Hydrogen odorization

Status and challenges

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Status and challenges

Like natural gas, hydrogen is odorless by nature. This can cause dangerous situations, for example if a leak occurs. That is why hydrogen - just like natural gas - is given a scent, a so-called odorant. In this white paper we take a closer look at the odorization of hydrogen. What exactly is an odorant? What types of odorants are there? And how do we know whether a certain odorant is sufficient?

An odorant is a compound added to a gas to make it smellable. As a result, a leak can be quickly detected and action can be taken. The natural gas distributed in the Netherlands is also provided with an odorant. This gas is mainly intended for household and small business users.

Explosion limit

Odorization is paramount in the safety of natural gas. It is aimed at ensuring that the smell of gas can be detected well below the lower explosion limit. The lower explosive limit is the lowest concentration of a gas (expressed as a volume percentage) at which a vapor-air mixture could explode by ignition. Such an odorant must have a pungent, unpleasant and recognizable smell, so that the alarming effect is guaranteed. The lower explosion limit of the Dutch 'Groningen' natural gas is 4.7% by volume. For hydrogen, this is 4.1% by volume. Also in this respect, hydrogen and natural gas do not differ much from each other.

Odorization is mandatory

The addition of an odorant is mandatory in the Dutch gas distribution network in accordance with the 'Ministeriële Regeling Gaskwaliteit' (Ministerial Gas Quality Regulation). The gas distribution network is the network that is managed by one of the regional network operators Liander, Enexis, Stedin, Cogas, Westland or RENDO. The pressure in the distribution network varies between 30 mbar and 8 bar. All households in the Netherlands and a number of small business users are connected to the gas distribution network and therefore receive odorized gas.

Odorized or unodorized?

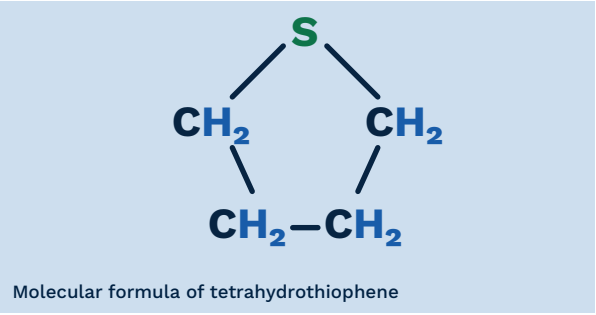
The gas in the Dutch main gas transport network (40 bar or 67 bar), which is managed by the national network operator Gasunie Transport Services, is provided with an odorant before it is transferred to the regional network operators. The odorant is added in the measuring and regulating stations. Large consumers, often in industry, who are connected to the national gas transport network can indicate whether or not they want to receive odorized gas, but in practice it is not always possible to choose. If a connection point is hooked up to the unodorized gas network, the customer must take its own safety measures, for example by using gas detection or by installing an odorizer itself.

Rotten eggs

Unodorized natural gas may have an odor. Although methane (the main component of natural gas) is odorless, there may be other compounds in natural gas with an odor. For example, higher hydrocarbons in natural gas have a slight odor that is not always experienced as unpleasant. There may also be small amounts of sulfur compounds, such as dihydrogen sulfide (H_2S) in natural gas. H_2S has an unpleasant odor that reminds many people of the stench of 'rotten eggs'. These and other sulfur compounds may be present in natural gas if the amount remains below a certain limit.

Tetrahydrothiophene

Not every type of natural gas is equally well smellable. In addition, the smell is not always the same and is not always perceived as repulsive and alarming. That is why a fixed amount of odorant is added to natural gas, so that it always smells the same. In the Netherlands we use the odorant tetrahydrothiophene, abbreviated as THT, for this. This is a sulfur-containing organic compound with the molecular formula C_4H_8S (see image below). This odorant is also used in countries such as Spain, France, Switzerland, Portugal, Greece, Norway and Poland.



Molecular formula of tetrahydrothiophene

Other odorants

Besides tetrahydrothiophene other odorants are also in use, mainly sulfur-containing compounds and often also mixtures of several sulfur-containing compounds. In England, for example, a mixture of tertiary butyl mercaptan and dimethyl sulfide is used. It is often impossible to find out why a gas transporter or distributor chooses a particular odorant. If an odorant suffices, this is generally not deviated from. After all, users are used to the smell and a change of odorant can lead to the smell not being recognized in the event of leaks or other calamities.

Environmental tax

When natural gas is burned, THT is completely converted into carbon dioxide, water and sulfur dioxide. Sulfur dioxide can cause acid rain. However, the amount of sulfur as a result of the addition of odorant is small. Due to measures such as the introduction of sulfur-free diesel and industry measures, sulfur dioxide emissions have fallen by a factor of 10 since 1990. The Netherlands is now well below the European guidelines for this exclusion. If we look at the influence of odorant in natural gas used by Dutch households, the contribution of natural gas odorant to sulfur dioxide emissions is just over 1.1%.

Sulfur-free odorant

Despite the limited influence of natural gas odorant on total sulfur dioxide emissions, the need for a sulfur-free odorant arose in the 1990's. At that time, acid rain was a serious problem and although it was known that the effect of sulfur-free odorants was limited, the idea was that every little bit helps. However, sulfur-free odorant is also attractive for another reason. Sulfur-containing compounds are generally bad for catalytic processes. Natural gas for industrial users is generally not odorized, but if this is the case, the gas must be cleaned and freed of contaminants, including odorants, that negatively affect the process. Fuel cells are also sensitive to sulfur contaminants. This differs per type of fuel cell, but all of them are more or less sensitive to sulfur contaminants. The gas must be cleaned of contaminants before it enters the fuel cell.

Public gas supply

Odorants are applied to natural gas used in the public gas supply to reduce the risk that a gas leak forms an explosive mixture and that an explosion that causes damage could occur when ignited. Liquid gases such as LPG and camping gas are also odorized to this end. In the case of LPG, this is usually done with the sulfur-containing compound ethyl mercaptan. Other odorants, such as THT, are also suitable as odorants for LPG, but ethyl mercaptan is used most often and switching to another odorant is not common practice for LPG either.

Hydrogen distribution

At the moment (2022), there is no large-scale distribution of hydrogen yet. There are now private hydrogen transport networks of several hundred kilometers from hydrogen producers in the Botlek area and in the southwest of the Netherlands, and Gasunie manages a twelve-kilometer hydrogen transport pipeline in the province of Zeeland. The hydrogen in these transport networks is not odorized. On 29 June 2022, the Dutch House of Representatives was informed about the development of the national hydrogen transport network. In 2025, the first hydrogen clusters on the North Sea and in the north of the Netherlands (Eemshaven) should be connected to a transport network. Through two subsequent phases, there will be a national hydrogen transport network for the industry in 2030, which will also allow import and export.

Pilot projects

The national hydrogen transport network will transport unodorized gas. Whether and when the current natural gas distribution networks or part of them will be connected to hydrogen is not yet known. However, small-scale pilot projects are now being started. There is not yet a legal framework for this, but these pilot projects are approved by the Dutch Authority for Consumers and Markets (ACM) because it is important to gain experience with the distribution and application of hydrogen. However, requirements will be set for the safety of these pilot projects. Given the results of research in the HyDelta research program (in which Kiwa also participates), it is very likely that hydrogen will be odorized in the built environment in order to meet the desired safety level. In natural gas distribution, odorization contributes to a high level of safety and this will be no different for hydrogen distribution.

Hydrogen odorant properties

An odorant for hydrogen should have the same properties as an odorant for natural gas. The international standardization organization ISO has drawn up the NEN-EN-ISO13734 guideline (‘Natural gas - Organic sulfur compounds used as fragrances - Requirements and test methods’).

This guideline includes properties that a natural gas odorant must meet:

1. It must smellable at a low concentration;
2. The smell must be unpleasant and not be confused with another smell, so that the smell has an alarming effect;
3. The odor character must remain the same in concentrated and in diluted form;
4. The odorant must be stable when mixed with (natural) gas and when storing gas;
5. The odorant must not condense in a pipeline;
6. When evaporating, no residues may remain in a pipeline;
7. The odorant must also be applicable at low temperatures;
8. No residual products may be left behind during combustion;
9. The odorant must not react with the gas.

Sulfur impurities

The requirements mentioned above should be taken into account, with the odor experience being the most important. A large proportion of people will have to be able to perceive the smell, experience it as unpleasant and also be able to recognize the smell. It is also important that the odorant has no harmful effects on humans and the environment. Since many catalytic processes, including fuel cells, are not very tolerant of sulfur contaminants, it is beneficial if a hydrogen odorant does not contain sulfur. It is possible to remove contaminants, including the odorant, before it is converted into a catalytic process or before it enters the fuel cell. However, it would be an advantage if the hydrogen odorant does not contain sulfur.

THT for now

The first experiments show that there is little difference between the smell of an odorant in hydrogen and the smell of the same odorant in natural gas. However, trace components such as higher hydrocarbons, aromatic compounds and sulfur compounds can slightly influence the odor. If a hydrogen network were to be commissioned now (2022), it would be logical that THT would be used because users are already used to this smell and associate this smell with danger and with a possible gas leak.

Experiments

In the long run, it would be better to develop a sulfur-free odorant that is not detrimental to the functioning of combustion appliances, gas engines, fuel cells and industrial processes that use hydrogen as a raw material. Experiments have shown that the only sulfur-free odorant currently used for natural gas still has an adverse effect on the operation of polymeric fuel cells (PEM FC). There are also doubts whether this odorant is sufficiently recognizable as a gas smell. There is therefore still a lot of work to be done before there is an odorant on the market that meets all requirements.

Responsible choice

In the past, the network operator played a major role in determining the odorant for natural gas. Obviously the Dutch government mine supervisor Staatstoezicht op de Mijnen - responsible for the safety of the network, the gas meter and the gas - also has a say in this. The health aspects of such a new odorant will most likely also have to be tested by an independent body. For a responsible choice the following questions will have to be answered positively:

- Is the odor strength sufficient?
- Is the odor experienced as repulsive and characteristic?
- Is the odorant stable?
- Are plastic pipes and other network components not affected?
- Is the odorant not harmful to combustion appliances and fuel cells?
- How does the odorant behave in the soil in case of an underground gas leak?

Testing

Kiwa Technology, specialized in research into the application of hydrogen in the built environment and the automotive sector, has an analytical chemical laboratory and a plastics laboratory with state-of-the-art test facilities. Kiwa can prepare and analyze gas mixtures and also has an odor setup where a panel can assess the odor strength and odor character. The stability of compounds can also be tested in the analytical laboratory. Kiwa also has experience in designing and building test setups to determine the properties of gases and odorants in the soil, and it even has its own hydrogen network and a unique hydrogen demo and training location. Material properties such as permeation, softening, absorption and mechanical strength can also be tested at Kiwa.

Want to know more?

Contact us by phone (+31 (0)88 998 35 21) of email (technology@kiwa.nl). Or check www.kiwa.nl/odorant-analysis.

Sources

The following sources were used for this white paper:

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  - The risk of non-odorizing hydrogen
  - Advice on odorant choice
- NEN-EN-ISO 13734:2000 en: Natural gas - Organic sulfur compounds used as fragrances - Requirements and test methods;
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