Application Note
Merox Process - pH and O_2

Oil & Gas: Refinery

Mercaptans (RSH) are organosulfur compounds that are often present in unrefined or partially refined hydrocarbon feedstocks. These chemicals have several undesirable attributes including strong odor (garlic smell), corrosivity, and degradation of downstream additives as well as the hydrocarbon end products. For these reasons mercaptans must be removed through a catalytic process. In this paper we will examine the Merox process and the Barben Analytical products used at different points throughout the treatment stages.

Merox Processes

Merox is an acronym for "Mercaptan Oxidation". The Merox process was first developed by UOP back in 1958. Over time, many variations of the Merox process have developed to solve different hydrocarbon refining applications. Caustic (NaOH) is favored for these processes since it reacts with both hydrogen sulfide (H_2S) as well as mercaptans (RSH). This paper will focus on the two general types of caustic-based Merox processes - Extraction & Sweetening:

Merox Extraction - A two stage process (caustic + oxidation) used to clean lighter molecular weight hydrocarbons such as LPG's (Liquefied Petroleum Gases), pentanes, and NGL's (Natural Gas Condensates).

Merox Sweetening - Single stage process used to directly convert mercaptans to disulfides in jet fuels, naphtha, diesel and kerosenes

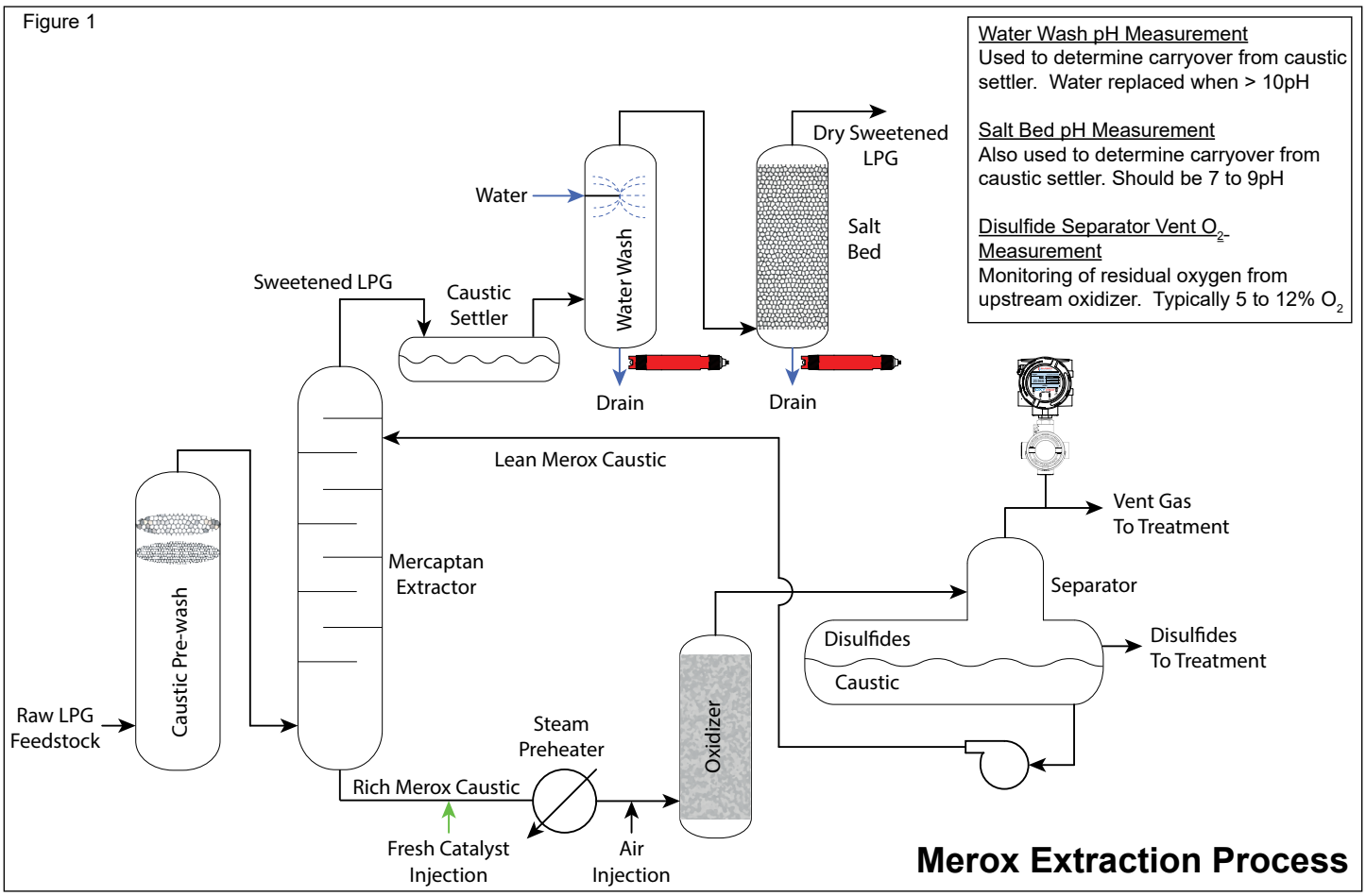
Merox Extraction Process

Merox extraction processes begin with H_2S removal. Often this is done upstream with an amine treatment unit. In cases where treatment is not available a caustic pre-wash is commonly used to remove H_2S from LPG feedstock. This sulfur removal step is necessary to avoid secondary reactions downstream when catalysts are introduced. The reaction is shown below.

$$H_2S + NaOH \blacktriangleright NaSH + H_2O$$

The LPG flows from the caustic pre-wash to the bottom of the mercaptan extractor vessel (Figure 1). The gas flows upwards through the vessel where it encounters

Figure 1



AMETEK®
THERMAL PROCESS MANAGEMENT

Application Note
Merox Process - pH and O_2

counter-current flow of caustic with entrained Merox catalyst (metal chelate). A series of perforated trays ensure thorough mixing of LPG and caustic as the two solutions pass through the vessel. The mercaptans react with the caustic mixture based on the following reaction:

$$2RSH + NaOH \blacktriangleright 2NaSR + 2H_2O$$

"R" denotes an organic group such as methyl, ethyl, or propyl

Pressure is kept elevated just above the bubble point so that the hydrocarbon gases remains in liquid form. The newly sweetened LPG exits from the top of the vessel while the mercaptan-rich Merox caustic flows from the bottom of the vessel. The sweetened LPG still contains caustic thus it is pumped to a horizontal caustic settling tank. The lighter LPG is pumped off the top of the tank. Depending on the feedstock, the LPG will go through multiple post-treatment steps including a water wash for final caustic removal, as well as moisture removal through a salt bed dryer. pH levels are closely monitored in these final treatment steps to avoid caustic carry-over in the final sweetened LPG product.

Back at the extractor, the rich caustic solution goes through a regeneration process to strip off entrained mercaptans. The caustic is heated and air is injected to convert the mercaptans to organic disulfide oils. The reaction follows:

$$4NaSR + O_2 + 2H_2O \blacktriangleright 2RSSR + 4NaOH$$

"R" denotes an organic group such as methyl, ethyl, or propyl

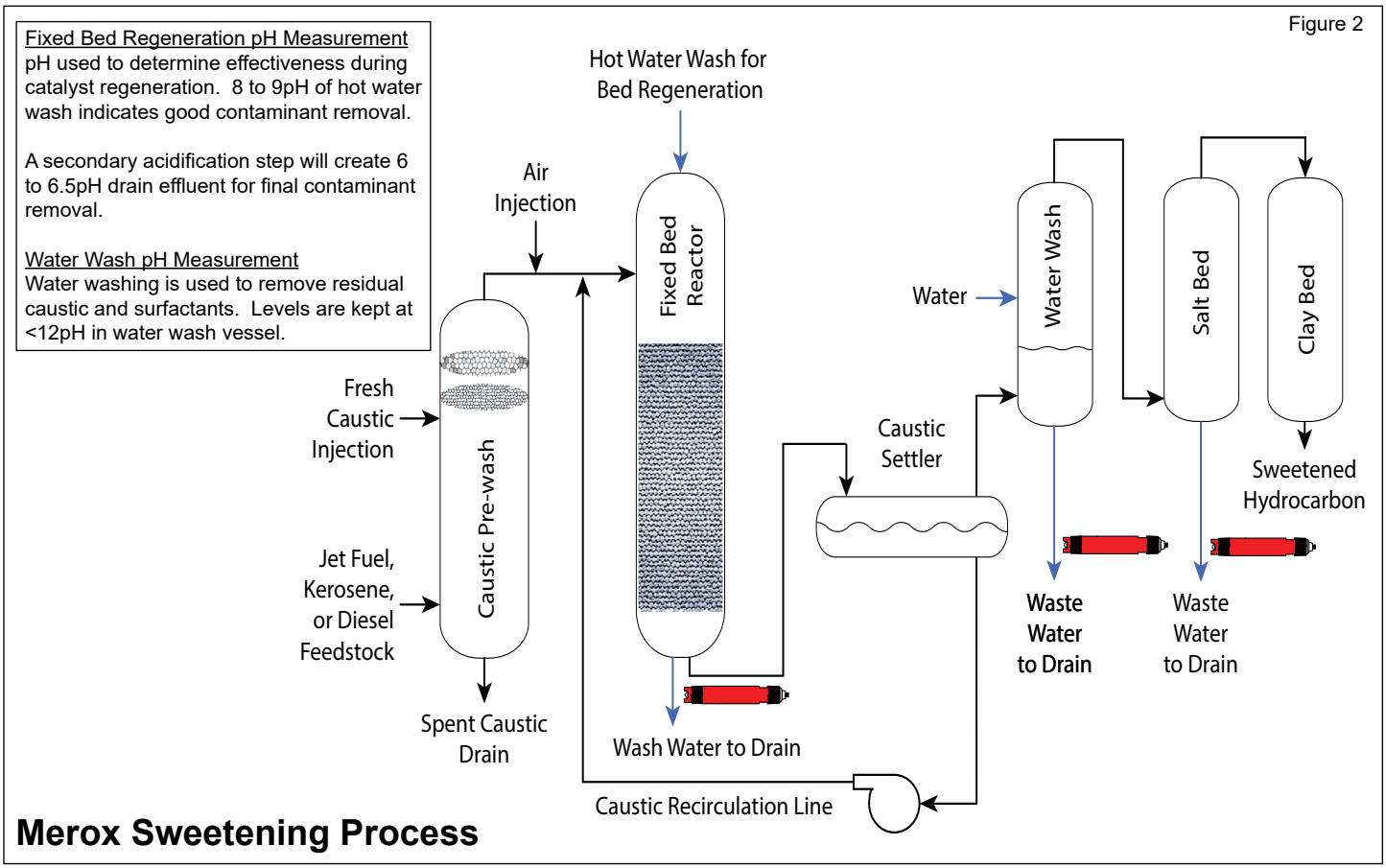
Oxidation occurs in a packed bed reactor. Since the disulfide oils (RSSR) are not soluble in caustic they are decanted in a horizontal separator vessel. Lean caustic is pumped off the bottom of the vessel for re-use in the process. Additional Merox catalyst may be added during regeneration to ensure a mercaptan removal back at the extractor vessel.

The disulfide separator vessel will have excess air from the oxidizer stage. The oxygen content of separator vent gas is monitored to determine the effectiveness of the oxidation stage. It is typically kept at 5 to 12% to ensure full conversion of mercaptan compounds.

Merox Sweetening Process

Merox sweetening processes (Figure 2) are reserved for heavier hydrocarbons such as kerosene, aviation fuels, and diesel. These fuels contain longer-chain mercaptans

Figure 2



which are not soluble in caustic. They require the conversion of mercaptans to disulfides in a single fixed-bed reactor in the presences of oxygen, caustic, and Merox catalyst. All of the fundamental chemical reactions in the sweetening process remain the same as in the prior extraction process.

Similar to the previously described extraction process; the feedstock for a sweetening process must be free of H_2S. A caustic pre-wash is used for sulfur removal. After pre-wash, both air and caustic are injected into the feedstock directly ahead of the fixed bed reactor. As the mixture enters the reactor it is exposed to activated charcoal containing the Merox catalyst. The charcoal serves to extend catalyst life by absorbing phenols, naphthenic acids and other contaminants which may harm the catalyst. The feedstock mixture with entrained caustic and air trickles through the fixed bed where exposure to the catalyst directly converts the mercaptans to disulfides. It should be noted that these disulfides are soluble in the hydrocarbon fuel but not soluble in caustic. They remain with the fuel throughout the sweetening process and will be removed in downstream processing if deemed necessary.

The newly sweetened solution drains from the bottom of the fixed bed reactor to a caustic settling tank. Caustic is pumped off the bottom of the settling tank for reuse in the process. The sweetened hydrocarbon is pumped to a water wash vessel for removal of any residual caustic. The water wash stage is typically a batch reaction where pH measurement is used to determine when too much caustic has carried over and fresh water must be added. A salt bed following the water wash is used to remove any residual moisture. pH may be measured on the drain from the salt bed if caustic carry-over is still a concern. Final treatment involves a clay filtration bed. Clay is used to absorb oil soluble surfactants, corrosion inhibitors and other final contaminants in the sweetened fuel.

To keep the sweetening process working smoothly periodic regeneration of the activated charcoal and catalyst within the mixed bed reactor is required. A hot water wash (approx. 190ºF) is used to unclog pores within the charcoal to expose catalyst. Residual caustic keeps pH well above neutral during the water wash. The water wash cleaning continues until the effluent water reaches 8 to 9 pH. The hot water wash is followed by a separate acetic acid wash. The acid removes any leftover salts trapped within the charcoal. pH of the effluent water will be monitored until is drops < 6.5pH. At this point, fresh catalyst will be added to the bed prior to restarting the process.

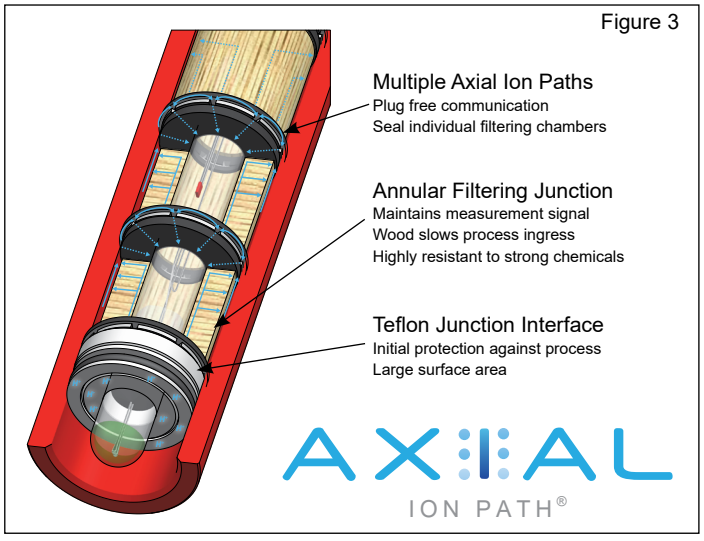
pH Measurement Challenges

Both extraction and sweetening Merox processes present challenges for pH measurement. Excess caustic combined with mercaptans, disulfides, and other contaminants can quickly poison the electrolyte and AgCl element used in most pH sensors. Once the sensor is poisoned the pH measurement becomes unreliable resulting in more frequent calibration. Residual oil passing by the sensor can plug the porous reference junction used in most conventional sensor designs leading to constant cleaning of the sensor tip and eventual lost measurement. Entrained catalyst fines can abrade the sensor causing premature failure of the measurement electrode.

pH Measurement Solutions

Barben Analytical Performance Series pH sensors are well suited for the various pH measurements found in refinery processes. The patented Axial Ion Path™ reference design (Figure 3) uses multiple internal filtering chambers to greatly slow the ion transfer of impurities from the process liquid, reducing contamination of the internal electrolyte. Each filtering chamber is separated with Barben's patented annular AIP seals. The seals ensure electrolyte flow perpendicular to the length of the sensor thus blocking chemical ingress from the process. The extremely large Teflon junction at the tip of the sensor helps to prevent plugging and coating from hydrocarbon build-up. All features of the Barben reference design ensure less frequent sensor cleaning and longer intervals between calibrations. The end result is the most reliable pH sensor for Merox applications.

Figure 3



BARBEN ANALYTICAL

Application Note
Merox Process - pH and O_2

Figure 4



The 551 Quick Change pH Sensor (left) with our B4992-1009 Flowcell (right).

Flowcells are available in 316 stainless and titanium with either 1/2" FNPT connections or 1/4" tube fittings. A drain port in the bottom of the flowcell provides an option for a sample tap or an easy purge location for sensor removal.

551 Quick Change pH Sensor with Flowcell

pH Sensor Specifications

Performance Series pH sensors should be specified with "CR" coating resistant glass electrodes. The coat resistant layer on the glass provides added protection for exposure to strong caustic solutions as well as oily build-up. Kynar (PVDF) should be specified as sensor body material due to its chemical compatibility. All seal / o-ring material are specified as FFKM (Kalrez) for process compatibility.

Merox pH measurements are often done on sample lines. In these applications the Barben 551 Quick Change pH Sensor with flowcell is recommended (Figure 4). The 551 Quick Change Sensor uses a union nut arrangement to affix the sensor within the flowcell. This design allows simple installation and removal of the sensor without torqueing the sensor body or twisting the cable.

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 by request from technical support.

Oxygen Measurement Challenges
Oxygen measurement is typically found on the vent gas of the disulfide separator used in the Merox extraction process. The vent gas will have traces of hydrocarbons and mercaptans which give it a garlic odor. If the sulfur content is low the vent gas can be flared. In some applications it may be routed through a carbon filter or used a fuel gas for other refinery processes. The gas content will be primarily nitrogen with oxygen content between 5 to 9% O_2. Besides vent gas there may also be trace oxygen measurements on inert gas blanketing applications on storage tanks surrounding the Merox unit.

These oxygen measurement applications can be difficult due to the moisture and contaminant gases in the stream. The presence of hydrocarbons eliminates zirconia-based oxygen sensors as due to high internal heat required to perform the measurement. Paramagnetic oxygen technology may be affected by residual water vapor which can condense and corrode small moving parts within the analyzer. Tunable Diode Laser (TDLAS) technology is a suitable yet costly solution. Frequently the end user turns to electrochemical cells for these applications due to their low cost; however they have multiple issues as well.

Electrochemical Sensor Issues
Electrochemical oxygen sensors function similar to a battery using a cathode and a lead (Pb) anode in an electrolyte solution. An oxygen permeable membrane allows oxygen molecules to enter the cell where they react with the electrolyte creating a voltage response to the changing oxygen level (Figure 5).

In disulfide separator applications contaminant gases within the flow stream continuously penetrate the sensor membrane and react with the electrolyte causing poisoning of the oxygen sensor. When this occurs, frequent recalibration is required to correct for zero drift caused by the poisoning of the sensor. Eventually the sensor response will become erratic and replacement is required. An electrochemical sensor may require an upstream H_2S scrubber to function in these applications. The scrubber adds to the significant investment in maintenance time and spare parts needed to keep the sensor functional.

Other downsides of electrochemical oxygen sensors include error due to changing flow and pressure. In separator vent gas applications surges of disulfide and caustic liquids in the tank frequently occur causing variable flow and pressure. These two factors affect the permeability of the membrane thus creating error in the oxygen reading.

A Better Approach to Oxygen Measurement
Barben Analytical's OXYvisor Optical Oxygen Analyzer uses a new technology to deal with the challenges of oxygen measurements within the refinery.

Quenched luminescent technology provides accurate oxygen measurement with no risk of damage to the sensor in the application. An oxygen sensitive luminophore sensor provides the measurement technology for the OXYvisor. Blue light is used to excite the luminophore sensor located in the process gas (Figure 6). Once excited, the luminophore emits red light back at a specific

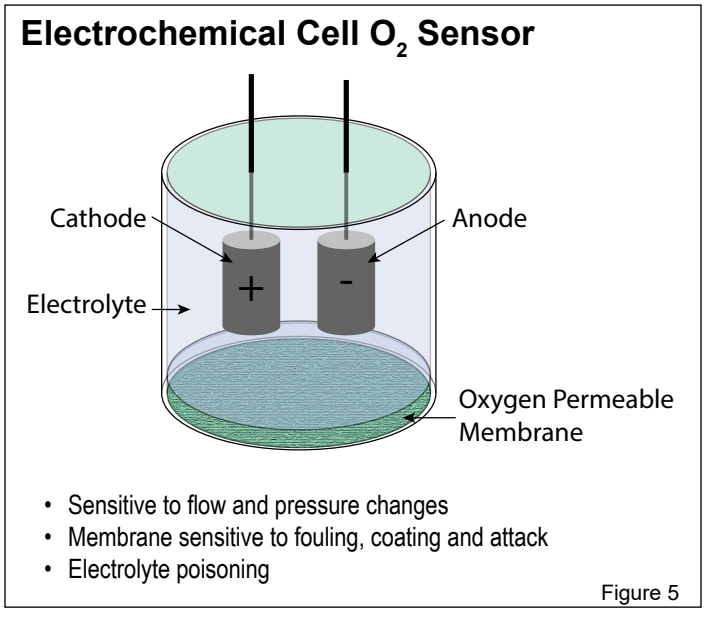
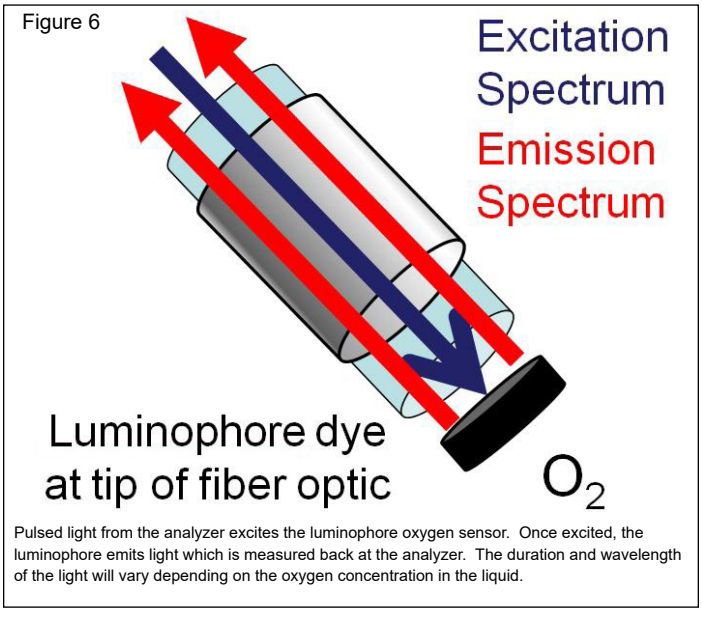


Figure 5



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.

wavelength and intensity. In the presence of oxygen, the emitted light is quenched, causing a time domain phase shift and reduced light intensity. The change in the luminophore output can be directly correlated to the partial pressure oxygen measurement. Advantages of the optical sensor design include no interference due to moisture, H_2S, and other contaminant gases. The oxygen measurement is independent of flow rate. The luminophore can withstand condensation and mild particulate build-up. The response time is extremely quick (T_{90} < 6 seconds) as is calibration time (3-5 minutes).

Because of these advantages, the OXYvisor Optical Oxygen Analyzer simplifies the sample system design. Contaminant gases do not need to be scrubbed prior to the measurement. The end result is increased reliability, better accuracy, and faster response in Merox gas measurement applications.

Installation

There are several options for installation of an Optical Oxygen Analyzer. A basic system includes the OXYvisor Analyzer, BOS Optical Sensor and Flow Cell (Figure 7). The OXYvisor Analyzer provides a local HMI interface and agency approval for non-incendive installations (Ex nA, Class I Division 2). The BOS Optical Sensor has several measurement range options depending on the amount of oxygen in the natural gas.

Sensor	Range
BOS1	0 - 4.2% O_2
BOS2	0 - 25% O_2
BOS3	0 - 300 PPM O_2 (1000 PPM over-range)

The BOS sensor consists of an armored fiber optic cable connected to a 12mm probe with the luminophore sensing element on the tip. Barben Analytical offers the 12mm probe and mating flow cell in 316 stainless steel, Titanium, and Hastelloy C-276 for full material compatibility. Temperature compensation of the oxygen measurement is provided by a external PT1000 RTD for quick response.

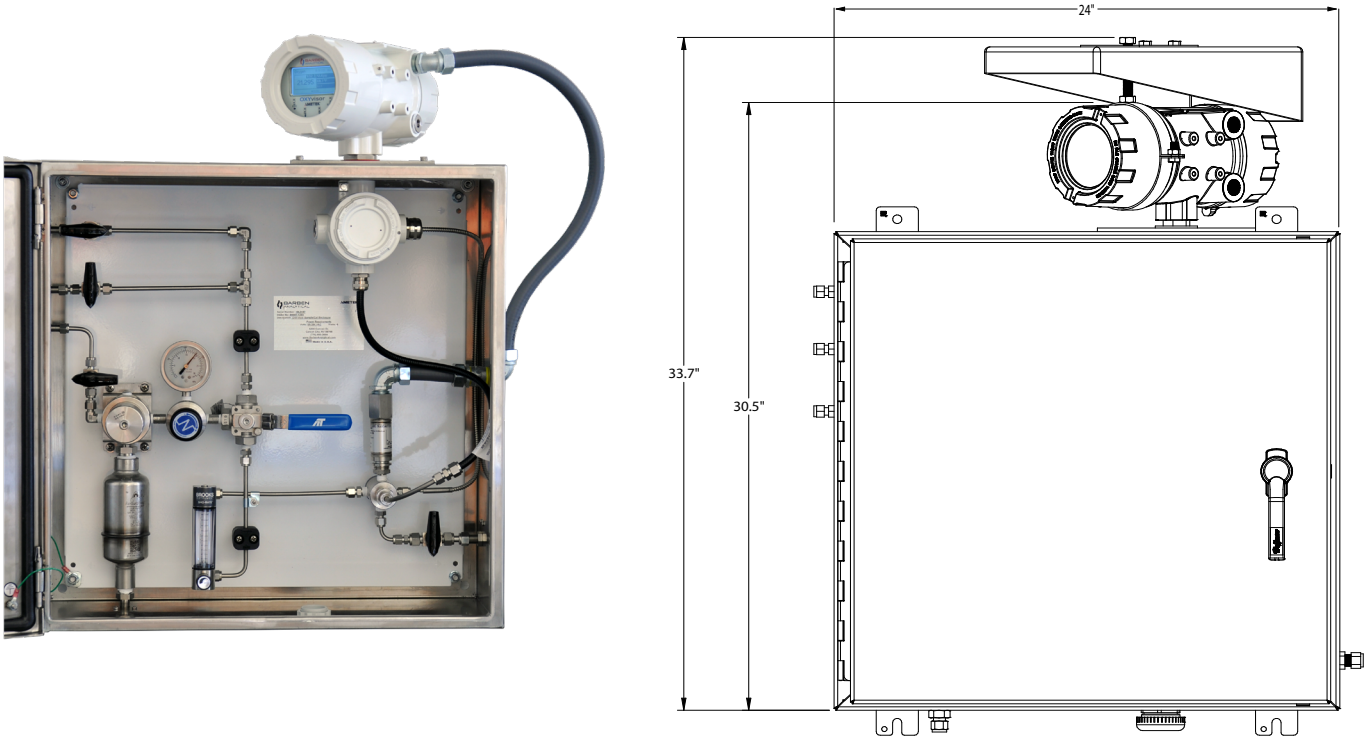
Barben Analytical also offers a pre-engineered sample calibration panel (Figure 8 & 9). The SCP panel provides connections for zero/span calibration gases as all related hardware for a proper installation. The panel design includes a fast loop to increases gas flow. The fast loop is a valuable feature to improve response time in applications where there process sample point is a long distance from the analyzer. The analyzer and related sensors ship pre-wired and mounted directly to the panel. The SCP panel can save considerable engineering and design work in new installations.

Figure 7



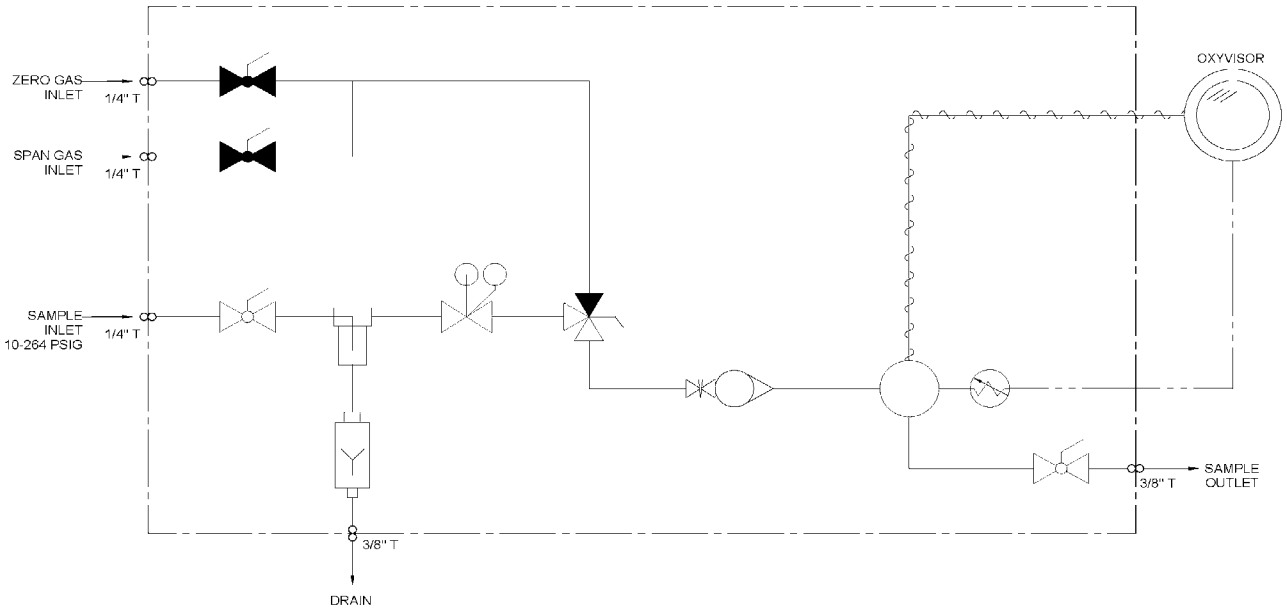
The OXYvisor Optical Oxygen Analyzer, BOS Sensor & Flow Cell (loose) shown above.

Figure 8



Part #B6001-1293 Pre-Engineered Sample Calibration Panel with integrated OXYvisor, designed for use in Merox processes.

Figure 9



Part #B6001-1293 Sample system flow diagram.

Application Note
Merox Process - pH and O_2

Summary

Barben Analytical pH and oxygen measurement products offer many benefits for improved measurement in the Merox process.

pH Measurement

- Less frequent cleaning and calibration intervals
- High pH measurement accuracy
- Increased sensor lifespan
- Less MRO inventory

Oxygen Measurement

- Increased reliability versus competing technology
- Reduced analyzer complexity
- Fully integrated sampling solutions

Hazardous Area Approvals

IEC Ex, ATEX, NA - Zone 1 & Zone 2 IIC
cULus (NRTL) - Class I, Div 2, Groups A, B, C, D T4

Contact Us

Barben Analytical is a leading supplier of analytical measurement technology targeting the industrial marketplace. It is a wholly owned subsidiary of AMETEK, Inc., a leading global manufacturer of electronic instruments and electromechanical devices.

AMETEK has over 15,000 colleagues at more than 120 manufacturing locations around the world. Supporting those operations are more than 100 sales and service locations across the United States and in 30 other countries around the world.

Barben Analytical
5200 Convair Drive
Carson City, NV 89706 USA

Toll Free: +1-800-993-9309
Phone: +1-775-883-2500
Fax: +1-775-883-6388
Email: Sales.Barben@Ametek.com
Web: BarbenAnalytical.com

Barben Analytical reserves the right to make technical changes or modify the contents of this document without prior notice. We reserve all rights in this document and in the subject matter and illustrations contained within.

Merox is a registered trademark of UOP (a Honeywell Company)
Kynar is a registered trademark of Elf Atochem North America Inc.
Kalrez is a registered trademark of DuPont, Inc.
Hastelloy is a registered trademark of Haynes International, Inc.

© 2020, by AMETEK, Inc. All rights reserved • BA-APP-MEROX-20RB