PG&E GAS R&D AND INNOVATION

WHITEPAPER

Biogas Upgrading

10/19/2018

Together, Building
a Better California

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Summary: Biogas and Syngas Upgrading

Definition: Upgrading technologies are those that use biogas or syngas as an input and, through a series of chemical or physical processes which separate, scrub/ absorb or adsorb contaminants in the raw gas, purify that gas into a gas with more methane per unit volume that also meets gas utility pipeline standards.

Figure 1 Biomethane Illustration

Generally, this process involves stripping the biogas of various *constituents of concern* (contaminant gases or particulates) that are present in biogas or syngas that pose hazards to the natural gas pipeline system, or to the health of end-users of that gas. In some cases, it also involves changing the composition of the gas to hit desired standards unrelated to safety (such as increasing the heating value that has repercussions for utility billing). Raw biogas from anaerobic digestion, for instance, is roughly 50-70% methane, 25-45% CO_2 and 5-15% of trace elements of water (H_2O), oxygen (O_2), nitrogen (N_2), ammonia, hydrogen sulfide (H_2S) among other compounds (U.S. EPA, 2012). Some of these must be removed for their corrosive effect on the pipeline (like water, H_2S and CO_2), their depressant effect on heating value (like N_2), or because they are poisonous to humans (like H_2S) or may degrade performance of appliance and engines (Like siloxanes). Taken together, the upgraded gas is often referred to as *Biomethane* to distinguish it from raw biogas.

In some cases, such as syngas produced from gasification or pyrolysis, the original synthetic gas has a *very* low composition of methane, sometimes only between 5-15% of the gas mixture (NETL, 2018). Syngas is comprised primarily of carbon monoxide (CO) and hydrogen (H_2) and if these elements of syngas were disposed of to select exclusively for methane, these thermal conversions would be so inefficient as to be uneconomical. Instead, after cleaning takes place to eliminate, tar, sulfur and CO_2. Cleaning also includes a water gas shift to bring the right stoichiometric ratio between H_2 and CO. The resulting gas goes through a process of *methanation*, where the CO and H_2 are combined to form methane (CH_4). The biomethane is then dried before injection in pipelines.

WHY EVEN BOTHER UPGRADING BIOGAS?

Raw biogas and syngas is burned to generate electricity in some areas of California and across the world today. Why would anyone go through the trouble of purifying and upgrading biogas to biomethane?

The Positive Case for Injecting Biomethane into the Gas System:

> *Clean transportation fuel credits combine to offer an incentive of $33/MMBTU of biomethane if injected into PG&E's gas pipeline – an astronomical amount that makes even early adopter systems profitable.*

While raw biogas can be burned for electricity, it cannot be injected into the gas pipelines because of stringent standards needed to assure that it does not impede the integrity of the system and is safe for customers. Injecting gas into the gas pipeline can often be a much more lucrative source of recurring revenue than electricity generation due to substantial incentives for producing renewable gas for transportation uses. These are incentivized through Renewable Identification Number (RIN) credits from a federal program called the Renewable Fuel Standard (RFS) run by the US EPA, and through a credit from the California Air Resources Board's Low Carbon Fuel Standard (LCFS) program. Combined, both credits can offer a subsidy of up to $33/MMBTU[1] of biomethane for use in the transportation sector – an astronomical sum. This is more than enough to make the economics of biomethane projects work out even in the earliest stages of the industry's development. (United States Environmental Protection Agency, 2016)

Additionally, the barriers to leveraging biogas-to-electricity at scale are mounting. While using biogas for local electricity generation can be economical, the electric grid in California is increasingly being dominated by renewable electricity sources such as solar and wind. These generation sources are not only 100% GHG free but also pollution free, and *very* cheap (as low as $0.04 to $0.10 per kWh (Dudley, 2018)). At the same time, they are incredibly inflexible resources with a challenging supply profile that utilities are increasingly working to accommodate. (Environmental Protection Agency, 2018)

[1] Sources: (California Air Resources Board, 2018), (California Air Resources Board, 2018), (Sheehy, September)

While biogas is GHG-free in carbon accounting terms, burning raw biogas still does generate CO_2 emissions, as well as particulate emissions like NOx and SOx. Biogas projects today are only marginally profitable, and so most biogas facilities are built close to where their biomass supply source is located. That means the vast majority of projects are located in California's Central Valley which has the vast majority of agricultural and livestock biomass resource. It also has one of most challenging air quality environments in the United States, and thus a much lower tolerance for the pollutants and GHGs that biogas produces when burned for electricity. Injecting the gas into utility pipelines resolves this challenge altogether.

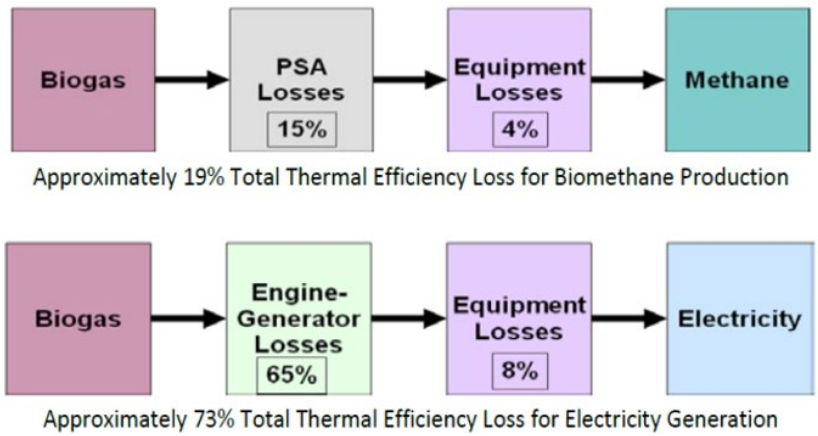


Figure 2 Biogas Utilization Thermal Efficiency Pathways (Krom, 2011)

Biomethane is also valuable to PG&E as a mechanism for raising demand for gas (more gas throughput makes our gas rates more affordable), reducing the carbon intensity of that gas, and continuing to maximize the use of our prior investments in the gas system.

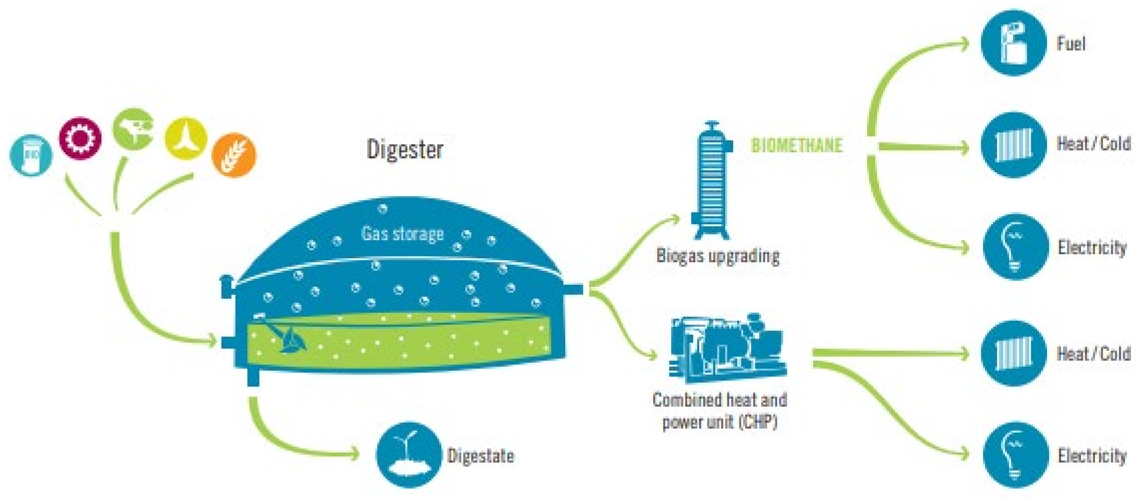


Figure 3 Flowchart of a Digester (Fachverband Biogas e.V., 2017)

Moving away from Biogas as Electric Generation:

Finally, with California's aggressive renewable energy policies, the use of renewable energy generation will continue to rise. Solar and wind are generally preferred to biogas, geothermal and small-hydro to fulfill renewable energy obligations. These resources, while powerful, are also intermittent, offering new challenges to managing the electric grid. With more intermittent renewables in the energy mix, sources of energy that are *flexible* and *storable* become more and more valuable. Renewable gas in PG&E's gas system can be easily stored, and can ramp to meet changing demands on the electric grid. By upgrading and injecting the gas into PG&E's pipeline, biogas takes on the most valuable properties of natural gas as a generator of electricity as well as a direct energy carrier in the new, renewable grid.

<u>More Resources on Upgrading:</u>

BioCycle: Basics of Biogas Upgrading

German Biogas Association: Biogas to Biomethane

Techniques for Transformation of Biogas to Biomethane: Scientific Paper

Biogas Upgrading: Technical Review

UC Davis / California Biomass Collaborative: Comparative Assessment of Technology Options for Biogas Clean-Up

SGC Biogas Upgrading: Review of Commercial Technologies

IEA Bioenergy: Biogas Upgrading Technologies - Developments and Innovations

PG&E's Rule 21: Gas Quality

Gas quality is determined in PG&E's gas pipeline system by Gas Rule No. 21. Raw biogas must be cleaned and upgraded to meet the specifications outlined in this rule, primarily for safety reasons, but also for billing reasons (i.e. Heating value, measured in BTU is how PG&E bills customers, so BTU levels are prescribed in this rule). All natural gas transported through PG&E's pipelines conform to this rule without exception.

However, since biomethane often contains gases that differ from traditional fossil fuels, a section of this rule (Section C. 13: Quality of Gas – Biomethane Requirements) identifies several constituents of concern impurities that must be removed from raw biogas in addition to the removal of elements already removed from traditional sources of natural gas. The most common impurities removed in biogas upgrading include:

- Carbon Dioxide (CO_2)
- Hydrogen Sulfide (H_2S)
- Water (H_2O)
- Oxygen (O_2)
- Silicon Organic Compounds (Siloxanes)
- Ammonia
- Physical particulates (dust, aerosols, metals, bacteria)

WHY REMOVE THESE THINGS?

H_2S is quite poisonous, and ammonia can be damaging to people when inhaled. Water, oxygen, ammonia, H_2S, CO_2, and other elements can cause corrosion of steel pipeline, which is a significant safety concern for gas pipeline operators. Siloxanes have an unusual property of forming a fine sand when combusted, which may have a problematic and unsafe effect on consumer and industrial appliances.

Current State of the Market: Existing Biogas Upgrading Technology

There are a variety of mature upgrading and conditioning technologies available on the market today. Below is an overview of the major categories of these technologies focusing on upgrading and conditioning and methanation.

PRESSURE SWING ADSORPTION

Pressure Swing Adsorption (PSA) is an upgrading system that 'swings' between high and low pressure to expose a purer stream of methane. Biogas is pumped into a chamber filled with a porous material. High pressure pushes smaller molecules like CO_2 into the pores of that material in a process called "adsorption." In high pressure, different molecules are attracted to solid surfaces at different intensities. This process relies on the smaller CO_2 molecule being attracted to the material at a very high rate, leaving primarily methane in the remaining space. The system is then blown down, channeling biomethane out of the system. The pressure is then lowered considerably, desorbing the CO_2-rich waste gas which can either be collected and disposed of, or recycled through the system to improve the system efficiency by up to 5% (Augelletti, 2016). Because this is a batch system, there are often several columns that are staggered to even out the methane outflow.

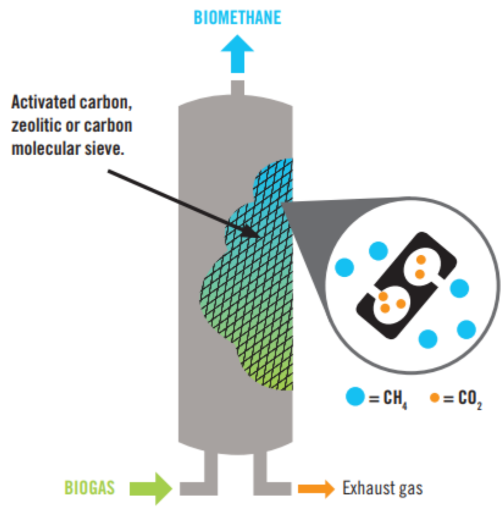


Figure 4 Pressure Swing Adsorption Process (Fachverband Biogas e.V., 2017)

The best adsorption materials are well established after years of successful operation of this mature technology. They generally fall into one of 4 categories:

1. Zeolites
2. Activated Carbon
3. Silica Gel and Aluminum Oxide
4. Molecular Sieves

There are many reasons why PSA has been an attractive means of upgrading gas – it has been used in the oil and gas industry for decades due to its relatively low energy consumption, lack of water consumption or water contamination, low maintenance costs, and efficacy. In part because this system does not require heating or cooling, it can work fast and requires less energy. Because the absorbent material is not used up in the process, it can also be reused again and again, which lowers a potentially significant source of variable cost. Some adsorption materials can even preferentially adsorb siloxanes (commonly found in wastewater). It is simple to operate and has a relatively small physical footprint.

However, compared to other upgrading technologies, PSA tends to lose a significant amount of methane in the waste gas, so often PSA systems recycle the waste gas through the system to improve the methane recovery rate. The methane loss can be between 1.5-2.5 vol% (Bauer, 2012). Additionally, the fast cycling between high and low pressures puts a significant strain on the equipment, and require precision in maintenance of the system. And unfortunately, the system works extremely poorly with gas that has not already been pre-treated to remove water and H_2S, so it can rarely be used in isolation. Add to that that these systems are not cheap – generally between $1-$5m per system, and the system becomes economical only in larger scale operations (Bauer, 2012).

Rapid Cycle PSA

Rapid Cycle PSA is a variant of PSA that operates at about 5-20x the speed of a conventional PSA (Xebex Adsorption, 2017). Rapid cycle PSA is carried out by using multi-port selector rotary valves and a many smaller adsorption chambers. They are of interest due to their smaller size, lower capital costs, lower pressure drops, and higher throughput. The downside of these new systems is that the methane recovery rate is lower – a tradeoff that might be acceptable to smaller biogas developers for the advantage of a smaller, more nimble system.

Ultimately, PSA is a well-established and straightforward system that is generally best used for upgrading already-cleaned biogas to a higher BTU by removing CO_2 and qualifying that gas for utility pipeline injection.

SCRUBBING: WATER SCRUBBING (R&D AND INNOVATION, 2018)

Water scrubbing is an upgrading technology that separates unwanted constituents, such as carbon dioxide, from methane since carbon dioxide has a much higher solubility in water than methane. By increasing the pressure and decreasing the temperature in the adsorption column, carbon dioxide is dissolved into the water. The adsorption of methane and carbon dioxide is described using Henry’s Law, which describes the relationship between partial pressure of a gas and the concentration of the gas in a liquid in contact with the gas.

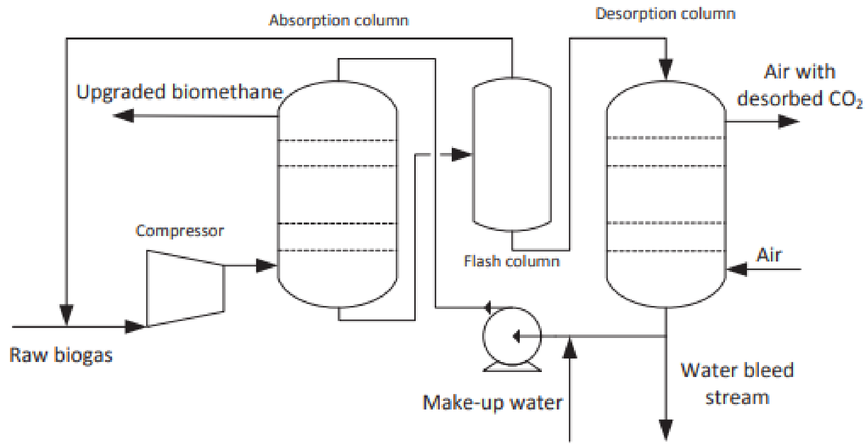


Figure 5 Typical water scrubbing process diagram (Bauer, 2012)

Typically, biogas is injected up into an adsorption column at an elevated pressure of 6-10 bar, while water is introduced from the top. In the adsorption column is a bed of random packing material that will increase the surface area between water and biogas to increase carbon dioxide adsorption efficiency. Counter-flow is important to minimize energy consumption and minimize methane loss. The two outputs are purer biomethane and water with adsorbed carbon dioxide.

The upgraded biomethane is sent out of the system to be used. Meanwhile, in the desorption column, the carbon dioxide is released from the water by addition of air at atmospheric pressure at 2.5-3.5 bar. The air with desorbed carbon dioxide is then exited out the top of the second column, while water is fed out the bottom and cycled through the system to be re-used. It is not uncommon for the separated carbon dioxide to be released to the atmosphere, however, it could be captured and repurposed.
The biogas water scrubber design impacts the efficiency and throughput of the system. The height of the packing material bed determines efficiency of the separation column, and the diameter of the column impacts throughput capacity.

There are two variations of the water scrubbing process that should be noted.

High Pressure Water Scrubbing (HPWS)

The main difference between HPWS and conventional water scrubbing is the very high pressure of the system, usually around 150 bar. Due to the high-pressure requirements, there is higher energy consumption. The approximate energy needed to operate is 0.4-0.5 kWh/Nm^3 of raw biogas. The produced biomethane is at such a high pressure that it could be used in a vehicle fuel filling station with only minor additions for compression. (Bauer, 2012)

Typically, the footprint of these systems is smaller because of the higher-pressure capability, however, the equipment will need to be designed to withstand the higher pressures. Also, the system is operated as a batch-wise system using two adsorption columns.

Rotary Coil Water Scrubber

This method of water scrubbing uses a rotating coil where the compression and scrubbing occur. A company called Biosling, based out of Sweden, has developed this method. Biogas and water are alternately input into the coils that are rotating. By rotating, you naturally increase the pressure from 2 to 10 bar (Bauer, 2012). In the process, the carbon dioxide will be dissolved into the water.

This process is not able to obtain counter-flow current, so the rotary coil method is not able to achieve 97% CH_4. The rotary coil method can output 94% CH_4 (Bauer, 2012). For this reason, this method is useful for applications where lower product purity is sufficient. A conventional water scrubbing unit can be used in series with this method. For the rotary coil system alone, the energy requirement is 0.15-0.25 kWh/Nm^3 of raw biogas. (Bauer, 2012)

Figure 6 Rotary Coil Water Scrubber (Bauer, 2012)

SCRUBBING: CHEMICAL SCRUBBING (R&D AND INNOVATION, 2018)

The process and main principles of chemical scrubbing are the same as water scrubbing. Instead of water, a chemical reagent is used to scrub the unwanted constituent from the biogas to result in a stream of purer methane. A water solution of amines (molecules of carbon and nitrogen) are commonly used due to their molecular ion form. Examples of solvents include Monoethanolamin MEA, Diethanolamine DEA, and Methyldiethanolamine MDEA. The scrubbing liquid is dependent on the properties of the targeted pollutant.

Operationally, the process of chemical scrubbing is the same as the process for water scrubbing. Chemical with a stronger affinity to the unwanted constituent result in minimized methane in the off gas. Although some chemicals have a high capacity and selectivity to make the process efficient, a drawback is getting the unwanted constituents to be released from the chemical during the desorption phase. This often results in a high energy requirement. The temperature will need to be elevated to as high as 160° Celsius in order to release the unwanted constituent (Bauer, 2012).

MEMBRANE SEPARATION

Membranes are selective barriers that allow certain molecules, ions, or particles to pass through and not others. They are very commonly found in biology (i.e. cell walls), but synthetic membranes are also now commonly produced for use in labs or in industry. Membranes in application for biogas upgrading work by creating a pressure difference between the two sides of the membrane. The membrane itself is designed to create openings large enough only for small molecules like CO_2, Oxygen, Water, or H_2S, and the pressure differential draws those out of the biogas, leaving only methane and some nitrogen, the much larger molecules (and more desired compounds).

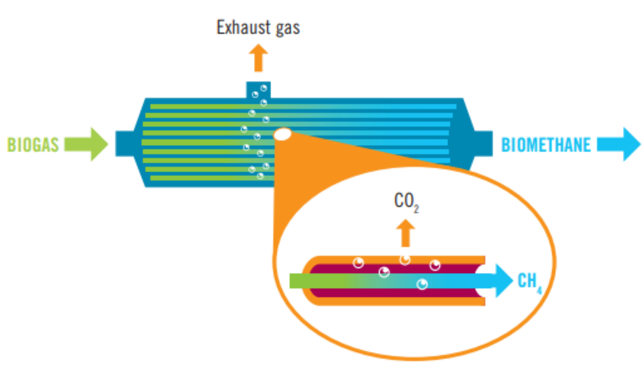


Figure 7 Membrane separation process (Fachverband Biogas e.V., 2017)

In practice, not all of the targeted molecules are captured from the gas, and some methane escapes. Effective membranes are typified by high *selectivity*, and high *permeability*.

Selectivity – Selectivity is a property of membranes that defines the purity of the recovered gas. It refers to the membrane's ability to "select" particular molecules for passing through (i.e. CO_2) and for preventing others from passing through (i.e. CH_4).

Permeability – Permeability is a property that measures the membrane's productivity, or how much gas it can purify in a given time. It is generally given as a rate.

Figure 8 Picture of an industrial membrane separation unit (Air Products, 2015)

The main challenge with membranes is that it there is an intrinsic tradeoff between these two properties. The more restrictive the selectivity (improving the purity of the resulting gas), the less gas that gets through in a given amount of time (which reduces the permeability measurements). Vice versa, if you want to upgrade gas at a higher rate (improving permeability), you must often reduce the selectively of the membrane which may compromise the purity of the resulting gas, or increase methane loss. *'Solution-Diffusion' theory is used to describe the mechanism of polymer membrane gas separations and can be found in detail in the Technical Analysis for Membrane Separation from Gas Operations R&D and Innovation.*

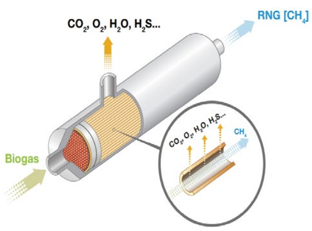
Types of Membranes:

Membrane upgrading systems are defined by the type of membrane in the system, as well as the configuration of the system in which the membranes are placed. Different membranes are used to optimize for separating different types of constituents of concern, and thus, it's unusual to use *only* membranes in upgrading and conditioning biogas. Frequently membranes are used in hybrid processes with other technologies (listed below) to improve efficiency and to lower costs.

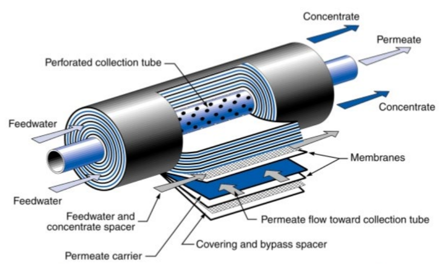
Table 1 Types of Membranes (R&D and Innovation , 2018)

Membrane Type	Sub-Types	Description
Polymer Membranes	Co-Polymer Cross-Linked Blend	Organic polymers are the most common form of commercial membranes. **Benefits:** Time-tested and cheap. Can scale to larger sizes for commercial purposes. **Limitations:** These membranes suffer from the permeability/selectivity tradeoff. Poor mechanical properties/plasticization at high pressure. Low separation factor. Sometimes vulnerable to corruption from H_2S
Inorganic Membranes	Metals Ceramics Zeolites Carbon Molecular Sieves	Inorganic membranes are based on materials like metal. **Benefits:** Inorganic membranes have excellent thermal and chemical stabilities. Some have higher gas fluxes and selectivity (e.g. zeolites and CSM) relative to polymer membranes. Size and shape discrimination led to the narrow pore size distribution resulting in high selectivity. **Limitations:** Mechanical properties make them difficult to fabricate (aka, they are expensive to manufacture). Physically fragile, so hard to use for large surface areas.
Mixed Matrix Membranes (*with Metal-Organic Frameworks, MOF)*	Combination of organic and inorganic polymers	Mixed matrix membranes (MMM) consist of organic polymer combined with inorganic (or organic) particles.

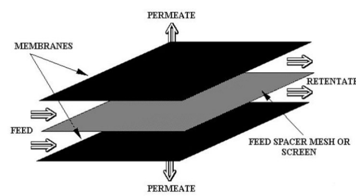
		Benefits: MMM prepared with metal-organic frameworks (MOF) with polymers matrices are good for CO2/CH4 gas separation. They have the potential for high selectivity, high permeability, or both. **Limitations:** Still relatively new technology and have yet to scale physically (to sizes needed for commercial use) or economically.
Module Types		



Hollow fiber (Air Liquide, 2018)



Spiral wound (Izaguirre, 2015)



Envelope (Lauren Burke, 2016)

Figure 9 Module types

<u>More Resources on Membranes:</u>

Membrane Gas Separation Technologies for Biogas Upgrading: [Review Paper]

[30 Years of Membrane Technology for Gas Separation: Article]

[Separation of Carbon Dioxide from Natural Gas Mixtures through Polymeric Membranes: Review Paper]

[Polymer Membranes for Separation of CO_2: An Overview]

CRYOGENY

Cryogeny makes use of low temperatures and pressures at which various gaseous components condense. All cryogenic technologies are useful for the removal of contaminants such as hydrogen sulfide, water vapor, carbon dioxide, helium, oxygen, volatile organic compounds (VOCs), siloxanes, and nitrogen from natural gas flows. It is important that these contaminants are removed to ensure no complications downstream. These complications include and are not limited to decreased energy content of biogas, corrosion in pipelines, combustion, mineral deposits, and erosion. Furthermore, cryogenic technologies also aid in the production of liquefied natural gas and liquefied carbon dioxide that can be stored at much higher volumes than in gaseous form and can also be used as fuel for large diesel trucks (Brendeløkken, 2016).

Biogas is upgraded by lowering system temperatures to extremely low temperatures that range between -90 degrees centigrade and -125 degrees centigrade. This process is ideal for large volumes of gases with high concentrations of carbon dioxide as more traditional methods such as membrane separation or water scrubbing require multiple stages and aren't as effective in carbon dioxide removal. Higher concentrations of carbon dioxide can be found in wetlands, landfills, sewers, farm lands, etc.

Domestic companies that provide cryogenic services include Morse Electric Incorporated, Cryogenic Industries, Linde Engineering North America Incorporated, Freeman and Curiel Engineers, Enerflex, Chart Industries, McDermott, UOP Russell, etc. Companies such as these can install modular cryogenic plants and develop new cryogenic processes. Some cryogenic processes include the Cryo Pur system, cryogenic distillation, cryogenic fractionation, cryogenic packed beds, CryoCell® separation, and others. It is important to note that all cryogenic processes have similar steps and outcomes. The table below shows pros and cons of common cryogenic separation technology. (R&D and Innovation, 2018)

Table 2 Comparative Analysis of Cryogenic Technologies (R&D and Innovation, 2018)

Cryogenic Technology	Pros	Cons
Cryogenic Distillation	• Low methane losses • Works well for carbon dioxide concentrated streams • Methane and carbon dioxide purity between 94.5% and 99.7%	• More expensive than traditional upgrading technologies • Does not work well for dilute carbon dioxide streams • Possibility of solid formations in column at different pressures
Cryo Pur System	• Low methane losses • Integrates biogas upgrading and biomethane liquefaction • Integrates cryogenic distillation column • Easily scalable • High heat recovery • Liquid methane and carbon dioxide purity of 99%	• More expensive than traditional upgrading technologies • Not domestic • Suitable for large gas flows at high concentrations • Energy intensive • High maintenance costs

Cryogenic Packed Bed	• Low methane losses	• More expensive than traditional upgrading technologies • Chance for choking and blockage in operation
CryoCell® Separation	• Low methane losses • Multiple configurations for different types of gas streams • No foaming or corrosion potential • Scalable	• More expensive than traditional upgrading technologies • High maintenance costs

For more information on cryogenic separation, please see PG&E R&D Technical Analysis on Cryogeny (PG&E R&D and Innovation, 2018)

METHANATION

Methanation is the critical step of conversion of syngas generated by thermochemical conversion of biomass (gasification and pyrolysis).

Methanation is a process that chemically creates synthetic natural gas (CH_4) from carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2). More recently, it has also been used as a second step in the production of synthetic methane from hydrogen generated from renewable electricity through electrolysis, a process known as power-to-gas. Power-to-gas is a process by which gas generated from renewable energy sources (in the form of Hydrogen/H_2) can be stored in the gas pipeline system safely as methane. *Power-to-gas is discussed in more detail in the Hydrogen Analysis from Gas Operations R&D and Innovation.*

A series of catalytic chemical reactions shift the balance of chemicals to eventually generate methane and water. The chemical reactions involved are as follows (R&D and Innovation, 2018):

Sabatier Reaction (Methanation)	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ $\Delta_r H_{298}$ = -165 kJ/mol
Reverse Steam Reforming Reaction (Methanation)	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ $\Delta_r H_{298}$ = -206 kJ/mol
Water Gas Shift Reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta_r H_{298}$ = -41 kJ/mol

Methanation usually occurs in one of four types of reactors. The central engineering challenge for methanation reactors is *cooling* – It is critical to control for the exothermic nature of these chemical reactions. The energy needs for methanation mean that there is about a 20% energy efficiency loss during the process (Zwart, Boerrigter, Deurwaarder, van der Meijden, & van Paasen, 2006). All reactor designs incorporate cooling mechanisms:

- **Adiabatic Reactors**: Heat is used to increase gas temperature, and rises until the temperature reaches a chemical equilibrium. Risk due to less than optimal CO_2 conversion at that temperature and risk of destroying the catalysts. Often to reduce these risks, the gas is diluted with an inert or other gas to reduce the temperature, or the gas is subject to cooling before it is injected. However, adding heat exchangers can make the reactor uneconomic or very complex.
- **Isothermal Operation**: Some reactors bundle the catalysts into pipe bundles surrounded by a circulating cooling medium to carry off the heat, such as boiling water. However, there are concerns about the pressure, and the lower rate of methane conversion from CO_2.
- **Fluidized Bed Reactors:** Disperses heat by moving the catalyst particles around inside the reactor, which allows the heat exchanger to function more effectively and to prevent hot spots.
- **Metal Monolith Reactors:** Heat is dispersed in a catalytic reactor by introduction of highly thermally conducting structures. This method coats the nickel catalyst on metal monoliths so hot spots can be reduced. This is still in the experimental stage of development.

Figure 10 Industrial methanation process (Automotive World, 2013)

One additional challenge associated with methanation is the sensitivity of methanation catalysts. Raw syngas must be conditioned before it is methanated because the catalysts (frequently nickel for its high activity and low cost) can be poisoned by H_2S or Siloxanes. The most common reactor types are listed below.

Table 3 Methanation reactor types (R&D and Innovation, 2018) (Automotive World, 2013)

Methanation Reactor Type	Description
Adiabatic Fixed-Bed Reactor	Simplest reactor design. The reactor is filled with catalytic pellets, and rather than being cooled its heat is instead used to increase the gas temperature. **Benefits:** Most common type of methanation reactor. Can be designed quite simply. **Limitations:** Very vulnerable to problems with excess heat. Often cooling that excess heat can lead to complex and expensive systems.
Multi-Tubular Fixed-Bed Reactor	Nickel-based catalysts are filled into small diameter tubes which are then cooled by a cooling medium. Used in power-to-gas applications (overall efficiency from electricity to methane is 45-56%) (Schildhauer, Reactors for Catalytic Methanation in the Conversion of Biomass to Synthetic Natural Gas, 2015)

	Benefits: Significantly reduces challenges and tradeoffs due to heat. **Limitations:** More complex equipment, reactor size depends strongly on heat performance, more costly.
Fluidized Bed Reactor	In fluidized bed reactors, methanation reactions occur within the fluidized bed of catalyst particles. **Benefits:** Allows for good mixing of gas and solid catalyst particles, resulting in high mass, heat transfer and near isothermal conditions. Allows for good process control. **Limitations:** Abrasion and entrainment of catalyst particles in the gas flow are a challenge.

Biomethane Injection into the Gas System: The Standard Injection Skid

Gas distributors need to odorize and measure both the quantity and quality of biomethane before allowing it to enter the grid, or to reject non-compliant gas. They also need to control pressure and add an odorant to the biomethane, which is required for safety reasons in case of leakages. This can be accomplished through a group of equipment as part of an interconnection facility. Often, these facilities can be combined into a skid-mounted modular system which can be pre-fabricated in bulk and transported to the point of interconnection (where any transfer of gas between the biomethane producer and the gas provider's pipeline system takes place). These skids are portable, mobile, and space efficient.

Creating a standardized skid designed specifically to meet all the unique needs for interconnecting biomethane projects could significantly reduce costs. By pre-fabricating or manufacturing these skids, providers can take advantage of economies of scale and can deliver the equipment more quickly and more on-demand. Both suppliers of interconnection equipment and producers can expect more transparency, standardization, and predictability in operations, equipment, and the timeline for execution of the interconnection process. That certainty reduces risk, and improves access to capital for biomethane producers and project developers.

PG&E has designed a personalized skid-mounted interconnection system for dairy biomethane pilots as of Summer 2018. In Europe and elsewhere internationally, skids are a mature concept, and are commonly used for gas pipeline interconnection.

Macro Challenges (High Level)

Upgrading is a relatively mature industry and the challenges associated with this step in the value chain are associated mainly with the many compounds that need to be cleaned out of the raw biogas.

- **H2S is poisonous –** One particular constituent of concern, H_2S, is toxic to humans, has corrosive properties in presence of water, and when combusted, generates SO_2, an environmental pollutant. The problem is *not* that there are no technologies in the market for protecting developers, utility employees, or the public against H_2S – there are. The problem *is* that it is *also* destructive to biological membranes and methane catalysts. There may be creative ways to avoid damaging these systems, such as combining multiple methods, or multiple stages that filter out H_2S first. The key is to do this cost-effectively.
- **Some upgrading technologies introduce problems while they solve others –** Occasionally, an upgrading system might introduce issues that cause ongoing O&M challenges. An easy example is water scrubbing. While it is a lower cost, simple method of removing most constituents of concern from biogas, it also introduces water.
- **Upgrading can be capital/energy intensive and suffer some methane loss** – Several commonly used technologies for upgrading have similar challenges as most other technologies associated with the biomethane supply chain. They are often capital intensive (an upgrading system might cost up to several million dollars) (Bauer, 2012), or can require additional energy to do the work. The challenge is to evaluate the efficiency of these technologies for biomethane applications – are they better than options like membranes which require no energy input at all? All forms of upgrading filter out some methane, and effective technologies minimize that loss. Technologies must be evaluated for capital and O&M cost, efficiency, and effectiveness.
- **Most technologies are mature, but have yet to be proven for biomethane in California –** While the technologies for biogas cleanup have been proven and are mature in international markets, many of these technologies must be re-proved in PG&E's system and approved in California's challenging regulatory environment. That process can take some time to complete even for low-risk, long-proven technologies.

Key Challenges to Address in Upgrading Technology (Medium Level)

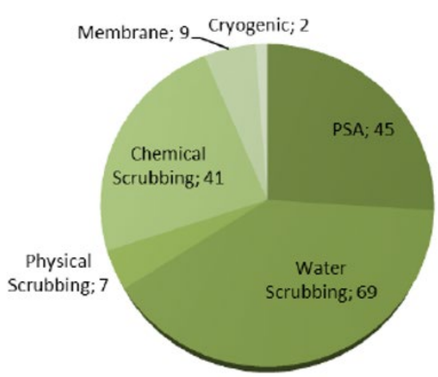
Successful upgrading technologies or processes will address the following:

1. **There are many constituents of concern that need to be removed from raw biogas - some require special treatment or different methods to separate.**
2. **There is an inherent tradeoff between selectivity and permeability – successful membrane separation technologies will work effectively while reducing methane loss.**

3. **Many internationally accepted technologies need development in the US/CA market.**
4. **Cost, energy intensity, and size are limitation factors.**
5. **Gas quality and heating value must be very accurately measured at biomethane injection for CA/PG&E's billing purposes.**

Upgrading is used frequently in Europe, where biomethane injection into gas pipelines (mostly on the distribution system) is common and a mature practice. Thus, many of these technologies and processes for cleaning and upgrading biogas are relatively well developed in Europe, and simply need to be approved by US utilities and US/state regulatory bodies before they can be used in the US market. However, most of the means for upgrading biogas and syngas to biomethane such as PSA (pressure swing adsorption) and scrubbing (chemical or water) have large capital costs and energy consumption requirements.

However, there are some technologies that use very little energy and are highly efficient. Membranes are one such technology. However, they face their own barriers to adoption, including ongoing membrane replacement costs, vulnerability to corruption from H_2S, and conflicts between permeability and selectivity. While membranes are already regularly used for biomethane upgrading, better types of membranes are in development, and there is an opportunity for R&D to identify these emerging technologies for potential deployment. Similarly, there are some newer options for upgrading, such as cryogeny, which are not yet commonly used, but might have potential as a more efficient and effective upgrading system.



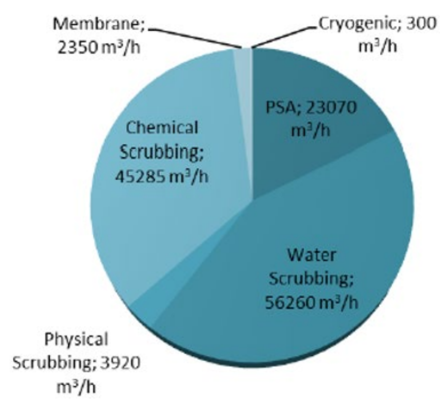


Figure 11 Number (left) and capacity (right) of upgrading plants in Europe in 2011 (Allegue & Hinge, 2012)

Biomethane Upgrading technology market share from Laura Bailón Allegue and Jørgen Hinge "Biogas and bio-syngas upgrading" DANISH TECHNOLOGICAL INSTITUTE December 2012

Potential R&D Projects for Gas Upgrading

These are the categories of technologies that are priorities in addressing some of the key challenges facing conversion technology adoption and usage in California. Since upgrading and interconnection technologies are the closest to PG&E's gas business, these technologies are likely to offer the opportunity for biggest impact on our business, and should be prioritized over other investments further away in the biogas/biomethane value chain.

1. SYNTHETIC OR H_2S-RESISTANT MEMBRANES

Membranes are a high efficiency, low maintenance, low energy consumption method for removing constituents of concern from biogas. In many ways, they are ideal. However, many commercially available membranes are organic polymers, meaning they can be corrupted easily by H_2S. Several new membranes are under development that are synthetic polymers or that use Mixed Matrix Membranes that are resistant to H_2S or that are effective at filtering H_2S. Such membranes would provide an effective and cheaper alternative to other forms of upgrading, or a complement in a hybrid system with another system.

Current PG&E Gas R&D Project: A researcher at Stanford University has demonstrated a new technology for gas separation via microporous polymer membranes. This method is a breakthrough in improving *both* selectivity and permeability. This tech would be especially attractive for smaller biomethane injection points, such as dairies, for which absorption and adsorption processes are too expensive.

Next Step: Membranes are not reusable – R&D can address Mixed Matrix Membranes/MOF – how to manufacture them more cheaply, and to increase the size for commercial use.

2. CRYOGENY LOW-TEMPERATURE DISTILLATION PROCESS

Cryogenic technology has not primarily been applied to large scale processes and it will be necessary to determine how to scale up different cryogenic processes for industrial use. Presently, there is an opportunity to research ways in which dilute carbon dioxide streams can benefit from this technology as the use of cryotechnology for rich carbon dioxide streams has proven to be the most cost effective.

3. RAPID CYCLE PSA

Rapid Cycle PSA has a smaller footprint, is cheaper, and is more nimble than traditional PSA systems. Many potential biogas developers are constrained by the upfront cost of upgrading systems, and the capacity of those systems may in fact be more than is needed. The ease of use, energy efficiency, small physical footprint, and low maintenance of these systems may be more value to this market of biogas developers than is lost through a slight increase in methane loss.

4. MODULARIZED, SMALLER GAS CHROMATOGRAPHY SYSTEMS

One piece of critical equipment that must be included in any biomethane interconnection point is gas quality measurement, often conducted by gas chromatography systems. Currently, one unit can measure only one or few compounds that must be measured for gas quality, so many units are needed for each injection point. These units are enormous, heavy, costly, and extremely complex – meaning that O&M costs are high due to a need for specialists, and replacing units is timely and costly.

Current PG&E Gas R&D Project: A solution currently under review is a new miniaturized technology (APIX) that performs the same function as a single gas chromatography unit, at the same accuracy, but at a tiny fraction of the size. The units are modular, simple to maintain and replace, and multiple units can be consolidated into less than ½ the size of a single older unit. While not cheaper, the size reduction, ease of use and maintenance, and modular structure offer significant compounded savings over time.

5. COMBINATION OF UPGRADING METHODS FOR EFFICIENCY, QUALITY

Hybrid processes can be more efficient. For example: membrane separation technology combined with pressurized water scrubbing (PWS), amine swing absorption(AS), pressure swing adsorption (PSA), temperature swing adsorption (TSA), cryogenic separation, and a combined heat and power engine or multi-membrane separation stages. These configurations can provide for lower costs (Chen, Membrane Gas Separation Technologies for Biogas Upgrading, 2015). As standalone processes: PSA is good for CO_2 removal and to an extent, siloxanes. Not good for water or H_2S. Membranes good for CO_2, Water, Oxygen. Not good for H_2S unless inorganic. Further study into various hybrid systems can improve process efficiencies and lower upgrading / operation costs.

6. GAS QUALITY STANDARDS BY BIOGAS SOURCE

Currently, PG&E measures all incoming biomethane projects for all constituents of concern, and developers must prove the quality of their gas to meet that standard. However, depending on the source of biogas, there may be a high probability of a particular contaminant, or nearly no probability of another contaminant (i.e. siloxanes are common in wastewater treatment projects, but almost nonexistent in woody-biomass biogas). R&D can help establish standards in partnership with worldwide partners with long experience to determine where PG&E can reduce extra or burdensome requirements for biogas project partners.

7. DE-SULPHERIZATION PROCESSES

Establishing the most effective and efficient method of reducing Sulphur in biogas is important because most conditioning and upgrading technologies do not tolerate H_2S well, making it a critical first step. Biological Desulpherization occurs with air injection for bacteria to convert H_2S to elementary Sulphur. Because nitrogen is common in air but unwanted in Biomethane however, this is not always a productive solution. Alternative methods include adsorption with activated carbon, iron hydroxide or iron salts injection, or caustic treatment with biological regeneration.

8. BIOMETHANE INJECTION SKID STANDARDIZATION

PG&E has an initial skid design completed for its first dairy interconnection pilots.

Next Step: Gas R&D has a history of importing mature processes and standards from overseas markets and proving them for the US/California market. In this case, several European providers have perfected more advanced versions of skid-mounted interconnection designs. R&D must identify the key modifications needed to adapt these best practices to the US market, and coordinate with other utilities to design Skid 2.0. The more standard the design across several markets, the more effective the cost reduction, ease of understanding for suppliers and gas producers, and advantages from just in time manufacturing.

Key Technologies to Investigate and Timeline

Because of the proximity of these technologies to PG&E's core business, these technologies offer the highest priority projects in the RNG value chain. It is important to prioritize technologies, standards and activities that will help PG&E reduce the time, cost or ongoing O&M of its own work, particularly in pipeline interconnection. Therefore, PG&E should prioritize a standardized, replicable skid design, as well as the technologies used within that skid design with a focus on continuous improvement and reduction of cost and complexity.

From there, PG&E should prioritize technologies that reduce the barriers that are most significant to developers who wish to upgrade biogas to biomethane, that also lie within PG&E's direct control. This is important because biogas producers have an easy substitute for biogas in burning it for electric generation. By reducing the cost or complexity of conditioning or upgrading, Potential projects might include:

1. PG&E can substantially reduce uncertainty, cost, and time by establishing a standard skid for biomethane pipeline injection. While PG&E's first standard skid has recently been approved for the earliest biomethane interconnection projects, the next step is to collaborate with experienced European utilities to identify potential improvements and advanced technology to include in Skid 2.0.
    a. Improved Gas Chromatography – APIX Project currently underway in partnership with SoCalGas. Currently, under evaluation for field testing at PG&E.
2. Establishing effective, quick, and efficient process for desulphurization is often a pre-requisite for using other upgrading technologies effectively and at low cost. Removing barriers to this, and methods for safe removal and disposal of H_2S will loosen a current upgrading bottleneck.
3. Membranes require little energy, are relatively low cost, and can scale down to accommodate smaller projects (like those needed for small dairy projects). Improving membranes might expand access to the biomethane market for smaller participants and reduce the need for additional energy to produce biomethane for injection.
    a. Gas Separation via multiparous polymer membranes – Current partnership with Stanford University for a new, more effective membrane.

Who are Experts in this field?

Experts specific to individual types of upgrading technologies:

Table 4 Individual and Technology Specific Experts

Industry Experts	Expert	Alternative
California		
United States	Stephen Kaffka (UC Davis), California Biomass Collaborative	

International	German Biogas Association	
Technologies		
Membranes	Kyle Goehring, Eisenmann Air Liquide Malmberg Alex Evans, Evonik	Bright Biomethane DMT Clear Gas Solutions
Water Scrubbing	H. Dekker, DMT Environmental Technology	
Chemical Scrubbing	Kerstin Hoyer, Energiforsk	
Pressure Swing Adsorption	Amir Ghasdi, Xebec	
Cryogeny	Cryo Pur Guenael Prince, WAGE-Energy	
Methanation	Haldor Topsøe A/S Paul Scherrer Institute in Switzerland (Fluidized Bed Reactor)	Zentrum für Solare Wasserstofferzeugung Reactor
Gas Quality Standards/Measurement	Amir Ghasdi, Xebec David Faulkner, APIX	
Constituent of Concern: H_2S	Jerry Hughes Martin II, North Carolina State University	
Constituent of Concern: Siloxanes	Adam Brandt, Stanford University GTI	
Standard Interconnection Skid	Honeywell Elster Emerson	

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