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20 ppm Anhydrous Ammonia Odor Agent Proposed for Hydrogen Fuel for Safe Detection of Leaks

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Abstract

Preferably 20 ppm anhydrous ammonia (NH_3) is proposed to be added to hydrogen fuel (H) made from renewable energy sources (green hydrogen), so that H leaks may be easily detectable by smell, but not dangerously toxic. Including this odor agent, would allow H to be distributed safely in pipes, as required by law, and it would allow H to be safely stored, transported, and exported for sale, and widely commercialized. Further research is suggested to identify optimum pressure, temperature, and automated technique for injecting NH_3 into H, and to chart the minimum concentration needed, as a function of temperature and humidity. An application to make hypersonic H burning aircraft safer for ground maintenance crews is proposed. An ability to make, store and distribute H, made from local sources of renewable energy, would reduce a need for fossil fuels, especially in poor, remote communities, where it could improve their economy by creating an export product for sale, while reducing pollution.

Keywords

Hydrogen, Renewable Energy, Anhydrous Ammonia, Hydrogen Gas Distribution System, Odorant, Odor Agent, Green Hydrogen, Hypersonic Aircraft

1. Introduction

Many remote locations of our planet are blessed with abundant natural, renewable energy sources, but electric power transmission lines from there to populated areas, where there is high demand for energy are not feasible, and electrical energy

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cannot be stored long-term in batteries. Such energy may be converted and stored in the form of hydrogen fuel (H). However, commercialization of H has been delayed, because some detectable odor agent or natural odor is required by law to be present in any fuel distribution system and mercaptans and other organic aromatic odor agents have molecular weights that are too heavy, relative to H, to travel with H, and to allow detection of H leaks by odor. Another problem has been that a flame of burning H is pale and difficult to see. At Quartz Media LLC, Akshat Rathi reported, Cadent, the biggest British gas distribution company, has proposed spending £600 million ($800 million) to test providing hydrogen, instead of natural gas, through the same pipes [1]. Also reported, therein, is an A$5 million (US $4 million) trial in Adelaide, Australia to produce hydrogen from excess wind or solar cell electricity, and to inject it into the gas grid, and Northern Gas Networks' £2-billion plan to convert all domestic users in Leeds, England to hydrogen [1]. Smeets *et al.* reported a mean odor detection threshold for ammonia to be 2.6 ppm [2]. However, no odor agent has been used, commercially, with H. At present, storing, transporting and burning H is considered too dangerous for public use. Therefore, there is a need to find an additive that adds an odor and travels well in H, so that leaks may be detected by smell, and to make a flame of burning H more easily seen at concentrations, which are not toxic.

2. Proposals to Use NH_3 as Odor Agent in Hydrogen Fuel

Renewable, clean energy such as solar, wind, magma, river, wave, tidal power, etc. may be converted into electrical power, and excess electrical power may be used to make hydrogen fuel (H), locally, by electrolysis from either water or methane or by steam-cracking methane or ammonia. It is proposed to add 20 ppm to 100 ppm, and preferably 20 ppm, of anhydrous ammonia (NH_3), as an odor agent, to this H to allow detection of leaks by smell by humans, and to satisfy laws, which require an odor agent in fuels in a distribution system. Ethyl mercaptan (CH_3CH_2SH), commonly used as odorant in natural gas and propane, is too big, having mass of 62 atomic mass units (amu), compared with 17 amu for NH_3. Anhydrous ammonia (NH_3) is about half the weight of air. Kanezashi discovered, NH_3 has kinetic diameter of 0.33 nm, which is comparable to 0.29 nm for that of molecular hydrogen [3]. **Figure 1** shows that hydrogen bonding of HN_3 with diatomic hydrogen is weak, even in liquid phase. Having twice the bond-length of covalently bonded hydrogen atoms, such weak bonding would be easily broken with heat, pressure, and agitation, as the fuel is pushed along a hydrogen fuel distribution system, so that the NH_3 molecule would be carried freely with the fuel. Hydrogen bonding is not prevalent in the gaseous phase, and is only a concern in the liquid phase at low temperatures and high pressures. For these reasons, NH_3 would travel well, and much better than CH_3CH_2SH, with H gas. Since it has no carbon atoms, it would leave no carbon soot residue, unlike mercaptans.

In a leaking H distribution system, NH_3 would diffuse rapidly upward into the

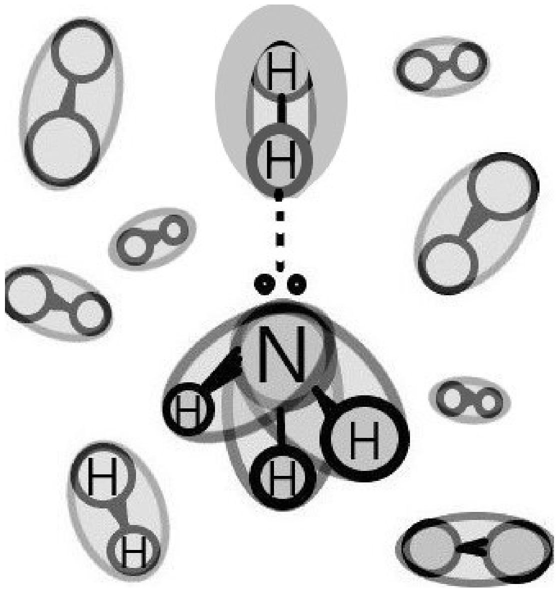

Figure 1. 3-D perspective drawing of one anhydrous ammonia (NH_3) molecule suspended among many diatomic molecules of hydrogen. The dashed line represents weak hydrogen bonding between NH_3 and one molecule of diatomic hydrogen. The elongated, shaded ellipse shows how a filled electron shell of the ammonia molecule, indicated by the 2 dots on top of it, pushes away the electron cloud of the hydrogen molecule, and induces a weak polarization on it, which enables weak hydrogen bonding in liquid phase.

surrounding air with the leaking H gas for quick and easy detection. If there is water vapor in the surrounding air, then some of this NH_3 would form the hydrate, $NH_3 \cdot H_2O$, which is commonly, but incorrectly, called, ammonium hydroxide, in proportion to such humidity. Since this hydrate is heavier than air and also detectable by smell, it would remain at lower levels, and serve to alert people to an H leak down there, too.

A mean odor detection threshold for ammonia, reported by Smeets *et al.*, in accordance with European Committee for Standardization guidelines in context of odor regulations, is 2.6 ppm [2]. So, after 20 ppm concentration of NH_3 in fuel is diluted, due to a leak into surrounding air 5 times in volume, to one-fifth of this concentration or 4 ppm, the sharp, pungent, characteristic smell of ammonia would be easily detectable in enclosed spaces. NH_3 in concentrations greater than 140 ppm in air is well-known, to produce not only a sharply pungent smell, but also a gaging, asphyxiating sensation. Therefore, a concentration of ammonia should never be higher than 140 ppm. When NH_3 in the range of 20 ppm to 100 ppm burns with H in a flame, it has no detectable odor. This is thought to be due to the high flame temperature of burning hydrogen in air of 2210˚C, which is much higher than the auto-ignition temperature of ammonia of 651˚C. The Occupational Safety and Health Administration (OSHA) limit for NH_3 is 25 ppm in air in a time-weighted average over eight hours. So, escaping NH_3 from a leak in an H distribution pipe would diffuse into surrounding air, where it would be greatly diluted from its concentration in the pipe. At low temperature and high pressure, or both, some of the ammonia precipitates from vapor to liquid phase, reducing its effectiveness, as odor agent. Sufficient amount must be added to H, such that a final concentration of ammonia vapor in leaking H, depending on temperature and humidity, is at least 5 ppm. For these reasons, NH_3 concentration range in fuel is recommended to be 20 ppm to 100 ppm, so that a final concentration, due to a leak diffusing into surrounding air, would be less than the OSHA limit of 25 ppm for safe, breathable air, and so that it would be above 5 ppm, after dilution in air, to allow such a leak to be easily detectable by smell by people.

NH_3, acting as an impurity in burning H, adds a golden color, which makes a flame of burning H more easily visible. This would help prevent burns. Additional elements, such as strontium, giving a red flame, or copper, giving a green flame, are proposed to be included at a site of a burner or as part of a burner alloy, as a colorant to fine-tune color and visibility of the flame to make burning of H for cooking, barbequing, and warming fires much safer than it is without any odorant or colorant.

It is proposed to include 50 ppm of NH_3 odorant to H to be burned by hypersonic aircraft that circulate their liquid fuel in the nose and leading edges to prevent them from melting. The concentration, in this case, is higher than the 20 ppm, proposed above, because either such aircraft would not be in an enclosed space, or they would be enclosed in a large hangar space, and much of the odorant would diffuse from a leak upward into the air, thus diluting it much more than in other commercial or domestic applications. Even in this liquid phase, hydrogen bonding, shown in **Figure 1** between NH_3 and H_2, or due to head-to-tail, daisy-chain hydrogen bonding with itself, would be disrupted by the high temperatures, pressures, and agitation occurring in hypersonic aircraft. So, this would not be a problem. This would enhance safety for ground maintenance crews by allowing early detection of leaks, while such aircraft are being serviced and tested. Automated electronic detectors connected to alarms are recommended to be required in all hydrogen fueled aircraft maintenance areas, but they can fail, lose power, and can go out of calibration, and they may be poorly located at a distance from where a leak may occur. For this reason, an odor agent is needed.

3. Discussion

The last thing one would think of when searching for an odor agent would be the inorganic, noxious, toxic chemical, anhydrous ammonia, because strong-smelling odorants are usually either aromatic carbon ring molecules or sulfur-containing molecules. But, for suspension with such a small molecule as diatomic hydrogen, there is no other choice, which would be small enough to be compatible. There are certain applications where odor agents and colorants are not recommended and not needed to be added to H, such as for use in rockets, hair-spray, and fuel-cell H engines, including those powering automobiles, ships, aircraft, and generators, because H fuel-cell polymer electrolyte membranes (PEM) are destroyed in the presence of even trace levels of ammonia, as low as 0.1 ppm, and because such engines would not be attached to H distribution systems, but would have separate, on-board H storage tanks. However, NH_3 may be used with alkaline H fuel-cells. Automated electronic sniffers connected to alarms are recommended to be used, as a backup safety measure, where H is used, because humans become less sensitive to odors over time, and people may think, incorrectly, that there is no longer any leak. Such detectors are widely available on the market for both NH_3 and H, but they may fail, lose battery power, and go out of calibration. Some people cannot smell mercaptans or they mistake them for cooking odors, but humans are genetically designed to be immediately strongly repelled by the odor of NH_3, which is what makes this odorant most effective, as a warning that a leak exists.

4. Conclusions

Considering the maximum allowable amount of NH_3 in breathable air, according to OSHA, and the minimum concentration, which can be detected by smell by humans, it is proposed to include 20 ppm NH_3, as odor agent in H, which would allow H to be used more safely in fuel distribution systems, without creating a toxicity problem. This would accelerate the commercialization of hydrogen fuel (H), as a new, clean, safe renewable energy product, which would be of great economic benefit to people, especially those living in remote locations anywhere in the world with abundant natural renewable energy sources. This would provide a new source of clean energy for all. An ability to make their own fuel from such local renewable energy, and to store it long-term, means that people living in such remote areas could rely on it, and would not need to buy fossil fuels, such as diesel fuel, to run back-up generators, for example. Excess H made in this way could be exported and sold for profit. Further research and development are encouraged toward this goal.

Anhydrous ammonia can form cyclic and straight head-to-tail weak formal bond daisy chains, also known as hydrogen bonding, in the liquid phase, if the temperature is too low and if the pressure and concentration are too high, which may cause it to settle to the bottom. So, further research is suggested to identify the optimum pressure, temperature, and automated injection technique to ensure that this does not happen so that it can travel well in an H distribution system. Further research is also suggested to determine what, if any, agitation means may be needed for H containing NH_3 odorant in cold weather conditions or for long-term storage to ensure that such hydrogen bonding and settling either does not happen or that it can be reversed. Since NH_3 is so hydrophilic and hygroscopic, it may be used in industrial applications, where pure hydrogen is required, to remove water from H by means of hydrogen bonding with water and precipitating out. In this use, hydrated ammonia is much heavier than anhydrous ammonia, would sink, and could be removed easily. In the case that it is used as an odor agent in H, an equal amount of NH_3 should, then, be added to replace that which has precipitated out with water molecules. In hot weather with low humidity only 20 ppm NH_3 odorant may be needed, and in cold weather with high humidity much higher concentrations may be needed, because the sense of smell is better in hot, dry weather and is less sensitive in cold, wet weather. Further research is suggested to chart the minimum detectable concentration of NH_3 odorant, as a function of temperature and of humidity.

The proposed odor agent, anhydrous ammonia, unlike mercaptans, is, itself, a clean, renewable, energy-dense form of stored energy, and its reaction products are nitrogen (N_2) and water (H_2O), when burned (oxidized) at the high combustion temperature of hydrogen. So, NH_3 odorant would not diminish the clean, renewable nature of hydrogen fuel into which it would be added. In fact, when anhydrous ammonia (NH_3) burns, its hydrogen atoms are oxidized to form water, just as occurs with hydrogen fuel, itself. Replacement of fossil fuels with clean-burning, safe, odorized hydrogen fuel, made from local, renewable energy sources, would greatly reduce incidence of cancer, disease, sickness, and early death in people, while eliminating emission of greenhouse gases, such as methane, carbon dioxide, carbon monoxide, etc., from the drilling, refining, and burning of fossil fuels.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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