Odorisation

WP2 – Odorisation of Hydrogen

D2.1 – Choice for a sulphur free odorant (EN version)

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Executive summary

This report describes the selection process of a potential third sulphur-free odorant for hydrogen within the framework of HyDelta WP2: Odorisation research programme.

Two odorants that are already known for natural gas, namely Tetrahydrothiophene (THT) and GASODOR® S-free, were already pre-selected. After a literature search, three odorants were tested on their odour character and the odour behaviour after a selection on the properties of the odorant.

The candidate odorant 2-hexyne was ultimately selected on the basis of the following properties:

- an unpleasant, distinctive characteristic odour
- a low odour threshold
- low toxicity
- sulphur-free
- workable dosage: nominal 15 mg/m^3(n), minimum 10 mg/m^3(n), maximum 35 mg/m^3(n).

The selected odorant will be further tested in the HyDelta WP2 study.

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1. Introduction

The Ministerial Regulation on Gas Quality (*MR Gaskwaliteit*) currently stipulates that operators are required to odorise natural gas that they distribute. In addition, the Connection and Transport Code of Natural Gas for Regional Grid Operators (*Aansluit- en transportcode gas RNB*) states an obligation to comply with standard NEN 7244. This standard says the following in relation to odorisation:

When gas does not naturally have an unpleasant, distinctive, alarming odour, an odorant must be added to the gas. The added odorant must be non-toxic and must be harmless in the concentration applied. The odour must disappear after combustion. Gas may be supplied without odorant for specific purposes. In such cases, other leakage detection systems must be permanently in operation in rooms where gas pipes are installed or gas installations are set up [1].

There is currently no requirement for the odorisation of hydrogen when used in the public gas supply network. However, it is expected that the same obligation and requirements will apply to hydrogen distribution according to the same argumentation. Hydrogen is a naturally odourless substance and it would be illogical to fit an entire pipeline network with leak detection equipment. Non-odorisation could be possible for a limited demonstration, such as one or two hydrogen homes with a short supply line, but not for large-scale application in the public gas supply network.

An odorant thus serves as an extra safety barrier that is added to allow users to smell a gas leak at a level that is well below the lower explosion limit and before the leaking gas can lead to an incident. The lower explosion limit of hydrogen is 4.1 vol% and that of natural gas is 5 to 6 vol% (depending on the type of natural gas, for G-gas it is 5.9 vol%) [2]. This means that the odorant we would choose for hydrogen should at least as easily detectable, at the same dosage, as the odorant we currently use for natural gas.

As part of the research study into the suitability of an odorant for hydrogen, two odorants have been selected in advance, namely tetrahydrothiophene (THT) and GASODOR®. The third odorant will be selected within the framework of the HyDelta study. A broad exploratory study has been conducted to find possible alternative odorants, preferably sulphur-free.

The aim of the study was to identify and analyse possible odorants, after which a selection was made based on known properties. The selected odorants were tested for odour characteristics and odour strength.

2. Selection criteria for an odorant

Standard NEN-EN-ISO13734 [3] provides good recommendations regarding the characteristics that an odorant for a gas should satisfy.

These are as follows:

1. it must be easy to smell at a low concentration;
2. the odour must be unpleasant and may not be confused with another odour, so that the odour has an alarming effect;
3. the odour character must remain the same in concentrated and diluted form;
4. the odorant must be stable when mixed with (natural) gas and when stored;
5. condensation of the odorant may not occur in the pipework;
6. no residues may be left in the pipe in case of evaporation;
7. the odorant must also be suitable for use at low temperatures;
8. no residue may remain after combustion;
9. the odorant may not react with the gas.

Not all characteristics are described in the literature, but most of them are. If an odour is assessed as sweet and pleasant, for example, it would be a reason for not selecting the odorant in question.

The same applies to an odour threshold that is too high. If the odour threshold is high, it means the gas will only be detected in higher concentrations, or that a lot of odorant needs to be added. Both situations are undesirable.

The boiling point of the odorant could also be a criterion for exclusion. If the odorant condenses under operating conditions, it might also dissolve in unforeseen liquids that are in the gas pipe, thus negating the effect of the odorant.

3. Ongoing research and incorporation into HyDelta

3.1 Literature study

Based on an internal literature study conducted by Kiwa, DNV and Stedin, a so-called longlist was made and is summarised in Table 1. Insofar as available, the relevant data of the individual odorants has been added to the table.

The literature study looked at other research, such as the Hy4Heat study in the UK, where eight odorants in total were screened. Earlier studies were also examined in which the application as an odorant is claimed by the authors.

3.2 Selection criteria

Prior to the study, a list of requirements that an alternative odorant has to meet was drawn up. These are largely based on the requirements that already apply to natural gas (see Chapter 2), supplemented by a specific requirement for hydrogen:

- The odorant must be chosen in a way that eliminates any confusion with other substances;
- The odorised gas must be properly detectable by a person with a normal sense of smell;
- The perception of the odour must be alarming;
- 1% of gas in air must still have a clearly recognisable alarming odour;
- The odour may not change when diluted;
- The odorant must remain stable in the gas system and may not react with the hydrogen;
- The odorant may not be harmful to components in the gas system;
- The odorant may not restrict the use of the hydrogen and may not leave any residual products;
- The odorant must be available and affordable.

The odorants found are classified into three groups:

- proven suitable;
- doubtful and/or less suitable. Further investigation may be required;
- proven unsuitable.

Ongoing investigation: odorisation study at Stedin with DNV. During an earlier stage, Stedin decided to carry out an initial inventory of possible sulphur-free alternative odorants. The study comprises a broad inventory of possible sulphur-free odorants.

Potential odorants were identified and three odorants were offered to more than 600 Stedin employees (colleagues who work in gas operations).

These odorants are summarised in table 1 according to the main criteria: odour threshold, odour character and solubility in liquids.

Table 1: gross list of candidate odorants [3 - 13]

Compound	Treshold odor value	Odor character	Water solubility
	[ppm]		
THT	0.00062	Unpleasant	Insoluble
Gasodor S-Free			Insoluble
2,3-butadione	0.002	Rotten butter	Insoluble
ethyl sugar lactone	10	Caramel	
ethylisobutyrate	0.000022	Fruity	865 g/l
5-ethyldiene-2-norbornene	0.014	Petroleum	Insoluble
cyclohexanen	2.5	Petroleum	Insoluble
methyl tert-butyl ether	0.0055	Alcohol/ether	5,1 g/l
tri-methylamine	0.48	Fishy/ammonia	Insoluble
2-hexyne	<0,0022	Characteristic	Insoluble
1-pentyne		Garlic and fish	1,05 g/l
ethyl isocyanide (enamine of isocyano ethane)	0.0006	"the Godzilla of scent"	Insoluble
n-butyl isocyanide		Sharp, unpleasant	
Methyl methacrylate	0.205	Sharp, sulphurous	15,8 g/l
DES (DiEthylStilbestrol)		Odorless	
1-butyne		acetylene	2,9 g/l
5-ethyl-3-hydroxy-4-methyl-2 (5h)furanone		Sweet, fruity, caramel	Insoluble
various selenides		Garlic	
mixture of aldehyde, acrylate and selenide		Fruity	Insoluble
cyclo-octyne		Characteristci, intensem unpleasant	
acetylene	226	Garlic, phosphine	1,185 g/l
phosphine		Garlic, fishy	

Based on the properties, the following top three odorants have been selected. The odorants have been purchased and odour tests have since been carried out.

The three odorants are:

- 5-Ethylidene-2-norbornene; the reason for selecting this odorant was because of its evaluation as a reasonably suitable odorant in the Hy4Heat project;
- Methyl tert-butyl ether; the odour character appears to be good. The odour threshold is low and the substance seems to be easy to produce and is not toxic. A disadvantage is that this substance is partially water soluble;

- 2-hexyne; the odour character seems good, the odour threshold is low, as is the toxicity, and the water solubility is poor.

3.3 Odour tests

After narrowing down the selection to three odorants, the first tests were performed by presenting the three odorants to more than 600 Stedin employees who work in the field. Although the ratings varied widely and were subject to interdependency, 2-hexyne was identified by nearly all employees as the most distinctive and alarming.

Odour tests were subsequently carried out on the top three odorants in the laboratory of DNV. Four people (experts in the field) smelled odour samples in a set-up where odorised hydrogen was mixed with air. The findings of the broad study at Stedin were not made known, nor was it stated which substance was offered (blind test).

The following criteria were determined:

- what is the odour strength at 100 times dilution?;
- what does the gas smell like?;
- how does the odour compare to that of nominally odorised THT (18 mg/m^3)?

Table 2: Panel experiences with the three candidate odorants

Compound	Concentration in H_2 (ppm)	Panel member	Odour character and strength
5-Ethylidene-2-norbornene	17	1	welding workshop. Not strong and only faintly alarming
		2	Dirty, burnt or rotten meat. Alarming. Strength OK
		3	Sweet. Not alarming. Strength OK
		4	Synthetic air, gas condensate, mildly alarming. Strength OK
Methyl tert-butyl ether	10	1	stale, air in a bicycle tyre. Not alarming. Strength is weak
		2	somewhat sweet, faintly alarming. Strength is weak
		3	smells something, but can't place it
		4	Urine? Very faint smell
2-hexyne	14	1	chemical, polyester mats, two-component adhesive. Stinks, but not alarming. Strength OK
		2	somewhat like THT Alarming. Strength OK
		3	doesn't smell much... petrol? THT? Not alarming.
		4	chemical, sulphuric. Alarming. Strength OK.

Supported by the experiences of the panel members, 2-hexyne was finally chosen.
The mixture of 14 ppm 2-hexyne odorant in hydrogen could still be smelled well at 2000-fold dilution, giving the substance a low odour threshold.
The strength was determined in relation to 100-fold diluted odorised G-gas. The concentration in the so-called mother gas was 14 ppm. At a 350-fold dilution level, the odour strength is comparable to 100-fold diluted G-gas, which is equivalent to 4 ppm, or 15 mg/m^3(n). The minimum and maximum concentrations have been set at 10 mg/m^3(n) and 35 mg/m^3(n) respectively.
The toxicity of 2-hexyne is also limited. The TWA value (time-weighted maximum concentration during 8 hours to which humans may be exposed) is 1000 ppm. This means that there is no toxicity risk when exposed to undiluted gas. Although authorisation as an odorant will most likely require a risk assessment to be performed, no barriers related to toxicity have been identified so far.

4. Conclusions and follow-up

Following on from a literature study, three odorants were selected and tested for their odour characteristics and odour behaviour.

The odorant 2-hexyne was finally selected on the basis of the following character traits:

- an unpleasant, distinctive odour;
- a low odour threshold;
- low toxicity;
- sulphur-free;
- a workable dosage: nominal 15 mg/m^{3}n, minimum 10 mg/m^{3}n, maximum 35 mg/m^3(n)

4.1 Follow-up

The selected odorant will be included in the continuation of the HyDelta test programme, together with the already selected odorants THT and GASodor®- S-free.

All three odorants will be subjected to the following tests within the framework of the HyDelta WP2; odorisation exploratory study:

- the stability of the odorant in hydrogen, measured over a period of 3 months;
- the odour perception by a panel of approx. 20 persons.

Before an odorant is approved for sale on the market, it usually requires more extensive testing than is currently performed. Further aspects should then be investigated, such as:

- the impact of odorants on pipe materials;
- the impact on regulators, valves, gas meters;
- the impact of odorants on combustion equipment and fuel cells;
- how does the odorant spread in the air?;
- screening for environmental and health aspects;
- perception of social support (broader representation than approx. 20 people);
- risk analyses; What is the best way to introduce a ‘new’ odorant?

These can possibly be examined in a subsequent phase of the HyDelta study.

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