GAS QUALITY CONSIDERATIONS

FUNDAMENTALS OF BIOGAS CONDITIONING AND UPGRADING

The composition of biogas constituents varies by feedstock and site. End use of the biogas typically guides the conditioning and upgrading requirements.

Part I

Diane Greer

BIOGAS QUALITY and energy content are critical to many applications generating heat and power or producing biomethane for vehicle fuel or injection into natural gas pipelines. A biogas conditioning and upgrading system typically integrates several technologies to meet equipment or process specifications for end-use applications. Selecting the right technologies for an application depends on gas composition, project scale, economics and operational considerations. Air quality and waste disposal regulations also come into play.

Biogas is primarily composed of methane (CH_4) and carbon dioxide (CO_2) with small amounts of hydrogen sulfide (H_2S) and ammonia (NH_3). Typically the gas is saturated with water vapor. Trace amounts of hydrogen (H_2), nitrogen (N_2), oxygen (O_2), dust and siloxane may be present. Part I of this article discusses contaminants found in biogas and processes available to remove them. Part II will look at how technologies to condition and upgrade biogas are combined. Case studies will range from heat and power generation to upgrading biogas to biomethane for pipeline injection and vehicle fuel.

BIOGAS COMPOSITION

The composition of biogas constituents varies by feedstock and site. Projects should first test biogas samples to determine the levels of key gas constituents, says Jan Scott, president of Unison Solutions in Dubuque, Iowa. If digester gas is unavailable, a biochemical methane potential (BMP) analysis can generate biogas from a small feedstock sample for testing, explains Kevin Jankowski, project engineer with Applied Technologies in Brookfield, Wisconsin.

Many biogas applications require removal of H_2S, siloxane, particulates and water vapor. Pipeline injection and vehicle fuel applications involve upgrading, which strips CO_2 from the biogas to increase its energy content. Hydrogen sulfide, produced during digestion of sulfur-bearing organic materials, is toxic and causes corrosion in pipelines, compressors, storage tanks and engines parts. Burning biogas containing H_2S produces sulfur dioxide (SO_2), a precursor to acid rain.

Manure digesters on dairy farms produce biogas with H_2S levels of 1,500 to 3,500-parts-per-million (ppm), says Norma McDonald, North American sales manager for Belgium-based Organic Waste Systems: "With food processing wastes, H_2S is typically lower, probably between 300 and 700-ppm."

H_2S in biogas generated by breweries and municipal wastewater is more variable.

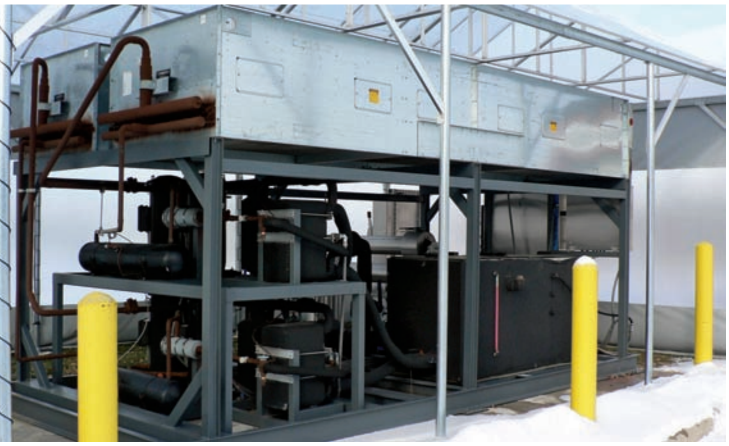
At the Madison, Wisconsin Metropolitan Sanitation District's wastewater treatment plant (WWTP), digester biogas flows into a vessel containing iron-impregnated wood chips (far right) to remove hydrogen sulfide, and then through two vessels that contain activated carbon media (right) to remove siloxanes.

"Breweries range from 2,000 to 3,000 ppm but we have also seen cases where they go all the way up to 30,000 ppm," Jankowski explains. "I have seen municipal sources as low as 200 ppm and I have also seen them over 30,000 ppm. It is really site specific." Chemicals used to control pH and clean equipment, such as sulfuric acid, can cause high H_2S levels. "Sometimes you have natural sulfur in the feedstock, like in meat and slaughterhouse waste," he adds.

Standards vary across the country — and utility by utility — when conditioning and upgrading biogas for injection into natural gas pipelines.

Biogas from wastewater treatment plants contain siloxanes, chemicals used in personal care products, pharmaceuticals, foods and lubricants. In a digester, siloxanes volatilize into biogas. When biogas is burned, siloxanes form microcrystalline silica deposits on spark plugs, pistons, valves, cylinder heads and other metallic surfaces in engines and turbines causing abrasion and fouling. At the Madison, Wisconsin Metropolitan Sanitation plant, moisture and siloxane levels of 2,000 to 4,000-parts-per-billion caused major damage to the cylinder and crank shaft of an engine producing electricity, explains Paul Nehm, director of operations and maintenance: "The engine required a $130,000 overhaul."

Biogas saturated with water may need to be dried. Changes in temperature and pressure can condense water vapor into water or ice causing corrosion and clogging in engines, pipelines and distribution systems. Corrosion results when water vapor reacts with H_2S to form sulfuric acid or with CO_2 to produce carbonic acid. CO_2 must be removed when upgrading biogas to natural gas standards for pipeline injection or use as vehicle fuel. CO_2, an inert gas, reduces the energy content of the biogas.



Water vapor in the biogas stream at the Madison WWTP is removed with a chiller (above).

Nitrogen and oxygen are typically not found in high concentrations unless oxygen is used in the digestion process to reduce H_2S levels. When combusted in engines, ammonia produces nitrogen oxides, which can form ozone, smog and particulate matter in the atmosphere.

BIOGAS QUALITY STANDARDS

Biogas quality standards vary by application. Biogas producers need to understand equipment specifications or the requirements of the utility purchasing or transporting the gas before selecting treatment systems. Typically boilers require H_2S concentrations under 1,000-ppm and the removal of water vapor to prevent the formation of sulfuric acid that causes corrosion. The type of materials used for piping, heat exchangers and chimneys is also a consideration due to potential corrosion issues.

Specifications for H_2S and siloxane levels in engines vary by the type of engine and manufacturer. "If it is a reciprocating engine sometimes it is less than 200-ppm but I have also seen specifications as high as 1,000-ppm," McDonald says. Some microturbines can tolerate very high H_2S levels. Capstone Turbine Corporation's line of biogas microturbines can tolerate H_2S up to 5,000-ppm.

Standards vary across the country — and utility by utility — when conditioning and upgrading biogas for injection into natural gas pipelines, McDonald adds. The specifications apply whether the utility is purchasing the gas or only transporting it to the final customer. Due to corrosion concerns, H_2S and water vapor limits for biomethane injected into pipelines are low. Pacific Gas and Electric Company (PGE) requires biomethane to contain no more than 4-ppm of H_2S. Water vapor exceeding 7 lbs/million cubic square feet at 800 psig is not permitted. One of Jankowski's pipeline projects limits water vapor to 0.5 lbs/million standard cubic feet of gas or less. "That comes out to be 0.1 percent water vapor," he says.

Particulates also need to be removed to prevent mechanical damage. Oxygen and nitrogen, i.e. air, are not permitted. PGE allows no more than one percent CO_2. "The lowest you are going to get away with in the pipeline is 94 percent methane," McDonald explains. "More commonly the specification is going to be 97 percent or higher."

Standards for compressed biomethane (CBM) for vehicle fuel strictly limit CO_2, H_2S, particulates and water vapor, although producers have more leeway with CO_2 levels. Engine manufacturers define requirements. "The most prevalent specification in the market is for a minimum of 90 percent methane," McDonald says. "They will provide a much larger operation window on two parameters — oxygen and nitrogen — that the pipeline won't."

Choosing how much CO_2 to remove is essentially a cost benefit analysis, she adds. Purer gas, with lower CO_2 levels, costs more to produce. Higher CO_2 content requires the producer to condense gas with less energy, reducing the mileage obtained from each cubic foot of CBM.

BIOGAS CLEANING OPTIONS

Biogas cleaning and upgrading technologies utilize a range of passive media, chemical and/or biological treatment techniques. There are tradeoffs between the effectiveness of the treatment method, capital costs, operating costs and operational complexity. Water utilization and disposal of media or chemicals, which may be toxic, can be an issue. This section describes biogas upgrade options based on the contaminant being removed.

Hydrogen Sulfide: Solid and liquid scavengers are the two main options for H_2S removal. The simplest solid scavenger is the iron sponge, typically made of wood chips covered with iron oxide or hydroxide. When biogas is filtered through a vessel containing a fixed bed of the media, the H_2S attaches itself to the iron on the wood chips. Over time the media become saturated and need to be replaced. "The waste basically is wood shavings that go out as a fertilizer," says Paul Tower, president of Applied Filter Technology (AFT) in Snohomish, Washington.

Several companies offer proprietary iron oxide media, such as SulfaTreat and Sulfr-Pack, which have greater surface areas and/or utilize chemicals to make the reaction more efficient, Jankowski explains. Activated carbon coated with alkaline or oxide solids to improve adsorption also are used to remove H_2S. Common coatings include sodium hydroxide, sodium carbonate, potassium hydroxide, potassium iodide and metal oxides.

Solid scavenger systems have the lowest capital cost and typically work best for lower concentrations of H_2S. "It is a good technology if you have 2,500-ppm or less of H_2S," Scott says. As H_2S levels rise, the media become saturated more quickly and needs to be replaced more frequently, increasing operating costs.

The performance curve for the media looks like a hockey stick, McDonald explains. "For a period of time it will keep the H_2S level near zero but as the media becomes coated, it adsorbs less and less. All of a sudden, H_2S starts to creep up and then spikes. So you have to replace those beds at that inflection point."

Media can be regenerated, typically using a lead/lag vessel approach. The lead vessel is used until it reaches its inflection point and then the system switches to the lag vessel while the lead vessel material is regenerated, McDonald adds: "Depending on which adsorbent media is chosen, the beds can be regenerated anywhere from three to five times."

Water scrubbing removes H_2S and CO_2 since both gases are soluble in water. The system works by feeding pressurized biogas into the bottom of a vessel. Pressurized water is sprayed from the top of the vessel in a counter-current to the gas. "The systems work well to remove H_2S but it also removes CO_2, which is in much higher concentrations," Jankowski says. "This is fine if you are upgrading the gas to pipeline quality standards that require CO_2 removal. But if CO_2 is not the target, the system still needs to be designed for high CO_2 concentrations and will produce large liquid streams that need to be treated or disposed."

Water scrubbing can fit well when a source of secondary water is available and the facility is located in an area where there is value to the wastewater generated by the process. Because the wastewater contains sulfur, it can be land applied by farmers. "They are able to get quite a bit more yield by having that trace of sulfur in the water," Tower explains. AFT recently introduced the SulfrStrip for applications with H_2S levels above 2,000- ppm. It utilizes a wet scrubbing process and a liquid catalyst to remove H_2S from biogas streams. The first stage absorbs H_2S into solution to create hydrosulfide ions. The second stage oxidizes the ions into elemental sulfur, which precipitates in solution.

"Liquid scavenger and water scrubber have higher capital costs than media based systems but have lower operating costs for high amounts of H_2S," says Jankowski. "Typically they try to recycle as much as possible and usually that keeps operating costs down, but sometimes it gets pricey. These systems can't compete on lower levels of H_2S but when you have higher loading they seem more applicable."

> Solid scavenger systems have the lowest capital cost and typically work best for lower concentrations of H_2S.

Biological processes to remove H_2S typically utilize microorganisms from the Thiobacillus family, which convert H_2S into sulfur and sulfates, explains Nicolas Abatzoglou, a professor at the Université de Sherbrooke in Quebec, Canada: "The sulfur is easily separated from the biomass."

The systems grow microbes on a fixed media bed in liquid. "Biogas is pumped in to the bottom of the vessel and flows out the top," Jankowski explains. "At the top you have a shower that trickles liquid and nutrients back down through the media."

Biological systems work best for applications with H_2S levels of 2,000-ppm or less, Tower explains. AFT licenses a system called BioStrip from Canadian-based Biorem. "BioStrip regenerates and you do not need to replace the media. You just feed it periodically," adds Tower.

Since biological systems do not require chemicals, their operating costs are lower than liquid scavenger systems. But the systems are more sensitive to operating parameters, such as heat and temperature. They also can't respond as fast to changes in H_2S levels, McDonald explains, although she notes companies are working on improving the capabilities of biological systems.

H_2S levels also can be reduced during digestion. At the Madison Metropolitan Sanitation plant, ferric chloride is added to the digesters to prevent formation of struvite, a phosphate mineral that causes fouling of digester components. "The ferric chloride ties up the phosphorous and also some of the sulfur, which will reduce H_2S levels," Nehm says. But sites need to be careful when adding ferric chloride. Adding too much iron in upflow anaerobic sludge bed reactors can plug the beds, Jankowski explains.

Adding small amounts of air, between 2 and 6 percent, into the head space of a digester will cause natural bacteria that convert H_2S to elemental sulfur to grow on exposed walls and roof beams in a digester. However, precipitating H_2S can cause stalactites of sulfur to form. "Then gravity takes over and you get pounds of sulfur falling from the top of the digester into your feedstock, creating higher inherent H_2S potential," McDonald explains.

Siloxane: "The vast majority of siloxane removal systems in the country are carbon-based," Scott explains. The systems utilize activated carbon, typically doped with proprietary chemicals to enhance adsorption. Setup is similar to an iron sponge. Biogas is passed through a fixed bed of the activated carbon. Spent media is typically swapped out and disposed, although some vendors offer regeneration systems.

Scott does not typically see media regen-

Water scrubbing in conjunction with pressure and temperature swing adsorption units removes CO_2 and H_2S for the production of compressed biomethane for vehicle fuel. The Greenlane Biogas upgrading equipment (left) is installed at a facility in France.

eration at smaller municipal wastewater plants: "Capital costs are higher and there is a high parasitic electrical use to operate the regeneration system. For smaller plants the cost of the media is just not that great."

Siloxanes can also be removed using silica gel or alumina adsorbents or by chilling the gas. Chilling is energy intensive and is not as effective as adsorption techniques unless the gas is cooled to very low temperatures (-70°C).

Water Vapor: Water vapor is commonly removed using refrigeration. Heat exchangers chill the gas, causing the moisture to condense. The dry gas is then reheated with the rejection heat from the heat exchanger. There are other methods, such as absorption with glycol or adsorption with drying agents such as silica gels. For many applications, refrigeration is the cheapest, says Paul Greene of O'Brien & Gere.

Some applications, such as pipeline injection, require extremely low moisture levels. In these cases chillers remove most of the water but the gas needs to run through another media bed for final polishing, Jankowski explains: "Pressure swing adsorption units or activated carbon beds assist in the final polishing of the moisture in addition to what they are designed to remove, whether it is CO_2, nitrogen or oxygen."

BIOGAS UPGRADING

Water Scrubbers: For applications with strict CO_2 limitations, a secondary processing step is often required to insure specifications are met. Water scrubbers, previously discussed, remove CO_2 and H_2S in one step. Swedish-based Greenlane Biogas Upgrading System employs water scrubbing in conjunction with pressure and temperature swing adsorption units (PSA/TSA) to remove CO_2 and H_2s for the production of compressed biomethane for vehicle fuel in Europe.

The system feeds pressurized biogas into the bottom of a vessel in a counter-flow to pressurized water sprayed into the top. Biomethane exiting the top of the tank goes through a PSA/TSA unit for drying and to remove impurities that made it through the water scrubbing process, explains Sean Mezei, North American president of Flotech Services. The company claims methane yields of 99 percent and the reduction of H_2S down to 0.1-ppm. Wastewater is sent to a second vessel where it is regenerated. "At low pressure we inject air in order to remove contaminants and then filter it to get rid of the sulfur," he adds.

Chemical Absorption: Organic solvents, such as Selexol and polyethylene glycol, can be used instead of water to absorb CO_2 and other impurities. Like water scrubbing, chemical absorption requires pressurized gas. Regeneration of the chemicals is achieved by lowering the pressure and applying heat. In general, methane yields from chemical absorption are high but the processes are generally not economical for smaller installations. Energy required to regenerate the chemicals pushes up operating costs.

Solvents tend to be used in applications where the gas also contains high levels of oxygen, such as biogas generated from landfills. Amine systems, which require lower pressure biogas, are more appropriate for large-scale digesters.

Pressure Swing Adsorption (PSA): PSA systems feed compressed biogas into the bottom of a vessel containing layers of adsorbent materials. As the gas flows upward through the bed, impurities such as CO_2, water, nitrogen and oxygen stick to the surfaces of the adsorbent particles. (The level and type of impurities removed depend on the composition of the bed.) Biomethane exits the top of the tank.

Once the adsorbent materials are loaded with impurities, the system switches to a second stage that lowers the pressure in the vessel. This causes the particles to release the impurities, which exit the system as exhaust gas. A small amount of methane is retained in the vessel and expelled with the exhaust stream.

PSA systems are typically composed of multiple vessels that alternate between high and low pressure so that at least one of the beds is producing biomethane at any given time. For applications with very restrictive CO_2 limits, sites use PSA in combination with membrane stages to remove the remaining CO_2 and moisture, Jankowski says.

Selecting a PSA system depends on the type and the size of the operation, McDonald explains: "Some systems have not, at least to date, been economically practical at very low volumes." Systems that can tolerate variations in flow rate are important in applications where biogas production fluctuates based on feedstock or time of year. "In California a covered lagoon might lose 50 percent of its gas production in the winter," she adds. "Some PSA system provides more flexibility in terms of changes in the rate of flow of the biogas." ■

Diane Greer is a Contributing Editor to BioCycle.