Odorisation

WP2 – Odorisation

D2.2 – Influence of sulfur containing odorant on end use appliances

Status: final

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Document approval

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Executive summary

In order to detect natural gas leaks in the built environment, the gas in the public distribution network is odorised. To maintain at least the same level of safety, hydrogen in the public distribution network will also have to be odorised. The final choice of the odorant for hydrogen has not yet been made, but there are good arguments for choosing tetrahydrothiophene (THT), which is also used in natural gas. The big advantage is that people in the Netherlands are familiar with the smell of THT and also link it to gas leakages. However, the disadvantage is that this odorant contains sulfur, which means that the use of odorised hydrogen is not possible in all end-user applications without pre-cleaning the gas.

Work package 2 of the Hydelta program investigated the effect of sulfur-containing odorants on the various end use applications. This is based on an odorant concentration of 10-40 mg THT/m^3(n), corresponding to 3.5-14.5 mg S/m^3(n), as specified for natural gas in the Dutch Ministerial Regulation on Gas Quality. A literature study was conducted for the study and additional discussions were held with manufacturers. The following applications have been considered:
- Central heating and hot water boilers;
- Kitchen appliances;
- Gas engines;
- gas turbines;
- Fuel cells;
- Feedstock and industry;
- Other applications, such as decorative fireplaces, outdoor heaters and patio heaters.

The impact of other gas quality parameters, the maturity and (economic) feasibility of the applications and the options for cleaning fell outside the scope of this study.

The results have shown that no insurmountable problems are to be expected for combustion equipment, such as central heating and hot water boilers, kitchen appliances, ornamental fireplaces, outdoor stoves and patio heaters, and gas engines when using hydrogen that is odorised with a sulfur-containing odorant, such as THT.

While these applications are relatively robust for low concentrations of sulfur (<14.5 mg S/m^3(n)) in the hydrogen, fuel cells are very sensitive to these impurities. The presence of sulfur in the hydrogen leads to irreversible damage to the fuel cell. This is an accumulating process, which already occurs at sulfur concentrations of 1 ppm (1.4 mg S/m^3(n)).

The development of hydrogen-driven gas turbines is still in full swing. Little is therefore currently known about the hydrogen specification ultimately required for gas turbines. In principle, gas turbines fall under ISO 14687 grade B, with a specified sulfur concentration of 10 molppm, corresponding to approximately 14 mg S/m^3(n). This concentration corresponds to the maximum specification that currently applies to natural gas distributed in the Netherlands. It is known from the past that natural gas-fired turbines are suitable for this sulfur load. It is up to the suppliers to make the gas turbines still to be developed suitable for this sulfur load.

For feedstock applications, where the hydrogen is used directly in the production process, impurities such as sulfur are highly relevant. These processes are so specific that no general statements can be made about the maximum permissible sulfur content in hydrogen. It is expected, however, that additional cleaning will have to be applied, as is now also the case for odorised natural gas.

It should be noted that almost all feedstock processes are connected to the high-pressure transport system (HTL). It is expected that, in accordance with the current HTL network, the hydrogen backbone will also not be odorised and the sulfur impact will not be increased. The impact of sulfurous hydrogen will therefore not be an issue for these applications.

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1. Introduction

In order to detect natural gas leaks in the built environment, the gas in the public distribution network is odorised. To maintain at least the same level of safety, hydrogen in the public distribution network will also have to be odorised [1].
The final choice of odorant for hydrogen has not been made yet, but there are good arguments for choosing tetrahydrothiophene (THT), which is also used in natural gas. The big advantage is that people in the Netherlands are familiar with the smell of THT and also link it to gas leakages. However, the disadvantage is that this odorant contains sulfur, which means that the use of odorised hydrogen is not possible in all end-user applications without pre-cleaning the gas.

Work package 2 of the Hydelta program investigated the effect of sulfur-containing odorants on the various end-user applications. This is based on an odorant concentration of 10-40 mg THT/m3(n), corresponding to 3.5-14.5 mg S/m3(n), as is now prescribed in the Ministerial Regulation on Gas Quality [2].
The impact of other gas quality parameters, as well as the maturity and (economic) feasibility of the applications and additional cleaning techniques are outside the scope of this study. A literature study was conducted for the study and additional discussions were held with manufacturers.

2. End use applications

In the following paragraphs, the impact of sulfur on the following hydrogen applications is considered:
- central heating and hot water boilers;
- kitchen appliances;
- gas engines;
- gas turbines;
- fuel cells;
- feedstock and industry;
- other applications, such as decorative fireplaces, outdoor heaters and patio heaters.

2.1. Central heating and hot water boilers

This category covers household appliances that are used for hot water and/or heating homes via the central heating system. In addition, commercial boilers are included for heating larger spaces and offices.

In general it can be stated that burners are very robust for the trace components present in hydrogen, such as sulfur. During combustion, the sulfur present in the hydrogen will be oxidized to sulfur dioxide (SO_2), as is also the case with natural gas-fired appliances. It is therefore to be expected that the impact of sulfur-containing odorants -in the concentration range that is now also used for natural gas- will be nil [3].

2.2. Kitchen appliances

In principle, it is possible to design kitchen appliances, such as stoves and ovens, that use hydrogen as fuel.

It is expected that the specifications for these types of appliances will not differ from those for central heating applications and no problems are expected due to low concentrations of sulfur in the hydrogen. [3]

2.3. Gas engines

Natural gas-fired gas engines are used to produce electricity and/or heat in the built environment (e.g. in horticulture, commercial sector, swimming pools, government buildings, etc.) and sometimes as an emergency power generator (e.g. in hospitals). These are often stationary engines that can run at a fixed speed at optimum load and efficiency. In addition, there are engines that are used as propulsion systems in vehicles.

After-treatment systems to reduce NO_X emissions can be sensitive to sulphur-containing trace elements. In the Hy4heat project, gas engine manufacturers have been approached and they have indicated that a sulfur limit of approximately 10 ppm (approx. 14 mg S/m^3n) is desirable for hydrogen engines that use SCR (Selective Catalytic Reduction) [4]. This limit corresponds to the maximum THT concentration as currently specified for natural gas in the Dutch MR Gas Quality [2], so it can be assumed that this will not lead to problems.

2.4. Gas turbines

Gas turbines are currently available that can use 100% hydrogen based on diffusion combustion [5]. There are currently no lean premixed systems that can use 100% hydrogen. EUTurbine has set itself the goal of developing such gas turbines for 100% hydrogen by 2030 [6].

The hydrogen specification ultimately required for gas turbines is therefore not yet available and will depend on the design of the turbine [3]. In principle, gas turbines fall under ISO 14687 grade B, with a specified sulfur concentration of 10 molppm corresponding to approximately 14 mg S/m^3(n) [7]. It has been known from the past that natural gas-fired turbines are suitable for this sulfur load. It is up to the suppliers to make the hydrogen gas turbines still to be developed also suitable for this sulfur load.

2.5. Fuel cells

Fuel cells can be used to generate electricity or as a replacement for CHP applications. While combustion equipment is relatively robust to impurities, fuel cells (depending on the type) are very sensitive to impurities in hydrogen and air. The operation of the most common fuel cells is briefly explained in the following subsections.

2.5.1. Polymer Electrolyte Membrane Fuel Cell (PEMFC)

PEMFCs are polymer membrane based cation fuel cells. The operating principle is based on a proton-conducting membrane where hydrogen is split into protons and electrons on the anode side, usually with the aid of a platinum catalyst. The protons are passed through the membrane and the electrons go to the cathode through an external circuit. Once at the cathode, the electrons and protons combine with the split oxygen ions to form water.

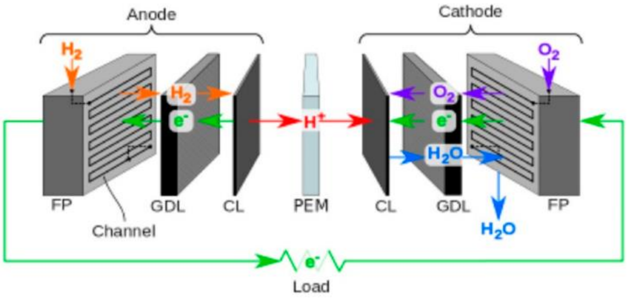

Figure 1: Schematic representation of PEMFC

Low temperature PEM fuel cells (LT PEMFC) use a sulfonic acid membrane. The cells operate at 60 - 70°C. The electrodes are mostly platinum based with typical loading of 0.05-0.6 mg Pt/cm².

High temperature PEM fuel cells (HT PEMFC) are based on an alkaline membrane, usually polybenzimadazole (PBI), which is saturated with phosphoric acid. Typical operating temperatures are 130 - 180°C. As with the LT technology, the electrodes are platinum based with a loading of 0.4-1 mg Pt/cm².

Sulfur-containing oxides in one of the reactant gases lead to degradation of the fuel cell [4,8,9]. After exposure to sulfur, some of the degradation can be repaired by reactivating the fuel cell through cyclic voltammetry, but there will always be permanent damage. The sulfur atoms in the molecule cover the platinum atoms in the electrode, preventing reactant gas from reaching the platinum electrode [10]. Hydrogen sulfide (H_2S) also results in degradation. The two hydrogen ions are electrolyzed from the sulfur ion, leaving (solid) sulfur. This solid sulfur then adheres to the surface of the platinum atoms in the electrode, rendering it inert. This effect is irreversible and irreversible [10].
As with LT PEMFC, the HT PEMFC does not tolerate sulfur components in its reactants. The degradation is slower due to the increased temperature, the higher loading and the presence of phosphoric acid. In the long run, the effect of the contamination is the same, namely irreversible degradation. In all cases the concentration is unimportant as the degradation is an accumulating effect. In the literature there are reports of degradations at sulfur concentrations of 1 ppm. [4,12]

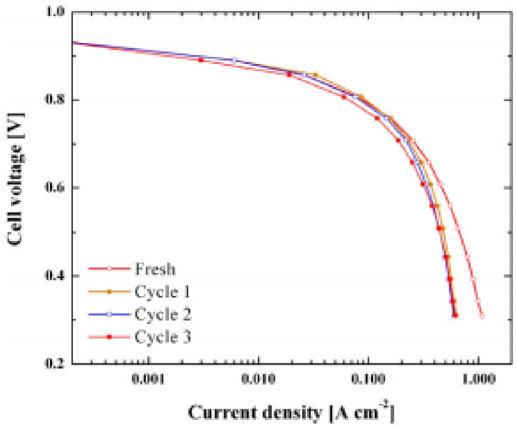

Figure 2: Degradation of a fuel cell *[11]*

Exposure 2 ppm H2S, after which multiple current-voltage (IV) curves were made. "Fresh" is a new MEA, which has not yet been exposed to H2S. The subsequent cycles amount to a period of exposure to 2ppm H2S. A performance difference of almost 50% can be observed between "Fresh" and "Cycle 1". [12]

2.5.2. Solid Oxide Fuel Cell (SOFC)

Solid Oxide Fuel Cells are fuel cells that use ceramic material and are operational at 500-1000 °C. In a SOFC, oxygen ions are passed through the membrane instead of protons. Because SOFCs are operated at particularly high temperatures, almost any hydrogen-containing source can be used as an anode reactant. The anode electrodes at SOFC are usually made of nickel in a yttrium-doped zirconium oxide (yttrium-stabilized zirconium) ceramic layer. Like the anode, the cathode is also a porous material, so mass transport is assured. Lanthanum strontium manganate (La1-xSrxMnO3) is usually used as the cathode. For SOFCs, the doping degree is approximately 0.16.

Because no platinum is used in the electrodes, SOFCs - unlike PEMFCs - are resistant to carbon monoxide. However, this does not apply to sulphur. As with PEMFCs, sulfur-containing components are electrochemically converted, leaving sulfur as an inert solid material. This inert sulfur then coats the catalyst material preventing absorption of reactant gas [13]. It is known from the literature that a reduction in power is already observed at concentrations of 1 ppm [4,14]. As with PEMFCs, SOFCs have an accumulative effect.

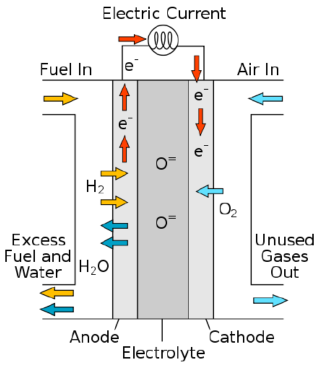

Figure 3: Schematic presentation of a SOFC

2.5.3. Molten Carbonate Fuel Cell (MCFC)

Molten carbonate fuel cells use a liquid membrane, which usually consists of molten sodium and potassium carbonate salts. Because the carbonate salts must be molten, this type of fuel cells are operated at temperatures of 600-700 °C. The anode electrodes are made of nickel, and often alloyed with chromium or aluminum. The cathode electrodes are either lithium nickel oxide or lithium metatitanate.

As with PEMFC, sulfur-containing components are electrochemically converted, leaving sulfur as an inert solid material. This inert sulfur then coats the catalyst material preventing absorption of reactant gas [15]. Also with MCFCs, reduced power is measured at sulfur concentrations of 1 ppm and sulfur has an accumulating effect [16].

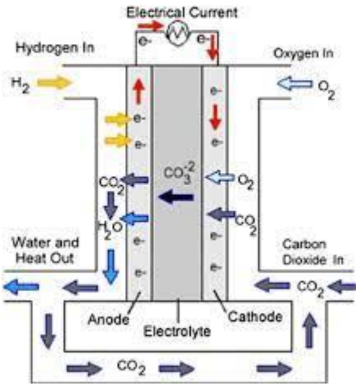

Figure 4: Schematic presentation of a MCFC

2.5.4. Other systems

In the preceding (sub) paragraphs, only the most common fuel cells have been considered. In addition, other types of fuel cells are under development, including the Phosphoric Acid Fuel Cell (PAFC). PAFCs are also not tolerant to sulfur-containing components [17]. The platinum catalyst becomes saturated with sulfur at the anode, preventing oxygen from entering and sulfur oxidation. There is a possibility to add a “bleed”, whereby a minimal air or oxygen flow is added in the anode. However, this bleed is also applicable to PEMFC. The PEMFC has a significantly better return than the PAFC, so that the economic feasibility for PAFC is currently estimated to be low [17].

An alkaline fuel cell (AFC, Alkaline Fuel Cell or AAEMFC, alkaline anion exchange membrane fuel cell) is also unlikely to be tolerant to sulfur-containing components because the system will also contaminate the catalyst. [18] However, this is not explicitly stated in the literature. In particular, the problems with carbon dioxide have been described in the literature. Carbon dioxide results in carbonate formation on the catalyst, which greatly shortens its life [19]. No information was found in the literature scans about the sulfur (in)tolerance when using the latest generation of AEM membranes. [20]

2.6. Feedstock and industry

A limited number of connected parties use the gas in a way other than for heat and/or power generation. This concerns so-called feedstock applications, which use the gas directly in their production process. For these processes, impurities, such as sulfur, are very relevant.

These processes are so specific that in general terms no statements can be made about the sulfur content in the hydrogen. It is expected, however, that additional cleaning will have to be applied, as is now also the case for odorised natural gas.

It should be noted that almost all feedstock processes are connected to the high-pressure transport system (HTL). It is expected that, in accordance with the current HTL network, the hydrogen backbone will not be odorised and the sulfur impact will not be increased. The impact of sulphur-containing hydrogen will therefore not be an issue.

2.7. Other applications

In addition to the usual applications described above, natural gas is also used in, among other things, fireplaces, outdoor stoves and patio heaters. In these applications, the gas is burned, as is used in central heating and hot water boilers and kitchen appliances.

It is therefore expected that a low sulfur concentration in hydrogen will not lead to problems for these appliances and that the specifications will match those for the boilers and kitchen equipment.

3. Conclusions

The study has shown that no insurmountable problems are to be expected for combustion equipment such as central heating and hot water boilers, kitchen appliances, ornamental fireplaces, outdoor heaters and patio heaters and gas engines when using hydrogen that has been odorised with sulfur-containing odorant, such as THT.
While these applications are relatively robust for low concentrations of sulfur (<14.5 mg S/m^3(n)) in hydrogen, fuel cells are very sensitive to these impurities. The presence of sulfur in hydrogen leads to irreversible damage to the fuel cell. This is an accumulating process, which already occurs at sulfur concentrations of 1 ppm (1.4 mg S/m^3(n)).

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