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Fuel cells and odorants for hydrogen

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Abstract

Odorants have been proposed as a reliable, inexpensive means to enable leak detection for hydrogen systems and increase public safety. However, traditional odorants cause problems for fuel cell systems. This paper examines the use of odorants for fuel cell systems, including the hydrogen storage. Current odorants and potential odorants have negative impacts on fuel cell performance. Odorants also appear to be problematic for most of the advanced hydrogen storage options. If odorants are used, the odorants will probably need to be removed from the hydrogen prior to the storage medium. Current hydrogen detectors are more reliable than the odorant–human detection system and should provide increased safety.

Keywords: Hydrogen; Odorant; Fuel cell; Hydrogen storage

1. Introduction

One of the main concerns with transitioning to a hydrogen economy is safety. The wide flammability range for hydrogen–air mixtures combined with the perceived difficulty in preventing hydrogen leakage has led some to propose that it will be necessary to add odorants to hydrogen similar to those used in natural gas and propane, to allow for easy detection of leaks and afford the public an acceptable measure of safety. However, the use of odorants for leak detection has its limitations. In addition, sulfur-based odorants used in natural gas have detrimental effects on fuel cell performance and on several high capacity hydrogen storage systems. This paper will address the use of odorants for leak detection in general, the potential for odorants for leak detection of hydrogen, the effects of potential odorants on fuel cell system performance, and alternative technologies to hydrogen leak detection.

2. A brief history of odorants in natural gas and LPG

The hazards of colorless, odorless gases are readily apparent, and were probably first realized by miners. Leaks of these gases can go undetected until the gas concentration builds up to toxic or explosive levels. The earliest solutions to this problem were crude. Candles were used for lighting and as detectors in mines. The candles on miners caps or carried by the miner would either go out from the lack of oxygen or the flame would get larger with a different coloring of the flame if certain gases were in the area. The open flames sometimes "detected" an explosive gas mixture, with fatal results. A more successful technique utilized canaries as small, portable gas detectors. Canaries were brought down into the mines in small cages. When the canary detector "sensed" coal gas, the canary would stop chirping (and likely die), and the miners knew there was a problem, and could head for the exits.

As we became more industrialized, coal gas, city gas, fuel gas and natural gas use increased. In an effort to aid in the detection of leaks of these gases, investigators began utilizing odorants. In the early 1900s work was being performed to develop an odorant for fuel gas. Several odorant products were developed, including amyl mercaptan. Some municipalities located near the industrial or natural gas producers would often utilize side streams of the unodorized gas. In 1937, an explosion occurred in a school utilizing unodorized residue gas for heating, killing 294 school children. After this tragedy, regulations were introduced requiring the use of odorants in gas [1].

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3. How odorants work

Odorants are chemicals that stimulate the olfactory sense. Although the human olfactory system is less complicated than those of most other animals, we can still detect some odorants in concentrations less than one part per trillion in air. The human perception of odor is quantified by the minimum level detectable and the minimum level identifiable. The minimum level detectable is the lowest concentration a certain specified percentage of the population (usually 50%) is aware of an odor without necessarily recognizing it. The recognition threshold is the minimum concentration recognized by a specified percentage of the population as having the characteristic odor quality. At the detection and recognition thresholds there will be a large number of individuals who do not detect or recognize the odor. Data indicate that the recognition threshold is approximately 10 times the detection threshold for many odorant compounds [2]. An additional factor of 10 is often used as a safety factor to account for differences in sensitivity among the population.

Natural gas and liquified petroleum gas (LPG: mainly propane and other hydrocarbons that can be liquefied under moderate pressure at normal temperature but are gaseous under atmospheric pressure) are now odorized with unpleasant smelling sulfur-containing molecules. The National Fire Protection Association (NFPA) has a requirement that LPG be odorized by the addition of a warning agent of such character that they are detectable by a distinct odor, down to a concentration in air of not over one-fifth of the lower limit of flammability. For natural gas, the lower flammability limit is 5.3%; for hydrogen, 4%; and for LPG ~1.9–2.2%. For LPG the requirement is that concentrations of ~0.4% of propane in air should be detectable. In other countries, the restrictions are more stringent. In Japan, the regulations require that when city gas or LPG leak into the air they can be detected at a ratio of gas to air of $\frac{1}{1000}$, i.e. a concentration of 0.1% [2].

A common odorant for LPG is ethyl mercaptan. The NFPA states that experience has shown a concentration of ethyl mercaptan in LPG of 1 lb per 10,000 gallons of liquid LPG has been recognized as an effective odorant to meet the requirements [3], (ethyl mercaptan concentration of ~25 ppmw). Many companies utilize a higher concentration as an additional safety measure. The NFPA requirements to detect at $\frac{1}{5}$th the lower flammability limit would require detection at concentrations of 1% and 0.8%, respectively, while the Japanese standard would require detection at about an order of magnitude lower concentration, 0.1%. To meet the Japanese requirements, the odorant in the gas must be present at a concentration 1000 times greater than the detection threshold.

An important aspect of the use of odorants in natural gas and LPG is that in the intended uses of the gas, the odorants are chemically changed, and converted to less-or-nonodorous materials. During combustion, the mercaptans are oxidized, and the effluent from the combustor is free from the odor imparted to the fuel gas by the odorant. Therefore, there is no interference to the detection of a leak by the exhaust gas from the process.

4. Advantages of odorants

Odorants allow for detection of a leak without any external equipment. The end user does not have any responsibility for maintaining equipment and, therefore, it is believed that equipment failures will not lead to undetected leaks. In addition, odorants allow for leak detection in locations where it may be difficult to place detectors, such as outdoor locations. Odorants can be used in small concentrations due to the sensitivity of the human olfactory system.

5. Limitations of odorants

Though addition of odorants to LPG and natural gas has improved safety and is a proven means of leak detection, the use of odorants has its limitations and disadvantages. The first limitation is detection. For an odor to be detected, someone needs to be in the vicinity to detect the odor. Even if someone is present, not all people detect the odors at the same odorant concentrations, and some individuals cannot detect the odor at all. Within an individual, the ability to detect an odor varies in time due to factors such as allergies, the common cold, exposure to other odors, whether they are awake or asleep, etc. The result of these limitations is that leaks in unoccupied areas will go undetected and detection of leaks in occupied areas will vary depending on the severity of the leak and the sensitivity of the person in that particular area at that particular time. For example, leaks in occupied areas during sleeping hours can go undetected.

Differences in the chemical and physical properties of the odorants and the fuel also lead to another limitation in their use. Odorants can be separated from the gas mixture by adsorption or other physical and chemical processes. In the case of hydrogen, there can be separation of the odorant from the hydrogen due to differences in adsorption, boiling and freezing points, permeation rates, and buoyancy factors. Differences in adsorption can separate the odorant from the fuel. This can be a problem if an adsorbent is used for hydrogen storage, but can also be problematic for cases of leaks in buried piping, depending on the odorant used and the composition of the soil. Differences in boiling and freezing points can lead to separation of the odorant from hydrogen when cryogenic hydrogen storage techniques are utilized. Hydrogen, due to its small molecular size, permeates much more readily through many materials than other larger gases such as those likely to be used as odorants. Permeation losses through some materials could lead to a build up of hydrogen to flammable levels, while the odorant would still be contained.

A third limitation with odorants is that they can have a negative impact on the end use of the fuel. In combustion technologies, odorants have little or no effects on the performance of the system. However, they do have an environmental impact, leading to emissions of sulfur oxides. In fuel cell systems, common odorants have a large negative impact on performance.