ALTERNATIVE ODORANTS FOR HYDROGEN

Identifying three sulphur free odorants and their suitability for hydrogen in the gas grid

Stedin and GRDF

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EXECUTIVE SUMMARY

The gas industry considers safety as a top priority. One of the activities to be able to maintain a high safety level is the odorisation of the gas distributed to the domestic market. The odorisation of natural gas in most European countries involves the addition of the organic sulphur compound tetrahydrothiophene (THT) to the natural gas. This component gives the natural gas a characteristic and alarming odor, so that it is detected in time in the event of a gas leakage.

Like natural gas, hydrogen is odorless by nature. Odorisation is a standard prodecure for natural gas distribution operation and has proven to be an efficient manner for gas leakage detection. To achieve the same safety level for hydrogen it should be odorised as well. Based on ongoing research, THT is also suitable for hydrogen odorisation. Using the same odorant for hydrogen as for natural gas has the advantage of the odor being familiar amongst the public. However, the use of THT in hydrogen has three drawbacks:

- THT should not be fed into certain hydrogen applications as it contains sulphur. Especially hydrogen fuel cells are extremely sensitive to small traces of sulphur. Furthermore, emissions of sulphur lead to environmental pollution and health risks;
- During the transition period from natural gas to hydrogen, parallel pipelines will contain one of both gases. Using the same odorant for both gas types will provide insight into whether there is a leak, but not in which pipe the leak occurred.

To achieve the widest possible application of hydrogen, Stedin, GRDF and DNV have investigated the possibility of using an alternative, sulphur-free odorant for hydrogen distribution. The goal of this research was to select a ‘top three’ of alternative odorants based on their characteristics found in literature and test their suitability for odorised hydrogen in fuel cell applications. The list of criteria is largely based on the criteria that now also apply to natural gas, supplemented with hydrogen-specific aspects:

- the odorant must have an unique odor so that confusion with any other substance is prevented;
- the odorised hydrogen should be easily perceived by a person with an average olfactory (sense of smell);
- the perception of the smell is alarming;
- 1% hydrogen in air should still have a clearly recognizable alarming smell;
- the smell should not change when diluted;
- the odorant must remain stable in the gas system and not react with hydrogen;
- the odorant must not be harmful to components in the gas system and/or gas applications;
- after use of the gas, the odorant may not lead to undesirable emissions and/or may not leave residual products behind;
- the odorant may not be toxic for humans;
- the odorant may not restrict the use of hydrogen;
- the vapour pressure should be that high that the odorant under all conditions is in the gaseous phase;
- the odorant must be available and affordable.

Furthermore, the stability of the long term stability has been studied. If a new odorant is chosen for the transition period and the existing natural gas pipelines are reused for hydrogen distribution, it is important to note that during a certain period of time the new odorant will be mixed with THT, as the pipelines will still contain traces of THT. For this reason, olfactometry tests were carried out with mixtures of the most promising odorant and THT in order to investigate the possibility of odor masking by THT.

Based on a literature search a long list of possible odorants have been made. Using the so-called elimination method, all candidate odorants were assessed, and three substances were selected for further research. The selected candidates are:

- 5-ethyldiene-2-norbornene;
- methyl tert-butyl ether;
- 2-hexyne.

All three candidate odorants are patent-free and none of them have been used as odorant commercially. The concentration level for 5-ethyldiene-2-norbornene has been determined at 84 mg/m^{3}n, as described in the Hy4Heat study. The concentration to be used for 2-hexyne has been determined on the basis of olfactometry. The concentration was adjusted in such a way that the odor strength corresponded to that of odorised natural gas. The experiments showed that 2-hexyne at a concentration level of 15 mg/m^{3}n gave the same odor strength as natural gas. For methyl tert-butyl ether the concentration was difficult to determine because a large part of the panellists could not distinguish and/or detect the ether. For this reason, it was decided, based on discussions with the safety expert and project members, to use a concentration of 100 mg/m^{3}n. This concentration is still considered to be safe and it is unlikely that higher concentrations will be useful in practice.

Mixtures in air were made of these three substances, selected for further research, in aluminium pressurised containers. These mixtures were then presented to approximately 600 Stedin employees. Although the ratings varied widely and were subject to mutual influence of the panel members, 2-hexyne was identified by nearly all employees as most distinctive, alarming and similar to THT. The odor of 5-ethyldiene-2-norbornene was largely not experienced as unpleasant - and therefore not as alarming to people smelling it. Approximately half of the panellists were unable to recognise? methyl tert-butyl ether from the environment.

All three odorants proofed not to have an adverse effect on the performance of Proton Exchange Membrane (PEM) fuel cells. As the PEM technology suffers the most from potential contaminants it has the highest chance of detecting potential harmful components. Therefore, it can be expected that other types of fuel cells also will not be negatively influenced by the three investigated odorants.

As for the stability of the odorants in hydrogen, it was found that contaminations of in particular oxygen-containing hydrocarbons in the gas system can lead to hydrogenation of 2-hexyne and 5-ethyldiene-2-norbornene, whereby the substance is (partly) converted into respectively hexane and 5-ethylnorbonane which decreases the smell. Tests have shown that increasing the temperature to 40 ^{o}C does not affect the stability of 2-hexyne.

Odor masking of 2-hexyne by THT was investigated. These additional tests were not carried out for the other two odorants, since the outcome of the forgoing described tests showed that only 2-hexyne can meet most of the specified criteria.

From the obtained results it can be concluded that a concentration of 15 mg/m^{3}n 2-hexyne -as expected- has approximately the same odor threshold and strength as is achieved with 18 mg/m^{3}n THT.

Based on the test results, the odor masking of 2-hexyne due to the presence of THT in the gas mixture is not expected to be an issue.

From this study, it can be concluded that 2-hexyne is the only one of the investigated substances that appears to be suitable for use as a sulphur-free odorant in hydrogen. Since the olfactometric measurement were carried out with a small panel, it is recommended to repeat those measurement with a larger group of people, who are preferably not working in the gas industry.

As the existing pipelines, that are used for distribution of natural gas for many decades, can contain THT and hydrocarbons it is recommended to investigate the optimal conditions for removing THT and to investigate the influence of materials and trace components on the stability of 2-hexyne.

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1 INTRODUCTION

In the near future, our energy system will undergo a transition to a system based on sustainable and renewable energy sources. Renewable energy sources are mainly distinguished from conventional, fossil energy sources due to their low life cycle carbon emissions and their intermittent nature.

Due to the intermittent nature of solar and wind energy in particular, matching the supply and demand of sustainably generated electricity will become increasingly challenging and the need for energy storage and a flexible energy infrastructure will increase. When incorporating more intermittent sustainable sources, the imbalance between supply and demand is therefore not easy to overcome. In order to facilitate sustainable electricity production as optimally as possible, options are being sought for alternatively deploying and/or storing the excess of sustainable produced electricity. Power-to-Gas (P2G) is a technology that enables flexible operation and buffering of electricity surpluses in the short and long term by storing electricity (as hydrogen) in the gas network. Hydrogen, as energy carrier, will play an important role in the decarbonisation of the energy system.

The gas industry strives for the highest standard of safety. One of the activities to be able to maintain this level is the odorisation of the gas distributed to the domestic market. The odorisation of natural gas involves the addition of the organic sulphur compound tetrahydrothiophene (THT) to the gas. This component gives the gas a characteristic and alarming odor, so that it is detected in time in the event of a gas leakage. Furthermore, THT does not react with other natural gas components and is stable in all type of materials that are used in the gas system. The requirements that odorised natural gas must meet are described in NEN 7244-1 [1].

Like natural gas, hydrogen is also odorless by nature. Odorisation has proven to be an efficient manner for gas leakage detection. To achieve the same safety level for hydrogen, also hydrogen should be odorised [2]. As far as ongoing research can tell, THT is also suitable for hydrogen. Using the same odorant for hydrogen as for natural gas has the advantage of the odor being familiar amongst the public. However, the use of THT in hydrogen has three drawbacks:

- THT contains sulphur, which implicates that it cannot be used directly in fuel cells and any other applications where sulphur leads to problems. The required additional cleaning step therefore can make such an application so expensive that the business case will be negative or come under heavy pressure;
- During the transition period, both natural gas and hydrogen distribution pipelines will be in use in certain areas. Application of the same odorant for both gas types provide insight into whether there is a leak, but not in which pipe the leak occurred[1];
- The use of THT leads to the undesirable emission of sulphur.

To achieve the widest possible application of hydrogen, Stedin, GRDF and DNV have investigated the possibility of using an alternative, sulphur-free odorant for hydrogen. The goal of this research was to select a ‘top three’ of alternative odorants based on their characteristics found in literature and test their suitability for hydrogen in fuel cells. Furthermore, the stability was studied.

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[1] If a new odorant is chosen for the transition period and the existing pipelines are reused for hydrogen, it is important to note that during a certain period of time the new odorant will be mixed with THT, as the pipelines will still contain traces of THT. Thus it is important that the new odorant is dominant over THT.

2 ODORANT CHOICE

2.1 Criteria

Prior to the study, a list of criteria was drawn up that an alternative odorant must meet. These are largely based on the criteria that now also apply to natural gas, supplemented with hydrogen-specific aspects:
- the odorant must have an unique odor so that confusion with any other substance is prevented;
- the odorised hydrogen should be easily perceived by a person with an average olfactory (sense of smell);
- the perception of the smell is alarming;
- 1% hydrogen in air should still have a clearly recognizable alarming smell;
- the smell should not change when diluted;
- the odorant must remain stable in the gas system and not react with hydrogen;
- the odorant must not be harmful to components in the gas system and/or gas applications;
- after use of the gas, the odorant may not lead to undesirable emissions and/or may not leave residual products behind;
- the odorant may not be toxic for humans;
- the odorant may not restrict the use of hydrogen;
- the vapour pressure should be that high that the odorant under all conditions is in the gaseous phase;
- the odorant must be available and affordable.

2.2 Pre-Selection

Based on own literature search, an inventory by Proton Technologies [3], the Hy4Heat study [4] and a quick scan performed within HyDelta [5], a so-called long list has been made, which is summarized in table 1. Insofar as available, the relevant data of the individual candidate odorants is added to the table. The data found are classified into 3 categories:
- green: proven suitable;
- yellow: doubtful and/or less suitable. Any further investigation is necessary;
- red: proven unsuitable.

Using the so-called elimination method, all candidate odorants were assessed and three substances were selected for further research. The results are summarized in table 2. The finally selected candidates are:
- 5-ethyldiene-2-norbornene (5E2N, CAS number 16219-75-3);
- methyl tert-butyl ether (MTBE, CAS number 1634-04-4);
- 2-hexyne (2HEX, CAS number 764-35-2).

Mixtures in air were made of these three substances, selected for further research, in aluminium pressurized containers. These mixtures were then presented to approximately 600 Stedin employees who work in the gas domain for assessment during the Stedin 'Gas Days'. Although the ratings varied widely and were subject to mutual influence, 2-hexyne was identified by nearly all employees as most distinctive and alarming. The odor of 5-ethyldiene-2-norbornene was largely not experienced as unpleasant - and therefore not as alarming. A large proportion of panellists were unable to distinguish methyl tert-butyl ether from the environment. The findings were later confirmed again during the olfactometry measurements carried out within the HyDelta study.

Name	Gas concentration [mg/m3n]	[ppm]	OTV (odour threshold va [ppm]	Flavour	End use - Fuel cell	Solubility in water	Health	Availability	Price [€/l] or [€/kg]
Tetrahydrothiophene (reference)	18	2,5	0,00062		3	insoluble			
Gasodor S-Free	8	1,9			1	insoluble		Good	as THT
2,3-butanedione	16	4,2	0,002	Putrid butter	1	soluble	LD50 (rat oral): 1580 mg/kg	Good	200
ethyl sugar lactone			10	Caramel	1			Good	3000
ethyl isobutyrate	11	2,1	0,000022	Fruity	1	865 g/l		Good	65
5-ethyldiene-2-norbornene	84	15,7	0,014	coal gas/petroleum	1	insoluble	LD50 (rat oral): 2830 ul/kg	Good	100
cyclohexane			2,5	petroleum	2	insoluble		Good	60
methyl tert-butyl ether			0,0055	Alcohol/chemical/ather	2	5,1 g/l	LD50 (rat oral): 2963 mgl/kg	Good	50
tri-methylamine	10	3,8	0,48	Fishy/amonia-like	3	soluble		Good	1000
2-hexyne	37	10,0	<0,0022	"Characteristic"		insoluble	TWA: 1000 ppm	Good	6000
1-pentyne				Garlic and bad fish mix		1,05 g/l	TWA: 1000 ppm	Good	2800
ethyl isocyanide (enamine or isocyano ethane)			0,0006	"the Godzilla of scent"		soluble	TWA: 40 ppm	Good	4000
n-butyl isocyanide				Pungent unpleasant				Good	>5000
Methyl methacrylate			0,205	pungent sulphureous	2	15,8 g/l	TWA: 5 ppm	Good	70
DES (DiEthylStilbestrol)				characteristic				Good	30000
1-butyne				acetylenic odor		2,9 g/l / insoluble		Bad	200
5-ethyl-3-hydroxy-4-methyl-2 (5h)furanone				Sweet, fruity, caramel		soluble		Good	1380
mix of selenides				garlic	3				26000
mix aldehyde, acrylates and selenide				fruity	3	slightly			500
cyclo-octyne				intense and unpleasant				Good	250
acetylene			226	Garlic like / phosphine		1,185 g/l	1800 mg/m3	Good	fair
Phosphine				Garlic / decaying fish			TWA: 0,3 ppm	Good	fair
Explaination									
			<0,1		1	No reported effect or small effect (<10 mV)			
			0,1-0,5		2	Significant reported effect >10mV, 100mV<			
			>0,5		3	Large reported effect >100mV, 500mV<			

Table 1: Longlist of possible odorants. THT is added as reference

Table 2: Assessment of the candidate odorants

*OTV: Odor threshold value

Name	Assessment
Gasodor S-Free	Suitable, but already being researched within HyDelta
2,3-butanedione	No unique scent
Ethyl sugar lactone	No unique scent. High OTV*
Ethyl isobutyrate	No unique scent. High OTV*
5-ethyldiene-2-norbornene	**Selected for further research**
Cyclohexane	No unique scent
Methyl tert-butyl ether	**Selected for further research**
Tri-methylamine	No unique scent
2-hexyne	**Selected for further research**
1-pentyne	Price and solubility may be a problem
Ethyl isocyanide (enamine or isocyano ethane)	No unique scent
n-Butyl isocyanide	No information about health effects
Methyl methacrylate	Toxic
DES (DiEthylStilbestrol)	No information about health effects
1-Butyne	Perhaps less distinctive scent and difficult to obtain
5-Ethyl-3-hydroxy-4-methyl-2 (5h)furanone	No unique scent
Mix of selenides	No unique scent
Mix aldehyde, acrylates and selenide	No unique scent
Cyclo-octyne	Little information. Possible ‘reserve candidate
Acetylene	High OTV*
Phosphine	Toxic

2.3 Concentration levels

The concentration level for 5-ethyldiene-2-norbornene has been determined at 84 mg/m^{3}n, as described in the Hy4Heat study [4].

The concentration to be used for 2-hexyne has been determined based on olfactometry. The concentration was adjusted in such a way that the odor strength corresponded to that of odorised natural gas. The experiments showed that 2-hexyne at 15 mg/m^{3}n gave the same odor strength as natural gas. [5]

For methyl tert-butyl ether the concentration was difficult to determine because a large part of the panellists could not distinguish and/or detect the ether. For this reason, it was decided, based on discussions with the safety expert and project members, to use a concentration of 100 mg/m^{3}n. This concentration is still considered to be safe and it is unlikely that higher concentrations will be useful in practice.

3 FUEL CELL TESTS

The influence of the three candidate odorants on the functioning and aging of fuel cells has been investigated. The tests were performed at concentrations levels as described in paragraph 2.3. For this purpose, a Proton Exchange Membrane (PEM) set-up, provided by Proton Technologies was built up at the DNV laboratory, with which the odorants could be tested in hydrogen. The reason the PEM technology was chosen was based upon the following considerations:

- PEM technology is the most likely technology to be applied in hydrogen to energy conversion technologies;
- As the PEM technology suffers the most from potential contaminants it has the highest chance of detecting potential harmful components. it can be said that if an odorant is applicable for PEM, it will be also applicable for other types of fuel cells[2].

Proton Technologies has developed a dedicated, easy to use 8 cm² fuel cell test platform to conduct these tests, shown in figure 1. It is developed in such a way that it allows for cost effective experimental work on operating conditions of Membrane Electrode Assembly (MEA) and its development.

The cell itself has a single serpentine flow field, made out of graphite plates, ensuring no water build up in the flow field. The MEA's have an active surface area of 8 cm² and can be easily exchanged as the cell is being compressed with a single pneumatic piston. All MEA configurations can be tested based or a novel approach. The test stand frame only allows for single cells, but by switching off the frame, multicell configurations can be tested as well.

Figure 1: Proton Technologies 8cm² test platform

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[2] Also anionic fuel cell systems could have been used for testing, though it's market potential is limited and can withstand contaminants harmful to PEM based systems.

The standard electronic load provided within this system can be disconnected from the cell, without limiting gas supply possibilities for the cell. This means that an external electronic load or potentiostat can be connected to the cell to run various measurements such as: electrochemical impedance spectroscopy, cyclic voltammetry, chrono amperometry and others. For this experiment we have been investigating the potential poisoning of an anode catalyst with an odorant added to the hydrogen gas. We use a measurement method called electrochemical surface analysis (ECSA) in which a potentiostat applies a cyclic voltammetry protocol. Cyclic voltammetry basically means a potential sweep takes place multiple times between a start and stop potential at a predetermined sweep rate.

With this analysis it can be measured whether a catalyst is poisoned by any contaminants in the supplied gas stream. The measurement basics depend on bonded hydrogen to the platina, wherein there are 2 hydrogen atoms bonded to the platina, which can be oxidized by applying a voltage on the platina. During the experiment only the hydrogen bonded to the platina will participate in the measurement.

When hydrogen is being oxidized a current signal can be detected, which corresponds to the platinum active surface area. When a catalyst is poisoned, it means that the active platinum has bonded to a different species than hydrogen for example carbon monoxide. As, for instance, carbon monoxide has a different offset potential compared to hydrogen, the carbon monoxide will remain to be bonded to the active platinum particle during the measurement thus reducing the surface area in the cyclic voltammogram. Typically, hydrogen is being released from the platinum between 0.06V and 0.4V, whereas all hydrogen bonded to the platina is being oxidized. Carbon monoxide on the other hand starts being oxidized at around 0.65V and is fully oxidized at around 0.9V. This spectral offset makes cyclic voltammetry a discriminate method for determining whether a catalyst is being poisoned by a contaminant. Carbon monoxide is used in this example, but any other contaminant will require higher voltage in order to be oxidized from the platinum. Thus, any reduction in the active platinum area while a contaminant, such as an odorant, is being introduced into the gas stream can be attributed to the adsorption of this contaminant to the platinum making it therefore unsuited for usage.

A “fresh” 8 cm² with 0.5 mg_{Pt}/cm^2 on both anode and cathode was used in this experiment. Which was first conditioned with pure hydrogen and air until the performance had reached a stable level. After the 30 minutes the anode was flushed with nitrogen for 5 minutes, while at the cathode pure hydrogen was introduced. Both gas flows were set at 50 ml/min. Next a cyclic voltammogram was recorded by sweeping the anode potential from 60 mV to 600 mV back and forth for 3 times with a scan rate of 20 mV/s. This test resulted in a baseline of how much platinum was active within the anode at beginning of life (BOL)

Following, 50 ml/min hydrogen with odorant was introduced in the anode for 30 minutes. After the 30 minutes the anode was flushed with nitrogen for 5 minutes and a cyclic voltammogram was recorded. This was done for all 3 of the odorised hydrogen gas samples and tests were conducted twice to rule out measurement error. After the 3 odorants were tested a final pure hydrogen test was performed in order to compare before and after the introduction of the odorised gasses and is described as end of life (EOL).

The cyclic voltammogram was corrected for background current and the surface area was calculated. This was done for all 5 measurements which have been gathered in figure 2.

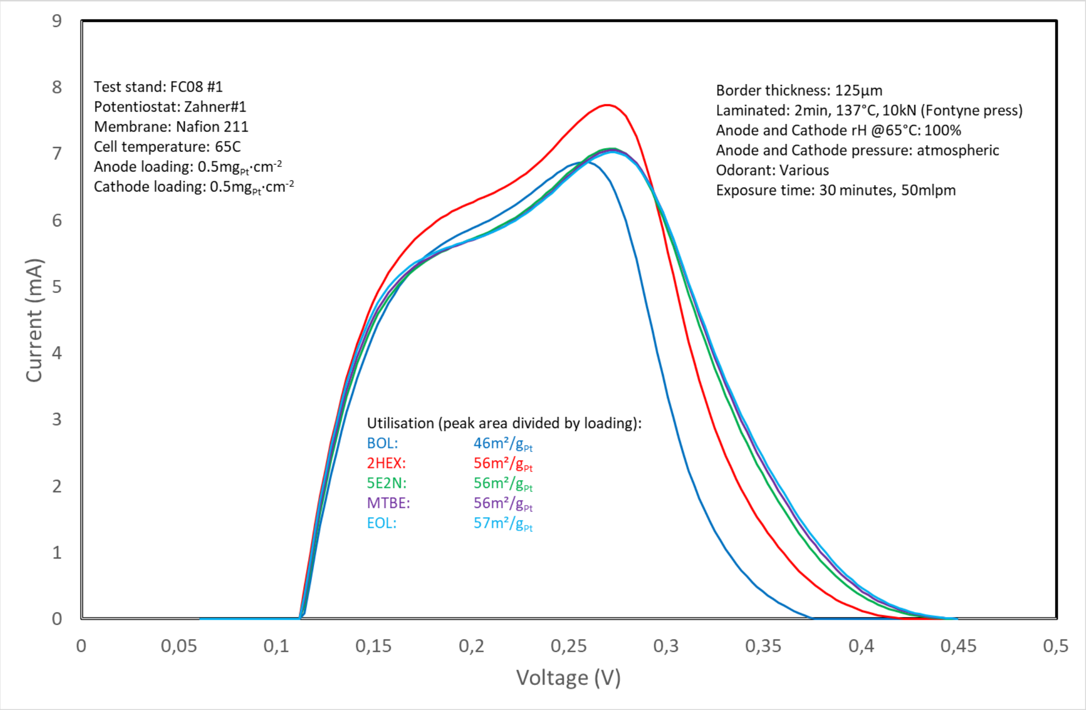

Figure 2: Corrected ECSA measurement plot

All 5 measurements result in more or less similar plot and surface area, clearly showing that there has not been any reduction of electro chemical active surface area. This concludes the investigation that the chosen odorants in the chosen concentrations within the hydrogen gas do not contaminate the PEM anode fuel cell.

4 LONG TERM STABILITY

The mixtures made by DNV for the fuel cell tests have been checked beforehand, during and afterwards the tests. During these analyses it was found that the concentrations of some of the mixtures decreased over time. Therefore, the three investigated odorants were subjected to stability tests.

4.1 Influence of various materials

During the tests, various cylinder materials (coated steel, copper, aluminium) were used. The tests were performed at pressures of 8-100 barg. Olfactometric tests were performed periodically, and the concentrations were determined by gas chromatography. The results are graphically presented in figure 3. As shown in the figure, the concentrations didn’t change over the test period, when using coated steel, copper and/or aluminium cylinders.

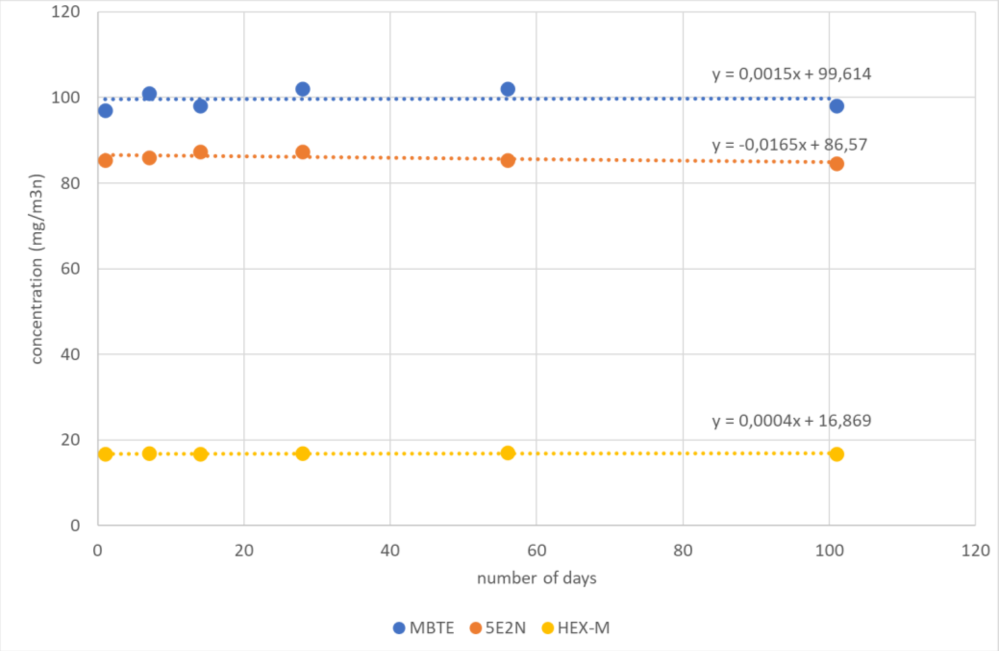

Figure 3: Results of long-term stability tests

4.2 Influence of pollutants

Also, gas mixtures were made in steel cylinders, that have been used for the delivery of hydrogen for many years. These cylinders were not cleaned prior to the filling process. The results show the conversion of the unsaturated hydrocarbons 2-hexyne and 5-ethyldiene-2-norbornene into their saturated versions, respectively hexane and 5-ethylnorbonane[3] (see figure 4). This so-called hydrogenation process was completed in instantaneously in one of the cylinders. In another cylinder the full conversion process took approximately one week.

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[3] Synonyms: 2-ethyl-norbonane and 2-thylbicyclo[2,,2,1]heptane

5-ethyldiene-2-norbornene 5-ethylnorbonane 2-hexyne hexane

Figure 4: unsaturated hydrocarbons and their saturated form (after hydrogenation)

Samples of both cylinders were analysed, using Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM/EDX).

SEM/EDX is the best known and most widely-used of the surface analytical techniques [6]. High resolution images of surface topography, with excellent depth of field, are produced using a highly focused, scanning (primary) electron beam. The primary electrons enter a surface with an energy of 20 keV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm).

In addition to low energy secondary electrons, backscattered electrons and X-rays are generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays (EDX analysis) emitted from the sample gives more quantitative elemental information.

SEM, accompanied by X-ray analysis, is considered a relatively rapid, inexpensive, and basically non-destructive approach to surface analysis. It is often used to survey surface analytical problems before proceeding to techniques that are more surface-sensitive and specialised.

In the figures 5 and 6 the SEM/EDX analyses of both cylinders are presented. The results of both analyses are summarized in table 3.

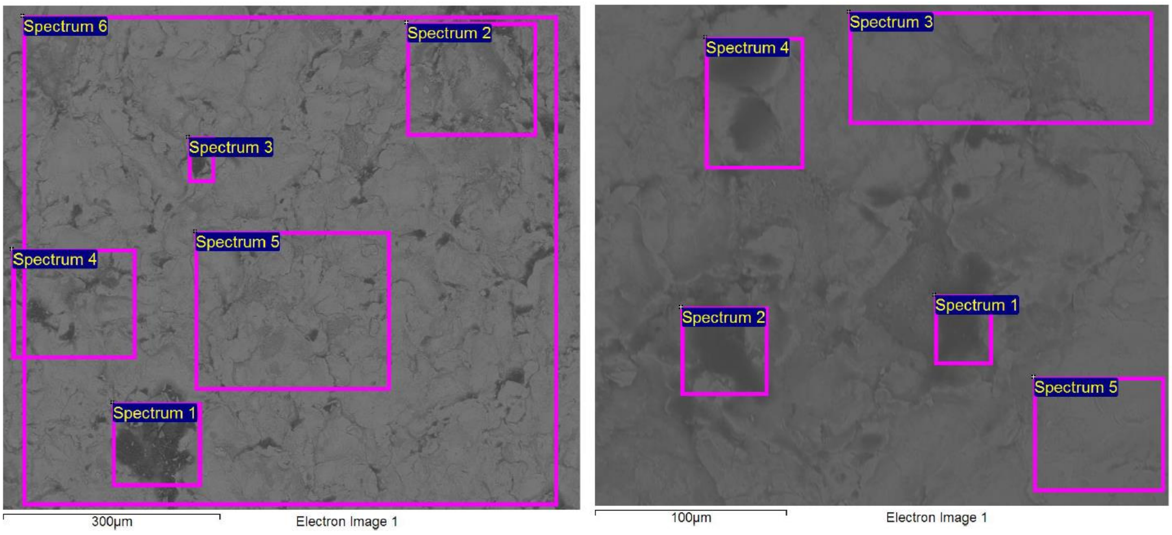

Figure 5: SEM/EDX analysis of cylinder #1 (slow conversion).

20keV. Magnification: left 400x, right 1000x

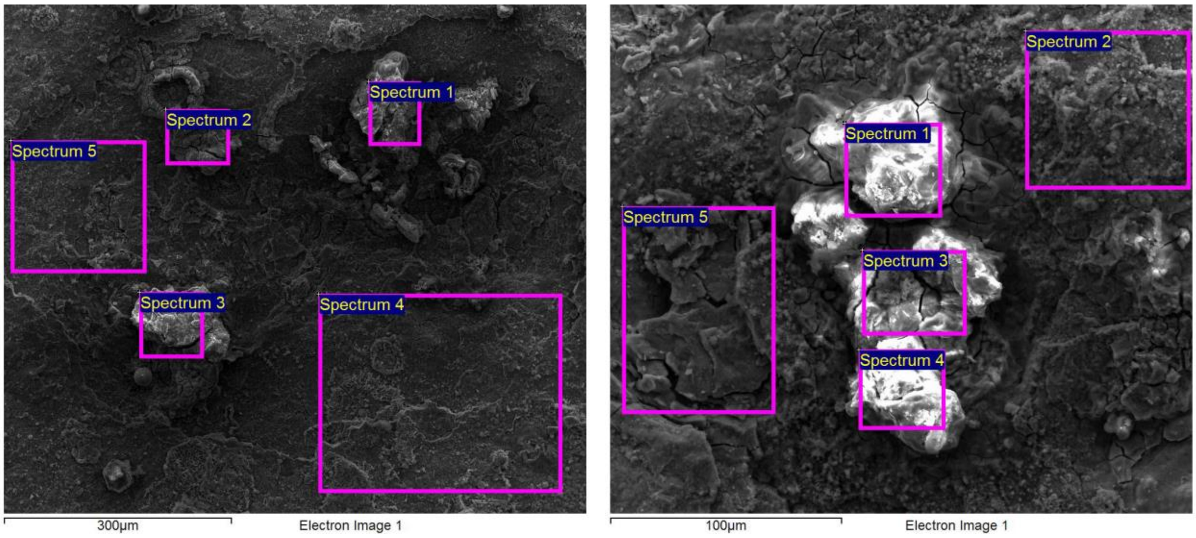

Figure 6: SEM/EDX analysis of cylinder #2 (immediate conversion).
20keV. Magnification: left 400x, right 1000x

Table 3: Results of the SEM/EDX analysis (normalized)

	Cylinder #1 (Slow conversion)		Cylinder #2 (Immediate conversion)	
Magnification	400	1000	400	1000
Spectrum	6	1	4	1
C	8.33	35.46	5.77	8.93
O	3.04	8.30	13.81	18.73
Na	-	-	-	-
Al	-	-	-	-
Si	0.42	0.93	0.37	0.24
P	-	-	-	-
S	0.20	0.11	0.01	-
Cl	0.16	0.19	0.07	0.19
K	-	-	-	-
Ca	-	0.18	0.34	-
Cr	1.34	0.64	-	0.21
Mn	0.72	0.43	0.51	0.70
Fe	85.79	53.64	79.14	70.96
Cu	-	-	-	0.07
Mo	-	0.12	-	0.32

The results, presented in the table above, are highly dependent on the size and location of the analysis, making it difficult to draw generic conclusions from the results.

It is clear that cylinder #1 contains more carbon and less iron and oxygen than cylinder #2. This will partly be the result of the type of steel being used, but also can be caused by the contamination found particularly in cylinder 2. The high oxygen content in the second cylinder indicates the presence metal oxides and/or deposited oxygen containing hydrocarbons, which may have resulted in the hydrogenation. Based on this SEM/EDX analysis it was not possible to draw conclusions. Therefore, additional research is required.

4.3 Influence of temperature

As hydrogenation is also temperature dependent, the stability of the odorants in hydrogen at elevated temperatures has been investigated. For this, mixtures are prepared in coated steel, aluminium and copper cylinders. Mixtures have also been prepared in plastics (HDPE and PVC), which are widely used in the gas distribution network. The filled gas cylinders were placed in a climate chamber, which could then be set at the desired temperature.

The maximum temperature was set at 40 ºC, corresponding with the maximum temperatures that generally are used in the Netherlands for HDPE and PVC. Under normal conditions this temperature will never be reached in practice, since the temperature of a gas pipe in the ground is approximately 8 ºC and elevated temperatures will only occur above the ground eq. inside houses, where 15-25 ºC is common.

Within the tested pressure and temperature ranges no conversion was observed. The results are shown in table 4.

Table 4: Influence of the temperature on the stability

Material	Pressure (barg)	Temperature range (ºC)	Result
Coated steel	8	0 – 40	No conversion
	16	0 – 40	No conversion
	40	0 – 40	No conversion
Aluminium	8	0 – 40	No conversion
	16	0 – 40	No conversion
	40	0 – 40	No conversion
Copper	8	0 – 40	No conversion
HDPE	8	0 – 40	No conversion
PVC	4	0 – 40	No conversion

5 ODOR MASKING BY THT FROM USED NATURAL GAS PIPELINES

It is known that THT adsorbs at the inner side of gas pipes. The desorption process of THT from the walls can take a very long period. Therefore, it can be expected that -when using old natural gas pipes for hydrogen transport- next to the new odorant also THT will be recognised. For this reason, the odor masking of 2-hexyne by THT was investigated. These additional tests were not carried out for the other two odorants, since the outcoming of the forgoing described tests showed that only 2-hexyne can meet most of the specified criteria.

For these olfactometric measurements, a test panel[4] was used, which was presented with five gas mixtures:
- 18 mg/m^{3}n THT in hydrogen (A);
- 3.75 mg/m^{3}n 2-hexyne and 13.5 mg/m^{3}n THT in hydrogen (75%A+25%B);
- 7.5 mg/m^{3}n 2-hexyne and 9 mg/m^{3}n THT in hydrogen (50%A+50%B);
- 11.25 mg/m^{3}n 2-hexyne and 4.5 mg/m^{3}n THT in hydrogen (25%A+75%B);
- 15 mg/m^{3}n 2-hexyn in hydrogen (B).

The questions to be answered by the test panel were:
- At what dilution can you recognize the odorant(s)?
- What do you recognize: 2-hexyne, THT or a mixture of both?
- Is the odor strength higher or lower than 15 mg/m^{3}n 2-hexyne?
- Is the odor strength higher or lower than 15 mg/m^{3}n THT?

The results are summarized in the tables 4-6 and figures 7-9.

Table 4: Detectability of the gas mixtures. *Based on 5 panel members.*

THT [mg/m^{3}n]	2HEX [mg/m^{3}n]								
Dilution factor		1000		500		250		100	
Perceptible		Yes	No	yes	No	Yes	No	Yes	no
18.00	0.00	20%	80%	100%	0%	100%	0%	100%	0%
13.50	3.75	20%	80%	100%	0%	100%	0%	100%	0%
9.00	7.50	0%	100%	100%	0%	100%	0%	100%	0%
4.50	11.25	0%	80%	100%	0%	100%	0%	100%	0%
0.00	15.00	0%	100%	100%	0%	100%	0%	100%	0%

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[4] The test panel consisted out of 5 persons. 4 of them are working at DNV and are familiar with the smell of THT

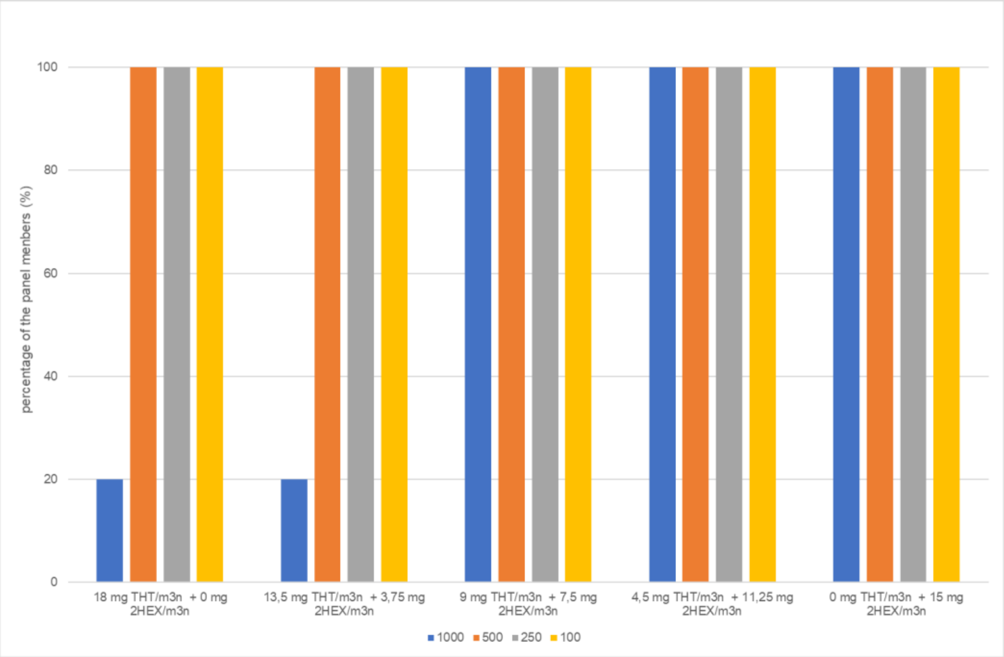
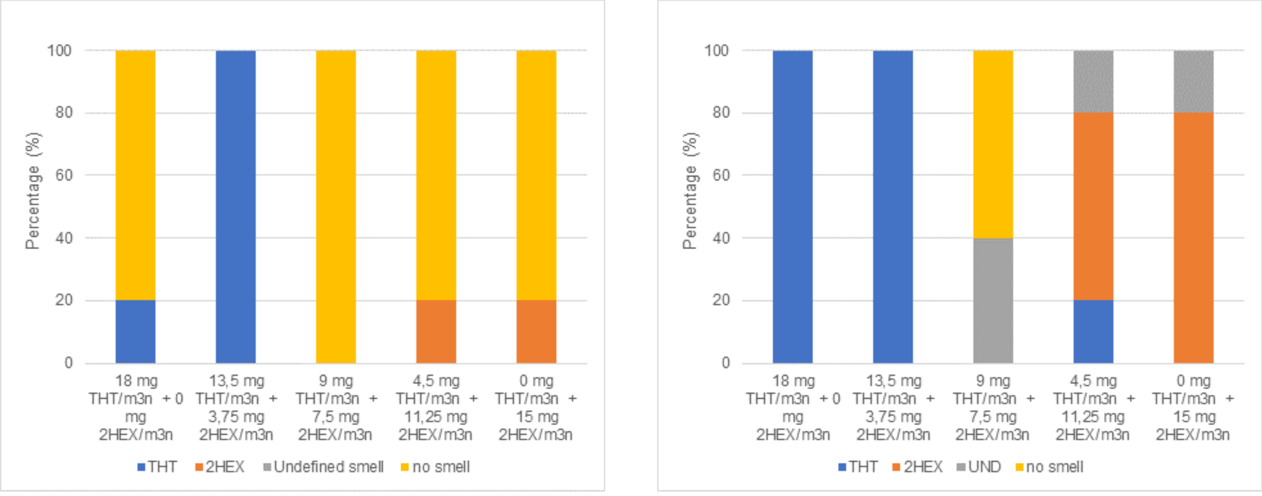


Figure 7: Detectability of the gas mixtures at various dilution factors

Table 5: Identification of the smell. *Based on 5 panel members. *UND: undefined smell.*

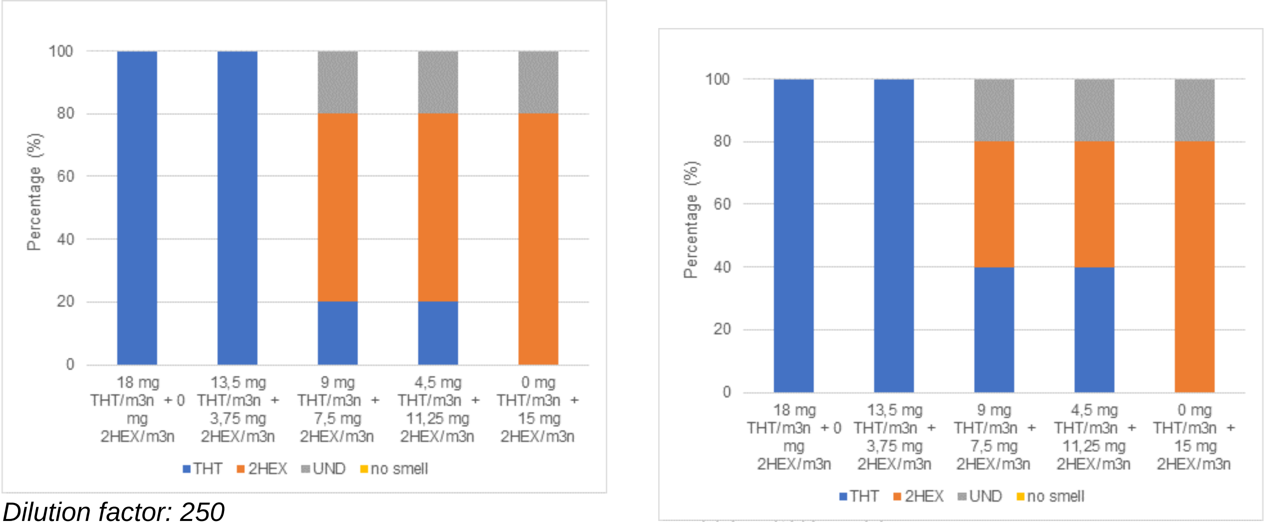
THT [mg/m^{3}n]	2HEX [mg/m^{3}n]												
Dilution factor		1000			500			250			100		
Identification		THT	2HEX	UND*	THT	2HEX	UND*	THT	2HEX	UND*	THT	2HEX	UND*
18.00	0.00	20%	0%	0%	100%	0%	0%	100%	0%	0%	100%	0%	0%
13.50	3.75	100%	0%	0%	100%	0%	0%	100%	0%	0%	100%	0%	0%
9.00	7.50	0%	0%	0%	0%	0%	40%	20%	60%	20%	40%	40%	20%
4.50	11.25	0%	20%	0%	0%	0%	40%	20%	60%	20%	40%	40%	20%
0.00	15.00	0%	20%	0%	0%	80%	20%	0%	80%	20%	0%	80%	20%

Figure 8: Identification of the smell at various dilution levels



Dilution factor: 1000

Dilution factor: 500

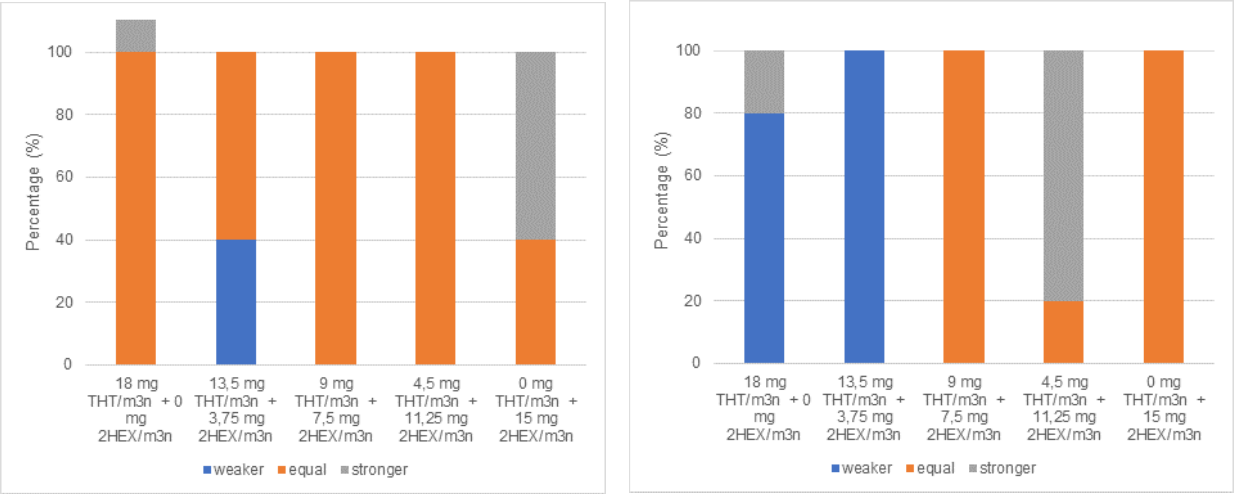


Dilution factor: 250

Table 6: Odor strength (intensity) at a dilution factor of 100, compared to THT and 2-hexyne reference material. *Based on 5 panel members.*

THT [mg/m^{3}n]	2HEX [mg/m^{3}n]	THT [18 mg/m^{3}n]			2HEX [15 mg/m^{3}n]		
		weaker	Equal	Stronger	Weaker	Equal	stronger
18.00	0.00	0%	100%	0%	80%	0%	20%
13.50	3.75	40%	60%	0%	100%	0%	0%
9.00	7.50	0%	100%	0%	0%	100%	0%
4.50	11.25	0%	100%	0%	0%	20%	80%
0.00	15.00	0%	40%	60%	0%	100%	0%

Figure 9: Odor strength (intensity) at a dilution factor of 100, compared to THT and 2-hexyne reference material



Reference: 18 mg THT/m^{3}n *Reference: 15 mg 2HEX/m^{3}n*

From the obtained results it can be concluded that 15 mg/m^{3}n 2-hexyne -as expected- has approximately the same odor threshold and strength as is achieved with 18 mg/m^{3}n THT.

Based on the test results, the odor masking of 2-hexyne due to the presence of THT in the gas mixture is not expected to be an issue. At a concentration of 4.5 mg/m^{3}n THT and 11.25 mg/m^{3}n 2-hexyne, 4 (=80%) of the panellists indicate that they perceive 2-hexyne. Only 1 (=20%) panellist perceives the odor as a mixture of both odorants. In all cases it can be said that the hydrogen has an alarming smell.

6 CONCLUSIONS AND RECOMMENDATIONS

From this study, it can be concluded that 2-hexyne appears te be suitable for use as sulphur-free odorant in hydrogen, as its smell is sufficient distinctive and alarming.

From the obtained results it can be concluded that 15 mg/m^{3}n 2-hexyne has approximately the same odor threshold and strength as is achieved with 18 mg/m^{3}n tetrahydrothiophene (THT) that is used as odorant in natural gas.

2-hexyne showed not to have an adverse effect on the performance of Proton Exchange Membrane (PEM) fuel cells. As the PEM technology suffers the most from potential contaminants it has the highest chance of detecting potential harmful components. Therefore, it can be expected that other types of fuel cells also will not be negatively influenced by the odorant.

It should be noted that contaminations of, in particular, oxygen-containing hydrocarbons in the gas system can lead to hydrogenation of 2-hexyne, whereby the substance is (partly) converted into hexane and the smell decreases. Tests have shown that increasing the temperature to 40 ^{o}C does not affect the stability of 2-hexyne.

During the transition, pipelines will still contain traces of THT. The odor masking of 2-hexyne due to the presence of THT in the gas mixture is not expected to be an issue. At a concentration of 4.5 mg/m^{3}n THT and 11.25 mg/m^{3}n 2-hexyne, 80% of the panellists indicate that they perceive 2-hexyne. 20% of the panellist perceives the odor as a mixture of both odorants. In all cases it can be said that the hydrogen has an alarming smell.

Since the olfactometric measurement were carried out with a small panel, it is recommended to repeat those measurement with a larger group of people, who are preferably not working in the gas industry.
As the existing pipelines, that are used for distribution of natural gas for many decades, can contain THT and hydrocarbons it is recommended to investigate the optimal conditions for removing THT and to investigate the influence of materials and trace components on the stability of 2-hexyne.

7 LITERATURE

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