas company that the produced biomethane meets requirements for introduction. The Verification Testing Program is based upon a similar and successful program jointly executed by a biomethane producer (Intrepid Technology and Resources, Inc.) and a natural gas company (Intermountain Gas) to bring forth a merchantable biomethane product in Idaho. The Verification Testing Program can be modified or expanded to suit particular situations, depending upon results of testing, biomass quality and variations over time, cleanup equipment, seasonal variations, etc. Introduction of new RNG fuels, such as biomethane, into the natural gas network often depends on multiple factors beyond specific gas quality objectives. Productive dialog between all parties is key.

Reference analytical values cited in this Document are further detailed in the American Gas Association’s (AGA) Report No. 4A - Natural Gas Contract Measurement and Quality Clauses (DRAFT update, 2009) The AGA Report 4A serves as an industry-wide reference tool pertaining to natural gas quality and measurement provisions in contracts or tariffs (see www.ferc.gov). This North American Guidance Document for Delivery of Dairy Waste Derived Biomethane into Existing Natural Gas Networks may supplement Report 4A information, focused on gas parameters particular to biomethane generated from anaerobic digestion of dairy waste. In some cases, analytical criteria for potential biomethane constituents are not included in industry tariffs (i.e., pesticides, pharmaceuticals, etc.) In these cases, independent evaluation of the compounds may be
necessary. References such as manufacturer tolerance levels, NIOSH and OSHA values may be helpful if applied in the appropriate context.

Although this Guidance Document has been devoted to waste from dairy operations, it may be applicable to other farming operations (pig, chicken, etc). This Document does not comment on or endorse specific methods or designs of cleanup technology employed to produce high quality biomethane; rather, gas quality itself is the focus. Values or numbers found in this report are not intended to take precedence over existing contract or tariff values. *It is strongly advised that individual company gas quality tariffs and other parameters be considered in evaluating the suitability of any proposed gas product for introduction to the pipeline network. Conditions for biomethane introduction may vary between natural gas companies and interconnection points. Tariff value ranges reported in this study may not be representative of actual delivered supplies into a specific market area. Readers are strongly advised to assess historically delivered supplies into a specific market area of concern in conjunction with appropriate tariff information.*

### 2.0 Guidance Document Background

This Guidance Document is the culmination of an effort by transmission and local distribution companies to evaluate the suitability of biomethane for inclusion into natural gas supplies. The purpose of the study was to understand biogas and biomethane production, to test representative samples of biogas and biomethane and evaluate them against the specific requirements of their respective analytical contract language for gas quality and prepare a Guidance Document. GTI has executed a nine-month, Three-Task Project, titled: **Pipeline Quality Biomethane: North American Guidance Document for Introduction of Dairy Waste Derived Biomethane in Existing Natural Gas Networks**. The full Report for this project includes the following:

- **Task 1 Report (Title: Technology Investigation, Assessment and Analysis)** is a detailed review of available information (national and international) to develop a knowledge base of existing information related to biogas production, biogas cleanup to pipeline quality biomethane, existing biogas and biomethane quality

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1 NIOSH and OSHA exposure limit criteria is specific to hazard assessments and use assessing personal exposure of constituents over a specified period of time. These reference limits are not intended to be used as surrogate gas quality constituent limits for contracts or tariffs and may not be transferable to this context.
standards, and biomethane quality test protocols. Although the specific focus of this Task is on biogas/biomethane from dairy sources, easily accessible information on biogas from all biomass sources was collected. No laboratory testing was part of this Task 1.

- **Task 2 Final Report (Title: Laboratory Testing and Analysis)** is the collection, preparation and analytical evaluation of more than 40 samples of “raw biogas” (no gas cleanup), “partially cleaned” biogas (removing only one/two constituents through scrubbing, etc.) and biomethane (cleaned biogas). Two natural gas samples and an ambient air sample were also collected. To this end, it should be noted that two biomethane suppliers offered samples for testing as part of the biomethane sampling effort and the results/conclusions are a reflection of this limited dataset. Each sample was subject to analytical testing and evaluation for all parameters using established protocols, detailed in this Guidance Document. No toxicology testing was performed as part of the biogas evaluation. Values obtained from testing of biomethane samples were compared against the range of values typical for each constituent as cite in AGA Report 4A (2001) and the analytical values required by the respective natural gas company to which the biomethane would be delivered. Of note, the contract language for biomethane delivery from the two suppliers was different. Therefore, the analytical requirements of the two biomethane sources were different. Results from this study and other reference documentation served as the basis for conclusions pertaining to “Recommended Biomethane Range” for specific biomethane parameters. Please refer to Task 2 Report for details on sampling, analysis and results of the analytical testing.

- **Task 3 Guidance Document (Title: Guidance Document for Introduction of Dairy Waste Derived Biomethane)** The scope of this Task 3 Guidance Document includes: 1) a parameter overview, 2) the biomethane range guidance, and, 3) representative analytical tests for the parameter. The Guidance Document also provides a sample verification testing procedure/test schedule and a list of terminology and definitions.

*Through the total work effort of this project executed by GTI, it is concluded and demonstrated that dairy waste based biomethane of high quality may be produced within existing tariff ranges for introduction into natural gas networks. Biogas needs to be conditioned, cleaned and/or filtered, depending on the specifics of the on-farm digester, and the specific pipeline network requirements. Pipeline network requirements may be different across North America, depending upon a variety of influencing factors.*
3.0 Guidance Document Goal

The goal of this Guidance Document is to provide the framework and recommend analytical methodologies for successful integration of biomethane from anaerobic digestion of dairy waste into existing natural gas transmission and distribution systems. This document can serve as a template for the evaluation of biomethane from other sources, such as landfill gas, wastewater treatment operations, co-digestion facilities, etc, although each of these sources have a unique set of characteristics which may or may not be specifically addressed in this document. The Guidance Document has been prepared with specific focus on dairy waste biomass. Depending upon the characteristics of biomass from other sources, resulting biomethane may contain a variety of organic and inorganic compounds, as well as other constituents. The Guidance provided here may serve as a resource for examination of other biomass conversion. This document may serve as reference for biomethane suppliers, for technical considerations of their product; natural gas companies may use this Document in establishing biomethane quality specifications for the purposes of contracts with suppliers. This Guidance Document is not intended to replace specific natural gas transmission and distribution company tariffs. Through consideration of the recommendations set forth herein, natural gas transmission and distribution companies can be more assured that biomethane of a consistent and suitable quality is supplied to their system, and biomethane producers will be able to verify their product as meeting gas company specifications. In this way, successful integration of this RNG with the existing natural gas supplies can be achieved.

4.0 Considerations For Introduction Of Biomethane To Natural Gas Network

Interchangeability is defined as, “the ability to substitute one gaseous fuel for another in a combustion application without materially changing operational safety, efficiency, performance or materially increasing air pollution emissions”. The ability to substitute or supplement an existing gas supply is dependent on quantitative evaluation of the combustion impacts of the proposed “interchange” using standard interchangeability evaluation methods such as AGA Bulletin 36, Weaver, or combinations of surrogate parameters such as Wobbe and Heating Value. Interchangeability evaluations are conducted based on knowledge of the constituents and parameters of historically delivered supplies into a defined market area relative to the constituent and associated parameters with the proposed “substitute” gas. Additional details regarding gas interchangeability can be found in the NGC+ White Paper on Natural Gas Interchangeability and Non-Combustion End Use (NGC+ White Paper, see references).
Each system operator is advised to conduct an overall interchangeability assessment. This assessment should include at a minimum:

- Assess historically delivered supplies into a market area (gas quality constituents and parameters that define interchangeability, aka “adjustment gas”, specific constituents of concern, etc.)

- Understand the proposed biomethane cleanup technology and maximum constituent concentrations (boundaries of cleanup system and proposed “substitute gas”)

- Model the zone of influence of proposed substitute gas and determine if the aggregated supply profile meets contract of tariff and/or contract requirements

- Assess any sensitive receptors within the zone of influence (end users that may be sensitive to changes in gas quality, including “node points” in the system where gas quality variations may be more substantial)

- Optimize the cleanup system and balance concerns of potentially sensitive end users (may include specific end use retrofits if limited in scope)

Referencing the AGA Report 4A, 2001, interchangeability is qualified through various indices (single index and multiple index) that have demonstrated broad applications to end-users. It has been suggested that interchangeability limits be evaluated and established for a specific market area, considering the nature of the installed appliance population or specific end-user requirement. Also noted in AGA Report 4A, 2009, caution needs to be exercised when using tariff value ranges suggested herein or within the Report 4A Document, as local requirements may vary. This Guidance Document addresses general interchange of biomethane and suggested tolerance limits. **Specific tariff requirements for individual gas companies should be consulted for the purpose of constructing a suitable contract for biomethane delivery.** These limits may not be representative of gas delivered into a specific market area and the reader is cautioned to completely understand the gas quality of actual delivered supplies in the evaluation process.

### 5.0 Unique Contract Considerations

Some of the parameters and monitoring techniques detailed in this Guidance Document are supplementary to typical General Terms and Conditions documents used for contracting purposes. Exact Terms and Conditions cannot be referenced herein because they will vary depending upon specific pipeline operator’s requirements and specific local conditions. As well, recommendations described herein are made based upon best
available information at the time of construction of the Guidance Document. Compliance to terms deemed necessary for safe gas interchange is generally mandatory, as appropriate parameters and tariff ranges are set forth by the Federal Energy Regulatory Commission (FERC).

There are parameters described within this Guidance Document that are considered by some contracting parties as supplemental to those normally found in tariffs. It is advised that both gas companies, pipelines and biomethane suppliers consider these additional parameters for safe interchange. This Guidance Document will explain each specific parameter and will verify that biomethane samples tested and evaluated against the applicable tariff met quality objectives.

6.0 Guidance for Biomethane Quality

Individual tariffs for individual gas companies may not include all parameters listed below. The Guidance provided herein encompasses parameters and language typical of natural gas tariffs. Individual tariffs and particulars specific to the point of proposed gas injection should be considered when assessing suitability of a fuel such as biomethane for introduction to the natural gas pipeline network. The intent of this Document is to assist the natural gas company; analytical parameters particular to biogas and biomethane may influence the overall gas quality within their pipeline network. It is highly advised that gas companies review all applicable tariffs and conditions for specific analytical boundaries.

“Raw” biogas is generally not considered suitable for interchange due to inherent characteristics. Therefore, raw biogas is generally “cleaned” to produce biomethane which may meet specific natural gas company requirements. The following are guidelines for consideration. Relative to “raw” biogas and partially cleaned biogas samples tested, the biomethane samples tested by GTI (2 systems tested) in Task 2 of this project were observed to produce a RNG with analytical values within ranges typical to natural gas (as compiled in the AGA Report 4A, 2009) and within the requirements set forth by the specific natural gas company receiving the gas.

6.1 Heating Value

6.1.1. Parameter Overview

Gross heating value, also known as Higher Heating Value (HHV), is defined as the amount of energy transferred as heat from the complete, ideal combustion of the gas with air, at a standard temperature, in which all the water formed by the reaction condenses to liquid.
Custody transfer of natural gas is generally based on an energy basis (per BTU/scf, using HHV). As a result, transportation of low Btu gas may reduce the economic efficiency of some pipelines. In addition, local distribution companies that meter gas considering its energy content may need to consider the influence of low BTU gas on its overall billing/accounting process.

6.1.2 Biomethane Range Guidance

The reported ranges typically found in tariffs for natural gas are between: minimum heat content (dry, HHV) of 950-1,000 Btu/scf and maximum heat content (dry, HHV) of 1,075 – 1,200 Btu/scf. Biomethane may yield a lower Btu range, and augmentation with other, higher Btu gases, such as propane, may be considered. Blending or aggregation with existing pipeline supplies may be possible to ensure compatibility.

Based upon results of biomethane testing as part of this GTI program, tariff values can be achieved without augmentation. It was shown that biomethane can be up to 99.6% methane, which corresponds to a Gross Dry Btu content of 1,010.3 Btu/SCF, at 60% and 14.73 psia. The Btu value is calculated at specific temperature and pressure conditions. The Gross Btu is defined as the amount of energy transferred as heat from the complete, ideal combustion of gas with air, at standard temperature, in which all the water formed during the combustion process condenses to liquid. Individual company tariffs and quality requirements for heating value requirements should be considered.

6.1.3 Representative Analytical Test For This Parameter

The heating value of a gas is determined from the molar compositional data obtained from gas chromatography (GC) analysis. Biomethane (methane) gas GC analyses can be performed following ASTM D1945 or GPA 2261. This analysis physically separates the major and minor components of a gas utilizing a gas chromatograph with detection by a thermal conductivity detector (TCD), or a combination of a TCD plus a flame ionization detector (FID). Historically, GC gas analyses reported hydrocarbons speciated out to pentane. All other hydrocarbons were backflushed from the GC column and reported as a C6+ fraction. Ratios were defined for the C6, C7, and C8 fractions and apply to the backflushed C6+ determination. This practice was adopted by the gas industry in the early days of GC analysis because it was performed isothermally.
The respective ideal gas value for each component is determined through ratio analysis, corrected using a compressibility factor calculated similarly. The procedure and ideal gas values are taken from Tables in ASTM 3588-98, GPA 2172, and GPA 2145.

6.2 Temperature

6.2.1 Parameter Overview

The effects and limitations of equipment, materials and fittings relative to gas temperatures should be considered. Temperature limitations serve to primarily protect external coatings, or pipe materials, as well as downstream gas processing and handling equipment.

6.2.2 Biomethane Range Guidance

The reported temperature ranges typically found in tariffs for natural gas are between: no less than 20°F (reported 20°F to 65°F) and no more than 120°F (reported 80°F to 120°F).

Based upon results of biomethane testing as part of this GTI program, tariff values for temperature can be achieved. Individual company tariffs and quality requirements for temperature should be considered.

6.2.3 Representative Analytical Test For This Parameter

Biomethane temperature may be continuously measured on-line using a sensor.

6.3 Hydrocarbon Dewpoint

6.3.1 Parameter Overview

The hydrocarbon dew point (HDP) is the temperature of the corresponding state condition at which the non-methane components of natural gas begin to condense into the liquid phase. The HDP of natural gas is regulated to prevent or control the formation of liquids in the pipeline. The formation of liquids has differing impacts on operations.
Gases containing heavy hydrocarbons have a higher dew point temperature resulting in the possibility of a hydrocarbon fluid forming when the pipeline gas temperature is colder than the HDP. This parameter is not considered particularly problematic in biomethane derived from dairy waste, as it is anticipated that there are few heavy hydrocarbons in the gas.

6.3.2 Biomethane Range Guidance

The reported hydrocarbon dewpoint values typically found in tariffs for delivered natural gas are between the range between 0 and 25°F at either fixed or operating pressures.

Based upon results of biomethane testing as part of this GTI program, tariff values can be achieved. Individual company tariffs and quality requirements for hydrocarbon dewpoint should be considered.

6.3.3 Representative Analytical Test For This Parameter

As with BTU analyses, hydrocarbon dewpoint analyses are performed following ASTM D1945 or GPA 2261. The accuracy of this practice varies depending on quality of the gas. For the most precise hydrocarbon dew point calculation, gases that are known to contain heavier hydrocarbons should be analyzed out to at least C20. However, this is less likely in biomethane. This usually involves a separate GC analysis utilizing a dedicated FID for greatest sensitivity.

The hydrocarbon dew point is calculated using the compositional data and a process simulation program containing an equation-of-state (EOS) model. The gas composition is determined by a GC analysis. A chilled mirror dew point tester and various types of real time analytical instrumentation are also utilized in industry for hydrocarbon dew point determination.
6.4 Water Content

6.4.1 Parameter Overview

The presence of water vapor in biomethane, as with natural gas, can pose many problems particularly associated with corrosion. Carbon dioxide (CO₂) and hydrogen sulfide (H₂S) are common components associated with raw biogas, as these are typical gases produced from anaerobic digestion of organic waste. Water combined with CO₂ and H₂S under certain conditions can form acidic mixtures, which are corrosive to pipeline systems. Water vapor is also limited to prevent condensation and to reduce hydrate formation. Hydrates are an ice-like mixture of water and hydrocarbons formed at high pressures where high water vapor is present.

6.4.2 Biomethane Range Guidance

The reported water vapor values typically found in tariffs for delivered natural gas are as follows: delivered free of liquid water and should contain between no more than four to seven pounds of water in vapor phase per million cubic feet (MMscf) of gas.

Based upon results of biomethane testing as part of this GTI program, tariff values for water vapor content can be achieved. Individual company tariffs and quality requirements for water vapor content should be considered.

6.4.3 Representative Analytical Test For This Parameter

Moisture can be tested on-line using a "chilled mirror technique" (ASTM D1142), an electronic moisture analyzer (ASTM D5454) containing sensors based on phosphorus pentoxide, aluminum oxide, or silicon among others or a detection sensor which utilizes laser technology.
6.5 Total Sulfur, Sulfide and Mercaptans

6.5.1 Parameter Overview

Total sulfur is the sum of the contribution of sulfur by all sulfur-containing compounds in gas and is calculated for individual sulfur containing compounds based on relative molecular weight of sulfur in the compound. Sulfur is corrosive with or without the presence of water. The primary sulfur compound found in raw biogas is hydrogen sulfide. It is generated from anaerobic microbial decomposition of sulfate and sulfur-containing organic matter in animal manure. Additionally, some on-farm water sources contain sulfate and hydrogen sulfide. The presence of H₂S and other sulfur-containing odorants are regulated because of their potential corrosive and destructive nature on pipeline materials. In the presence of water, sulfur compounds can eventually form sulfuric acid, a strong acid with an aggressive corrosion potential. Sulfur species corrosion is synergistic if other compounds are present, especially CO₂ and O₂.

Mercaptans are sulfur compounds which may be naturally occurring or added to natural gas as an odorant. Lower molecular weight mercaptans, such as methyl mercaptan, are typically found in biogenic gases. When present in concentrations greater than 1 ppmv, these mercaptans can severely degrade the quality of odorization and cause operational problems in distribution systems. Some pipeline tariffs or related industry regulations include a limit on mercaptan concentrations.

6.5.2 Biomethane Range Guidance

The reported total sulfur and hydrogen sulfide values typically found in tariffs for delivered natural gas are as follows: total sulfur compounds (as sulfur) within the range of 0.5 and 20 grains per one hundred standard cubic feet (scf) of gas (conversion to ppm Sulfur (S): 1 gr S/100scf = 16.96215 ppmS(v) (@ 15°C & 101.325 kPa), therefore the equivalent range would be 8.48 to 339.24 ppmS(v)) and hydrogen sulfide concentrations within 0.25 and 1.0 grains per one hundred scf of gas. Mercaptan concentrations range between 0.20 and 2.0 grains per one hundred scf of gas. However, it is clear from testing of raw and partially cleaned biogas that methyl mercaptan can be found in concentrations above 1 ppmv; consideration of mercaptan concentrations in biomethane is therefore important. Based upon testing of biomethane, below detection limit (0.05 ppmv) can be achieved for all mercaptan compounds.

Based upon results of biomethane testing as part of this GTI program, typical reported tariff values for total sulfur, hydrogen sulfide and mercaptan content can be achieved. Individual company tariffs and quality requirements for these constituents should be considered.
6.5.3 Representative Analytical Test For This Parameter

Off-line sulfur species analysis is usually performed by gas chromatography following either ASTM D6228 or D5504. The two methods use different techniques for detection of sulfur species. D6228 uses a flame photometric detector (FPD) and D5504 uses a sulfur chemiluminescence detector (SCD). Total sulfur analysis can be performed by ASTM D3246 using oxidative microcoulometry.

Because the presence of an odorant in fuel gas is mandated by law, real-time or near-real time monitoring systems that measure sulfur compounds are very common in the fuel gas and gas transmission industries. This "on-line" sulfur analysis is also performed by GC techniques. Various detectors are used including sulfur chemiluminescence (D5504), flame photometric (D6228), electrochemical cell (currently considered by ASTM D03 committee), oxidative cell and reductive cells.

6.6 Dusts, Gums and Biologicals

6.6.1 Parameter Overview

Particulate matter, such as dust, gums and biologicals, can be introduced into the gas distribution network from a variety of sources. In the case of biomethane production, particulate matter may be carried along from the production process into the final biomethane gas product. Another source may be chemical interactions between concomitant gas species in the raw biogas. Specific microbes contained in the bioreactors/digesters may induce/exacerbate pipeline corrosion (microbial induced corrosion or “MIC”). Depending upon reactor conditions and starting biomass, a variety of microbial populations may exist in the resulting gas stream. The amount and size of particulate matter in the biomethane stream should be minimized to avoid contamination, clogging and erosion of processing plant and distribution line components. Particles can usually be removed by filters, sedimentation or centrifugal collectors.

6.6.2 Biomethane Range Guidance

Some tariffs for natural gas state that the gas is to be “commercially free of dusts and gums” or solid particles must be within the range of 3 – 15 microns. There is no specific requirement for biologicals (microbes and spores). However, biological agents may be considered as particulate matter, as they can be filtered from the gas stream.
Based upon results of biomethane testing as part of this GTI program, typical tariff values for dust and gum particulate matter can be achieved through in-line filtration (1 micron filter). However, biological matter may require a .3 micron filter, as spores and bacteria can pass through a 1 micron filter. Individual company tariffs and quality requirements for particulate matter should be considered.

6.6.3 Representative Analytical Tests For This Parameter

6.6.3.1 Dust and Gums

Filters may be installed in-line after the biogas cleanup process, collected on a periodic basis and subjected to analysis for the presence of particles. Analysis for particulate matter can also be achieved through on-line instrumentation using an isokinetic sampling method (like EPA Method 5).

6.6.3.2 Biologicals

Where the downstream pipeline environment is conducive to microbially induced corrosion, it is recommended that .2 or .3 micron filters be installed for proper filtration of microbes. Please refer to the Appendix for further specifics on this topic.

6.7 Inert and Diluent Gases Total

6.7.1 Overview

Inert and diluent gases are non-hydrocarbons and reduce the overall heating value of the biomethane. Inerts (nitrogen, argon, helium, etc.) are not chemically reactive with the surrounding environment. However, diluents gases may chemically react with the surrounding environment; the primary diluent in biomethane is carbon dioxide, but others such as oxygen may be present. Some pipelines group all non-hydrocarbon gases together as “total inerts”, but may also have specific limit values for each inert gas.

Concentrations and combinations of inerts and/or diluents may impart various impacts to pipeline operations, gas facilities and end-use equipment. These are detailed in the following sections.
6.7.1.1  **Carbon Dioxide (CO₂)**

Carbon dioxide is considered a diluent and is an odorless, colorless gas. Carbon dioxide reduces the overall heating value of the gas stream per unit volume. Carbon dioxide is non-corrosive in the absence of water, but if water is present, under certain conditions, it can form carbonic acid. Additionally, carbon dioxide can act synergistically with H₂S and O₂, thereby enhancing the corrosion of pipeline materials.

6.7.1.2  **Oxygen (O₂)**

Oxygen may be present under the conditions of biogas production. The presence of oxygen is critical because it increases both the effect and rate of other corrosion mechanisms. In combination with free water and/or with other constituents such as carbon dioxide, hydrogen sulfide and bacteria (naturally occurring), enhanced corrosion can result. Therefore, a dry biomethane product is desired. Small amounts of oxygen can support colonies of sulfate-reducing bacteria, especially in the presence of moisture.

6.7.1.3  **Nitrogen (N₂)**

Nitrogen is an inert gas that is colorless, odorless and non-corrosive. It is usually regulated because it affects the calorific value of the gas or gas used as feedstock (fuel cells, hydrogen production and natural gas liquefaction). At elevated concentrations, combustion operations may be impacted, possibly causing poor flame stability and producing a flame with yellow tipping and lifting.

6.7.2  **Biomethane Range Guidance**

Reported tariff values for total diluents gases (total inerts) in natural gas ranges between no more than 2 - 6% of total by volume. Reported tariff values for carbon dioxide ranges from 1 – 3 % by volume, oxygen ranges from 0.001 – 1% by volume and nitrogen ranges from 1 – 4% by volume.

Based upon results of biomethane testing as part of this GTI program, typical tariff values for inert and diluents gases can be achieved. Individual company tariffs and quality requirements for these gases, separately or in total, be considered.
6.7.3 Representative Analytical Test For This Parameter (Carbon Dioxide, Oxygen and Nitrogen)

Carbon dioxide, oxygen and nitrogen can be determined by gas chromatograph analysis with a thermal conductivity detector following ASTM D1945/1946.

6.8 Other Trace Constituents

6.8.1 Overview

Depending upon the quality and composition of the starting biomass material and the conditions under which the biomass is anaerobically digested, it is possible that higher organic compounds and other so-called “trace” substances could be introduced into the resulting biogas. Microbes are able to degrade or transform a wide variety of organic and inorganic compounds by way of enzymatic action or incomplete digestion. As well, some compounds are simply volatilized through agitation in the bioreactors (digesters). Some trace constituents may be problematic to the pipeline network (inducing/exacerbating corrosion, contributing to odorant fade, accumulating on pipeline walls, etc), end-use equipment (burner tip accumulation, equipment/product compromise, feedstock applications etc.). While it is unlikely that trace constituents are found in significant quantities in cleaned biogas from dairy waste conversion, examination for such constituents may be useful. Ranges of tariff specifications in the area of “Trace Constituents, Contaminants and Objectionable Material” vary throughout the industry; individual companies should consider specific requirements for their particular system and customer base. Testing for the presence of specific trace constituents may be achieved by gas chromatography, or other methods, as required. However, testing should be designed around the specific compounds of interest and testing should include quality standards for comparison purposes.
6.8.2 Heavy Metals

Heavy metal concentrations are of particular concern when dealing with biomethane generation because volatile metals may be released through the degradation of concentrated plant materials and metal-containing products used in dairy operations, such as fungicides which contain copper.

Heavy metals may cause toxicological and environmental problems. The primary impact from the presence of some heavy metals in the gas stream is potential corrosion of aluminum metal and alloys used to construct gas processing equipment. This is particularly problematic because heavy metals, such as mercury, may concentrate in cryogenic liquids and other processing fluids.

Sampling for volatile metals can be performed on-line using a sparger containing a mix of hydrogen peroxide and nitric acid, returned to the lab, and analyzed by ICP or AAS. (The sparger technique is similar to EPA Method 29 for stack gas sampling, where a known volume of gas is passed through a gas bubbler.)

Routine analysis for mercury can be done following ASTM D5954 or D6350. These methods utilize on-site collection on gilded silica sorbent tubes followed by lab analysis by atomic absorption or atomic fluorescence spectroscopy. These techniques require knowledge of the total gas sampled via a dry test meter (preferred) or rotameter. On-line analyzers are available for continuous monitoring.

Metals should be extracted from the biomethane at the point of gas sampling. Accurate mercury analysis cannot be performed through collection of the biomethane in a cylinder and shipment to the laboratory for further analysis.

Individual company tariffs and quality requirements for heavy metals should be considered.

6.8.3 Hydrogen

Hydrogen is not a typical constituent of natural gas, but some raw natural gas wells or storage fields may contain hydrogen; it may be present in biomethane. Hydrogen can be problematic when in contact with steel; hydrogen stress cracking or hydrogen embrittlement may occur. Hydrogen stress cracking is a degradation process that steel can undergo due to the extreme solubility of atomic hydrogen in the iron alloy lattice. Atomic hydrogen may result from spontaneous dissociation of molecular hydrogen. The presence of hydrogen sulfide in the gas accelerates the permeation of atomic hydrogen into the iron lattice. Other concerns are with reactions between hydrogen and sulfur and
chlorine-containing compounds, especially in the presence of water, forming sulfuric and hydrochloric acids.

Hydrogen can be determined on-line using a solid state sensor, or in the laboratory from a field sample using gas chromatography with a thermal conductivity detector (ASTM D1945/1946). Other detectors can be used to reduce detection limits if hydrogen presence is a concern.

Based upon results of biomethane testing as part of this GTI program, typical tariff values for hydrogen can be achieved. The reported hydrogen value typically found in tariffs for delivered natural gas is between 400 – 1000 ppm. Individual company tariffs and quality requirements for hydrogen should be considered.

### 6.8.4 Ammonia

Some of the excess nitrogen fed to cows in the form of feed proteins results in slurry with high urea content. This urea can be converted to ammonia through enzymatic processes. The presence of ammonia could impact on downstream gas processing equipment and odorization of pipeline gas. When present in a gas that is combusted, it could form nitrogen oxides that would have an impact on end use operations. Nitrogen oxides are an environmental concern because they are known to assist in the creation of smog, foster the depletion of the ozone layer, and contribute to acid rain.

Ammonia can be determined on-line or in the laboratory from a field sample using a nitrogen chemiluminescence detector.

Individual company tariffs and quality requirements for ammonia should be considered.

### 6.8.5 Siloxanes

Siloxanes are organic compounds that contain silicon, oxygen, hydrogen, and carbon. Due to the increase in silicon-containing personal hygiene, health care, and industrial products, the presence of siloxanes in waste streams has increased. However, dairy farms do not normally use siloxanes in their operations so the occurrence of siloxanes in biogas is minimal. As the silicon-containing waste stream is digested and treated in the anaerobic digester, the silicon converts to siloxane compounds that volatilize and become entrained in the biogas. When this gas is combusted under high heat and pressure, silicon dioxide is formed. This silica dust damages internal combustion engines, turbines, and add-on air pollution control devices. While there are no generally accepted pipeline
specification for siloxane concentrations in natural gas, its introduction into the gas system is to be avoided.

Analysis for siloxanes is performed by two methods. One method to detect these compounds utilizes an inerted gas sample collection cylinder that can be directly analyzed in the lab with no additional sample preparation. The final analysis is by GC-AED. The Atomic Emission Detector is an element specific detector that can look exclusively at silicon emission responses. Another technique uses alcohol filled glass spargers that the gas is bubbled through. This sample collection must be performed in the field with the final analysis by GC-MS in the laboratory.

Individual company quality requirements and end use tolerance for siloxane concentrations should be considered.

6.8.6 Pesticides

Pesticides are commonly used on farms and may be unintentionally introduced into dairy manure. The specific target chemicals should be determined based on their known or suspected use at each dairy farm. It is not anticipated that pesticides would be present in the resulting biomethane. Testing of biogas and biomethane samples from dairy farms throughout the US as part of the Task 2 GTI work included analysis of the following pesticides identified as typical to dairy farm operations: a-BHC, b-BHC, G-BHC, d-BHC, heptachlor, aldrin, heptachlor epoxide, g-chlordane, endosulfan I, dieldrin, 4,4’-DDE, Endrin, Endosulfan II, 4,4’-DDD, Endrin aldehyde, endosulfan sulfate, 4,4’-DDT, Endrin ketone and Methoxychlor.

Sampling for pesticides in biogas, can be performed on-line using XAD-2 sorbent tubes. The sample should be collected using two sorbent tubes attached in series connected to a personal air pump capable of sampling at a rate of up to 5 L/min. Samples should be collected for four hours at a rate of 2L/min. This XAD sorbent tube sampling method is similar to NIOSH Methods 5600/5601.

Individual company tariffs and quality requirement for pesticides should be considered.

6.8.7 Pharmaceuticals

Many types of drugs and other chemical products are used on conventional dairy farms to promote and maintain the health of cows; this is not the case on organic farms. These chemicals, either through digestion or through external application to the cows, may be
present in manure or eventually carried over into the digester and product biogas. Consequently, it is recommended that dairy biomethane samples be analyzed for animal drugs and care products. Testing of biogas and biomethane samples from dairy farms throughout the US included analysis of the following pharmaceuticals identified as typical to dairy farm operations: ampicillin, amoxicillin, oxytocin, florfenicol, tripelennamine hydrochloride, ceftiofur, tilmisosin, furosemide, flunixin meglumine, fenbendazol and doramectin.

The suggested sampling method (which is similar to existing NIOSH methods) can be performed on-line using Porapak-R sorbent tubes. The sample should be collected using two sorbent tubes attached in series connected to a personal air pump capable of sampling at a rate of 5 L/min. The sample should be collected at a rate of 1 L/min for 4 hours. The samples should subsequently be analyzed using GC/MS and/or LC/MS for determination of animal drugs and care products, using known standards.

Individual company tariffs and quality requirements for pharmaceuticals should be considered.

6.8.9 Higher Organics/Chlorinated Compounds (PCBs)

Polychlorinated biphenyls (PCBs) are addressed under the category of Trace Constituents and Objectionable Matter and PCBs are routinely sampled in natural gas pipelines and are highly regulated chemicals in the natural gas industry. Although the presence of PCBs is highly unlikely in dairy waste biomethane, analysis of these set constituents was tested as part of Task 2 biogas sampling and analysis.

Sampling for PCBs in biomethane can be performed on-line using XAD-2 sorbent tubes. The sample should be collected using two sorbent tubes attached in series connected to a personal air pump capable of sampling at a rate of up to 5 L/min. Samples should be collected for four hours at a rate of 2 L/min. This XAD sorbent tube sampling method is similar to NIOSH Methods 5503. The samples should be analyzed using EPA Method 8082 for determination of PCBs.

Individual company tariffs and quality requirement for chlorinated compounds should be considered.

6.8.10 Semi-Volatile and Volatile Compounds (VOCs and SVOCs)

Biogas produced from dairy waste, or cow manure, typically consists of methane and other major components but can also contain hundreds of other chemicals -- most of
which are known as "non-methane organic compounds" or NMOCs. Most NMOCs are volatile organic compounds (VOCs). Volatile organic compounds are formed as intermediate metabolites in the degradation of organic matter in manure. Under aerobic conditions, any VOC formed are rapidly oxidized to carbon dioxide and water. Under anaerobic conditions, complex organic compounds are initially degraded microbially to volatile organic acids and other volatile organic compounds before complete conversion to methane and carbon dioxide by methanogenic bacteria. When the metabolic activity of the methanogenic bacteria is not inhibited, virtually all of the VOCs are consumed and the potential for VOC emissions is nominal. However, the inhibition of methane formation results in a buildup of VOCs in the manure and ultimate volatilization to the biogas.

Sampling for volatile and semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), can be performed on-line using XAD-2 sorbent tubes. The sample should be collected using two sorbent tubes attached in series connected to a personal air pump (or other suitable pumping apparatus) capable of sampling at a rate of up to 5 L/min. Samples should be collected for four hours at a rate of 2 L/min. This XAD sorbent tube sampling method is similar to NIOSH Method 5515. There are also real time analytical instrumentations available which monitor and record specific and total VOCs; these instruments are GCs which utilize FID or TCD detectors.

Individual company tariffs and quality requirement for VOCs and SVOCs should be considered.

6.8.11 Halocarbons

Halocarbons are organic compounds containing carbon, hydrogen, and chlorine, fluorine, and bromine. They are used in various applications, such as air conditioning systems, refrigeration systems, firefighting agents, aerosols, and foam-blowing agents. For example, the various forms of Freon are halocarbons. Some halocarbons may be present in products used on the farm, but levels of such compounds is expected to be very low overall.

Halocarbons present in the gas stream can cause operational problems for gas processing. When combusted, chloride ions form, causing potentially corrosive conditions to the pipeline. Even small amounts of halocarbon compounds can produce noxious and corrosive acids in gas flames affecting many manufacturing processes. While it is unlikely that trace constituents are found in significant quantities in cleaned biogas from dairy waste conversion, examination for such constituents may be useful.
Analysis for halocarbons is by gas chromatography using a electron capture detector (ECD) or an electrolytic conductivity detector (ELCD). Both the GC-ECD and GC-ELCD techniques are capable of detecting chlorine-containing compounds. The former GC detector is much more sensitive than the latter. However, sulfur-containing organics and aromatics also respond to the ECD, reducing the selectivity to halocarbons. The latter technique is more selective, making positive identification of halocarbons much easier.

Individual company tariffs and quality requirement for halocarbons should be considered.

6.8.12 Others

Depending upon the biomass material digested, materials introduced into the digester, conditions under which the material is digested, quality of gas cleanup, gas volumes produced and introduced, local conditions of the pipeline network, end-use applications or human health and environmental considerations, and other considerations, concentrations of additional organic/inorganic or biological constituents may be necessary.

7.0 An Example Program for Biomethane Quality Verification

7.1 Purpose

Prior to introduction to the natural gas pipeline network, it is suggested that the biomethane product be monitored for quality for a discreet test period. Depending upon the specifics pertaining to any individual natural gas company, this test period may vary in length. As an example and for the purposes of this Document, a test period of three months has been constructed. During the test period, field samples are regularly retrieved and tested by independent laboratories for quality and accuracy with on-line instrumentation. It is recommended that the test period be executed prior to introduction to the natural gas pipeline network. The following is a sample of such a test program, termed the “Biomethane Verification Program”. This example test program offers a model for gas testing and is aimed at confirming that biomethane from a discrete system, given a discrete biomass input, can consistently achieve required value ranges for specific compounds in the product.

This example Verification Program achieves 3 goals:
1) The natural gas company is able to monitor and assure the quality of the new fuel product and the routine production of the product over a trial period of time,

2) The biomethane provider is able to verify that the product is consistent and safe for pipeline interchange, and,

3) Both parties may better understand the nature of specific gas quality parameters and constituents necessary to optimize the cleanup process prior to introduction to the pipeline network.

A three month intensive testing program, following by a continued yet reduced program, is proposed.

7.2 Sample Analytical Package

In order to impart security in the sustainable quality of a biomethane system, it is proposed that the biomethane be intensively monitored for an agreed upon test schedule period. A sample test period of 3 months is proposed here, titled the Biomethane Verification Program. Each individual gas company should evaluate the appropriateness of this test program for their purposes; it is not prescriptive.

A test/verification period should cover changes in the system as the feed manure changes and the system matures. Until the variability of a specific process is thoroughly understood, use of an on-line GC test with Btu calculation is proposed and readings should be performed as frequently as possible. Modern on-line instruments would customarily allow for an analysis every 5-15 minutes (depending on which analyzer is used). The Btu content is measured frequently at custody transfer points because gas is sold on an energy basis, not a volume basis. Other surrogate testing may achieve similar levels of confidence.

It is also recommended that an on-line sulfur analyzer be installed, to remove concerns about sulfur stability and holding time in cylinders, as well as all other on-line monitors described above (moisture, particulate matter, etc).

It is recommended that all on-line measurements be available for independent viewing by qualified personnel for verification of quality during the test period. This period of testing and system analysis is for the protection of the receiving pipeline system and will provide data which assures routine and rigorous gas quality.
As a point of reference, when the EPA monitors sulfur emissions from a stationary source (gas-fired combustion engines), monthly analysis for 1-3 years is required. This is required even though existing natural gas sources are utilized.

Once verification of minimum gas quality has been routinely reported, a “maintenance” testing schedule can be established. If reporting is satisfactory after the sample three month Verification Testing Program has been completed, it is suggested that reporting be decreased but maintained over the next two years. On-line verification of Btu content, through installed instruments to the biomethane processing system, should remain open for the receiving pipeline system verification of quality. If deemed necessary, a program of continued testing should be established at the end of the three-month test period, based upon test period results.
### 7.3 Sample: Biomethane Verification Program

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analysis</th>
<th>Referenced Method</th>
<th>Reported Tariff Ranges</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Value</td>
<td>Gas Chromatography</td>
<td>ASTM D1945 or GPA 2261</td>
<td>950 - 1000 Btu/scf (min) 1075 – 1200 Btu/scf (max)</td>
<td>Continuous real-time or near-real-time monitoring and weekly field samples for independent confirmation. NOTE: Heating Value, HCDP, Water Content, Total Sulfur, H2S, CO2, O2, N2 and Inerts can effectively been monitored all at the same time, on a real time basis, as required.</td>
</tr>
<tr>
<td>Temperature</td>
<td>On-line Analysis</td>
<td>NA</td>
<td>20°F - 120°F</td>
<td>Continuously measured on-line</td>
</tr>
<tr>
<td>Hydrocarbon Dew Point</td>
<td>Equation-of-state (EOS) model</td>
<td>NA</td>
<td>0°F - 25°F @ either fixed or operating pressures</td>
<td>Continuous real-time or near-real time monitoring and weekly field samples for independent confirmation</td>
</tr>
<tr>
<td>Water Content</td>
<td>Chilled Mirror Technique or an Electronic Moisture Analyzer</td>
<td>ASTM D1142 or ASTM D5454</td>
<td>4 – 7 lb./MMscf</td>
<td>Continuous real-time or near-real time monitoring and monthly field samples for independent confirmation</td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>Oxidative Microcoulometry</td>
<td>ASTM D3246</td>
<td>0.5 - 20 grains total sulfur/100 scf</td>
<td>Continuous real-time or near-real time monitoring and weekly field samples for independent confirmation</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>Lead acetate reaction rate method</td>
<td>ASTM D4084</td>
<td>0.25 – 1 grain of hydrogen sulfide/100 scf</td>
<td>Continuous real-time or near-real time monitoring and weekly field samples for independent confirmation</td>
</tr>
<tr>
<td>Max. Solid Particle Size</td>
<td>On-line instrumentation using an isokinetic sampling method</td>
<td>Similar to EPA Method 5</td>
<td>3 – 15 microns</td>
<td>In-line or on-line filters be collected monthly for determination of particulates</td>
</tr>
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<td>--------------------------</td>
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<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Biologicals</td>
<td>Quantitative Polymerase Chain Reaction (qPCR), Most Probable Number, NASA Protocol for Spore Testing</td>
<td>Spores enumeration via modified NASA Protocol for Spore Testing NHB 5340.1D</td>
<td>Refer to Individual Company Requirements</td>
<td>In-line or on-line filters be examined weekly for determination of live and dead bacteria and spores throughout the test schedule. Bi-weekly testing for MIC bacteria is advised through the test period.</td>
</tr>
<tr>
<td>Volatile metals</td>
<td>Inductively Coupled Plasma or Atomic Absorption Spectroscopy</td>
<td>NA</td>
<td>Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
<tr>
<td>Mercury</td>
<td>Atomic Absorption or Atomic Fluorescence Spectroscopy</td>
<td>ASTM D5954 or ASTM D6350</td>
<td>Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Gas Chromatography with a Thermal Conductivity Detector</td>
<td>ASTM D1945/1946</td>
<td>400 - 1000 ppm</td>
<td>Monthly*</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Gas Chromatography</td>
<td>ASTM D1945/1946</td>
<td>1 - 3%</td>
<td>Continuous real-time or near-real time monitoring and weekly field samples for independent confirmation</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Gas Chromatography</td>
<td>ASTM D1945/1946</td>
<td>1 - 4%</td>
<td>Continuous real-time or near-real time monitoring and weekly field samples for independent confirmation</td>
</tr>
<tr>
<td>Substance</td>
<td>Analysis Method</td>
<td>Standard/Method</td>
<td>Concentration Range</td>
<td>Monitoring Frequency</td>
</tr>
<tr>
<td>----------------------</td>
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</tr>
<tr>
<td>Oxygen</td>
<td>Gas Chromatography</td>
<td>ASTM D1945/1946</td>
<td>0.001 - 1%</td>
<td>Continuous real-time or near-real time monitoring and weekly field samples for independent confirmation</td>
</tr>
<tr>
<td>Siloxanes</td>
<td>Gas Chromatography with an Atomic Emission Detector</td>
<td>NA</td>
<td></td>
<td>Monthly*</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Gas Chromatography, Nitrogen Chemiluminescence Detector</td>
<td>ASTM D1945/1946</td>
<td>Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Gas Chromatography with an Electron Capture Detector</td>
<td>EPA Method 8081</td>
<td>Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>Gas Chromatography with a Mass Spectrometer or Liquid Chromatography with a Mass Spectrometer</td>
<td>NA</td>
<td>Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
<tr>
<td>Polychlorinated Biphenyls</td>
<td>Gas Chromatography with an Atomic Emission Detector</td>
<td>EPA Method 8082</td>
<td>Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
<tr>
<td>Semi-volatile and Volatile</td>
<td>Gas Chromatography with a Mass Spectrometer or Liquid Chromatography with a Mass Spectrometer</td>
<td>EPA Method 8270</td>
<td>Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
</tbody>
</table>
### Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass Spectrometer</th>
<th>Company Requirements</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halocarbons</td>
<td>Gas Chromatography with an Electron Capture Detector or and Electrolytic Conductivity Detector</td>
<td>NA Refer to Individual Company Requirements</td>
<td>Monthly*</td>
</tr>
</tbody>
</table>

*Increased or decreased frequency, depending upon concentrations at first sample point.
8.0 Terminology/Definitions

The definitions provided here are intentionally limited in scope and are offered for general information only.

**Biogas** - The gas resulting from the anaerobic digestion of biomass. Depending upon the digestion process used and conditions of digestion, biogas consists of 40 – 65% methane. The remaining 35 – 60% of the biogas consists of “other” gases, with carbon dioxide being the major other gas along with trace gases including nitrogen compounds (ammonia, etc), water vapor, sulfur compounds (hydrogen sulfide, etc) and other constituents, depending upon the biomass used for digestion. Biogas is considered “raw” unless cleaned or “conditioned” to meet the requirements of end use or inclusion within natural pipeline systems. “Raw” biogas is not considered suitable for interchange within natural gas pipeline networks.

**Biomass** – Organic materials that may be converted to gaseous fuel through digestion (breakdown) or high temperature conversion (gasification). These materials may include all organic substances, but some biomass materials possess more caloric value than others, thereby producing more energy. Biomass sources vary widely and include animal wastes, livestock operation residues, forest and mill residues, agricultural crops and wastes, wood and wood wastes, aquatic plants, fast-growing trees and plants, and municipal and industrial wastes.

**Biomethane** - The portion of biogas which consists primarily of methane. Biomethane is generally extracted from raw biogas through cleanup or “conditioning”, to remove “other” gases which impact gas quality. Using effective biogas cleanup (removal of gases which effect overall gas quality), biomethane can be up to 99% methane, with concentrations of “other” gases. However, “raw” biogas may contain only 35 – 65% methane. Biomethane is considered suitable for many end-use applications and may be considered suitable for inclusion in general pipeline systems, depending upon other characteristics of the gas and specific tariff requirements.

**Biomethane Verification Testing Program** - A period of time in which the gas resulting from a biomethane production process is subject to analytical testing and review, to confirm biomethane quality. Such a program is advised, as the quality of biogas and biomethane varies with process design, biomass input, choice of cleanup unit and other parameters. It is advised that the verification program be executed prior to introduction of the biomethane product to the natural gas system, so that analytical compliance may be demonstrated over a period of time.

**Biweekly** - Every other week.
**Chromatograph** - An analytical instrument that separates a gas sample into its components for measuring and is used to determine gas quality data such as heating value, relative density (specific gravity), and compressibility.

**Conventional Dairy Production** – The practice of modern dairy farming in the U.S. were chemicals are used as labeled to control invasive insects and bacteria that are harmful to crop production and vaccines, antibiotics and other drugs to treat or prevent dairy cattle disease.

**Dairy Waste** – Manure from dairy cattle along with other byproducts generated when operating a dairy farm such as stored feed that has spoiled, unconsumed feed, milking equipment cleaning water, etc. Both barn “flush” and “scrape” manure handling practices were considered in the preparation of this document.

**Detection Limit** - Detection limit is defined here as 50% of the reporting limit. Reporting limit is defined as the sample equivalent of the lowest linear calibration concentration for the target analyte. Therefore, if a concentration is reported as “below detection limit” (BDL), the analyte was not detected at a concentration greater than the specified detection limit.

**Digester (Anaerobic)** – A tank, covered lagoon or other covered vessel designed to convert biomass to biogas. Conversion of the biomass in the digester depends upon bacterial degradation or transformation of compounds, both carbon-based and other, to gaseous products, which are then present in the resulting biogas. Digesters vary in complexity and design. The maximum quantity of biogas generated from digestion of biomass is dependent upon the design of the digester (temperature and hydraulic retention time), biologically degradable fraction of the raw material and other factors. Biogas generated through anaerobic digestion of biomass in digesters requires further cleanup prior to use (interchange) within natural gas pipeline systems.

**Gas Cleanup** - Used in reference to cleaning raw biogas resulting from biomass conversion (anaerobic digestion or landfill digestion). The goal of the gas cleanup unit is to remove constituents within the raw biogas in order to produce a clean “biomethane” product, suitable for further end use or potential inclusion within gas pipeline networks. Cleanup efficiencies for particular constituents vary between cleanup or “conditioning” units.

**Grain** – A measurement of weight. 7,000 grains = 1 lb.

**Halogens** - The elements fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At), which make up the seventh period in the periodic table of the elements. Compounds which consist of these elements are often used in disinfectant solutions. Upon degradation, the elements may be released as gases.
Heavy Hydrocarbons - Heavier molecular weight hydrocarbons are more prone to condense from the natural gas stream and are the major constituents of hydrocarbon condensate.

Heavy Metals - Heavy metals refers to a group of mostly toxic metals that have high atomic weights. Some are always toxic (e.g. lead, mercury, cadmium, arsenic, chromium) and others are toxic at high concentrations (e.g. zinc, copper). They are found everywhere in the environment because they are naturally part of the earth's crust or are concentrated in waste streams due to the use of a compound that incorporates a heavy metal element. When a compound that contains a heavy metal is degraded, the element can be released as a toxic gas.

Interchangeability – The ability to substitute one gas for another, in the context of natural gas replacement, without materially changing or influencing environmental health and safety, end use performance or pipeline integrity.

Manure – The mixture of urine and feces excreted by dairy cattle.

Microbial Induced Corrosion (MIC) - Corrosion caused by bacteria present in a pipeline network. Specific groups of bacteria can produce acids that deteriorate pipes through pitting and oxidation. MIC bacteria groupings include, but are not limited to: sulfate-reducing bacteria (SRB), acid-producing bacteria (APB), including acetic-acid producing bacteria (total group) and butyric-acid producing bacteria (total group), iron-oxidizing bacteria (IOB), denitrifying bacteria (DNB), and methanogens – microbes which produce methane (in the Archaea domain). MIC can be very deleterious to pipeline integrity and has been associated with pipeline failure.

Organic Dairy Production - The practice of modern dairy farming in the U.S. were chemicals are not used to control invasive insects and bacteria that are harmful to crop production and vaccines, antibiotics and other drugs are not used to treat or prevent dairy cattle disease.

Pesticides - Chemical products used to reduce or eliminate unwanted organisms, regarded as "pests". Pesticides are often used on agricultural land, gardens, roadsides, and golf courses to eliminate species considered undesirable or damaging. Pesticides may incorporate elements which are deleterious to human health and the environment and, when degraded, may release compounds/elements of concern.

Pharmaceuticals - Pharmaceuticals are substances that are aimed to cure, prevent, or recognize diseases and relieve pains through their application in the organism. These products are in the routine or special care of animals. Breakdown or volatilization of pharmaceutical products may pose secondary health effects in receptors for which the products were not intended.
Siloxane - Any chemical compound composed of units of the form R₂SiO₂, where R is a hydrogen atom or a hydrocarbon group. A siloxane has a branched or unbranched backbone of alternating silicon and oxygen atoms, -Si-O-Si-O-Si, with side chains R attached to the silicon atoms. The word siloxane is derived from the words silicon, oxygen and alkane. Siloxanes can be found in products such as cosmetics, deodorants, water repelling windshield coatings, food additives and some soaps. When combusted, the siloxane molecules are reduced to silicon dust; this is extremely abrasive and damaging to internal engine components. Combustion of siloxanes also causes a glass-like build up around burner tips and on the tubes of heat exchangers. Silicon dust, resulting from the combustion of siloxanes, may pose health risks to humans and other receptors.

9.0 References


White Paper on Natural Gas Interchangeability and Non-Combustion End Use, NGC+ Interchangeability Work Group, February 28, 2005
Appendix A: Introduction to MIC

Microbially-induced corrosion (MIC) is one of the leading causes of pipe failure in the natural gas industry. This corrosion is caused by bacteria produced acids which cause pitting in the pipes. This is especially prevalent in gas lines in which moisture has collected, or in wet gas systems. Bacteria associated with MIC can be difficult to enumerate and identify. Traditionally, corrosion-causing bacteria are detected and quantified through simple bacterial growth tests that incorporate different enrichment media. In these tests, samples are collected and provided with growth medium (food and nutrients) on which the bacteria grow. However, there are problems with these types of tests: 1) the bacteria may not grow on the selected medium, 2) the bacteria may be very slow to grow and are therefore not counted, and, 3) the conditions (temperature, etc) are not correct for the growth of target bacteria. Bacteria which cause MIC are difficult to grow and, using the plate growth method, are often overlooked or misrepresented in final numbers. Also, given the conditions of biomethane production and cleanup, bacteria may be present in the cleaned gas stream but may not be alive. Traditional plate tests, commonly used in the natural gas industry, cannot account for the presence of dead bacteria.

One of the most traditional growth methods is called the Most Probable Number test or MPN test. It relies on liquid samples containing live bacteria, and takes up to 4 weeks to obtain the results. Unfortunately, as numerous researchers have shown, only 0.1% to 10% of total live bacteria can actually grow in an artificial medium such as that used in the MPN tests and a significant portion of bacteria growing in the media are actually not the target bacteria. Therefore, this growth test is unable to accurately quantify the target bacteria in the samples.

New methods have been developed to more accurately assess microbial populations. Common and widely used molecular biology techniques can be deployed to assay for live and dead bacteria (16s rRNA analysis). GTI, for instance, has developed and patented a procedure based upon a common and referenced molecular biology technique to test specifically for the bacteria which cause MIC in pipeline, to overcome the problems with the MPN testing. The technique allows for direct detection and quantification, without prior growth, of corrosion-causing microorganisms typically found in pipes and other equipment used by the natural gas, petroleum, chemical, water, and wastewater industries. This test allows for quantification and identification of live and dead bacteria because it does not involve bacterial growth. This test specifically targets functional genes (segments of DNA) associated with bacteria that cause corrosion. In other words, it looks specifically for the DNA sequences within the dead or live bacteria, which are associated with MIC-corrosion capabilities. The testing technique is far more accurate than traditional microbial growth tests with an accuracy of ± 10%, and can analyze.
almost any type of samples (liquid, biofilms, or solid samples), including dried solid samples, which only contain dead bacteria. It is also rapid; genetic tests can be completed in 24 to 48 hours. This testing is called qPCR (Quantitative Polymerase Chain Reaction). The test of qPCR is a common molecular biology technique and has been used in many types of microbial testing programs, but GTI has developed the test specific to MIC testing and identification. Other qPCR, protein or nucleic acids tests may also be useful.

Another consideration of transmission of bacteria into the natural gas system is the introduction of pathogens to gas supplies. Identifying bacterial strains which may be pathogenic is achieved through Genbank analysis. Consideration of the transmission of pathogenic microbes and spores has been mentioned in research documents generated in Europe (BONGO Collective).

**Description of MIC Bacteria/Microbes**

Corrosion producing bacteria can be arranged into five basic groups:

- Sulfate-reducing bacteria (SRB)
- Acid-producing bacteria (APB)
  - Acetic-acid producing bacteria (total group)
  - Butyric-acid producing bacteria (total group)
- Iron-oxidizing bacteria (IOB)
  - *Leptothrix* and *Sphaerotilus* genus
  - *Gallionella* genus
- Denitrifying bacteria (DNB)
- Methanogens – microbes in the Archaea domain that produce methane

Of the set listed above, SRB, APB and IOB are widely considered the most aggressive corrosion-causing bacteria, even though SRB are often not the most abundant microbes in pipeline samples. The DNB and methanogens are frequently retrieved from pipeline samples, and also cause corrosion. Of note, the total APB number reported in Task 2 of this project includes both acetic acid–producing bacteria and butyric acid-producing bacteria, which are two most common APB in the pipes. The total IOB number reported here includes *Leptothrix*, *Sphaerotilus*, and *Gallionella*, which are the most common IOB
related to corrosion. Methanogens do not belong to Bacteria Domain; they are a very primitive organism, and belong to Archaea domain.

**Description of Spores**

A bacterial spore is a hard protective coating that encases the key parts of the bacterium, produced by the bacterium when conditions for growth are adverse. Bacterial spores are approximately 0.8 to 1.2 microns in size and consist of protective membrane layers, wrapping essential genetic elements necessary for bacterial survival in the future. They can be spherical and ellipsoidal. Within these membranes and the hard coating, the dormant bacterium is able to survive for weeks, even years, through drought, heat and radiation. When conditions become more favorable again (more water or food available), the bacterium "comes to life" again, transforming from a spore back into a cell. Some bacterial spores have possibly been revived after they lay underground for thousands of years.

Specific types of bacteria in the environment readily produce spores. Some bacteria which convert biomass to methane or perform accessory degradative processes within anaerobic digesters are among the groups that produce spores. Bacteria that produce spores are found among aerobes (require air to grow) and anaerobes (grow without air). Spores can be collected, enumerated and identified.

For confirmatory biological collection and testing, filters of size 0.2 microns, encased in a stainless steel pressure filtration funnel, may be installed in-line after the biogas cleanup and primary biomethane filtering process. The filters can be collected on a periodic basis and evaluated for the presence of microbes and spores. Filtering time depends upon the quality and volume of biomethane that passes through the filter. Filters are folded inward and placed in sterile plastic bags for overnight shipment to the laboratory. Bacteria/spore counts are recorded as number per 100 standard cubic feet of gas.

For testing for the presence of live and dead bacteria, all samples can be tested to the level of type of bacterium using qPCR primers (GTI) or other qPCR testing to the grouping level (test for genetic segments which indicate the presence of the MIC-bacteria, etc. listed in Section 8.0). These tests can determine the total number of bacteria (live and dead) in the sample and can identify the bacteria as associated with MIC.

Live bacteria can be enumerated through traditional bacterial MPN testing (TG Media, Commercial Microbiology). In MPN tests, 10-fold dilution series of filter suspension are inoculated, in triplicate, in the thioglycolate medium to quantify live bacteria and
incubated at 37°C for one week. The positive and negative readings of each culture bottle and the resulting most-probable-number values are then determined according to manufacturer’s instructions.

For samples with positive MPN results (live bacteria present), the MPN culture can be used for DNA isolation and qPCR analysis to determine the types of bacteria present after growth in the medium.

Spore testing can be achieved by using the NASA standard assay NHB 5340.1D. The filter sample used to retrieve bacteria can be used for spore testing. GTI Task 2 testing included taxonomic identification of spores found in biomethane samples through Genbank analysis. Identification of spores may be desirable if there is a concern for pathogenic carryover.

Refer to Task 2 for further information regarding microbial testing.