Hydrogen Detection **in Oil Refineries**

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MSA Gas Detection: Hydrogen Gas Detection in Oil Refineries

Oil refineries are large producers and consumers of hydrogen gas. Hydrogen plays a pivotal role in many refining operations, from hydrocracking—reduction of heavy gas and gas oils to lower molecular weight components—to treatment of gas streams, to catalytic reforming. In the latter, the gas is also used to prevent carbon from reacting with the catalyst to maintain production of lighter hydrocarbons and to extend catalyst life. Not surprisingly, refineries use large volumes of hydrogen that may be produced on site or purchased from hydrogen production facilities.

Demand for hydrogen is growing. Changes to gasoline and diesel fuel specifications prompted by environmental legislation have resulted in greater hydrogen use for improving the grade of gasoline. At the same time, higher crude oil prices have enhanced commercial prospects of heavier crudes, requiring new investments in conversion processes and more extensive hydrotreating and hydrocracking applications.

Scale and growth of hydrogen demand raise fundamental questions concerning safe hydrogen use. Hydrogen's chemical properties pose unique challenges within the processing plant environment. Hydrogen gas is colorless, odorless and is not detectable by human senses. It is lighter than air and hence difficult to detect where accumulations cannot occur, nor is hydrogen gas detectable via infrared gas sensing technology. Added to challenges of detection are safety risks posed by hydrogen gas itself.

In this paper, we provide a practical approach for deployment of fire and gas detectors that maximize detection efficiency. This approach is based upon the notion that any single detection technique cannot respond to all hazardous events and consequently, risk of detection failure is reduced by deploying devices that offer different strengths and limitations.

Improved Safety through Diversity

Hazards associated with hydrogen include respiratory ailments, component failure, ignition, and burning. Although a combination of hazards occurs in most instances, hydrogen's primary hazard is production of a flammable mixture that can lead to fire or explosion. As hydrogen's minimum ignition energy in air at atmospheric pressure is approximately 0.2 mJ, hydrogen is easily ignited.

In addition, hydrogen can produce mechanical failure of containment vessels, piping and other components due to hydrogen embrittlement. Long-term hydrogen gas exposure may result in some metals and plastics loss of ductility and strength, leading to formation of cracks and eventually, possible ruptures. A form of hydrogen embrittlement takes place via chemical reaction; at high temperatures, hydrogen reacts with one or more components of metal walls to form hydrides that weaken the material's lattice structure.

In oil refineries, the first step in fire escalation and detonation is loss of gas containment. Hydrogen leaks are typically caused by defective seals or gaskets, valve misalignment or failures of flanges or other equipment. When released, hydrogen diffuses rapidly. If the leak occurs outdoors, cloud dispersion is affected by wind speed and direction and can be influenced by atmospheric turbulence and nearby structures. With gas dispersed in a plume, detonation can occur if the hydrogen and air mixture is within explosion range and an appropriate ignition source is available. Such flammable mixture can form at considerable distance from the leak source.

In order to address hazards posed by hydrogen, fire and gas detection system manufacturers work within the construct of layers of protection to reduce hazard propagation. Using such a model, each layer acts as a safeguard, preventing the hazard from becoming more severe. *Figure 1* illustrates a hydrogen gas leak hazard propagation sequence.

Hazard Sequence for Hydrogen Disposal				
Equipment Rupture	Gas Dispersal	Ignition	Fire/Explosion	Property Damage Personal Injury

Figure 1. *Hazard sequence for hydrogen dispersal. Layers of protection separate each hazard state.*

Detection layers encompass different detection techniques that either improve scenario coverage or increase the likelihood that a specific hazard type is detected. Such fire and gas detection layers can consist of catalytic sensors, ultrasonic gas leak monitors and fire detectors (*Figure 2*). Ultrasonic gas leak detectors can respond to high pressure releases of hydrogen, such as those that may occur in hydrocracking reactors or hydrogen separators. In turn, continuous hydrogen monitors such as catalytic detectors can contribute to detection of small leaks, for example, due to a flange that is slowly deformed through use or failure of a vessel maintained at close to atmospheric pressure. To further protect a plant against fires, hydrogen-specific flame detectors can supervise entire process areas. Such wide coverage is necessary; due to hydrogen cloud movement, a fire may ignite at considerable distance from the leak source.

When a containment system fails, hydrogen gas escapes at a rate that is proportional to orifice size and internal system pressure. Such leaks can be detected using ultrasonic monitors that detect airborne ultrasound produced by turbulent flow above a pre-defined sound pressure level. Using ultrasound as a proxy for gas concentration is a major advantage of this technique, as ultrasonic gas leak detectors do not require transport of gas to the sensor element to detect gas, and are unaffected by leak orientation, gas plume concentration gradient and wind direction. Such features enable ultrasonic gas leak detectors to be an ideal choice for supervision of pressurized pipes and vessels in open, well ventilated areas. Ultrasonic gas leak detectors supervise areas for noise higher than 24 kHz. Frequencies in the audible range, spanning approximately 20 Hz to 20 kHz, are removed by a band pass filter. Another advantage of these instruments is their wide coverage area per device. Depending upon the level of background ultrasound, for example, a single detector can respond to a small hydrogen leak at approximately 8 m from the source. As illustrated in *Figure 3*, even small leaks can generate sufficient ultrasonic noise to afford detection within most industrial environments. While audible acoustic noise typically ranges between 60 and 110 dB in industrial sites, ultrasonic noise levels (frequency range of 25-100 kHz) span from 68 to 78 dB in high noise areas where rotating machinery such as compressors and turbines are installed, and rarely exceed 60 dB within low noise areas. Consequently, ultrasonic gas leak detectors can detect hydrogen leaks without being affected by background noise. And as instruments respond to the gas release rather than the gas itself, instruments can alarm rapidly, often within milliseconds.

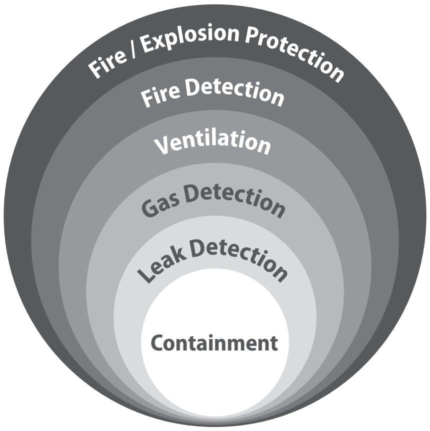

Figure 2. *Schematic of protective barriers for a hydrogen accident sequence*

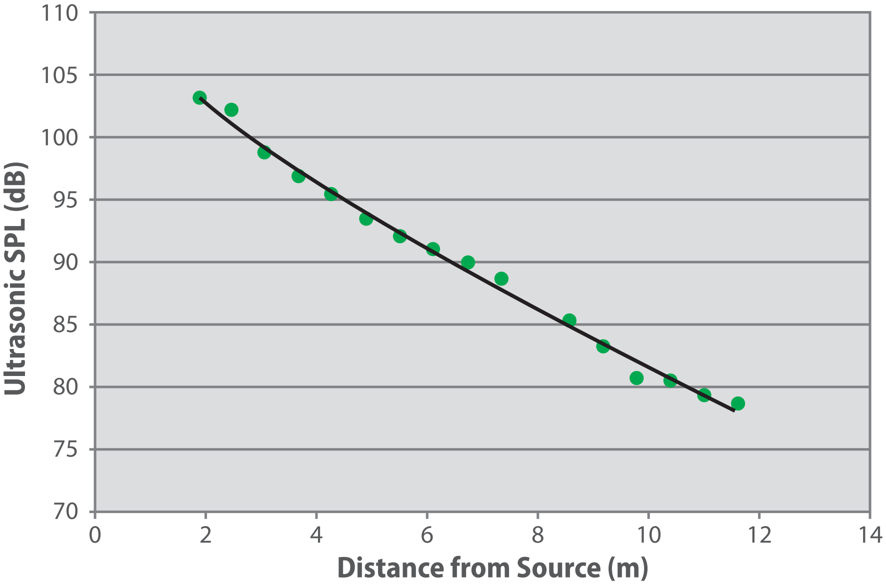

Figure 3. *Sound pressure level as a function of distance for hydrogen leaks. Leak size = 1 mm-diameter orifice, differential pressure = 5,515 kPa (800 psi), leak rate = 0.003 kg/s. The curve is to guide the eye.*

A second protective measure is direct gas detection using catalytic combustible gas detectors, used for hydrogen applications for more than 50 years. These sensing devices consist of a pair of platinum wire coils embedded in a ceramic bead. The active bead is coated with a catalyst; the reference bead is encased in glass and consequently is inert. Upon exposure to hydrogen, the gas begins to burn at the heated catalyst surface per the reaction: $2H_2 + 2O_2 \rightarrow 2H_2O + O_2$.

Hydrogen oxidation releases heat, causing the wire's electrical resistance to change. This resistance is linear across a wide temperature range (~ 500 – 1,000° C) and proportional to concentration. For hydrogen-specific catalytic detection, the reaction temperature and catalyst are tailored to prevent combustion of hydrocarbons in the substrate. This scenario's simplicity enables catalytic detectors to be suitable for many applications. Where gas accumulations can occur, catalytic sensors can establish hydrogen presence with fair accuracy and repeatability. Hydrogen-specific catalytic detectors also provide fast response times, typically 5 to 10 seconds, and offer good selectivity. These parameters vary widely among sensor manufacturers, but are generally tailored for maximum selectivity and speed of response. As referenced earlier, hydrogen cannot be detected by infrared absorption, allowing catalytic detection to be a highly reliable technology for hydrogen gas detection.

In addition to catalytic and ultrasonic gas leak detectors, hydrogen-specific flame detectors add another barrier against hydrogen hazard propagation. These instruments simultaneously monitor infrared and ultraviolet radiation at different wavelengths. Radiation is emitted in the infrared by water molecules created by hydrogen combustion; emission from such heated water or steam is monitored in the wavelength span from 2.7 to 3.2 mm. An algorithm that processes IR radiation modulation allows these detectors to avoid false signals caused by hot objects and solar reflection. The UV detector is typically a photo discharge tube that detects deep UV radiation in the 180 to 260 nm wavelength range. Due to absorption by the atmosphere, solar radiation at these wavelengths does not reach the earth's surface; thus the UV detector is essentially immune to solar radiation. This combination of IR and UV detection improves false alarm immunity, while producing detectors that can detect even small hydrogen fires at a range of 5 m. *Figure 4* shows the detection range of a hydrogen-specific flame detector for a plume 15 – 20 cm (6 – 8 inches) high and 15 cm (6 inches) in diameter. As observed in this case, the flame detector can detect the on-axis range of 4.6 m (15 ft) up to ± 55°, providing broad angular coverage.

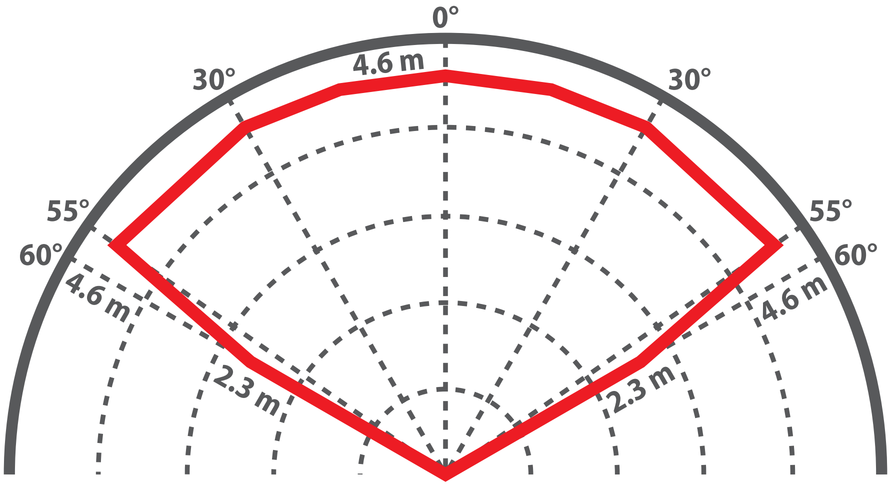

Figure 4. *Detection range of a MSA FlameGard UV/IR – H_2 Detector.*
Size of hydrogen fire: 15 cm (6 in) diameter and 15 – 20 cm (6 – 8 in) high.

Ultrasonic gas leak detection, catalytic gas detection and hydrogen flame detection have different strengths and vulnerabilities, and respond to different hazard manifestations —whether the gas, the source of the gas or the fire. Further, each technology operates in a different area of regard, with catalytic detectors as point instruments and ultrasonic leak detectors and hydrogen flame detectors as area monitors. As for their unique properties, the combination of detectors increases the odds that hydrogen gas dispersal or fire is identified early on, either before ignition or when an explosion occurs.

An illustration of the use of these technologies can be found in catalytic reforming*. In this process, a stream of heavy gas oils is subjected to high temperature (480 – 524°C) and pressure (1,379 – 3,447 kPa; 200 – 500 psi) and passed through a fixed-bed catalyst. Upon reaction, the oils are converted to aromatics that yield much higher octane ratings for gasoline. Because of operating conditions and continuous hydrogen production, a rupture in the reactors, separator or pipe system of the unit can have grave consequences. *Figure 5* shows the detector allocation across a reforming unit.

Of course, the scheme shown in this example does not preclude use of other detection systems, nor does it eliminate the need for operating procedures, instrumentation and control systems and adequate training, all necessary for safety. Condition monitoring instruments such as x-ray pipe testing equipment play a pivotal role in spotting defects before loss of pipe network integrity. Likewise, thermal conductivity sensors can ensure detection coverage within oxygen deficient environments and thus complement catalytic sensors when used above the LEL. Experience suggests that choice of detection instruments must be carefully weighed to match hazard types associated with the particular refinery's chemical process and that each detection type offsets vulnerabilities of the other.

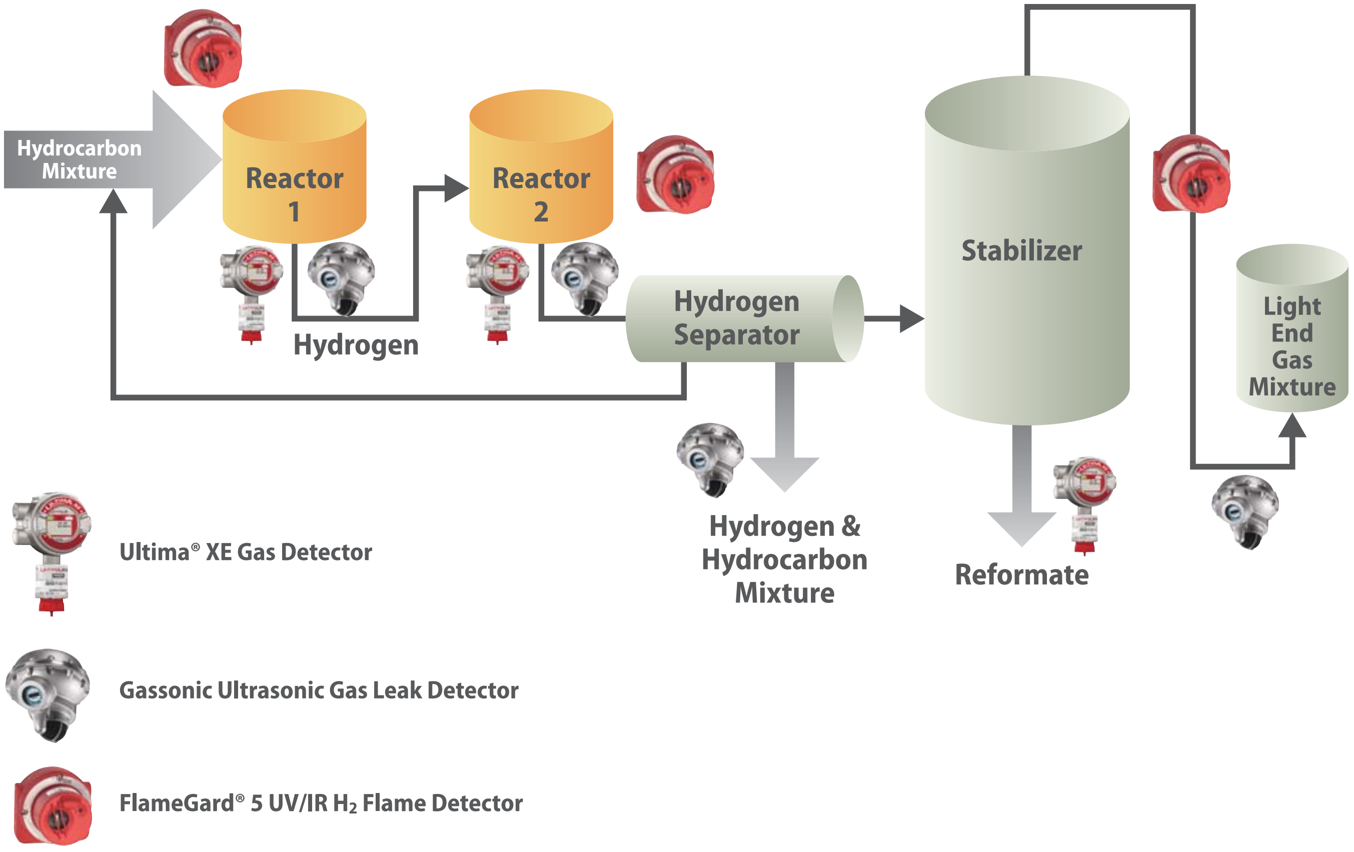

Figure 5. *Schematic of dual-stage reforming unit showing possible locations of gas and flame detectors.*

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* *Berger, W. D. and Anderson, K. E., Modern Petroleum: A Basic Primer of the Industry, Second Edition, PennWell Publishing, Tulsa, Oklahoma, 1981.*

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Conclusion

Hydrogen production continues to grow, fueled by environmental legislation and demand for cleaner, higher grade fuels. However, rising production must be matched by a comprehensive approach to plant safety. New facilities that use hydrogen should be designed with adequate safeguards from potential hazards; the design of old facilities should also be revisited to ensure that sufficient barriers are available to minimize accidents and control failure. Safety systems that deploy a diversity of detection technologies can counteract possible effects of leaks, fire and explosions, preventing equipment or property damage, personal injury and loss of life.

A combination of catalytic and ultrasonic gas leak monitors and fire detectors is particularly effective because they are complementary. Vulnerabilities of one are offset by strengths of the others; hazards have fewer chances to propagate undetected. Such diverse safety systems, combined with design that prevents leakage and eliminates possible ignition sources, offer a sound approach for managing hydrogen processes.

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