

# Hydrogen Detection in Oil Refineries



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Oil refineries are some of the largest producers and consumers of hydrogen gas. Hydrogen plays a pivotal role in a whole host of refining operations, from hydrocracking – the reduction of heavy gas and gas oils to lower molecular weight components – to the 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 the production of lighter hydrocarbons and extend the life of the catalyst. Not surprisingly, refineries use large volumes of hydrogen, which may be produced on site or purchased from hydrogen production facilities.

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

The scale and growth of hydrogen demand raises fundamental questions about the safe use of the gas. Due to its chemical properties, hydrogen poses unique challenges in the plant environment. Hydrogen gas is colorless, odorless, and not detectable by human senses. It is lighter than air and hence difficult to detect where accumulations cannot occur. Nor is it detectable by infrared gas sensing technology. Coupled with the challenge of detection are the safety risks posed by the gas itself.

In this note we offer a practical approach for the deployment of fire and gas detectors that maximizes detection efficiency. The approach is based on the notion that any one detection technique cannot respond to all hazardous events; and consequently, the risk of detection failure is reduced by deploying devices that have different strengths and limitations.

## Improved Safety through Diversity

There are several hazards associated with hydrogen, ranging from respiratory ailment, component failure, ignition, and burning. Although a combination of hazards occurs in most instances, the primary hazard with hydrogen is the production of a flammable mixture, which can lead to a fire or explosion. Because its minimum ignition energy in air at atmospheric pressure is about 0.2 mJ, hydrogen is easily ignited.

In addition to these hazards, hydrogen can produce mechanical failures of containment vessels, piping, and other components due to hydrogen embrittlement. Upon long term exposure to the gas, many metals and plastics can lose ductility and strength, which leads to the formation of cracks and can eventually cause ruptures. A form of hydrogen embrittlement takes place by chemical reaction. At high temperatures, for instance, hydrogen reacts with one or more components of metal walls to form hydrides, which weaken the lattice structure of the material.

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

In order to address the hazards posed by hydrogen, manufacturers of fire and gas detection systems work within the construct of layers of protection to reduce the incidence of hazard propagation. Under such a model, each layer acts as a safeguard, preventing the hazard from

becoming more severe. Figure 1 illustrates a hazard propagation sequence for hydrogen gas leaks.

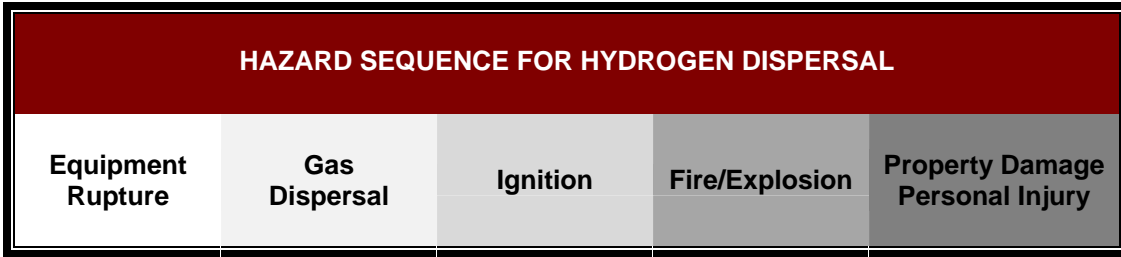


Figure 1. Hazard sequence for hydrogen dispersal. Layers of protection separate each hazard state.

The detection layers themselves encompass different detection techniques that either improve scenario coverage or increase the likelihood that a specific type of hazard 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 like catalytic detectors can contribute to detecting small leaks, for example, due to a flange slowly deformed by 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: Because of hydrogen cloud movement, a fire may be ignited at a considerable distance from the leak source.

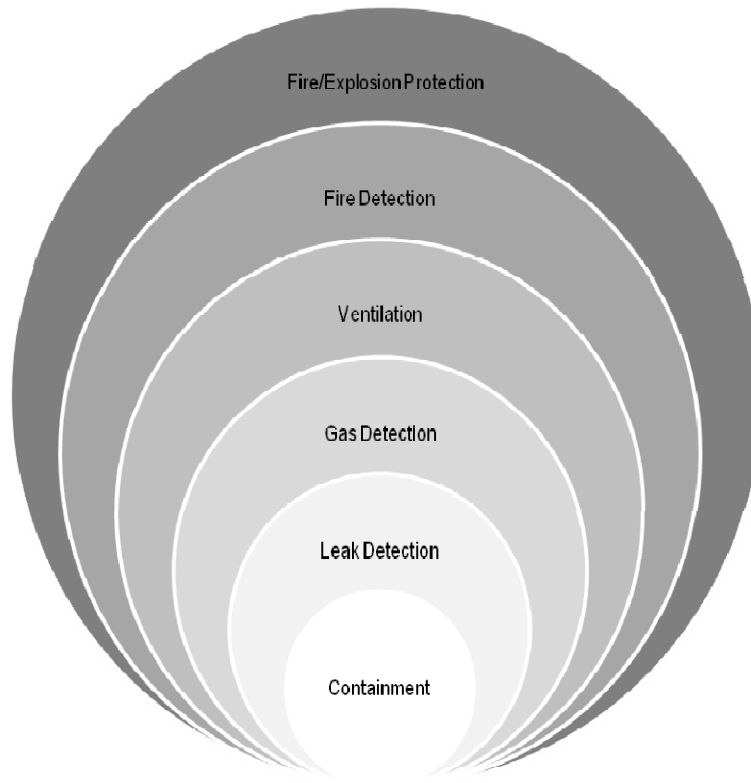


Figure 2. Schematic of protective barriers for a hydrogen accident sequence.

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

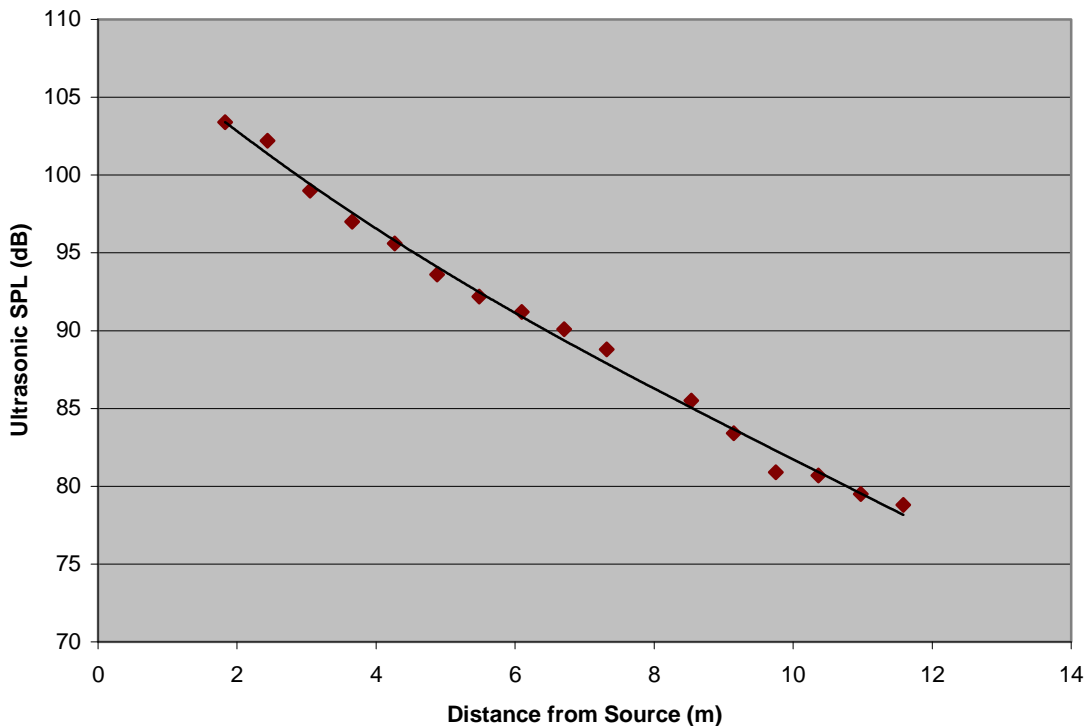


Figure 3. Sound pressure level as a function of distance for hydrogen leaks. Leak size = 1 mm-diameter orifice, differential pressure = 5,515 kPa (800 psi), leak rate = 0.003 kg/s. The curve is to guide the eye.

A second measure of protection is the direct detection of the gas by means of catalytic combustible gas detectors. They have a long pedigree and have been 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, while the reference bead is encased in glass, and consequently, is inert. Upon exposure to hydrogen, the gas begins to burn at the heated surface of the catalyst per the reaction:  $2\text{H}_2 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

The oxidation of hydrogen releases heat, which causes the electrical resistance of the wire 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 the combustion of hydrocarbons in the substrate. The simplicity of this scheme makes catalytic detectors suitable for many applications. Where gas accumulations can occur, catalytic sensors can establish the presence of hydrogen with fair accuracy and repeatability. Hydrogen-specific catalytic detectors also have fast response times, on the order of 5 to 10 seconds, and offer good selectivity. These parameters vary widely among the various manufacturers of these sensors, but are generally tailored for maximum selectivity and speed of response. As pointed out earlier, hydrogen cannot be detected by infrared absorption. This makes catalytic detection one of the most reliable technologies for the detection of hydrogen gas.

Along with catalytic and ultrasonic gas leak detectors, hydrogen-specific flame detectors add another barrier against the propagation of hydrogen hazards. The instruments simultaneously monitor infrared and ultraviolet radiation at different wavelengths. Radiation is emitted in the infrared by the water molecules created by the combustion of hydrogen; the emission from such heated water or steam is monitored in the wavelength span from 2.7 to 3.2  $\mu\text{m}$ . An algorithm that processes the modulation of IR radiation 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  $\pm 55^\circ$ , providing broad angular coverage.

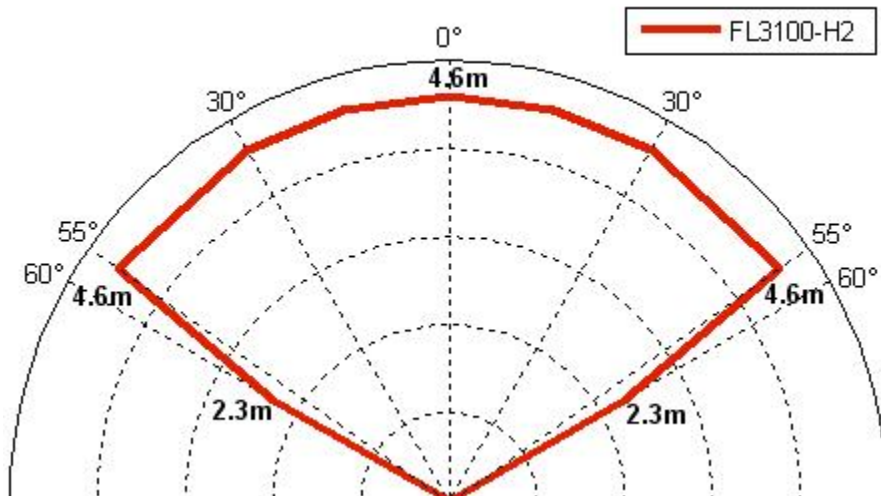


Figure 4. Detection range of a General Monitors FL3100 UV/IR – H<sub>2</sub> detector. Size of hydrogen fire: 15 cm (6 in) diameter and 15 – 20 cm (6 – 8 in) high.

Ultrasonic gas leak detection, catalytic gas detection, and hydrogen flame detection have different strengths and vulnerabilities, and respond to different manifestations of the hazard – 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 of 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<sup>1</sup>. 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, which yield much higher octane ratings for gasoline. Because of the operating conditions and the continuous production of hydrogen, 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.

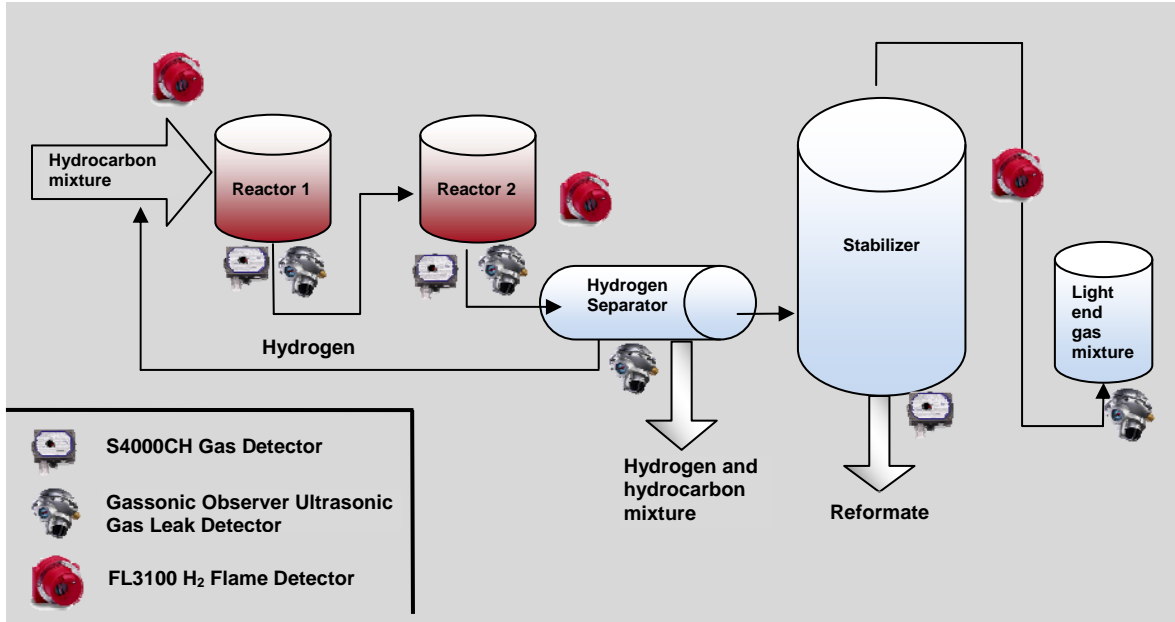


Figure 5. Schematic of dual-stage reforming unit showing possible locations of gas and flame detectors.

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

### Conclusion

Hydrogen production will continue to grow, fueled by environmental legislation and demand for cleaner, higher grade fuels. But 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 sufficient barriers are available to minimize accidents and control failure. Safety systems that deploy a diversity of detection technologies can counteract the possible effects of leaks, fire and explosions, preventing equipment or property damage, personal injury, and loss of life.

<sup>1</sup> Berger, W. D. and Anderson, K. E., *Modern Petroleum: A Basic Primer of the Industry*, Second Edition, PennWell Publishing, Tulsa, Oklahoma, 1981.

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

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