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# Guidance Document for the Introduction of Landfill-Derived Renewable Gas into Natural Gas Pipelines

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## Legal Notice

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## Executive Summary

The Gas Technology Institute (GTI) has constructed an updated *Guidance Document for the Introduction of Landfill-Derived Renewable Gas into Natural Gas Pipelines* as part of a larger project that collected 27 samples of high-BTU landfill-derived renewable gas. As recommended by project sponsors, three specific cleanup technologies were investigated: Physical Solvent, PSA (Pressure Swing Adsorption), and Gas Separation Membrane. Four samples of pipeline quality natural gas were also collected to serve as comparators. The sampling rationale, analytical data, and statistical analysis of the high-BTU landfill-derived renewable gas data are presented in a separate report.

The purpose of the guidance document is to identify criteria that stakeholders should consider when developing a landfill gas recovery facility for introduction of biomethane into a natural gas pipeline. This document provides a structured approach that pipelines, developers and landfill operators can use to begin the critical process of technical collaboration necessary to understand each other's requirements and ultimately, to make each landfill gas development project a success story for all involved parties. Landfill biogas is recognized as a valuable, relatively untapped resource which when appropriately processed to acceptable pipeline quality levels becomes a fungible zero-emission product.

The guidance document also includes considerations for performance testing of high-BTU landfill-derived renewable gas to aid both developers and pipeline operators in process design optimization ultimately leading to the most efficient and effective processing options. **Such testing, and the list of constituents of interest, would transpire <u>only</u> if mutually agreeable to both the developer and the pipeline operator.**

It is a common practice for the natural gas industry to measure various parameters at custody transfer points, city gates, or odorization stations. The primary purpose is because gas is sold on an energy basis, not a volume basis and the data is needed to calculate the heating value of the gas. Sulfur content is monitored for odorization control. Both sulfur and water are tracked for corrosion control purposes. Temperature is measured so that deviations from the base temperature condition are documented and correction of the metered volume can be made. High-BTU landfill-derived renewable gas should be treated similarly.

The guidance document is not prescriptive; it is meant to provide a framework for productive discussions regarding high-BTU landfill-derived renewable gas quality. It is not intended to provide specific operational parameters for such gas. It is expected to serve as an industry-wide reference covering basic high-BTU landfill-derived renewable gas quality and characteristics. This version of the guidance document is revised and edited from prior releases based on new information gained from the additional sampling and analysis work, and the 2009 edition of American Gas Association (AGA) Report 4A.[1]

While specific gas quality tariffs vary from company to company, many common basic quality parameters exist. The guidance document contains a review of these common gas quality parameters, analytical ranges typical to pipeline tariffs for the parameters, and representative analytical tests. A brief comparison to high-BTU landfill-derived renewable gas data and natural gas data is made. Tables 1A and 1B summarize the findings. Other constituents of interest are reviewed based on past historical data and potential impact.

From the results obtained in this project it can be concluded that high-BTU landfill-derived renewable gas of high quality may be produced within agreed-upon tolerance specifications for introduction with natural gas supplies. These results are specific to the facilities and their gas treatment trains, which represent state-of-the-art facilities. Results should not be extrapolated to other high-BTU landfill-derived renewable gas without considering their characteristics. Further, the results are presented here for guidance purposes only. The results are not intended to replace specific tariff requirements negotiated in contracts for gas delivery.

Highlighted below are study findings that should be considered as part of the collaborative discussion between pipeline operators and project developers / process system operators:

- No vinyl chloride was detected. Dichlorodifluoromethane (CFC-12 or Freon-12) was found in 6 of 27 samples and chloroethane was found in 3 of 27 samples, both in the 0.1 to 2.3 ppmv range.
- Volatile organic compounds (VOC), including hydrocarbons heavier than methane, were at single digit ppmv levels or below the detection limit (BDL). A subset of VOCs is the family of aromatic hydrocarbons that include benzene, toluene, ethyl benzene, and xylene (BTEX). No benzene or ethyl benzene was found in any samples. Toluene and xylene were found in 3 and 2 samples, respectively, at levels no more than 1.4 ppmv.
- Siloxane was below detectable levels in 22 of 27 samples, and ranged from 0.1 to 0.4 mg $Si/m^3$ in 5 of the 27 samples. The only species found was D4 (octamethylcyclotetrasiloxane).
- The net heating value and Wobbe Number may be below typical tariff ranges.
- Data from the net heating value and the sum of the diluent and/or inert gases suggest an initial performance test to avoid exceeding common tariff levels.
- Biologicals were examined as part of this project and levels were found to be similar to those seen in the natural gas samples collected as a comparator data set.
- Sub percent (less than one percent) levels of hydrogen were found in 21 out of 27 samples analyzed.

It is important to recognize the relative differences in typical gas quality parameters and constituent values in flowing pipeline gas in order to assess the relative nature of introduction of renewable gas. Tables 1A and 1B also summarize typical ranges of reported tariff and contract values as documented in the recent revision of AGA Report No. 4A.[1] Most tariffs enforce specifications at the pipeline receipt point. Actual delivery ranges may be different depending on market area proximity relative to production, receipt points, and other common practices associated with pipeline aggregation of supplies.

In reporting the results of the testing of samples taken at the various landfill gas projects, GTI recognizes that the selection of a technology to produce high-BTU landfill-derived renewable gas by a project owner is influenced by capital costs, operating expenses, and the ability of a given technology to meet the minimum pipeline specifications of the natural gas pipeline into which the high-BTU landfill-derived renewable gas is to be delivered. Although an alternative technology may be available to produce high-BTU landfill-derived renewable gas with either fewer trace components or lower levels of those components at either a higher capital or operating cost, a project owner's decision as to selection of a given processing technology is strongly influenced by a technology's ability to continuously meet the minimum pipeline specifications at the lowest combination of capital costs and operating expenses. Thus, the selection of a processing technology by a project owner may have impacted the test results summarized in Table 1.

Tables 1A and 1B are provided solely to illustrate components and parameters that could be considered during contract or tariff negotiations for the introduction of renewable gas, *not to propose actual values*. Individual tariffs may not include all the properties listed in the table and/or may include others not listed, e.g., interchangeability criteria, trace constituents, helium, specific hydrocarbon limits, and others. Readers are advised to consult with appropriate technical and engineering support personnel in an effort to make an informed decision regarding specific contract or tariff specification criteria for a specific market area. This should take into consideration the nature of historical supplies, end use applications within the market area, pipeline integrity, and environmental considerations, as well as the Federal Energy Regulatory Commission (FERC) Policy Statement.

> **NOTE:** *Readers are strongly advised to review applicable tariffs*[2] *and consult with individual pipelines serving their market area for additional information regarding specific constituent or parameter limits as well as information regarding historical gas quality.*

Depending on the nature of supply aggregation and the ability of a pipeline to reasonably manage its system, a pipeline tariff may include Safe Harbor provisions for some parameters to provide suppliers with some degree of certainty about the acceptance of gas into the pipeline. Appropriate language about a pipeline's ability to manage receipts of renewable gas into its system balanced against the needs of market area deliveries is critical for the practical application of component or property limits.

The ranges of gas property specifications vary across the pipeline grid, and exceptions to specified levels at renewable gas receipt points may be considered on a case-by-case basis if the pipeline has determined that variations do not adversely impact its ability to safely transport gas and to meet customer requirements. However, regulatory authorities may require notifications, such as operational flow orders (OFOs) for short term excursions, and posting of these exceptions in accordance with current North American Energy Standards Board (NAESB) guidelines.

As the composition of gas supplies may vary from one receipt point to another, waivers and/or pairing agreements may be considered for any gas not meeting pipeline specifications. Some pipelines may have other options available. This situation provides additional flexibility for landfill gas recovery developers working with the pipelines to optimize processing necessary to maximize available supplies into the pipeline and to satisfy customer requirements. This capability varies from pipeline to pipeline and within individual pipeline systems.

> **NOTE:** ***Caution needs to be exercised when using tariff value ranges highlighted in Tables 1A and 1B to assess interchangeability****. While the tariff value ranges may be representative of some deliveries that are in relatively close proximity to associated receipts into the pipeline from production areas, other delivery points further downstream may have historically experienced much narrower ranges of gas quality, and it cannot be assumed that gas at the extremes of the tariff value range have been delivered and acceptably utilized in these systems. In these cases, tariff values are not representative of historically delivered supplies or the Adjustment Gas for a region. Each party should review historical deliveries into their specific market area.*

> **NOTE:** ***The renewable gas from each of the landfills sampled, analyzed and summarized in Tables 1A and 1B meets the applicable pipeline specification for the natural gas pipeline to which it is interconnected. Those pipeline specifications vary widely.*** *The range of results summarized for the renewable gas analyzed for the various constituents arises from the extent of processing equipment installed and the intensity or lack of intensity of processing required to meet an applicable pipeline specification tariff. Some of the constituents for which results are included are not constituents found in most of the applicable pipeline specification tariffs that must be met by renewable gas sampled for this study.*

[2] All tariff data filed with FERC can be viewed via the FERC web site at www.ferc.gov

Table 1A. Selected Parameters and their Associated Ranges

| Common Tariff Parameters | | | |
|---|---|---|---|
| **Parameter** | **Typical Tariff & Contract Constituent and Property Considerations from AGA 4A – Reported Maximum and Minimum Range** | **Range Found in 27 High-BTU Landfill-Derived Renewable Gas Samples** | **Range Found in Four Natural Gas Samples** |
| Heating Value | minimum<br>900 to 1000 BTU/SCF<br>maximum<br>1075 to 1200 BTU/SCF | 930 to 1010, BTU/SCF | 1009 to 1022, BTU/SCF |
| Wobbe Number | minimum<br>1279 to 1340 , BTU/SCF<br>maximum<br>1380 to 1400 , BTU/SCF | 1200 to 1350, BTU/SCF | 1322 to 1336, BTU/SCF |
| Hydrocarbon Dew Point | maximum HDP between 0°F and 25°F maximum CHDP between 15°F and 20°F | < -100°F | -17 to 16 °F |
| Total Sulfur | maximum 0.5 to 20 grains per 100 SCF | BDL to 0.3 grains per 100 SCF | 0.06 to 0.24 grains per 100 SCF |
| Hydrogen Sulfide | maximum 0.25 to 1.0 grains per 100 SCF | BDL | BDL to 0.03 grains per 100 SCF |
| Diluents + Inerts | maximum 3 to 6 vol % | 0.6 to 8 vol %[a] | 1.7 to 2.3 vol % |
| Carbon dioxide | maximum 1 to 3 vol % | BDL to 2.2 vol % | 1.0 to 1.7 vol % |
| Oxygen | maximum 0.001 to 1 vol %<br>majority: 0.1 to 0.2 vol % | 0.1 to 0.9 vol % | BDL to 0.1 vol % |
| Nitrogen | maximum 1 to 4 vol % | 0.5 to 6 vol %[b] | 0.4 to 1.2 vol % |

[a] Samples from only one of the landfill sites had values outside of the AGA4A suggested range for Diluents + Inerts.

[b] Samples from only one of the landfill sites had values outside of the AGA4A suggested range for Nitrogen.

Table 1B.  Selected Parameters and their Associated Ranges

| **Other Parameters <u>Not</u> Included in Common Tariffs** | | | |
|---|---|---|---|
| **Parameter** | **AGA 4A – Reported Maximum and Minimum Range** | **Range Found in 27 High-BTU Landfill-Derived Renewable Gas Samples** | **Range Found in Four Natural Gas Samples** |
| Hydrogen | maximum 0.04 to 0.1 vol % | BDL to 0.9 vol % | BDL |
| Total Bacteria | No range specified | $5.13x10^5$ to $3.29x10^8$ # per 100 SCF | $6.30x10^6$ to $6.39x10^7$ # per 100 SCF |
| Mercury | No range specified | BDL to 0.05 µg/$m^3$ | BDL to 0.01 µg/$m^3$ |
| Other Volatile Metals | No range specified | insignificant | insignificant |
| Siloxanes (D4) | No range specified | BDL to 0.4 mg Si/$m^3$ | BDL |
| Ammonia | No range specified | BDL | BDL |
| Non-Halogenated Semi-Volatile and Volatile Compounds | No range specified | BDL to single digit levels, ppmv (toluene, xylene) | BDL to 22 ppmv (1,3-butadiene, acrylonitrile, benzene, toluene, xylene) |
| Halocarbons | No range specified | BDL to single digit levels, ppmv (Freon-12, chloroethane | BDL |
| Aldehyde/Ketones | No range specified | sub ppmv | sub ppmv |

## Introduction

The Gas Technology Institute (GTI) has constructed an updated Guidance Document for the Introduction of Landfill-Derived Renewable Gas into Natural Gas Pipelines as part of a larger project that collected 27 samples of high-BTU landfill-derived renewable gas. As recommended by project sponsors, three specific cleanup technologies were investigated: Physical Solvent, PSA (Pressure Swing Adsorption), and Gas Separation Membrane. Four samples of pipeline quality natural gas were also collected to serve as comparators. The sampling rationale, analytical data, and statistical analysis of the high-BTU landfill-derived renewable gas data are presented in a separate report.[3]

This version of the Draft Guidance Document is revised and edited from prior releases based on new information gained from the sampling and analysis of the recommended high-BTU landfill-derived renewable gas supplies, and the 2009 edition of American Gas Association (AGA) *Report No. 4A - Natural Gas Contract Measurement and Quality Clauses*.[1]

The purpose of this updated *Draft Guidance Document* is to identify criteria that stakeholders should consider when developing a landfill gas recovery facility for introduction of biomethane into a natural gas pipeline. This document provides a structured approach that pipelines, developers and landfill operators can use to begin the critical process of technical collaboration necessary to understand each other's requirements and ultimately to make each landfill gas development project a success story for all involved parties. Landfill biogas is recognized as a valuable, relatively untapped resource which, when appropriately processed to acceptable pipeline quality levels, becomes a fungible zero-emission product.

This Document will not provide specific operational parameters for high-BTU landfill-derived renewable gas. Rather, it is meant to serve as an industry-wide reference covering basic high-BTU landfill-derived renewable gas quality and characteristics. This document outlines those analytical parameters in high-BTU landfill-derived renewable gas which may be of importance, referenced by way of the range of typical natural gas tariffs in North America (where available). A list of definitions and terminology follow the main text. The intent of this document is to create common understanding of the product between all stakeholders: natural gas companies, landfill owners/operators, developers, and providers of biogas cleanup technologies. Introduction of new renewable gas fuels, such as high-BTU landfill-derived renewable gas, into the natural gas network often depends on multiple factors beyond specific gas quality objectives. Productive dialog between all parties is key.

The Guidance Document is organized as follows: each parameter has an overview, a range of values for contract consideration, and, a brief description of the representative analytical tests suitable for analysis of the parameter. Constituents not commonly included in pipeline tariffs that are of interest due to the circumstances applicable to a specific pipeline to which a developer proposes to interconnect its project, should be identified in advance and discussed by the developer and the pipeline operator. Such discussions should include the type and frequency (i.e. only at start-up, periodically, or continuously) of any performance testing requested or required by a pipeline operator. Testing of any particular constituent of interest should consider the range of its proposed concentration, and the integrity of the natural gas pipeline to which the renewable gas project is proposed to interconnect. These considerations can be modified or expanded to suit particular situations, depending upon the results of testing, biomass quality and variations over time, cleanup equipment, seasonal variations, etc.

Reference analytical values cited in this document are further detailed in AGA Report 4A. This document serves as an industry-wide reference tool pertaining to natural gas quality and measurement provisions in contracts or tariffs. Most tariffs enforce specifications at the pipeline receipt point. Actual delivery ranges may be different depending on market area proximity relative to production, receipt points, and other common practices associated with pipeline aggregation of supplies.

This Draft Guidance Document is intended to supplement Report 4A information, with a specific focus on gas parameters particular to high-BTU landfill-derived renewable gas. In some cases, analytical criteria for potential constituents may not be included in industry tariffs. In these cases, independent evaluation of the compounds may be necessary. References such as manufacturer tolerance levels may be helpful if applied in the appropriate context.

Seven sources of high-BTU landfill-derived renewable gas were collected and analyzed as part of Task 2 of the project. The gas was sampled in triplicate, with two sites receiving two separate sampling visits, for a total of 27 high-BTU landfill-derived renewable gas samples. Four natural gas samples were also collected and analyzed. The range of analytical data obtained for both sample types is presented in this document as a comparison. Caution must be exercised in interpreting the natural gas data since four samples comprise only a limited data set and the samples were not taken in replicate.

The draft guidance document has been prepared based upon the information available through this study (compiled in Task 2 of the project). Task 2 results include the following:

- High-BTU landfill-derived renewable gas of high quality may be produced <u>within existing tariff ranges</u>.
- Heating value and Wobbe Number vary slightly from traditional natural gas.
- The constituents present in high-BTU landfill-derived renewable gas can vary between landfills and upgrading equipment.
- High-BTU landfill-derived renewable gas profiles may change with time but the constituent concentrations are much more stable than was seen in raw biogas collected in past projects.
- Some analytes may be present in high-BTU landfill-derived renewable gas in greater concentrations than in natural gas. (The specific constituents found in this study are nitrogen, dimethyl sulfide, propionaldehyde, crotonaldehyde, butyraldehyde, mercury, iron-oxidizing bacteria.)
- Some analytes not present in natural gas may be present in high-BTU landfill-derived renewable gas. (The specific constituents found in this study are hydrogen, CFC-12, chloroethane, formaldehyde, methyl ethyl ketone, valeraldehyde, p-tolualdehyde, caproaldehyde, D4 siloxane, lead, anaerobic bacteria, and spores)
- Biologicals are present in both high-BTU landfill-derived renewable gas and natural gas.

Neither this document, nor the Task 2 report,[3] comment on or endorse specific methods or designs of cleanup technology employed to produce high quality landfill-derived renewable gas. As recommended by project sponsors, three specific cleanup technologies were investigated: Physical Solvent, PSA (Pressure Swing Adsorption), and Gas Separation Membrane. The data herein came from state-of-art treatment systems. These conclusions may not be valid for all facilities.

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 high-BTU landfill-derived renewable gas 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.

Gas quality itself is the primary focus. The data collected is provided solely to illustrate components and parameters that could be considered during contract or tariff negotiations for the introduction of renewable gas. Values or numbers found in this report are not intended to take precedence over existing contract or tariff values. Individual tariffs may not include all the properties listed in the table and/or may include others not listed, e.g., interchangeability criteria, trace constituents, helium, specific hydrocarbon limits, and others. Readers are advised to consult with appropriate technical and engineering support personnel in an effort to make an informed decision regarding specific contract or tariff specification criteria for a specific market area. This should take into consideration the nature of historical supplies, end use applications within the market area, pipeline integrity, and environmental considerations, as well as the Federal Energy Regulatory Commission (FERC) Policy Statement.

> **NOTE:** *Readers are strongly advised to review applicable tariffs and consult with individual pipelines serving their market area for additional information regarding specific constituent or parameter limits as well as information regarding historical gas quality.*

### Interchangeability Considerations for Introduction of High-BTU Landfill-derived Renewable Gas to a Natural Gas Network

Interchangeability is defined (for combustion applications) in AGA Report 4A as, "the ability to substitute one gaseous fuel for another without materially reducing operational safety, efficiency, and performance, and without materially increasing air pollutants". The ability to substitute or supplement an existing gas supply is dependent on quantitative evaluation of the combustion impact of the proposed substitute gas using standard interchangeability evaluation methods such as those outlined in AGA Bulletin 36[6] or by Weaver[7], or by using simpler surrogate parameters. One surrogate parameter that is easy to calculate, and that is used world-wide, is the Wobbe Number. Another surrogate parameter, calculation of the higher (gross) heating value (HHV), while historically important, is not generally viewed as a sufficient assessment of interchangeability because it only examines heat content. The Wobbe Number takes both HHV and the relative density of the gas into consideration and accounts for both heat content and gas flow through a fixed orifice.

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 site-specific market area tariff provisions may be considered to address constituents not commonly reported in either natural gas or high-BTU landfill-derived renewable gas. This may also include constituents found in natural gas but not in high-BTU landfill-derived renewable gas such as higher chain hydrocarbons that add to the heating value of natural gas. Additional details regarding gas interchangeability can be found in the NGC+ White Paper on Natural Gas Interchangeability and Non-Combustion End Use[8] (NGC+ White Paper, see references).

Each system operator is advised to conduct an overall interchangeability assessment. This assessment should occur collaboratively and cooperatively with the renewable natural gas developer proposing to deliver high-BTU landfill-derived renewable gas by interconnection to the pipeline owned or operated by such system operator before the initiation of the design phase of the gas cleanup system and well prior to commencement of construction of such gas cleanup system. Such assessment could include:

- Assessment of historically delivered and expected future delivered supplies into a market area with respect to gas quality constituents and parameters that define interchangeability.
- Assessment of the projected volumes of renewable gas in relationship to the historically delivered supplies of natural gas in the market area.

- Assessment of the potential to ameliorate any interchangeability concerns that may exist by the planned blending with renewable gas of a higher density, higher heating value fuel, such as propane, or by other means.
- Understanding of the proposed landfill-derived renewable gas cleanup technology and maximum constituent concentrations that may be present in the proposed substitute gas.
- Modeling of the zone of influence of the proposed substitute gas and determine if the aggregated supply profile meets tariff and/or contract requirements.
- Assessment of any sensitive receptors within the zone of influence. These might be 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.

As noted in AGA Report 4A, caution needs to be exercised when using any suggested tariff value ranges, as local requirements may vary. 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. Specific tariff requirements for individual gas companies must be consulted for the purpose of constructing a suitable contract for any substitute gas delivery.

### *Unique Contract Considerations*

Some of the parameters and 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, suggestions described herein are made based upon best available information at the time of construction of the guidance document.

It is advised that gas companies, pipelines and high-BTU landfill-derived renewable gas suppliers consider these supplemental parameters for safe interchange. This guidance document will explain each specific parameter and will assist all parties in verifying that high-BTU landfill-derived renewable gas samples are collected, tested, and evaluated against the applicable tariff and that they meet minimum quality objectives.

Depending on the nature of supply aggregation and the ability of a pipeline to reasonably manage its system, a pipeline tariff may include Safe Harbor provisions for some parameters to provide suppliers with some degree of certainty about the acceptance of gas into the pipeline. Appropriate language about a pipeline's ability to manage receipts of renewable gas into its system balanced against the needs of market area deliveries is critical for the practical application of component or property limits.

The ranges of gas property specifications vary across the pipeline grid, and exceptions to specified levels at renewable gas receipt points may be considered on a case-by-case basis if the pipeline has determined that variations do not adversely impact its ability to safely transport gas and to meet customer requirements. However, regulatory authorities may require notifications, such as operational flow orders (OFOs) for short term excursions, and posting of these exceptions in accordance with current North American Energy Standards Board (NAESB) guidelines.

As the composition of gas supplies may vary from one receipt point to another, waivers and/or pairing agreements may be considered for renewable gas not meeting pipeline specifications. Some pipelines may have the flexibility to aggregate supplies and to benefit from consequential blending. This situation provides additional flexibility for landfill gas recovery developers working with the pipelines to optimize processing necessary to maximize available supplies into the pipeline and to satisfy customer requirements. This capability varies from pipeline to pipeline and within individual pipeline systems.

**NOTE:** ***Caution needs to be exercised when using tariff value ranges highlighted in the report to assess interchangeability***. *While the tariff value ranges may be representative of some deliveries that are in relatively close proximity to associated receipts into the pipeline from production areas, other delivery points further downstream may have historically experienced much narrower ranges of gas quality, and it cannot be assumed that gas at the extremes of the tariff value range have been delivered and acceptably utilized in these systems. In these cases, tariff values are not representative of historically delivered supplies or the Adjustment Gas for a region. Each party should review historical deliveries into their specific market area.*

## *Cleanup Technologies Examined*

There are many landfill gas upgrading technologies available for a developer to use. The exact choice of any specific processing technology is driven by many different factors. These include economic factors, system technical requirements, or the pipeline specification in effect for the natural gas pipeline that is anticipated would accept the high-BTU landfill-derived renewable gas. GTI and the project sponsors/participants worked together to determine which specific processing technologies to include in this study. GTI saw the selection process as a cooperative effort - the industry must define what systems merit testing, and then create access to obtain samples.

After careful consideration and input from the High-Btu Group at the Solid Waste Association of North America (SWANA), three gas cleanup technologies were selected. The three specific gas cleanup technologies chosen are:

- Physical Solvent
- PSA (pressure swing adsorption)
- Gas Separation Membrane

While the gas cleanup technologies are divided into the three categories based on their $CO_2$ removal technology, these systems utilize multiple unit operations designed to remove other components such as oxygen and water. These add-on units are located either upstream or downstream from the main cleanup system. The complete set of data is found in Appendix B and further discussed in the Task 2 report. The specific gas cleanup system is documented for each site sampled.

Specific tariffs for individual gas companies may not include all parameters listed below. Individual tariffs and particulars specific to the point of proposed gas injection must be considered when assessing suitability of a fuel such as high-BTU landfill-derived renewable gas for introduction to the natural gas pipeline network. The guidance provided herein encompasses parameters and language typical of natural gas tariffs as outlined in AGA Report 4A. The intent of this document is to assist all parties involved in determining which analytical parameters may influence the overall gas quality within a pipeline network.

## *Compositional Dependent and Other Physical Parameters*

Most distributed pipeline gas is not a pure compound but instead is a mixture of different hydrocarbon compounds along with inert gases, diluent gases, and other trace constituents. Inert and diluent gases are non-hydrocarbons and reduce the overall heating value of a fuel gas. Pipeline quality natural gas can vary widely depending on its geologic source or amount of processing. The actual composition of a fuel gas governs many of its physical parameters, such as its energy content and specific gravity. These parameters are important to consider when evaluating the potential for gas interchangeability.

Any compositional dependent or physical parameter must be calculated or determined using the same base conditions in order for comparisons to be consistent. Correction factors must be applied if measurements are made under different conditions. The North American Energy Standards Board (NAESB) recommends a standard base condition of 14.73 psia at 60°F, for dry gas measured in cubic feet, and 101.3 kPa at 15°C, for dry gas measured in cubic meters.

### Heating Value

***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. Another commonly seen heating value parameter is net heating value, or Lower Heating Value (LHV). The difference between HHV and LHV is that the water produced by combustion remains in the vapor state when determining the LHV. The energy gained by the condensation of the water vapor is not realized so the heating value is lower. Heating values are also often reported as wet or dry. Wet gas refers to gas that is completely saturated with water vapor. A wet gas has a lower heating value per volume than a dry gas because some of the gas volume is occupied by the water vapor, so the absolute amount of combustible gas is less. The NAESB recommends utilizing the HHV expressed on a dry basis. For the purposes of this document, the term “HHV” as used here will mean “dry-basis HHV”.

Custody transfer of natural gas is generally based on an energy per volume basis; one example is BTU/SCF. As a result, transportation of low BTU (British Thermal Unit) gas may reduce the economic efficiency of some pipelines. A local distribution company, metering gas by its energy content, may need to consider the influence of low BTU gas on its overall billing/accounting process. Both low and high BTU gas may have detrimental effects on end use equipment and may not be compatible with many systems.

***High-BTU Landfill-derived Renewable Gas Range Guidance***

AGA Report 4A reports ranges for dry basis HHV typically found in tariffs for natural gas are between a minimum of 900 to 1000 BTU/SCF and a maximum of 1075 to 1200 BTU/SCF. It should be noted that few companies use such a low minimum HHV tariff, a more typical lower HHV tariff is 950 BTU/SCF.

This more stringent limit reinforces the need to consider individual company tariffs and quality requirements for heating value specifications. It is a common practice to monitor natural gas BTU content at custody transfer points and/or city gates and high-BTU landfill-derived renewable gas should be treated similarly.

Based upon the results as part of this GTI program, tariff values can be achieved with proper conditioning or upgrading of landfill-derived biogas. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the calculated HHV ranged in from 929 to 1008 BTU/SCF, depending on which upgrade technology is used. Based on the project results, the high-BTU landfill-derived renewable gas can be up to 99 % by volume methane, corresponding to a dry HHV of over 1000 BTU/SCF, at 60°F and 14.73 psia.

Four natural gas samples were collected and tested for this project. The HHV ranged from 1009 to 1022 BTU/SCF.

***Representative Analytical Test for this Parameter***

Historically the HHV was directly determined using a combustion calorimetry technique (ASTM D1826, *Standard Test Method for Calorific (Heating) Value of Gases in Natural Gas Range by Continuous Recording Calorimeter*). This method has largely been replaced by gas chromatography (GC) whereby each individual major and minor constituent is directly measured and its contribution to the total heating value is calculated from its ideal gas value; these values are then adjusted by means of a calculated compressibility factor and summed.

Standard GC analysis techniques follow ASTM D1945 (*Standard Test Method for Analysis of Natural Gas by Gas Chromatography)*, ASTM D1946 *(Standard Practice for Analysis of Reformed Gas by Gas Chromatography)* ASTM D7164, *(Standard Practice for On-line/At-line Heating Value Determination of Gaseous Fuels by Gas Chromatography)*, or GPA 2261 *(Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography)*. 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). In the early days of GC gas analyses, hydrocarbons were speciated only out to pentane (C5) because the analysis was performed isothermally. The other hydrocarbons were determined and reported as a lump hexane+ fraction. Ratios were defined for the hexane (C6), heptanes (C7), and octane (C8) fractions and applied to the C6+ determination. Modern instrumentation has improved the analysis and speciation out to C8 is more common, eliminating the need for approximating the C6, C7, and C8 ratios.

The procedure to calculate the HHV and ideal gas values are found in ASTM 3588 *(Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels)*, GPA 2172 *(Calculation of Gross Heating Value, Relative Density, Compressibility and Theoretical Hydrocarbon Liquid Content for Natural Gas Mixtures for Custody Transfer)*, and GPA 2145 *(Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas Industry)*.

## Relative Density and Wobbe Number

***Parameter Overview***

The relative density of a gas is defined as the ratio of the mass density of the gas to the mass density of air (where the molecular weight of air is defined as 28.9625 grams per mole), both at a defined pressure and temperature. This property, along with the heating value, is used to determine the Wobbe Number, an interchangeability parameter that takes both HHV and the relative density of the gas into consideration and accounts for both heat content and gas flow through a fixed orifice. Noteworthy are the recommendations for interchangeability specifications given in the NGC+ White Paper, particularly the proposed acceptable variation of Wobbe Index of +/- 4% from historical values and the upper limit of 1400 BTU/SCF.

Differences in the relative density, and by extrapolation the Wobbe Number, generally come from the presence of other hydrocarbons or diluent and inert gases such as carbon dioxide or air (nitrogen plus oxygen). These gases are much denser than methane thus raising the relative density, and the inert gases have no heating value, thus lowering the HHV. The final impact would lower the Wobbe Number. Hydrogen, another potential gas present, would lower the relative density and raise the Wobbe Number.

### *High-BTU Landfill-Derived Renewable Gas Range Guidance*

Typically the relative density of a gas does not have tariff limits. The Wobbe Number is more often included in custody transfer contracts. AGA Report 4A reports ranges typically found in tariffs for delivered natural gas for dry basis Wobbe Number as between a minimum of 1279 to 1340 BTU/SCF and a maximum of 1380 to 1400 BTU/SCF. The 1400 BTU/SCF upper limit corresponds with the upper limit recommended by the NGC+ committee. It is a common practice to calculate the Wobbe Number of natural gas at custody transfer points and/or city gates and high-BTU landfill-derived renewable gas should be treated similarly.

Based upon the results as part of this GTI program, tariff values can be achieved with proper conditioning or upgrading of landfill-derived biogas. However, 19 of the tested gases had a Wobbe Number lower than the lowest minimum (1279 BTU/SCF). In the 27 high-BTU landfill-derived renewable gas samples collected for this project the Wobbe Number varied from 1200 to 1350 BTU/SCF depending on which upgrade technology is used. Generally, the lower Wobbe Number results appear to have nitrogen present.

Four natural gas samples were collected and tested for this project. The Wobbe Number ranged from 1322 to 1336 BTU/SCF.

### *Representative Analytical Test for this Parameter*

Historically the relative density was directly determined using several different techniques, a pressure balance, a displacement balance, and measurement of centrifugal force or kinetic energy (ASTM D1070, *Standard Test Methods for Relative Density of Gaseous Fuels*). These methods have largely been replaced by gas chromatography (GC) whereby each individual major and minor constituent is directly measured and its contribution to the relative density is calculated from its ideal gas value; these values are then adjusted by means of a calculated compressibility factor and summed.

Standard GC analysis techniques follow ASTM D1945, ASTM D1946 ASTM D7164, or GPA 2261 as previously described. The procedures to calculate the relative density and ideal gas values are found in ASTM 3588, GPA 2172, and GPA 2145.

The Wobbe Number is calculated by dividing the HHV by the square root of the relative density.

$$W = \frac{HHV}{\sqrt{RD}}$$

## Hydrocarbon Dewpoint Temperature

***Parameter Overview***

The hydrocarbon dew point temperature (HDP) is the temperature of the corresponding state condition at which the non-methane hydrocarbon components of natural gas begin to condense into the liquid phase. Ethane, propane, and other gases heavier (more carbon atoms) than methane can drop out of the vapor phase under certain pressures and temperatures. Typically, the greater the carbon number is, the greater the tendency for the phenomenon to occur. It is the heaviest weight components that first condense and define the HDP temperature of the gas. The hydrocarbon dew point temperature also changes in relation to pressure.

Gases containing heavier hydrocarbons have a higher hydrocarbon dew point temperature resulting in the possibility of a hydrocarbon fluid forming when the pipeline gas temperature is colder than the HDP. The HDP of natural gas is regulated to prevent or control the formation of condensate liquids in the pipeline. The impact on gas processing or end use operations can vary depending on where the condensation occurs.

The hydrocarbon dewpoint temperature can be measured directly at the specified operating pressure or calculated from a compositional measurement using one of the many equations of state. A calculated HDP is known as the cricondentherm hydrocarbon dewpoint (CHDP) and is taken from the highest temperature observed from the calculated retrograde phase envelope.

***High-BTU Landfill-Derived Renewable Gas Range Guidance***

AGA Report 4A reports that the maximum hydrocarbon dewpoint temperature values typically found in tariffs for delivered natural gas are between 0°F and 25°F at either a fixed and specified pressure, or at the operating pressure. The calculated CHDP typically varies from 15°F and 20°F. There is no minimum tariff. It is a common practice to calculate hydrocarbon dewpoint temperatures of natural at custody transfer points and/or city gates. High-BTU landfill-derived renewable gas is likely to meet hydrocarbon dewpoint specifications due to the absence of higher hydrocarbons. Consequently, measurement frequencies for this parameter may be lower than for natural gas.

Based upon the results as part of this GTI program, tariff values can be achieved. The absence of significant amounts of non-methane hydrocarbons renders the HDP or CHDP very low, typically less than -100°F.

***Representative Analytical Test for this Parameter***

The direct measurement of HDP temperature is by variations on the chilled mirror technique. One version of this instrument is used as a spot analyzer. Another version serves as an on-line automatic optical condensation dew point analyzer. The concept for both instruments is similar, the gas is cooled until a condensate forms on a mirror or other surface, and the temperature at which this happens is recorded as the HDP.

The indirect measurement calculates the CHDP from a compositional analysis by GC following ASTM D1945, ASTM D7164, 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). It is important when analyzing natural gas that an extended hydrocarbon analysis be performed, preferably out to at least C20 (eicosane), but minimally out to C8 (octane). One thing to note is that the heavier components will condense out first. Large measurement errors will occur if these components are not accurately taken into account. Grouping the C6+ hydrocarbon components can add a minimum of 3°F to 5°F to the calculated CHDP, depending on the hydrocarbon distribution. The CHDP is finally calculated using the compositional data and a process simulation program containing an equation-of-state (EOS) model.

### Temperature

***Parameter Overview***

Most pipeline tariffs specify a maximum gas temperature and many specify a minimum temperature. 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.

***High-BTU Landfill-derived Renewable Gas Range Guidance***

AGA Report 4A reports the temperature ranges typically found in tariffs for delivered natural gas are between a minimum of 20°F to 65°F and a maximum of 80°F to 140°F. It is a common practice to monitor the temperature of natural gas at custody transfer points and/or city gates and high-BTU landfill-derived renewable gas should be treated similarly.

While temperature was not measured for this project, because the gas is processed, tariff values for temperature can be achieved.

***Representative Analytical Test for this Parameter***

High-BTU landfill-derived renewable gas temperature may be continuously measured on-line using thermocouple sensors.

## *Compositional Parameters*

Natural gas, as well as renewable gas, is not simply fuel consisting of methane, nor is it homogenous in chemical and physical makeup. Natural gas is typically composed of methane and other light hydrocarbons such as ethane, propane, butane and pentane. It additionally contains other diluent and inert gases, which include carbon dioxide, nitrogen, oxygen and helium. The actual composition for a specific gas is complex and a function of many factors, including the resource supply characteristics and level of gas processing.

*Major component* profiling is the first priority in determining gas quality because many physical gas properties are dependent on the hydrocarbon and inert gas compositional distribution. *Trace components* are those with concentrations below 0.01 volume %.

The chief portion of trace constituents may consist of naturally occurring species such as paraffinic and aromatic hydrocarbons, a wide range of volatile and semi-volatile organic compounds, and sulfur compounds (natural odorants and those added to natural gas by law). Some naturally occurring constituents originate from the gas source. Biologicals, such as microbes and spores, have also been found.

### Water Content

***Parameter Overview***

The presence of water vapor can pose many problems particularly associated with corrosion. Usually the upgrading process will reduce the water content significantly. The presence of water is an issue because water, combined with $CO_2$ and $H_2S$ 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 ice-like mixtures of water and hydrocarbons formed at high pressures where high water vapor is present.

***High-BTU Landfill-Derived Renewable Gas Range Guidance***

AGA Report 4A reports ranges for maximum water vapor concentration typically found in tariffs for delivered natural gas as between 4 to 7 pounds of water in vapor phase per million cubic feet (MMSCF) of gas.  Gas should be delivered free of any liquid water.  It is a common practice to monitor natural gas water content at custody transfer points and/or city gates and high-BTU landfill-derived renewable gas should be treated similarly.

While water vapor content was not measured for this project, because the gas is processed, tariff values for water vapor content can be achieved.

***Representative Analytical Test for this Parameter***

Moisture content can be spot tested using the chilled mirror technique (ASTM D1142, *Standard Test Method for Water Vapor Content of Gaseous Fuels by Measurement of Dew-Point Temperature*).  On-line analysis uses an electronic moisture analyzer (ASTM D5454, *Standard Test Method for Water Vapor Content of Gaseous Fuels Using Electronic Moisture Analyzers*) containing sensors based on phosphorus pentoxide, aluminum oxide, or silicon.  New detection technology is becoming available that utilizes laser technology.

### Total Sulfur, Hydrogen Sulfide, Mercaptans and Other Sulfur Compounds

***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 the relative molecular weight of sulfur in the compound.  Specific sulfur-containing compounds can be either naturally occurring, or added by law to a fuel gas to serve as a warning in the case of a gas leak.

Hydrogen sulfide is found at various levels in both natural gas and landfill-derived renewable gas.  Its presence in renewable gas is due to its formation during the anaerobic microbial decomposition of sulfate and sulfur-containing organic matter; the primary sulfur compound found in raw biogas is hydrogen sulfide.  It can also be found in natural gas as a naturally occurring contaminant.  Hydrogen sulfide is colorless and smells like rotten eggs.

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, can be found in biogenic gases.  Higher molecular weight mercaptans, such as t-butyl mercaptan (TBM) are added as part of an odorant blend along with other mercaptans, dimethyl sulfide (DMS), or tetrahydrothiophene (THT).  Other sulfur compounds that can potentially be present include carbonyl sulfide, sulfur dioxide, and polysulfides, the latter due to sulfur species interactions in the pipeline.

The presence of $H_2S$ and other sulfur-containing compounds are regulated because of their potential corrosive and destructive nature on pipeline materials.  Sulfur can be corrosive with or without the presence of water.  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 $CO_2$ and $O_2$ (from the presence of air).  When present in sufficiently high enough concentrations (>1 ppmv), lower molecular weight mercaptans can degrade the quality of odorization and induce odor fade or odor masking.  Pipeline tariffs typically include a limit on hydrogen sulfide concentration and total sulfur, and many limit total mercaptans.

Sulfur compounds are reported in units of ppmv and grains per 100 SCF. The conversion to ppmv total sulfur is 1 grain sulfur per 100 SCF equals 17 ppmv sulfur (at standard conditions).

### *High-BTU Landfill-Derived Renewable Gas Range Guidance*

AGA Report 4A reports the maximum total sulfur concentration typically found in tariffs for delivered natural gas ranges from 0.5 to 20 grains per 100 SCF. This is equivalent to 8.5 to 340 ppmv as sulfur.

The maximum hydrogen sulfide concentration typically found in tariffs for delivered natural gas ranges from 0.25 to 1 grains per 100 SCF. Maximum mercaptan concentration ranges between 0.20 and 2.0 grains per 100 SCF. It is a common practice to monitor natural gas sulfur content for odorization and corrosion control purposes and high-BTU landfill-derived renewable gas should be treated similarly.

Based upon the results as part of this GTI program, typical reported tariff values for total sulfur, hydrogen sulfide and mercaptan content can be achieved. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the total sulfur varied from BDL to 0.3 grains sulfur per 100 SCF (BDL to 5.5 ppmv S) depending on which upgrade technology is used. No hydrogen sulfide or mercaptans were detected, the only sulfur compounds seen were carbonyl sulfide (3 out of 27 samples), sulfur dioxide (2 out of 27 samples), and dimethyl sulfide (9 out of 27 samples). The detectable concentration levels of the first two sulfur compounds were below 0.3 ppmv. The detectable concentration levels of dimethyl sulfide ranged from 0.1 to 5.5 ppmv.

Four natural gas samples were collected and tested for this project. The total sulfur ranged from BDL to 0.24 grains per 100 SCF. The gases contained sulfur dioxide, hydrogen sulfide, carbonyl sulfide, methyl mercaptan, isopropyl mercaptan, t-butyl mercaptan, and dimethyl sulfide. The latter four compounds are all added as part of an odorization program.

### *Representative Analytical Test for this Parameter*

An inerted gas sample collection cylinder is commonly used to collect a grab sample of gas that can be directly analyzed in the lab with no additional sample preparation. Sulfur compounds are reactive, so analysis should be performed as quickly as possible after collection, preferably within 24 hours.

Off-line sulfur species analysis is usually performed by gas chromatography following either ASTM D6228 *(Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection)*, or D5504 *(Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence)*, or GPA 2199 *(Determination of Specific Sulfur Compounds by Capillary Gas Chromatography and Sulfur Chemiluminescence Detection)*. The two methods use different techniques for detection of sulfur species. D6228 uses a flame photometric detector (FPD) or pulsed flame photometric detector (PFPD) and D5504 (or GPA 2199) uses a sulfur chemiluminescence detector (SCD).

Total sulfur analysis can be performed by ASTM D3246 *(Standard Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry)* using oxidative pyrolysis to convert the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion.. New ASTM techniques include GC coupled with atomic emission spectroscopy (D6968, *Standard Test Method for Simultaneous Measurement of Sulfur Compounds and Minor Hydrocarbons in Natural Gas and Gaseous Fuels by Gas Chromatography and Atomic Emission Detection*) and total sulfur by combustion followed by UV fluorescence detection (D7551, *Standard Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases and Natural Gas by Ultraviolet Fluorescence*).

Because the presence of an odorant in fuel gas is mandated by law (49 CFR Section 192.625), real-time or near-real time monitoring systems that measure sulfur compounds are very common in the fuel gas and gas transmission industries to supplement the human "sniff" test. On-line sulfur speciation analysis is usually performed by GC techniques. In addition to the detectors listed above, many of which are not practical for on-line analysis, detection using an electrochemical cell (D7493, *Standard Test Method for Online Measurement of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatograph and Electrochemical Detection*) is available.

On-line hydrogen sulfide analysis can be performed using lead acetate technology (ASTM D4084, *Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)*). The same technology can be adapted for total sulfur (D4468, *Standard Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry*).

Older techniques using combustion followed by titration are available (Wickbold method), but not commonly used since the advent of more automated techniques.

## Particulates (Dusts and Gums)

### *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 high-BTU landfill-derived renewable gas production, particulate matter may be carried along from the production process into the final high-BTU landfill-derived renewable gas product.

The amount and size of particulate matter in any fuel gas 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.

### *High-BTU Landfill-derived Renewable Gas Range Guidance*

AGA Report 4A reports a typical maximum solid particle size range typically found in tariffs for delivered natural gas to be between 3 and 15 microns. Some tariffs for natural gas state that the gas is to be "commercially free of dusts and gums", or "commercially free of objectionable matter". 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.

While particulates were not specifically measured for this project, typical tariff values for dust and gum particulate matter can be achieved through in-line filtration (1 micron filter). The recognized standard for removing microorganisms, called "sterile filtration" requires a 0.2 micron filter.

### *Representative Analytical Tests for this Parameter*

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 (*Determination of Particulate Matter Emissions From Stationary Sources*).

## Biologicals

***Parameter Overview***

Bacteria/Microbes

Microbial-influenced corrosion (MIC) can degrade the integrity, safety, and reliability of pipeline operations and is one of leading causes of pipeline failure in the oil and gas industry. Cost-effective MIC management requires the early detection of MIC problems, which can only be achieved by routine monitoring of the characteristics of pipeline systems.

Depending upon the starting biomass, or the originating geological formation, a variety of microbial populations may exist in the resulting gas stream, in both high-BTU landfill-derived renewable gas and natural gas, respectively. MIC corrosion is caused by acids produced by bacteria; it is this acid which induces pitting in metal pipes. MIC can be especially prevalent in gas lines in which moisture has collected, or in wet gas systems. Appendix A gives a brief overview of MIC.

Corrosion producing bacteria/microbes can be arranged into five basic groups:

- Acid-producing bacteria (APB)
  - Acetic-acid producing bacteria
  - Butyric-acid producing bacteria
- Iron-oxidizing bacteria (IOB)
  - Leptothrix and Sphaerotilus genus
  - Gallionella genus
- Sulfate-reducing bacteria (SRB)
- 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. 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 includes Leptothrix, Sphaerotilus, and Gallionella, which are the most common IOB related to corrosion.

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 (e.g., 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 both aerobes (require air to grow) and anaerobes (grow without air). Spores can be collected, enumerated, and identified.

As noted previously, the recognized standard for removing microorganisms, called “sterile filtration”, requires a 0.2 micron filter.

### *High-BTU Landfill-Derived Renewable Gas Range Guidance*

AGA Report 4A does not report any tariff ranges or maximum limits for biologicals in delivered gas. Ranges of tariff specifications in the area of “Trace Constituents, Contaminants and Objectionable Material” vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base. Introduction of biologicals into the gas system is to be avoided. Where the downstream pipeline environment is conducive to microbial induced corrosion, 0.2 micron filters can be installed for proper filtration.

Biologicals were examined as part of this project and levels in the 27 high-BTU landfill-derived renewable gas samples were found to be similar to those found in the natural gas samples collected as a comparator data set. In the 27 samples collected for this project the total bacteria count ranged from $5.13 x 10^5$ to $3.29 x 10^8$ per 100 SCF. Bacteria were found in all 27 samples. Some samples were higher than levels in the collected natural gas samples and some were lower. APB counts ranged from $8.99 x 10^3$ to $2.02 x 10^5$ per 100 SCF, in 24 of the 27 samples collected. These results are within to slightly lower than the range for the collected natural gas samples. IOB counts ranged from $1.27 x 10^4$ to $7.67 x 10^4$ per 100 SCF, in 15 of the 27 samples collected. These results are within the same range as in the collected natural gas samples. SRB counts ranged from $2.27 x 10^3$ to $2.52 x 10^4$ per 100 SCF, in two of the 27 samples collected. These results are within the same range as in the collected natural gas samples. Live bacteria were found in only four of the 27 samples tested. Only one sample had spores

Four natural gas samples were collected and tested for this project. The results ranged from $6.30 x 10^6$ to $6.39 x 10^7$ total bacteria per 100 SCF. Bacteria were found in all four samples. ABP counts ranged from $1.09 x 10^4$ to $5.09 x 10^5$ per 100 SCF, in all four samples. IOB counts ranged from $1.04 x 10^4$ to $4.98 x 10^4$ per 100 SCF, in all four samples. SRB counts ranged from $1.94 x 10^4$ to $2.76 x 10^4$ per 100 SCF, in two of the four samples collected. No live bacteria or spores were detected.

The sampling procedure for this parameter may kill biological materials due to desiccation from flowing gas, high pressure, or other system constraints. This is true for any gas stream. It should be noted that any bacteria found were live at one time.

### *Representative Analytical Tests for this Parameter*

For confirmatory biological collection and testing, 0.2 micron filters, encased in a stainless steel pressure filtration funnel, may be installed in-line after the biogas cleanup 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. This collection technique requires knowledge of the total gas sampled via a dry test meter (preferred) or rotameter.

The filter samples are tested for total bacteria and bacteria type (SRB, APB and IOB) using the quantitative polymerase chain reaction (qPCR) method. qPCR is a technique that detects and quantifies specific genes of target bacteria, which are essential for the metabolism of the corrosion causing bacteria in the samples. Bacteria can be either dead or alive, this technique measures both.

Live bacteria can be enumerated through traditional bacterial Most Probable Number (MPN) testing. In MPN testing, a 10-fold dilution series of filter suspension are inoculated, in triplicate, in a thioglycolate medium to quantify live bacteria and incubated at 37º 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.

Spore testing can be achieved by using the NASA standard assay NHB 5340.1D *(Nasa Standard Procedures For The Microbial Examination Of Space Hardware)*.

## Total Inert and Diluent Gases

***Parameter Overview – Total Diluents and Inerts***

Inert and diluent gases are non-hydrocarbons and reduce the overall heating value of a fuel gas. Inerts (nitrogen, argon, helium, etc.) are not chemically reactive with the surrounding environment. However, diluent gases may chemically react with the surrounding environment; the primary diluents in high-BTU landfill-derived renewable gas are carbon dioxide and oxygen. 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 have various impact to pipeline operations, gas facilities and end-use equipment. These are detailed in the following sections.

***Parameter Overview – Carbon Dioxide ($CO_2$)***

Carbon dioxide is considered a diluent and is an odorless, colorless gas. It 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 hydrogen sulfide and oxygen, thereby enhancing the corrosion of pipeline materials.

***Parameter Overview – Oxygen ($O_2$)***

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 high-BTU landfill-derived renewable gas product is desired. Small amounts of oxygen can support colonies of sulfate-reducing bacteria, especially in the presence of moisture.

***Parameter Overview – Nitrogen ($N_2$)***

Nitrogen is an inert gas that is colorless, odorless and non-corrosive. It is usually regulated because it affects the calorific value and relative density of the gas. At elevated concentrations, combustion operations may be impacted, possibly causing poor flame stability and producing a flame with yellow tipping and lifting. High concentrations of nitrogen also may affect compressibility of the gas.

***High-BTU Landfill-Derived Renewable Gas Range Guidance – Total Diluents and Inerts***

AGA Report 4A reports the maximum total of diluent plus inert gases typically found in tariffs for delivered natural gas ranges from 3 to 6 % by volume. It is a common practice to monitor natural gas for total diluents and inerts at custody transfer points and/or city gates (as part of the major constituent analysis to calculate BTU content), and high-BTU landfill-derived renewable gas should be treated similarly.

Based upon the results as part of this GTI program, typical tariff values for inert and diluents gases can be achieved. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the total diluent and inert content varied from 0.6 to 8 % by volume, depending on what upgrade technology is used. While the 8 % value was higher than the typical tariff value, only one site had data over the highest maximum tariff. The largest contributor is nitrogen.

Four natural gas samples were collected and tested for this project. The total diluents and inerts ranged from 1.7 to 2.3 % by volume.

### *High-BTU Landfill-Derived Renewable Gas Range Guidance – Carbon Dioxide*

AGA Report 4A reports the maximum carbon dioxide concentration typically found in tariffs for delivered natural gas ranges from 1 to 3 % by volume. As stated above, it is a common practice to monitor natural gas for carbon dioxide concentration at custody transfer points and/or city gates (as part of the major constituent analysis to calculate BTU content), and high-BTU landfill-derived renewable gas should be treated similarly.

Based upon the results as part of this GTI program, typical tariff values for carbon dioxide can be achieved. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the carbon dioxide content varied from BDL to 2.2 % by volume, depending on what upgrade technology is used.

Four natural gas samples were collected and tested for this project. Carbon dioxide content ranged from 1.0 to 1.7 % by volume.

### *High-BTU Landfill-Derived Renewable Gas Range Guidance – Oxygen*

AGA Report 4A reports the maximum oxygen concentration typically found in tariffs for delivered natural gas ranges from 0.001 to 1 % by volume. It should be noted that the majority of respondents to the AGA survey reported maximum tariffs from 0.1 to 0.2 % by volume. As stated above, it is a common practice to monitor natural gas for oxygen concentration at custody transfer points and/or city gates (as part of the major constituent analysis to calculate BTU content), and high-BTU landfill-derived renewable gas should be treated similarly.

Based upon the results as part of this GTI program, typical tariff values for oxygen can be achieved. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the oxygen content varied from 0.1 to 0.5 % by volume, depending on what upgrade technology is used.

Four natural gas samples were collected and tested for this project. The oxygen content ranged from BDL to 0.1 % by volume.

### *High-BTU Landfill-Derived Renewable Gas Range Guidance – Nitrogen*

AGA Report 4A reports the maximum nitrogen concentration typically found in tariffs for delivered natural gas ranges from 1 to 4 % by volume. As stated above, it is a common practice to monitor natural gas for nitrogen concentration at custody transfer points and/or city gates (as part of the major constituent analysis to calculate BTU content), and high-BTU landfill-derived renewable gas should be treated similarly.

Based upon the results as part of this GTI program, typical tariff values for nitrogen can be achieved. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the nitrogen content varied from 0.5 to 6 % by volume, depending on what upgrade technology is used. As explained in the total inerts plus diluents section above, while the 6 % value was higher than the typical tariff value, only one site had data over the highest maximum tariff.

Four natural gas samples were collected and tested for this project. The nitrogen content ranged from 0.4 to 1.2 % by volume.

***Representative Analytical Test for this Parameter (Carbon Dioxide, Oxygen and Nitrogen)***

Carbon dioxide, oxygen and nitrogen can be determined by gas chromatographic analysis with a thermal conductivity detector following ASTM D1945, ASTM D7164, or GPA 2261. Online sensors for oxygen are commonly used (ASTM D7607, *Standard Test Method for Analysis of Oxygen in Gaseous Fuels (Electrochemical Sensor Method)*), and may be available for carbon dioxide, but nitrogen cannot be routinely detected in the same manner.

### Hydrogen

***Parameter Overview***

Hydrogen is not a typical constituent of natural gas, but some raw natural gas wells or storage fields may contain hydrogen; it may also be present in high-BTU landfill-derived renewable gas. It is not strictly a diluent gas because it can impart some calorific content to the fuel gas. The impact from high levels of hydrogen on pipeline materials of construction can depend on a multitude of variables. Cases where the presence of hydrogen is a concern should be addressed on an individual basis by determining upper and lower boundary conditions and checking the literature for empirical examples and/or theoretical predictions.

***High-BTU Landfill-Derived Renewable Gas Range Guidance***

AGA Report 4A reports the maximum concentration of hydrogen typically found in tariffs for delivered natural gas ranges from 400 to 1000 ppmv (0.04 to 0.1 % by volume), but most companies (209 out of 224 respondents) do not specify a tariff. Hydrogen is a parameter that is not routinely analyzed.

Based upon the results as part of this GTI program, low concentration values for hydrogen can be achieved. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the hydrogen content varied from BDL to 0.9 % by volume, depending on the landfill site and upgrade technology combination. Hydrogen was found in 21 samples.

Four natural gas samples were collected and tested for this project. These samples did not exhibit any hydrogen content.

***Representative Analytical Test for this Parameter***

Hydrogen can be determined on-line using a solid state sensor. Palladium is commonly used because it selectively absorbs hydrogen gas and forms palladium hydride. In the laboratory hydrogen can be analyzed from a field sample using gas chromatography with a thermal conductivity detector following ASTM D1945. Some field on-line GCs do not have the capability to detect hydrogen.

## *Other Trace Constituents Not Specifically Found in Typical Tariffs*

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 trace constituents could be introduced into the resulting high-BTU landfill-derived renewable gas. Microbes are able to degrade or transform a wide variety of organic and inorganic compounds by way of enzymatic action or incomplete digestion. Some compounds are simply volatilized through agitation in the bioreactors (digesters) or under landfill gas extraction. Although only low concentrations of constituents not commonly found in typically tariffs were found in the samples of high BTU landfill-derived renewable natural gas analyzed for this project, higher concentrations of certain trace constituents, were they to occur, may be problematic to the pipeline network (inducing/exacerbating corrosion, contributing to odorant fade, accumulating on pipeline walls, etc.), and end-use equipment (burner tip accumulation, equipment/product compromise, feedstock applications etc.).

## Volatile Metals

***Parameter Overview***

Volatile metals such as mercury and arsenic may be present in any source of fuel gas. In renewable gas generation they may be released into the raw gas through the degradation of concentrated plant materials and metal-containing products. Mercury in natural gas can be from both natural and artificial sources. It is believed to permeate from the carboniferous formations from which the gas itself originates. Artificial sources are likely mercury-containing devices that measure pressure and gas flow through the pipeline. It is generally supposed that any arsenic in natural gas comes from the geological gas formations.

The primary impact from the presence of mercury in the gas stream is potential corrosion of aluminum metal and alloys used to construct gas processing equipment. This is particularly problematic because mercury may concentrate in cryogenic liquids and other processing fluids. The primary impact from the presence of arsenic in the gas stream is potential formation of particulates of alkyl arsine sulfides at pressure reduction points along the gas network. The presence of arsenic compounds in the gas phase can lead to poisoning of palladium and platinum catalysts used in gas processing operations. For both parameters there are potential health hazards associated with pipeline workers performing odorant sniff tests and end use applications.

***High-BTU Landfill-Derived Renewable Gas Range Guidance***

AGA Report 4A does not report any tariff ranges or maximum limits for volatile metals in delivered gas. Ranges of tariff specifications in the area of "Trace Constituents, Contaminants and Objectionable Material" vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base.

Based upon the results as part of this GTI program, low concentration values for volatile metals can be achieved. In 25 of the 27 high-BTU landfill-derived renewable gas samples collected for this project the mercury content varied from BDL to 0.05 $\mu g/m^3$. Mercury was found in six samples ranging from 0.03 to 0.05 $\mu g/m^3$. Two samples were not analyzed for mercury because the collection tube was compromised or broken. No arsenic was found. Small amounts of other volatile metals were seen but only in three samples out of twenty-seven. Copper and zinc compounds were also detected but these were found in the field blanks also so their presence in collected samples is not statistically significant.

Four natural gas samples were collected and tested for this project. Mercury content ranged from BDL to 0.01 $\mu g/m^3$. No other elements at reportable levels were found. Copper and zinc compounds were also detected but these were found in the field blanks also so their presence in collected samples is not statistically significant.

***Representative Analytical Test for this Parameter***

Sampling for arsenic and other 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 (inductively coupled plasma atomic emission spectroscopy, either directly or by mass spectroscopy), or by AAS (atomic absorption spectroscopy either directly or by graphite furnace excitation). The sparger technique is similar to EPA Method 29 *(Determination of Metals Emissions from Stationary Sources)* for stack gas sampling.

Routine analysis for mercury can be done following ASTM D5954 *(Standard Test Method for Mercury Sampling and Measurement in Natural Gas by Atomic Absorption Spectroscopy)* or D6350 *(Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy)*. These methods utilize on-site collection on gold-coated silica sorbent tubes followed by lab analysis by atomic absorption or atomic fluorescence spectroscopy. On-line mercury analyzers utilizing both techniques are available for continuous monitoring.

Both the sparger technique and the gilded silica sorbent collection technique require knowledge of the total gas sampled via a dry test meter (preferred) or rotameter. Sampling for volatile metals should be performed at the point of gas sampling. Accurate analysis cannot be performed through collection of the high-BTU landfill-derived renewable gas in a cylinder and shipment to the laboratory for further analysis.

## Ammonia

***Parameter Overview***

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 a 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 may possibly degrade the quality of odorization and induce odor fade or odor masking.

***High-BTU Landfill-Derived Renewable Gas Range Guidance***

AGA Report 4A does not report any tariff ranges or maximum limits for ammonia in delivered gas. Ranges of tariff specifications in the area of “Trace Constituents, Contaminants and Objectionable Material” vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base.

Based upon the results as part of this GTI program, low concentration values for ammonia can be achieved. No ammonia was found in any of the 27 high-BTU landfill-derived renewable gas samples collected for this project.

Four natural gas samples were collected and tested for this project. None of the samples exhibited any ammonia.

***Representative Analytical Test for this Parameter***

Ammonia can be determined on-line or in the laboratory from a field sample using a gas chromatograph coupled with a nitrogen chemiluminescence detector. Sparger sampling following EPA Conditional Method 27 (*Procedure for Collection and Analysis of Ammonia in Stationary Sources*) can also be performed with off-site analysis of ammonia by various spectrophotometric or titration techniques. The sparger technique requires knowledge of the total gas sampled via a dry test meter (preferred) or rotameter.

## Siloxanes

***Parameter Overview***

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 silicon in waste streams has increased. As the silicon-containing waste stream is anaerobically digested, 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.

***High-BTU Landfill-derived Renewable Gas Range Guidance***

AGA Report 4A does not report any tariff ranges or maximum limits for siloxanes in delivered gas. Ranges of tariff specifications in the area of "Trace Constituents, Contaminants and Objectionable Material" vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base.

Manufacturers of energy generating equipment have set their own recommended maximum siloxane limits for their equipment, these range from 0.03 to 28 $mg/m^3$ as the actual siloxane compound. Considered as D4 (octamethylcyclotetrasiloxane), the only siloxane found in high-BTU landfill-derived renewable gas on this project, the range is from 0.01 to 11 mg $Si/m^3$. The limits vary considerably from manufacturer to manufacturer.

Based upon the results as part of this GTI program, low concentration values for siloxanes can be achieved. In the 27 high-BTU landfill-derived renewable gas samples collected for this project the siloxane content varied from BDL to 0.4 mg $Si/m^3$. Most gas streams sampled were BDL (22 samples out of 27). The only siloxane compound found was D4 (octamethylcyclotetrasiloxane).

Four natural gas samples were collected and tested for this project. None of the samples exhibited any siloxanes.

***Representative Analytical Test for this Parameter***

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 coupled with an atomic emission detector (GC-AED). The AED 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. The sparger technique requires knowledge of the total gas sampled via a dry test meter (preferred) or rotameter. Sample collection is performed in the field with the final analysis by gas chromatography with (typically) a mass spectral detector (GC-MS) in the laboratory.

## Higher Organics/Chlorinated Compounds (PCBs)

***Parameter Overview***

PCBs are synthetic chlorinated chemicals that were produced for approximately 50 years between the 1920s and the 1970s. In 1976 Congress passed the Toxic Substances Control Act (TSCA) which banned their use. The general chemical formula for a PCB is $C_{12}H_{10-n}Cl_n$ where n varies from one to ten. There are 209 distinct compounds, commonly referred to as congeners, defined by the number and location of the chlorine atoms on the parent molecule. Polychlorinated biphenyls (PCBs) are addressed under the category of *Trace Constituents and Objectionable Matter*. Liquid condensates found in natural gas pipelines and pipeline surface wipe samples are routinely tested for PCBs.

***High-BTU Landfill-derived Renewable Gas Range Guidance***

AGA Report 4A does not report any tariff ranges or maximum limits for PCBs in delivered gas. Ranges of tariff specifications in the area of "Trace Constituents, Contaminants and Objectionable Material" vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base.

PCBs have not been detected in any raw or processed landfill gas samples at concentrations greater than detection limits (sub-ppb level), based on previous work. The current project did not sample for PCBs. This absence is expected since the typical vapor pressure of PCB congeners is around $10^{-5}$ torr at ambient temperature. A completely saturated gas would have only ppb levels present. PCBs are no longer in use, although they are very stable and linger in the environment. There is some concern about the presence of PCBs in natural gas condensates (liquids) present at low points in the distribution system.

***Representative Analytical Test for this Parameter***

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. Samples should be collected for four hours at a rate of 2L/min. The sorbent technique requires knowledge of the total gas sampled via a dry test meter (preferred) or rotameter. This XAD sorbent tube sampling method is similar to NIOSH Method 5503 *(Polychlorobiphenyls)*. The samples should be analyzed using EPA Method 8082, *Polychlorinated Biphenyls (PCBs) by Gas Chromatography*.

### Non-halogenated Volatile and Semi-Volatile Compounds (VOCs and SVOCs)

***Parameter Overview***

Biogas produced from landfill biomass sources 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 volatile or semi-volatile organic compounds (VOCs and SVOCs). These are typically compounds containing carbon, hydrogen, and sometimes oxygen. These can be present directly in the landfill waste stream, or formed biogenically. Under the anaerobic conditions found in a landfill, complex organic compounds from the initial waste stream can be degraded by microbial action to volatile organic compounds before complete conversion to methane and carbon dioxide. Because this reaction does not usually go to completion it results in a buildup of volatile or semi-volatile organic compounds in the landfill and ultimate volatilization to the gas phase.

Many non-halogenated VOCs and SVOCs are present in natural gas as well, originating from the geological basin from which the gas was extracted. Non-halogenated VOCs and SVOCs can be a concern due to potential health hazards associated with pipeline workers performing odorant sniff tests, and end use applications.

Volatile halogenated compounds (containing chlorine, fluorine, and bromine), and aldehydes and ketones may also be present and are discussed as separate topics.

***High-BTU Landfill-derived Renewable Gas Range Guidance***

AGA Report 4A does not report any tariff ranges or maximum limits for non-halogenated volatile or semi-volatile organic compounds in delivered gas. Ranges of tariff specifications in the area of “Trace Constituents, Contaminants and Objectionable Material” vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base.

Based upon the results as part of this GTI program, low concentration values for non-halogenated volatile or semi-volatile organic compounds can be achieved. Toluene (three out of twenty-seven) and xylene (two out of twenty-seven) were found in a few samples of high-BTU landfill-derived renewable gas collected for this project at the single digit ppmv level, but most of the samples were at BDL levels. No benzene was detected. Other volatile organics detected were some cycloalkanes (five out of twenty-seven), non-specifically identified C3 benzenes (three out of twenty-seven), and some C6+ hydrocarbons (nineteen out of twenty-seven), all at or very near the detection limit. Phthalate compounds were also detected at ppbv levels but these were found in the field blanks also so their presence in collected samples is not statistically significant. The phthalates are likely trace contaminants in the sorbent tube outer packaging.

Some compounds were found in the four natural gas tested for this program, specifically 1,3-butadiene, acrylonitrile, benzene, toluene, and xylene. Concentration levels ranged from single digit ppmv up to 22 ppmv. Benzene and toluene were in general the compounds with the highest concentration, ranging from 13 to 22 ppmv and 8 to 16 ppmv, respectively. The other compounds were single digit ppmv. Three samples also had single digit ppbv levels of two methylnaphthalene isomers. Phthalate compounds were detected at ppbv levels but these were found in the field blanks also so their presence in collected samples is not statistically significant.

#### *Representative Analytical Test for this Parameter*

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. Samples should be collected for four hours at a rate of 2 L/min. The sorbent technique requires knowledge of the total gas sampled via a dry test meter (preferred) or rotameter. This XAD sorbent tube sampling method is similar to NIOSH Method 5515, *Polynuclear Aromatic Hydrocarbons by GC*. Final analysis is by GC mass spectrometry. 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. Detection limits are in the ppmv range.

### Halocarbons

#### *Parameter Overview*

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. One halocarbon example common in landfill-derived gases are the various forms of Freon. These halocarbons are very stable and do not typically undergo any degradation reaction.

If not directly present in the refuse found in the landfill, the pathway of formation is similar to that seen with the VOC and SVOC parameter. Under the anaerobic conditions found in a landfill, complex organic compounds from the initial waste stream can be degraded by microbial action to volatile halocarbons before complete conversion to methane and carbon dioxide. Because this reaction does not usually go to completion it results in a buildup of halocarbons in the landfill and ultimate volatilization to the gas phase.

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.

#### *High-BTU Landfill-Derived Renewable Gas Range Guidance*

AGA Report 4A does not report any tariff ranges or maximum limits for halocarbons in delivered gas. Ranges of tariff specifications in the area of "Trace Constituents, Contaminants and Objectionable Material" vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base.

Based upon the results as part of this GTI program, low concentration values for halocarbons can be achieved. Dichlorodifluoromethane (CFC-12 or Freon-12) and chloroethane were found in a few samples of the 27 high-BTU landfill-derived renewable gases collected for this project at the single digit ppmv level, but most of the samples were at BDL levels. No vinyl chloride (chloroethene) was detected in any samples.

No halocarbons were found in the four natural gas tested for this program.

***Representative Analytical Test for this Parameter***

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. Other sampling methods use solid sorbents to preconcentrate the gas sample and offer lower detection limits, but caution must be made to not lose the very volatile species of interest. The sorbent technique requires knowledge of the total gas sampled via a dry test meter (preferred) or rotameter.

Final analysis for halocarbons is by gas chromatography using an electron capture detector (ECD) or an electrolytic conductivity detector (ELCD). Both the GC-ECD and GC-ELCD techniques are capable of detecting halogen-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.

## Aldehydes and Ketones

***Parameter Overview***

Aldehydes and ketones are organic compounds that contain hydrogen, carbon and oxygen atoms. This chemical class is generally associated with odor. Aldehydes and ketones can be found in landfill waste streams such as building materials such as OSB (oriented strand board), MDF (medium-density fiberboard), carpet and linoleum/vinyl flooring, other pressed wood products, hardwood and plywood paneling, upholstery fabrics, latex-backed fabrics, fiberglass, urea formaldehyde foam insulation.

Aldehydes and ketones can also be formed through anaerobic degradation of synthetic polymers, adhesives, and other waste streams. Under the anaerobic conditions found in a landfill, complex organic compounds from the initial waste stream can be degraded by microbial action to volatile aldehydes and ketones before complete conversion to methane and carbon dioxide. Because this reaction does not usually go to completion, it results in a buildup of aldehydes and ketones in the landfill and ultimate volatilization into the gas phase.

Aldehydes and ketones present in the gas stream can cause operational problems for gas processing and end use applications. Their presence may possibly degrade the quality of odorization and induce odor fade or odor masking.

***High-BTU Landfill-Derived Renewable Gas Range Guidance***

AGA Report 4A does not report any tariff ranges or maximum limits for aldehydes and ketones in delivered gas. Ranges of tariff specifications in the area of “Trace Constituents, Contaminants and Objectionable Material” vary throughout the industry; individual companies will need to consider specific requirements for their particular system and customer base.

Based upon the results as part of this GTI program, low concentration values for aldehydes and ketones can be achieved. Formaldehyde, acetaldehyde, acetone, and 2-butanone were found in many of the samples of high-BTU landfill-derived renewable gas collected for this project. Propionaldehyde, crotonaldehyde, butyraldehyde, valeraldehyde, p-tolualdehyde, and caproaldehyde were found in only a select few samples. However, all levels were sub-ppm.

Four natural gas samples were collected and tested for this project. Some compounds were found in the natural gas samples, specifically acetaldehyde, acetone, butyraldehyde in the four samples tested. Propionaldehyde and methacrolein were found in one sample. Crotonaldehyde was found in two samples. All levels were sub-ppm.

***Representative Analytical Test for this Parameter***

Sampling for aldehyde and ketone compounds can be performed using DNPH-impregnated sorbent tubes. The sample should be collected using two sorbent tubes attached in series. Samples should be collected for four hours at a rate of 1 L/min. The sorbent technique requires knowledge of the total gas sampled via a dry test meter (preferred) or rotameter. This DNPH sorbent tube sampling method is similar to EPA Method TO-11 *(Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC))*. Final analysis can be by GC mass spectrometry or HPLC.

### 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, and other considerations, concentrations of additional organic/inorganic or biological constituents may be necessary.

## Parameters for Performance Considerations

Prior to introduction to the natural gas pipeline network, the parties involved should consider performance testing of the high-BTU landfill-derived renewable gas. Such testing would provide assurance that the quality and production of the high-BTU landfill-derived renewable gas is consistent. These considerations 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.
Table 2 outlines some parameters for consideration. It is aimed at demonstrating that high-BTU landfill-derived renewable gas from a discrete system, given a discrete biomass input and gas cleanup technology, can consistently achieve required value ranges for specific compounds in the product. Although not typically performed, certain testing may be specified by a system operator and/or a producer of natural gas or renewable gas. It would be dependent on the analysis and risk assessment by all parties to address those operating conditions peculiar to any specific pipeline system. Each individual combination of producer and pipeline operator should evaluate the appropriateness of a test program for their purposes; it is not prescriptive.

It is a common practice for the natural gas industry to measure various parameters at custody transfer points, city gates, or odorization stations. The primary purpose is because gas is sold on an energy basis, not a volume basis and the data is needed to calculate the heating value of the gas. Sulfur content is monitored for odorization control. Both sulfur and water are tracked for corrosion control purposes. Temperature is measured so that deviations from the base temperature condition are documented and correction of the metered volume can be made. High-BTU landfill-derived renewable gas should be treated similarly.

Table 2. Parameters for Performance Consideration and their Testing Frequency

| **Common Tariff Parameters** | **Typical Frequency for High-BTU Landfill-Derived Renewable Gas** | **Typical Frequency for Natural Gas** |
|---|---|---|
| Heating Value | Continuous real-time or near-real time monitoring | Continuous real-time or near-real time monitoring |
| Temperature | Continuously measured on-line | Continuously measured on-line |
| Water Content | Continuous real-time or near-real time monitoring | Continuous real-time or near-real time monitoring |
| Sulfur, including Hydrogen Sulfide | Continuous real-time or near-real time monitoring | Continuous real-time or near-real time monitoring |
| Carbon dioxide | Continuous real-time or near-real time monitoring | Continuous real-time or near-real time monitoring |
| Nitrogen | Continuous real-time or near-real time monitoring | Continuous real-time or near-real time monitoring |
| Oxygen | Continuous real-time or near-real time monitoring | Continuous real-time or near-real time monitoring |
| **Other Parameters** | **Typical Frequency for High-BTU Landfill-Derived Renewable Gas** | **Typical Frequency for Natural Gas** |
| Hydrogen | Not typically tested[1] | Not typically tested[1] |
| Biologicals | Not typically tested[1]<br>Levels found in this project are comparable to natural gas | Not typically tested[1] |
| Mercury and/or other Metals | Not typically tested[1]<br>Levels found in this project are comparable to natural gas | Not typically tested[1]<br>Levels found in this project are at the one one-hundredths μg/m$^3$ range |
| Siloxanes | Not typically tested[1]<br>Levels found in this project are at the sub mg Si/m$^3$ range | Not typically tested or found in natural gas[1] |
| Semi-volatile and Volatile Compounds | Not typically tested[1]<br>Levels found in this project are lower than in natural gas | Not typically tested[1]<br>Levels found in this project are at the double digit ppmv range |
| Halocarbons | Not typically tested[1]<br>Levels found in this project are at the single digit ppmv range | Not typically tested or found in natural gas[1] |
| Aldehydes and Ketones | Not typically tested[1]<br>Levels found in this project are comparable to natural gas | Not typically tested[1]<br>Levels found in this project are at the sub ppmv range |

[1] The decision by the parties to include as a tariff condition with performance testing at a specified frequency or time (e.g., only immediately prior to commercial sale, at specified intervals or continuously in real time or near real time) for any of the constituents not typically tested for either high BTU landfill-derived renewable gas or natural gas will depend on site-specific analysis of the landfill gas to be

converted to high BTU landfill-derived renewable gas and to circumstances and policies of the natural gas pipeline proposed for interconnection to receive the high BTU landfill-derived renewable gas.

## Terminology and Definitions

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

**ASTM –** American Society for Testing and Materials

**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 domestic wastes, 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 those constituents which impact gas quality. Using effective biogas cleanup (removal of gases which effect overall gas quality), biomethane can be up to 99% 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.

**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.

**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. Digesters are common to the wastewater treatment industry as well as in farming operations for manure management. 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.

**Grab sample –** A single sample taken at a specific time or over a short period of time.

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

**GPA –** Gas Processors Association

**Halocarbons –** Organic compounds containing the elements fluorine (F), chlorine (Cl), bromine (Br), and iodine (I), 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.

**Inerted Gas Sample Collection Cylinder –** Sample collection cylinders containing and inert coating or otherwise passivated so that the cylinder exhibits very low reactivity to labile compounds such as sulfur odorants or $H_2S$.

**Labile Compounds –** A chemical compound that can readily or continually undergoing chemical, physical, or biological change or breakdown.

**Volatile Metals –** Volatile 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.

**Landfill Gas –** Gas which is emitted from the breakdown of materials in a landfill. This gas is considered "raw" and requires upgrade for introduction to the pipeline network.

**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.

**Quantitative Polymerase Chain Reaction (qPCR) Method –** qPCR is a technique that detects and quantifies specific genes of target bacteria, which are essential for the metabolism of the corrosion causing bacteria in the samples. Bacteria can be either dead or alive.

**Siloxane -** Any chemical compound composed of units of the form $R_2SiO_2$, 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 soaps. When combusted, the siloxane molecules are reduced to silica dust; this is extremely abrasive and damaging to internal engine components. The combustion process can cause a build up around burner tips and on the tubes of heat exchangers. Silica dust may also pose health risks to humans and other receptors.

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## Appendix A – Brief Introduction to MIC

Microbial-induced corrosion (MIC) is one type of metallic pipe failure in the natural gas industry. This corrosion is caused by bacteria produced acids which induce pitting in the pipes. It can be 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. This test, qPCR (Quantitative Polymerase Chain Reaction), was developed to be specific to MIC testing and identification.

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.

## Appendix B – Landfill and Natural Gas Data

The following pages tabulate the data used to construct the Draft Guidance Document. The Task 2 report presents the sampling rationale, analytical information, and statistical analysis of the high-BTU landfill-derived renewable gas data.