BARBEN ANALYTICAL

Application Note
Biogas - pH & O_2

Oil & Gas: Renewable Natural Gas

Biogas is a common term for a hydrocarbon gas mixture generated from landfills, waste water treatment, animal manure, and other sources. It is estimated that there are 2000+ biogas generation sites in the United States and over 10,000 sites within Europe. Biogas is considered environmentally friendly since it is a carbon neutral energy source. In this paper we will look at the analytical measurements used in biogas purification.

Overview

Biogas is a byproduct of the of the breakdown of organic matter. Anaerobic bacterial digestion produces a gas mixture roughly comprised of the following:

Percentage	Component
50-60%	Methane (CH_4)
30-40%	Carbon Dioxide (CO_2)
0-5%	Nitrogen (N_2)
0-1%	Hydrogen Sulfide (H_2S)
<2%	Oxygen (O2)
<1%	Hydrogen (H_2)
<1%	Trace Gases (NH_3, Siloxane)

The composition of the biogas varies depending on the feedstock. For example, animal manure tends to have higher levels of H_2S and NH_3, while landfill gas is relatively clean. Temperature also plays an important role in gas composition and generation.

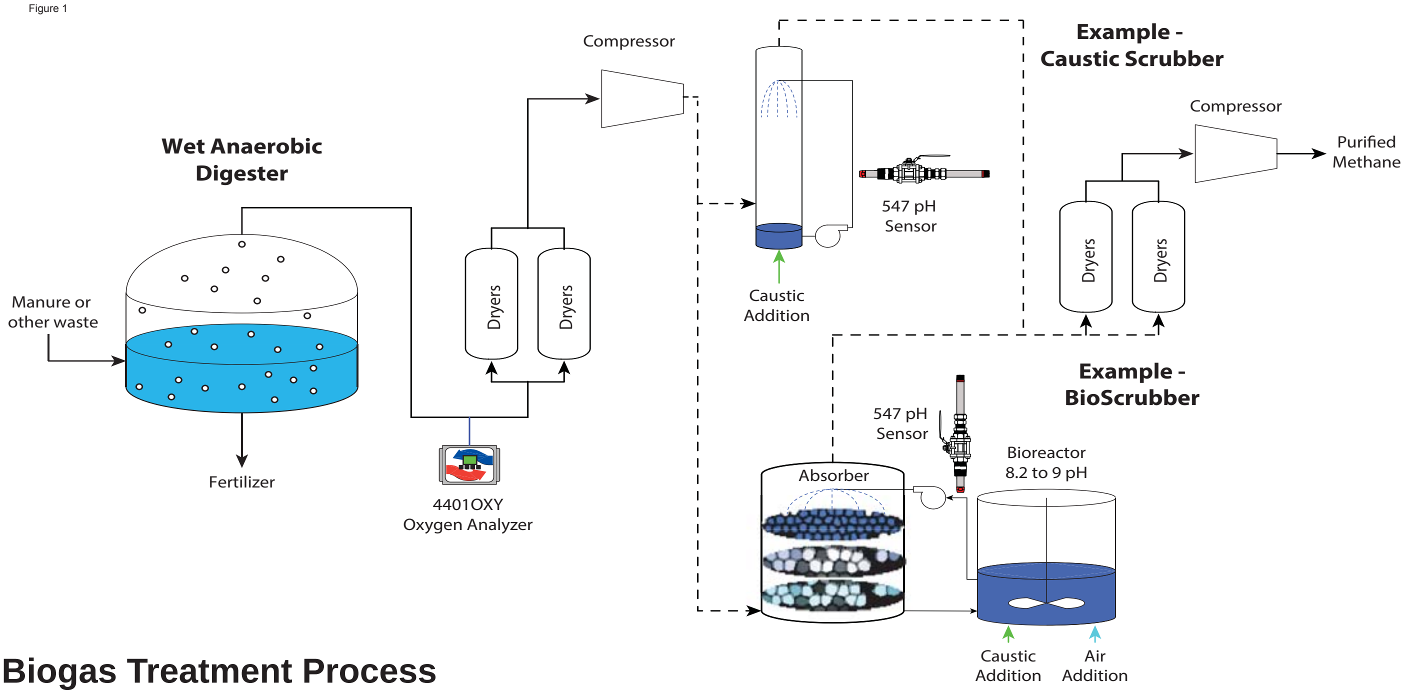
Production

Raw biogas is not suitable for most combustion processes. It must go through multi-stage purification to get the methane content to a usable value (>95% CH_4) for power generation. Gas at the exit of the digester is saturated with moisture. The moisture combined with H_2S and CO_2 may create acidic condensation. First stage gas clean-up requires moisture removal by passing the biogas through a dryer. Drying can be accomplished through a heat exchanger or through dessicant drying. After the dryer, second stage clean-up involves removing H_2S. There are several strategies for sulfide removal. Small biogas facilities use packed bed iron oxide (Fe_2O_3) absorbers to react with H_2S. This design is often referred to as an "iron sponge". Large scale biogas operations often choose liquid scrubber technology to clean up the impurities. Caustic water wash scrubbers can effectively remove both H_2S and CO_2 to produce sales grade biogas in the following reactions.

$H_2S + NaOH \blacktriangleright NaHS + H_2O$
$CO_2 + 2NaOH \blacktriangleright Na_2CO_3$
$Na_2CO_3 + H_2S \blacktriangleright NaHS + NaHCO_3$

A second option is to use a bioscrubber. Bioscrubbers use chemotropic bacteria to consume both the H_2S and CO_2. With either strategy the purified methane must go through final drying for moisture removal before usage.

Figure 1



Biogas Treatment Process

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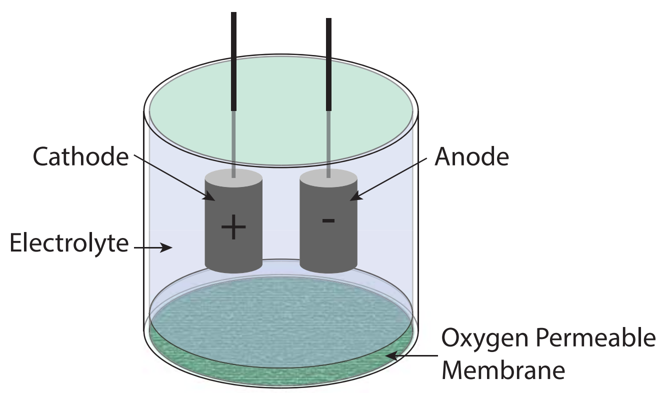
Measurement Challenges - Oxygen
Methanogenic bacteria used in the digester cannot survive in the presence of oxygen; thus monitoring O_2 levels is critical for the generating capacity of the biogas facility. An increase in oxygen indicates detrimental leaks in the digester structure as well as air ingress at compressor and pump seals. A secondary purpose for oxygen measurement is to provide a safety check to avoid exceeding low explosive limits (LEL) in the biogas. Most biogas operations try to keep oxygen measurements below 1%.

Biogas oxygen is best measured at the digester outlet. For traditional electrochemical cells (figure 2 - also known as Clark cells or galvanic cells) this can be a challenging application. The raw biogas is saturated with moisture and contains various trace level contaminant gases. High moisture creates measurement errors in traditional electrochemical cells due to condensation blocking oxygen diffusion through the hydrophobic membrane. Hydrogen sulfide in raw biogas will permeate the electrochemical cell membrane and poison the electrolyte. High levels of CO_2 may have a similar effect on the electrochemical cell causing the output of the sensor be inaccurate. If these types of sensors are used, then a complex sample conditioning system may be required to drop out moisture and the other trace gases. A sample system is often maintenance intensive and adds to the response time of the critical oxygen measurement.

Barben Analytical's 4401OXY Optical Oxygen Analyzer provides a better method to handle biogas O_2 measurements. Fluorescence quenching technology provides trace PPM oxygen measurement with no risk of damaging the sensor in the application. An oxygen sensitive luminophore sensor provides the measurement technology for the 4401OXY. Blue light is used to excite the luminophore. In return, the luminophore emits light back at a specific wavelength and intensity (figure 3). When oxygen is present the emitted light undergoes a phase shift and reduced light intensity. The change in the luminophore output can be directly correlated to the partial pressure oxygen levels in both gas and liquid phases.

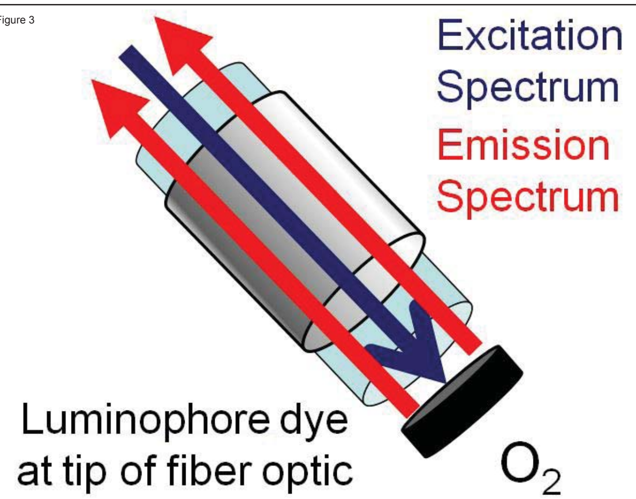
Electrochemical Clark Cell O_2 Sensor



- Sensitive to flow and pressure changes
- Membrane sensitive to fouling, coating and attack
- Electrolyte poisoning

Figure 2

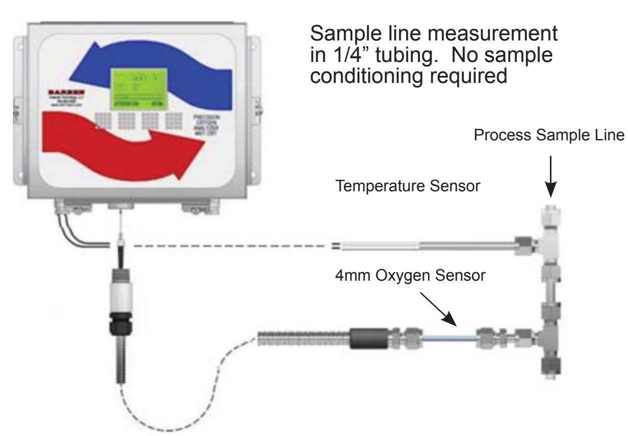
Figure 3



Pulsed light from the analyzer excites the luminophore oxygen sensor. Once excited, the luminophore emits light which is measured back at the analyzer. The duration and wavelength of the light will vary depending on the oxygen concentration in the liquid.

Advantages of this design include no interference due to moisture, H_2S, CO_2, and other contaminant gases. The 4401OXY also simplifies the sample system design as the contaminant gases do not need to be scrubbed prior to the measurement. The end result is increased reliability, better accuracy, and faster response in biogas applications.

Figure 4



Example - Barben 4401 Optical Dissolved Oxygen with BOS1 Sensor

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Measurement Challenges - pH
pH levels in the biogas digester are maintained slightly above neutral (7.4 to 8.0pH) to provide the best enviroment for bacterial growth. This measurement is typically done with a portable analyzer or in the laboratory since the mass balance of the digester system rarely changes.

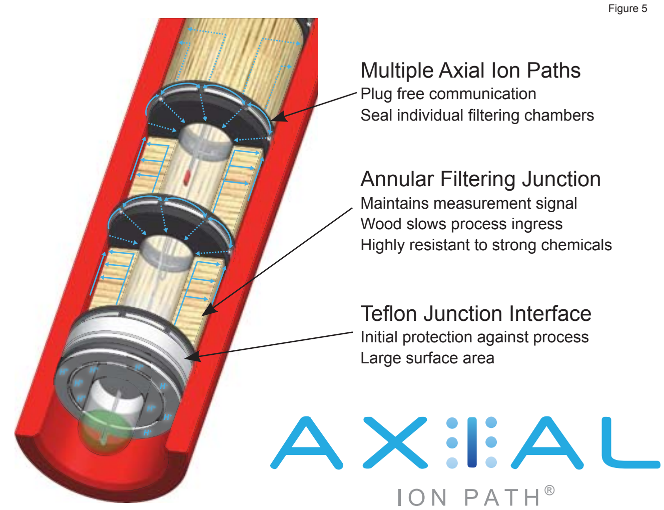
Online pH control does become a critical parameter in downstream liquid scrubbing applications. Caustic scrubbers rely on continuous pH measurements for proper dosing of chemicals. As H_2S and CO_2 are dissolved into the solution the pH drops as acids are formed. Hydrogen sulfide can poison pH sensors in the same way as described with electrochemical oxygen sensors. Sulfides will contaminate the KCl electrolyte used in the pH sensor and eventually attack the Ag/AgCl element causing instability of reading.

In bioscrubber applications H_2S is converted to solid sulfur by thiobacillus bacteria. The pH of bacteria liquid solution is maintained at 8.2 to 9.0 to provide optimum bacterial growth. Online pH is used to control dosing of nutrients and caustic to the bioreactor. The bioreactor sits adjacent to the absorber and provides additional retention time for the bacteria to consume the H_2S. Residual H_2S poses a problem in bioscrubber applications as well, with poisoning of the sensor as the primary concern. The bacteria and elemental sulfur forms a liquid slurry, which can plug up the porous reference junction of conventional sensors causing sluggish response to changing pH levels.

Barben Performance Series pH sensors provide a unique solution for online pH measurement in scrubber applications. The Axial Ion Path® reference design greatly slows the ingress of H_2S providing two to three times the lifespan when compared with traditional double junction pH sensor designs. A large Teflon junction used in the front of the Barben pH sensor provides a difficult to plug, large surface area, which is easy to clean in high build-up applications.

Barben pH sensors should be specified with “R” or “CR” high-temperature glass electrodes for these applications. Viton seals and Kynar (PVDF) should be specified as the sensor wetted material for best chemical compatibility and integrity at elevated temperatures.

Figure 5



For scrubber applications Barben pH sensors should be mounted directly into recirculation pipelines to provide quick response. A retractable “hot tap” sensor such as the 547 (figure 6) is recommended for these installations. The flow rate past the sensor tip helps to keep the sensor free of any coating or build-up. If the sensor is mounted in a pre-existing sample line then the Barben 551 Quick Change sensor (figure 7) with flow cell provides an easy way to install and remove the sensor.

547 Retractable “Hot Tap” Sensors

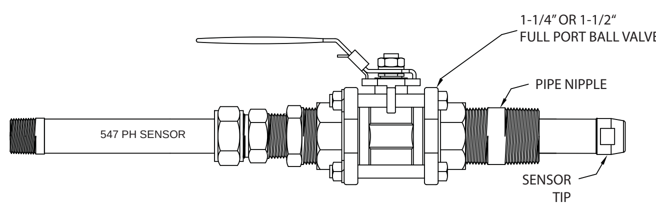


Figure 6

551 Quick Change Sensors

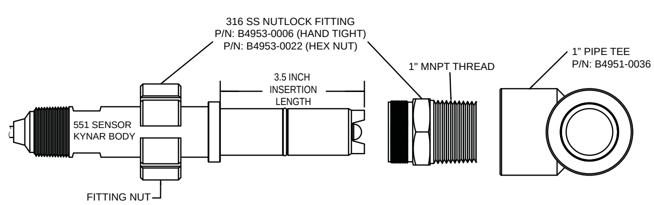


Figure 7

Barben pH sensors easily connect to most modern pH analyzers in use today, Wiring diagrams for commonly available instruments can be found on www.BarbenAnalytical.com or via request from technical support.

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Summary

Barben Analytical products provide many measurement advantages for biogas purification. The 4401OXY Optical Oxygen Analyzer solves the problems related to oxygen measurement in raw biogas while simplifying installation and reducing maintenance.

Barben Performance Series pH sensors help solve problems related to gas purification if downstream liquid scrubbers are used. Advantages include the following:

- Less frequent cleaning and calibration intervals
- High pH / ORP measurement accuracy
- Increased pH / ORP sensor lifespan
- Simplified sensor specification

Maintenance expenses are decreased as spares inventory is reduced and fewer calibration hours are required to keep measurements accurate.

Contact Us

Barben Analytical is a leading supplier of analytical measurement technology targeting the industrial marketplace. It is a wholly owned subsidiary of Ametek.

Ametek has nearly 14,000 colleagues at over 120 manufacturing locations around the world. Supporting those operations are more than 80 sales and service locations across the United States and in more than 30 other countries around the world.

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