ODORISATION OF NATURAL GAS AND HYDROGEN MIXTURES

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Contact

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ABOUT MARCOGAZ

Founded in 1968, MARCOGAZ is the technical association of the European gas industry. It represents 30 member organisations from 20 countries. Its mission encompasses monitoring and policy advisory activities related to the European technical regulation, standardisation and certification with respect to safety and integrity of gas systems and equipment, rational use of energy as well as environment, health and safety issues. It is registered in Brussels under number BE0877 785 464.

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1. Odorisation issue related to the addition of hydrogen in natural gas

1.1. Background information

Hydrogen was one of the major components of the town gas (cracking treatment produced around 10-20% of hydrogen, while reforming produced up to 60%). In this case, however, odorisation wasn't required because of the self-odour of the town gas.

The addition of hydrogen modifies natural gas composition and – consequently - the physical properties, so a question could be raised if odorisation is affected by these changes.

1.2. Preliminary works

The Final Report of the GERG Project "Admissible Hydrogen Concentrations in Natural Gas Systems" (October 2013) doesn't deal about odorisation, considering that safety parameters are non-critical aspects.

The Final Report of CEN/CENELEC Sector Forum Energy Management / Working Group Hydrogen (2016) deals, in a dedicated chapter, about odorisation of hydrogen injected into natural gas. The Final Report recommends "*the standardization in order to harmonize the performance indicators for odorants used for H2NG*". Two standards are to consider: ISO TR 16922:2013 (which specifies the principles for the odorisation technique and the control of odorisation of natural gas) and ISO 13734:2013 (specifies general requirements for odorants and the physical and chemical properties of commonly used odorants)[1]. Odorisation is recalled in other chapters of the same document. It is written: "*Also performance tests on the propagation of smell depending on hydrogen concentrations for new odorants are recommended in the near term and should be addressed before 10 vol% is injected into the natural gas grid.*" It is also mentioned that "*Performance tests to determine the suitability of odorants for different H2NG mixtures are recommended in the near term*". Another recommended study is to "*investigate the propagation of smell for new odorants in presence of hydrogen*".

[1] The ISO TC 193 / WG 5 "Odorisation" is in charge to review the current ISO standards.

2. Effects of hydrogen addition to natural gas odorisation

In this chapter, some information is presented to try to give some answers to the questions raised, even if some new tests could be necessary.

The injection of hydrogen into natural gas grids can be investigated through different potential impacts:

- Possibility of chemical reactions between hydrogen and odorants,
- Physical effects in the grid,
- Possibility of odorant masking by hydrogen.

2.1. Possible chemical reactions between hydrogen and odorants

The answers listed below were obtained from exchange of information with the gas odorants suppliers (Th. Geyer GmbH for the Sulphur-Free odorant, Chevron Philipps and Arkema for the THT (Tetrahydrothiophene) and the blends of mercaptans). More information is given in Annex A (§.7).

Sulphur odorants are, from the chemical point of view, reduced compounds, so a reaction with hydrogen is not expected. Usually problems with odorants are produced by oxidation (more with mercaptans than sulphides), mainly in presence of iron oxides.

The common reaction of hydrogen with organic compounds is hydrogenation, which typically is the addition of pairs of hydrogen atoms to a molecule, often to an unsaturated bond.

Sulphur-based odorants (like THT, mercaptans) are all saturated, therefore no reaction with elemental hydrogen seems to be likely at the conditions typically found in the gas distribution systems.

Sulphur-free odorants (such as acrylates) exhibit a C=C double bond which makes them prone to addition reactions. Addition of hydrogen however requires a metal catalyst with an active surface. Nevertheless, it is known that in steel pipelines corrosions products and solid deposits may contain some pyrophoric iron, which exhibits an extremely reactive surface due to its fine granularity. These deposits may be able to catalyze an electrophilic addition of hydrogen to the C=C double bond. This may lead to a depletion of the odorant, as a consequence of a reaction unlikely but possible.

Note:

- In case of high purity hydrogen used for fuel cells supply, Sulphur containing odorants shall be avoided because of the poisoning of the cells.

2.2. Physical effect of hydrogen addition in natural gas

2.2.1. Density and vapour pressure

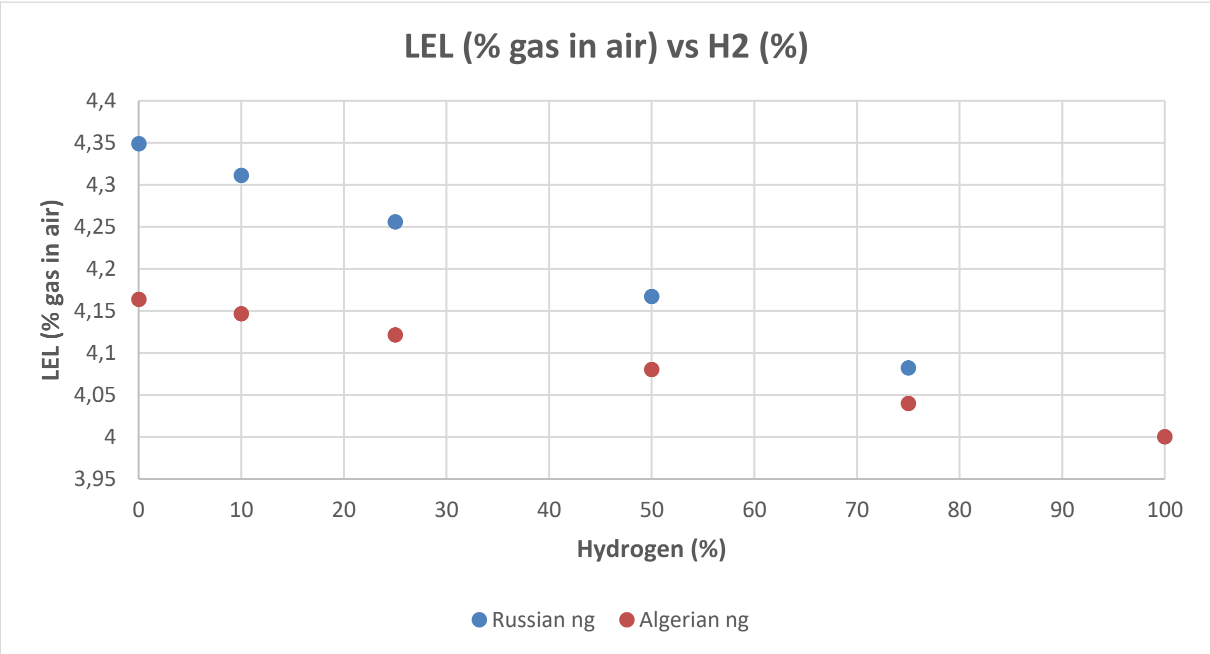
Care must be taken in the choice of the odorant if the amount of hydrogen in the H2NG mixture affects significantly the density and vapour pressure of the gas. If the gas density is reduced, the odorant, which is liquid, should be chosen according to the properties of the H2NG mixture. Odorants with lower density and higher vapour pressure could better fit for higher amounts of hydrogen in the H2NG mixture. Care should also be taken when odorant is a blend (due to possible differences in the physical properties of the components of the blend).

2.2.2. Lower Explosion Limits (LEL) of H2NG

Gas odorisation is, in most countries, a legal or regulatory requirement that specifies that natural gas in air has to be readily detectable by odour at a concentration of 20-25 % of the LEL (Lower Explosion Limits).

Hydrogen and natural gas have almost similar LEL values, so the LEL of the mixture doesn't change significantly when hydrogen is injected.

Simulations[2] were done to calculate the LEL of mixtures of two natural gases (Russian-type and Algerian-type) at increasing concentrations of hydrogen:



Data calculated in reference to atmospheric conditions: pressure of 101,3 kPa and temperature of 20°C.

[2] Using the method in Schroeder V. "Calculation of flammability and lower flammability limits of gas mixtures for classification purposes" (BAM Berlin, 09-09-2016) and using the values of Li and Kk from EN ISO 10156:2010,

2.3. Odorant masking by hydrogen addition in natural gas

No evidences of masking effects are available up to now.

2.4. Measurement of odorant in the H2NG

Although no problems were reported with gas chromatographs, odorant measurement with chemical sensors could be influenced by hydrogen.

3. Hydrogen injection into natural gas at MOP ≤ 16 bar

These data were collected by MARCOGAZ members, based on available information at the time of the report was made.

3.1. France

An experimental project (called GRHYD, coordinated by ENGIE from 2014 until 2020) is injecting progressively hydrogen, up to 20% in concentration, into natural gas in a local, new and dedicated odorized natural gas grid. The decision is to not odorize hydrogen, because the dilution factor used (even the maximum one) and the concentration of the THT of the mixed natural gas are still in adequacy with the technical requirement of the distribution operators. A µGC (micro-Gas Chromatograph) will measure on-line the concentration of THT before the injection of hydrogen.

3.2. Germany

Several injections of hydrogen (with a concentration up to 2%) into natural gas grids are operated, but, so far, no effect of the hydrogen onto the odorisation has been reported:

- Near Hamburg, hydrogen is injected into the grid of HanseGas which is odorized with the odorant mercaptan mixture based on TBM (Tert-butyl-Mercaptan). No report on odorisation problems raised, too.

- In Frankfurt, hydrogen is injected into the local grid, which is odorized with a mercaptan mixture based on TBM. In that grid, there were severe problems with the odorisation, but those could be identified not being caused by the hydrogen injection. The source of the problem was two biogas plants feeding their biomethane into the gas grid. The biomethane was conditioned with LPG to achieve the Wobbe-index of the natural gas, and the trouble came from interferences with the odorant in the LPG.

- There are some more injections of hydrogen in Germany, but at the moment there is no information about that.

The German National Committee on odorisation gives the following indications:

- To odorize natural gas/hydrogen mixtures, the odorants specified in (EN) ISO 13734 will suffice.

- To odorize "pure" hydrogen grids, there will only be the need for odorisation if the hydrogen replaces the natural gas delivered to "ordinary" customers. So far, all hydrogen grids existing or projected for the future end in chemical or other industrial plants as e. g. power stations, i. e. without the need for odorisation. However, there may be such grids reaching normal "tariff" customers in some years and given the option that also some fuel cells will be run in such grids, there may develop the need for adapted odorants without Sulphur.

- Hydrogen odorants may be in demand in the near future: a need for standardization probably will raise.

3.3. Italy

Up to now in Italy there are no injection of hydrogen into the natural gas grids, so there is no direct experience on a possible interference between odorant and hydrogen. Anyway, there were experiences with odorisation of manufactured gases. A confidential study dated 1983 refers on rhino-analytical controls of grids distributing natural gas and manufactured gas containing hydrogen, both odorized with mercaptans: no differences were noted.

The composition of manufactured gas was roughly the following:

- Methane: 45 %;
- Hydrogen: 28 %;
- Carbon Monoxide: 8 %;
- Carbon Dioxide: 8 %;
- Oxygen: 2 %;
- Nitrogen: rest.

3.4. The Netherlands

During 2019-2020, a research was organized by Gasunie Transport Services (GTS) and Netbeheer Nederland in order to state if increasing hydrogen concentrations can affect the effectiveness of odorisation.

DNV GL and SGS Nederland prepared 12 different mixtures of Groningen natural gas (L-gas) at four different concentrations of Hydrogen (0%, 15%, 85% and 100%) and three different odorants: THT, Spotleak 1001® (TBM+DMS 80:20) and Gasodor ® S-Free.

The different samples were anonymously assessed by a panel of smellers of the Odor Laboratory Bureau Blauw B.V. It was concluded that mixtures of natural gas and hydrogen and pure hydrogen can be sufficiently odorized with the tested odorants.

No significant effects caused by hydrogen addition were found.

3.5. United Kingdom

In October 2019, Hy4Heat published a report on "Hydrogen Odorant" (Project Closure Report - Hydrogen Odorant and Leak Detection - Part 1 - Hydrogen Odorant", from SGN), the aim of which was to identify a suitable odorant for use in a 100% hydrogen gas grid (domestic use such as boilers and cookers).

The research involved a selection of five odorants to be tested about the effects of the mixtures on pipeline (metal and plastic), appliances (a hydrogen boiler provided by Worcester Bosch) and PEM fuel cells. For the olfactory test, each odorant was evaluated by 6 panellists.

The odorants:

	Odorant name (including alternative names)	Compound	Rationale
1	Odorant NB, NB	78% 2-methyl-propanethiol, 22% dimethyl Sulphide	Primary odorant used by Scotia Gas Network and other UK gas networks
2	Standby Odorant 2, NB Dilute	34% Odorant NB, 64% Hexane	Diluted form of Odorant NB used by SGN if supply of Odorant NB is compromised
3	Odorant THT, THT	100% tetrahydrothiophene	Most commonly used odorant within European gas networks
4	GASODOR-S-FREE, Acrylates	37.4% ethyl acrylate, 60.1% methyl acrylate, 2.5% 2-ethyl-3methylpyrazine	Sulphur-free gas odorant in use within some German gas networks
5	5-ethylidene-2-norbornene, Norbornene	5-ethylidene-2-norbornene	Odorant with an unpleasant odour that is suitable for fuel cell applications

The results:

	Odorant NB	Standby odorant 2	Odorant THT	GASODOR-SFREE	5-ethylidene-2-norbornene
Health/environment	green	green	green	green	green
Olfactory	green	green	green	green	yellow
Pipeline	green	green	green	green	green
Flame boiler	green	green	green	green	green
Fuel cell	red	yellow	red	yellow	yellow
Economic (*)	green	yellow	yellow	yellow	yellow

(*) Please note that the economic evaluation is referred to UK conditions and, generally speaking, cannot be considered applicable as it is to all Europe.

All the odorants were judged suitable for use in a 100% hydrogen gas grid for combustion applications, but further research would be required if the intention is to supply grid hydrogen to stationery fuel cells or fuel cell vehicles.

The olfactory testing suitability was based on odour concentration (how easily the odorant could be detected), the intensity (on the Sales scale) and character (whether it would be distinguishable from other possible odours such as food). All odorants met the testing criteria for odour concentration and intensity. All odorants except 5-ethylidene-2-norbornene met the requirements for character testing, as they were perceived as unpleasant and gave smells that could be characterised as sulphur or oil. The 5-ethylidene-2-norbornene was perceived as fruity (as well as sulphur and oil), which indicated that some customers would not immediately recognise a gas leak if this odorant was used in the gas grid.

3.6. PRCI State of the Art on hydrogen

In this study, done with the overall goal to develop a concrete path forward to define the necessary projects that need to be completed for companies to safely and reliably inject hydrogen into their pipelines at certain blend levels, there is the following table regarding odorisation:

Topic	Key results, knowledge is available	Gaps, ongoing research or needs further investigation
Odorants	• At this time, there is no known odorant suitable for hydrogen that is light enough to "travel with" hydrogen at an equal dispersion rate. • Existing projects for hydrogen blending in natural gas, up to 20%, generally use the standard odorization for natural gas. • A recent study of common odorants THT, Spot-leak® 1001, and Gasodor® S-Free concluded that all odorants were detectable in a range of hydrogen blending in natural gas (from 0% to 100%), however the experimental set up did not allow for consideration of hydrogen separation from the natural gas. • (NOTE: the last sentence is referring to 3.4).	• Evaluation of typical odorants for natural gas and their effectiveness under situations of hydrogen blending at various blend percentages, for practical situations such as pipeline leaks and leaks in buildings where hydrogen may separate from the natural gas and odorant. • Particularly for situations of pipeline leaks, the stratification of hydrogen from natural gas, and therefore from the odorant, needs to be better understood to advise safety protocols during leaks and repairs. It would be useful to be able to evaluate a timescale for gas separation/concentration gradient at ambient pressure (i.e., does it take hours/days for hydrogen to separate from the natural gas and odorant?). • Assessment of alternative options for identifying leaks and specifically hydrogen gas when blending hydrogen at higher percentages. • Conflicting data exists regarding the effectiveness of common natural gas odorants for detecting pure hydrogen; further investigation is required to assess if hydrogen separated from natural gas following leakage could be effectively identified.

4. Hydrogen injection into natural gas at MOP > 16 bar

These data were collected by MARCOGAZ members, based on available information at the time of the report was made.

4.1. The Netherlands

At the moment there is a single part of the grid where refinery gas, containing up to 15% of hydrogen, is odorized with THT at 18 mg/m^3(n). Every 3 weeks the degree of odorisation is measured with a µGC, without any reported failure in odorant concentration. No olfactory test can be performed due to the presence of CO in the gas.

So far, no other data is available on odorisation effect from the injection of hydrogen in gas network at MOP > 16 bar.

4.2. France

The Jupiter 1000 project (coordinated by GRTgaz since 2014) is the first industrial demonstrator of Power-to-Gas (P2G) in France with a power rating of 1 MWe for electrolysis and a methanation process with carbon capture. The scope is to convert renewable power surplus into green hydrogen and syngas, injecting it into the gas grid. On Jupiter 1000 platform, pipelines are made of stainless steel, such as the transmission network. Maximum 6% of hydrogen will be injected in transmission pipelines containing natural gas. No odorisation addition are performed due to the low level of dilution of hydrogen in natural gas. Also, no control of the level of THT after the hydrogen injection in natural gas are scheduled.

5. Conclusions and Actions

No evidence of problems in odorisation after addition of hydrogen to natural gas were found yet, but experiences are small, up to now. Some olfactory results show that the odorisation of natural gas/hydrogen mixtures could be performed with the same odorants and concentrations as for natural gas; some concern, however, can rise about the possibility of a separation of natural gas and hydrogen when pipeline leaks occur, due to the differences in physical properties: in this case the odorant could not be equally distributed in the leak. For this reason, we suggest to consider a safe concentration of hydrogen in the natural gas - for odorisation – up to 15% of hydrogen. However, MARCOGAZ is awaiting new data on the topic in order to assess and determine whether this threshold can be increased.

It is not easy to extend the information from distribution grids to transmission grids, due to the higher pressure, even if the hydrogenation is not expected in absence of catalysts.

In addition, more information is needed regarding the following items:

- Possible effects on odorisation due to differences in physical properties of the mixture of gas and odorant (density, vapor pressure, …),
- Possible chemical reaction between hydrogen and odorant at high pressure condition,
- Possible effects of high concentrations of hydrogen on gas odorant,
- Influences from possible impurities from hydrogen production.

6. Bibliography

- GERG Project "Admissible Hydrogen Concentrations in Natural Gas Systems (HIPS)" (Final report - Hydrogen Consortium - October 2013).
- Sector Forum Energy Management / Working Group Hydrogen Final Report; EUR 27641 EN; 10.2790/66386 (2016).
- Hy4Heat: Project closure report - Hydrogen Odorant and Leak Detection - Part 1, Hydrogen Odorant - October 2019 - A consolidated summary report by Dr Arul Murugan, Senior Research Scientist (NPL).
- Odor assessment of selected odorants in hydrogen and natural gas-hydrogen mixtures. Gasunie Transport Services B.V. and Netbeheer Nederland - Report n°: OGNL.194132 -Date: 22-07-2020.
- PRCI (DRAFT) - Emerging fuels – Hydrogen - SOTA, Gap Analysis, Future Project Roadmap - MEAS-15-02 Catalog No. PR-720-20603-R01 - Authors: Kim Domptail, Shannon Hildebrandt, Graham Hill, David Maunder, Fred Taylor, Vanessa Win - Release Date: October 1, 2020.

7. Annex A: Information on Odorants for Hydrogen received by Odorants Companies

7.1. Annex A.1 - Information from Arkema – GRL (Jean-Benoit Cazaux)

From the odorant perspective, no chemical compatibility issue to whatever hydrogen concentration are foreseen. A challenge might be to correct the measure H_2 flowrate and concentrations to adjust the dosage.

Physical data:

Odorant	density at 273K (kg/m^3)	density at 288K (kg/m^3)	Vapor pressure at 273K (mbar)	Vapor pressure at 288K (mbar)
THT+ EA (Ethyl Acrylate)	950	910	11	27
THT	1016	1003	5,8	13
TBM+IPM+NPM	825	810	82	169
TBM+MES	828	813	71	152
TBM+DMS (UK+IE)	830	814	114	230
TBM+DMS (CZ)	837	817	140	246
EM	861	844	246	486

7.2. Annex A.2 - Information from Chevron Phillips (Alex Pauwels)

Hydrogen was already used in a distant past as it was in a large proportion present in the so called "town-gas". This gas contained traces of several mercaptans that gave it its typical "gassy" odor. Once town gas has been replaced by natural gas it became standard practice the odorize the natural gas with mercaptans, mixtures of mercaptans and or sulphides. The obvious selection for these compounds was to copy the so called "gassy odor" from town gas that was recognized by the general public as an odor that might warn for a gas leak. No reason why also these odorants would not be the best choice to odorize natural gas containing hydrogen since this will only be copying the historical "town-gas".

Name	Density at 273K (kg/m³)	Density at 288K (kg/m³)	Vapour pressure at 273K (bar)	Vapour pressure at 288K (bar)
THT (SCT)	1015,73	1002,78	0,00554	0,014
TBM-IPM-NPM (SC E)	824,33	810,8	0,00842	0,17
TBM-DMS (SC F20)	830,09	814,36	0,1226	0,23
THT-TBM (SC TB5)	907,83	893,1	0,0406	0,084
EM (SC A)	861,32	844,31	0,246	0,474

7.3. Annex A.3 - Information from Th. Geyer GmbH (previously Symrise)

- No experience concerning the effect of minor concentrations of H_2 (up to 20%) on the "Gasodor™S-Free". This will have to be tested in further investigations.

- On the other side, already in the year 2006, they developed a product called "Gasodor™Hydrogen", which purpose is to be used with pure hydrogen with respect to PEM-fuel-cells.

- The reason for the new product was the fact, that the well-known "Gasodor™S-Free" exhibits 2-Ethyl-3-methylpyrazine as a nitrogen source which may have undesirable effects on catalysts.

- This new product, Gasodor™Hydrogen, however, is not yet being used anywhere in the world, therefore is not yet commercially available and not yet approved.