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Odor assessment of selected odorants in hydrogen and natural gas-hydrogen mixtures

Gasunie Transport Services B.V. and Netbeheer Nederland

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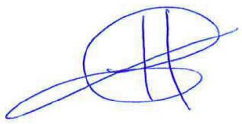

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1 SUMMARY

A trend can be observed within Europe to replace fossil gases by hydrogen in the near future. Before it is clear whether this goal is feasible, research is needed. One of these topics is the question whether it is possible to odorize pure hydrogen, or mixtures of hydrogen and natural gas, so that it 1. can it be smelled sufficiently and 2. does the amount of hydrogen influences the odor intensity and characteristics? The aim of this research project is to find out with a few simple experiments how the odor of hydrogen and mixtures of hydrogen and natural gas, which have been odorized with various common odorants in Europe, is assessed by an independent odor panel.

Gasunie Transport Services (GTS) and Netbeheer Nederland have asked DNV GL and SGS Nederland to prepare and analyze several gas mixtures with some selected odorants for an odor assessment of hydrogen and mixtures of hydrogen with natural gas. A total of 12 different mixtures were prepared with the odorants THT, Spotleak® 1001 and Gasodor® S-Free. These mixtures were anonymously assessed by a panel of Odor Laboratory Bureau Blauw B.V. on October 28 and 29 of 2019 in Wageningen, The Netherlands. The odor panel consisted of 6-7 panelists.

It can be concluded for 11 mixtures that the odors can already be classified as slightly annoying upon observation or just above threshold. In addition, a standard dilution (= 156 times) of all samples was presented to the panel, which showed that the odor intensities were assessed as "very" to "extremely unpleasant". Of the 12 samples, 7 samples were recognized, 5 of which were directly associated with (natural) gas.

THT is well recognized by most panelists as (natural) gas in all mixing ratios between natural gas and hydrogen. For Spotleak 1001 and Gasodor S-Free, the odor is less known and is less often associated with natural gas. A common recognition/description was respectively "chemical" and "(burnt) rubber/plastic". The odor thresholds for Spotleak 1001 and Gasodor S-Free are lower than those for THT (therefore less is needed to achieve enough odor intensity).

For all three odorants, a slight trend can be observed that odor intensities increase with an increase in hydrogen concentration. Possibly a decrease of natural gas concentration is less masking the odorant, which increases odor intensity.

Overall, it can be concluded that mixtures of natural gas and hydrogen and pure hydrogen can be sufficiently odorized with some commonly used odorants across Europe. Adding THT results in the best recognition and association with (natural) gas, which is to be expected with a Dutch odor panel, because THT is the only odorant in The Netherlands used for natural gas.

2 INTRODUCTION

A trend can be observed within Europe to replace fossil gases by hydrogen in the near future. Before it is clear whether this goal is feasible, research is needed. One of these topics is the question whether it is possible to odorize pure hydrogen, or mixtures thereof with natural gas, so that it can be smelled sufficiently and/or the amount of hydrogen influences the perception. To be effective, odorization must give an odor that is easily noticeable by a person with a normal sense of smell and is also alarming (unpleasant). The odorant must be chosen in such a way that confusion with other substances is virtually eliminated. The Dutch standard NEN 7244-1 specifies the following requirement for odorization: for the natural gas distributed in the Netherlands, the lower explosion limit is approximately 5 % by volume of natural gas in air. A gas concentration of 1 vol % natural gas in air (= 20 % LEL) should therefore be easily recognized. The same applies to hydrogen and mixtures of natural gas and hydrogen.

The aim of this research project is to find out with a few simple experiments how the odor of hydrogen and mixtures of hydrogen and natural gas, which have been odorized with various common odorants in Europe, is assessed by an independent odor panel.

Gasunie Transport Services (GTS) and Netbeheer Nederland have asked DNV GL and SGS Nederland to prepare and analyze several gas mixtures with some selected odorants for an odor assessment of hydrogen and mixtures of hydrogen with natural gas. These mixtures were anonymously assessed by a panel of Odor Laboratory Bureau Blauw B.V. on October 28 and 29 of 2019 in Wageningen, The Netherlands. They are accredited by the Dutch Accreditation Council (registration number L400) for performing olfactometric assessments in accordance with the European/Dutch standard NEN-EN 13725 and performing hedonic assessments in accordance with the requirements of standard NVN 2818 (2005).

This report provides an overview of the approach and odor perception of odorized hydrogen and mixtures of natural gas/hydrogen with THT, Spotleak 1001 and Gasodor S-Free by an independent odor panel.

3 PREPARATION OF MIXTURES

The study was conducted with three different odorants, namely: TetraHydroThiopheen (THT, from a stock tank of M&R Haren and also standard odorant in the Netherlands), Spotleak® 1001 and Gasodor® S-Free. Spotleak® 1001, from Arkema (France), consists of a mixture of 80% Tert-ButylMercaptane (TBM) and 20% DiMethylSulfide (DMS). This is the odorant that is applied in the United Kingdom and Ireland for the odorisation of natural gas. Gasodor® S-Free, from Symrise (Germany), consists of a mixture of acrylates (37.5% methyl acrylate and 60% ethyl acrylate) and methyl ethyl pyrazine (2.5%). The latter odorant does not contain sulfur and could potentially be a good candidate for the odorisation of pure hydrogen considering end users (think of fuel cells that are poisoned in the presence of traces of sulfur). Gasodor® S-Free is used by several local grid owners (Stadtwerke) in Germany.

Four different mixtures have been prepared for each odorant:

1. 100% natural gas + odorant;
2. 85% natural gas + 15% hydrogen + odorant;
3. 15% natural gas + 85% hydrogen + odorant;
4. 100% hydrogen + odorant.

A total of 12 mixtures were prepared in 5-liter aluminum cylinders, the internal coating of which is suitable for sulfur-containing components. The maximum filling pressure is 80 bar, making approximately 400 liters of sample gas available for the odor laboratory.

The odorant in question has been added to the mixtures in accordance with the nominal concentration in natural gas as far as possible, respectively 18 mg/$m^3_{(n)}$ THT, 6 mg/$m^3_{(n)}$ Spotleak® 1001 and 10 mg/$m^3_{(n)}$ Gasodor® S- Free.

Pseudo G gas from compressor station Beverwijk was used as the basis for natural gas (the gas composition is stated in Appendix 1). Pseudo G gas is currently the most commonly distributed gas quality in the Netherlands. At Beverwijk compressor station, two 50-liter cylinders were filled with a booster to a pressure of 180 bar. This pseudo G gas contains a small amount of hydrogen sulfide (H_2S), with a concentration of 0.8 mg /$m^3_{(n)}$ (as S).

The 12 mixtures were prepared gravimetrically in the DNV GL laboratory in Groningen. The liquid odorant was weighed with a precision syringe (injection volume 0 - 10 µl) and injected into an evacuated cylinder. Natural gas and/or hydrogen was then added to a filling pressure of 80 bar and weighed with a balance. The odorant content of each cylinder was analyzed for validation. To be able to do this for Gasodor® S-Free, an attempt was made to develop and calibrate an analytical method with a gas chromatograph (GC) in combination with a mass spectrometer (MS).

Tables 1a, 1b and 1c provide an overview of the prepared mixtures. These mixtures have been validated before and after the odor assessments, using an analytical technique based on gas chromatography. However, it turned out to be impossible to determine the concentration of Gasodor S-Free with a suitable analytical technique. The acrylates were found to have no unique fragmentation mass when using mass spectrometry and coelute with the natural gas matrix. The gravimetrically determined concentration is therefore used for Gasodor S-Free. In pure hydrogen (= no coelution with natural gas matrix) the Gasodor S-Free content is 9.3 mg/m^3(n) (based on relative response factors with a flame ionization detector (FID).

The results for THT and Spotleak 1001 are shown in Tables 2a and 2b. It can be concluded that these mixtures have remained virtually stable. However, there is a significant deviation between the gravimetrically determined value of the odorant content with the weight of the syringe. This is most likely caused by cylinder wall adsorption and desorption phenomena while injecting the fluids into the evacuated cylinders.

Table 1a. Gravimetrically prepared THT-mixtures.

Component	Unit	Cylinder			
		D566189	D248062	D566116	D566212
Natural gas	mol %	100	85.920	16.829	0
Hydrogen	mol %	0	14.080	83.171	100
THT	mg/m$^3_{(n)}$	*	13.2	21.3	18.9

**no result due to wrong reading.*

Table 1b. Gravimetrically prepared Spotleak 1001-mixtures.

Component	Unit	Cylinder			
		D566154	D247462	D247597	D566217
Natural gas	mol %	100	85.827	16.880	0
Hydrogen	mol %	0	14.173	83.120	100
Spotleak 1001	mg/m$^3_{(n)}$	8.2	5.2	8.2	7.2

Table 1c. Gravimetrically prepared Gasodor S-Free mixtures.

Component	Unit	Cylinder			
		D566122	D247606	D215952	D247561
Natural gas	mol %	100	86.134	19.256	0
Hyrdogen	mol %	0	13.866	80.744	100
Gasodor S-Free	mg/m$^3_{(n)}$	13.4	11.7	11.7	11.9

Table 2a. Validation THT-mixtures.

THT	Unit	Cylinder			
		D566189	D248062	D566116	D566212
26-09-2019	$mg/m^3_{(n)}$	18.6	17.6	18.6	22.2
09-12-2019	$mg/m^3_{(n)}$	18.9	17.8	18.8	17.9

Table 2b. Validation Spotleak 1001 mixtures.

Spotleak 1001	Unit	Cylinder			
		D566154	D247462	D247597	D566217
26-09-2019	$mg/m^3_{(n)}$	4.9	4.4	5.0	3.8
12-12-2019	$mg/m^3_{(n)}$	4.9	4.4	5.0	3.8

4 ODOR PANEL

On October 28 and 29, 2019, the odor laboratory of Buro Blauw carried out the odor testing on the 12 mixtures from DNV GL [lit 1] on behalf of SGS Nederland B.V.

The aim of the study was to determine the odor concentration by employing 12 independent panelists per mixture. In addition, an assessment of the hedonic value at a previously requested standard dilution/ concentration (1: 100). This dilution is derived from the fact that gas leaks must be detectable at 1 vol% (natural) gas in air.

Buro Blauw quickly ran into a number of problems/challenges when planning and performing the assessments. The initial odor concentration of 5 mixtures turned out to be so high that it had to be pre-diluted on the day of the odor assessment, because the dilution range of the olfactometer was found to be insufficient. Pre-dilution was done with nitrogen by means of a so-called stack diluter, in which the mixtures were pre-diluted by approximately a factor of 34. However, these actions took time. The intended first days of testing turned out differently than initially planned. Because the schedule had to be changed, it was difficult to arrange a complete panel of the desired 12 panelists (an odor panel requires at least four panelists).

During the first tests and after the assessments, (worrying) questions came from the panelists. Panelists were concerned about their health. Because a high odor concentration with a predetermined dilution of about 100 times (in practice a dilution of 156 times) had to be tested, the room in which the assessments were carried out was contaminated. As a result, extra time was taken between assessments and a single rather than a double sequence of odor concentrations was tested.

4.1 Odor concentration

Odor is a sensory perception. Odor concentrations are therefore sensory determined with a panel of panelists. Odor-free air and odor samples diluted with clean (odor-free) air are presented to a selected panel. It is determined at which dilution number (the diluted volume divided by the original volume) the "average" panelist can distinguish the diluted sample correctly and with certainty from odor-free air. This dilution number is the value of the odor concentration in the undiluted odor sample and is expressed in European odor units per m^3 air (ou_E/m^3). NEN-EN 13725 "Determination of odor concentration by dynamic olfactometry" is followed. The odor concentrations of the 12 mixtures are shown in table 3. Herein the mixtures are classified per odorant with increasing hydrogen concentrations of 0 - 100 mol%. The odor laboratory's original sample identifier consists of the following series "2019LO-105-XXX", where "XXX" is the sample ID in the presented tables. Appendix 3 gives an overview of the order in which the mixtures were tested by the odor panel on October 28 and 29 in 2019.

Tabel 3. Odor concentration of the mixtures.

Cylinder	Odorant	[odorant] $mg/m^3_{(n)}$	SampleID	Dilution	[Odor] Analysis ou_E/m^3	[Odor] Total ou_E/m^3
D566189	THT	18.6	199	1	10,451	10,451
D248062		17.6	103	1	10,442	10,442
D566116		18.6	022	1	12,609	12,609
D566212		22.2	036	1	12,075	12,075
D566154	Spotleak 1001	4.9	192	33.7	12,653	426,406
D247462		4.4	141	33.3	20,989	698,934
D247597		5.0	084	33.7	18,757	632,111
D566217		3.8	029	34.1	23,414	798,417
D566122	Gasodor S-Free	13.4*	050	1	13,921	13,921
D247606		11.7*	002	1	16,785	16,785
D215952		11.7*	010	1	14,599	14,599
D247561		9.3	014	34.1	5,898	201,122

**gravimetrical value*

4.2 Hedonic tone

In addition to determining the odor threshold, the panelists can also assess the nature of the odor. This is done by offering a sequence of different upper threshold odor concentrations. The panelists give their opinion as the so-called hedonic tone (H). This is determined in one of the 9 categories below:

-4	-3	-2	-1	0	1	2	3	4
extremely unpleasant				neutral				extremely pleasant

The concentration at which an odor is found unpleasant is a measure of the hindrance potential. The lower the concentration at, for example, H = -1 or -2, the greater the chance of nuisance. The hedonic assessment (and the reporting) is carried out in accordance with NVN-2818 "Odour quality - Sensory determination of hedonic tone of an odor using an olfactometer".

Table 4 shows the average hedonic tones of the mixtures for the requested predetermined dilution of approximately 100 times. In practice, however, a dilution of 156 times has been applied. Appendix 2 provides an overview of the odor concentrations for a number of standard hedonic tones.

Tabel 4. Hedonic tone at a specific dilution.

Cylinder	Odorant	[odorant] $mg/m^3_{(n)}$	SampleID	Presented odor concentration ou_E/m^3	Average hedonic tone ou_E/m^3
D566189	THT	18.6	199	67	-3.7
D248062		17.6	103	67	-2.7
D566116		18.6	022	81	-3.6
D566212		22.2	036	77	-3.7
D566154	Spotleak 1001	4.9	192	81	-3.1
D247462		4.4	141	135	-2.5
D247597		5.0	084	120	-2.8
D566217		3.8	029	150	-3.2
D566122	Gasodor S-Free	13.4*	050	89	-2.9
D247606		11.7*	002	108	-2.6
D215952		11.7*	010	94	-3.0
D247561		9.3	014	38	-2.3

** gravimetric value*

4.3 Questionairy

Additionally, a questionnaire has been prepared for the panelists if a 1: 100 dilution is assessed. These are questions that were also asked in earlier research, but instead of asking for natural gases from different sources, questions are now being asked for different natural gas/hydrogen mixtures. The following questions were asked:

A) (Re) know this odor?

B) What does this odor remind you of?

C) Do you think the odors/samples were always the same? If the odor is not the same, can you describe the difference in odor?

Table 5-7 gives the answers to the questions asked for each odorant in three separate tables (a-c).

Table 5a. Recognition of THT-mixtures.

Panelist	**Question A: Recognition?**			
	D566189 2019LO-105-199	D248062 2019LO-105-103	D566116 2019LO-105-022	D566212 2019LO-105-036
1	Yes	No	Yes	Yes
2	Yes	Yes	Yes	Yes, gas from stove, but dirtier
3	Yes	Yes	Yes	Yes
4	No	Yes/No	No	No
5	Yes	Yes	Yes	Yes
6	Yes	Yes	Yes/No	Yes
7	Yes	Yes	Yes	Yes
Score Yes/No	**6/1**	**6/2**	**6/2**	**6/1**

Table 5b. Description of THT-mixtures.

Panelist	Question B: Description			
	D566189 2019LO-105-199	D248062 2019LO-105-103	D566116 2019LO-105-022	D566212 2019LO-105-036
1	Petrochemistry; gas, oil	-	Petrochemistry, gas, oil	Household gas; petrochemistry (Pernis refinery)
2	Looks more like stove gas than 036; penetrating pungent odor	Gas smell	Gas from a stove	Unnatural, unhealthy.
3	Chemical	Natural gas	Gas from a stove	Gas, chemical
4	Same as previous sample; natural gas	Smells like gas station	Natural gas, sulfurous	Bit like gas from a stove, sulfurous, stinky cheese
5	Natural gas, or something identical	Gas	Fossil gas, can't place it further	Probably natural gas
6	Gas smell; increasingly present	Gas from a stove, pungent and dangerous because of association with gas	Smells like soap with a different concentration, high concentration of gas odor	Natural gas
7	Stove	Gas stove	Gas from a stove	Gas from a stove

Tabel 5c. Comparison of THT-mixtures.

Panelist	Question C: Comparison			
	D566189 2019LO-105-199	D248062 2019LO-105-103	D566116 2019LO-105-022	D566212 2019LO-105-036
1	Comparable	-	Comparable with 036 and 199	-
2	Less dirty than 036; more sterile	Yes/no, pungent odor	Looks like sample 199	-
3	Same as 036	No, smells different	Looks like others (036 en 199), but not like 050 and 002	-
4	Same as 036	-	Looks like 036 and 199, makes you light-headed	-
5	The scents are all alike	No	Not a big difference compared to 036 and 199	-
6	Do not smell any differences, very strong	Other than 141, 029, 084 and 192	No and yes, remains gas smell	Softer and weaker than 199
7	Not the same, this more like gas from a gas stove	-	Same as 036	Something other than 199, slightly rubber/plastic odor

Table 6a. Recognition of Spotleak 1001 mixtures.

Panelist	Question A: Recognition			
	D566154 2019LO-105-192	D247462 2019LO-105-141	D247597 2019LO-105-084	D566217 2019LO-105-029
1	-	Yes	Yes	Yes
2	-	No	No	No
3	No	Yes	No	Yes
4	No	No	No	No
5	No	No	No	Yes
6	No	Yes	Yes	Yes
7	Yes			
8	Yes/No			
Score (Yes/No)	**2/5**	**3/3**	**2/4**	**4/2**

Tabel 6b. Description of Spotleak 1001 mixtures.

Panelist	Question B: Description			
	D566154 2019LO-105-192	D247462 2019LO-105-141	D247597 2019LO-105-084	D566217 2019LO-105-029
1	-	Chemical, animal waste	Smells like mega livestock farming, natural gas	Gas, chemical
2	-	Kind of boiling oil odor	Smells like gas leakage	Smells like gas leakage
3	Natural gas	Chemical, initially herbal, but still chemical	Not clear	Gas
4	Frying oil	A fart from someone? Oil puddle left in combustion engine	Old combustion engine, or odor coming out of it	Again, as if someone farted
5	Chemical? Unions	Strong odor	-	Looks like sample 192
6	Oil-pungent smell like 141	Butane	Butane, gas stove	Butane
7	The 'dirty' page of a Geronimo Stilton book			
8	Butane gas, engine or marine working			

Tabel 6c. Comparison of Spotleak 1001 mixtures.

Panelist	Question C: Comparison			
	D566154 2019LO-105-192	D247462 2019LO-105-141	D247597 2019LO-105-084	D566217 2019LO-105-029
1	-	No	Yes, similar 141, 029	Looks like 141
2	-	Comparable to other samples	-	-
3	No not comparable	No	No	No
4	No not comparable	No	Looks like 141	Looks like 141
5	No	-	Looks like 192	Looks like sample 192
6	Comparable 141	No different from the others	-	Looks like sample 141
7	-			
8	-			

Tabel 7a. Recognition of Gasodor S-Free mixtures.

Panelist	Question A: Recognition			
	D566122 2019LO-105-050	D247606 2019LO-105-002	D215952 2019LO-105-010	D247561 2019LO-105-014
1	Yes	Yes	No	Yes
2	Yes	Yes	No	No
3	No	No	No	Yes
4	No	No	No	No
5	Yes	Yes	Yes	No
6	No	Yes	No	Yes
7	Yes	Yes	Yes	-
Score Yes/No	**4/3**	**5/2**	**2/5**	**3/3**

Tabel 7b. Description of Gasodor S-Free mixtures.

Panelist	Question B: Description			
	D566122 2019LO-105-050	D247606 2019LO-105-002	D215952 2019LO-105-010	D247561 2019LO-105-014
1	Molten rubber/plastic	Molten rubber/plastic	Molten rubber/plastic	Smelled something like wood glue? Hardware store?
2	Rubber/plastic odor	Rubber/plastic	Dirty chemical candy that I wouldn't eat; rubber/plastic odor	Oil, such as in car parts store
3	None	Chemical	Also chemical	Burnt plastic
4	Manure-like	Rubber/plastic	Smells like potato; higher concentrations also rubber	Irony, plastic scent
5	Gluey	Liquid glue	Type of glue	-
6	Egg smell	Candies, rubber	Burned; later more gas smell, sometimes more "Maggi-aroma", then gas/coal again	Rubber or plastic
7	Rubber/plastic	Rubber/plastic	Rubber; soft plastic	-

Tabel 7c. Comparison of Gasodor S-Free mixtures.

Panelist	Question C: Comparison			
	D566122 2019LO-105-050	D247606 2019LO-105-002	D215952 2019LO-105-010	D247561 2019LO-105-014
1	Comparable to 010	Comparable to 010	Not comparable	-
2	Comparable to 010 and 002	Comparable to 010	Completely different from 036 and 199, sweeter and less pungent than the first two	-
3	None	No	Completely different from 036 and 199	-
4	Different from all others (036, 199, 010, 022 002), mild, not tasty but also not disturbing, farmland	Comparable to 010	It smells different from 036 and 199; not so chemical, is more pleasant, warmer	-
5	Same as 002	Looks like one of the previous (010)	Also strong smell, but completely different from 103, 036 and 199	-
6	Does not look like others	No	Does not look like previous samples (103, 036 and 199)	-
7	-	Yes, comparable to others with the same description (010)	Same as 002	-

5 DISCUSSION AND CONCLUSIONS

12 odor samples were anonymously tested for odor assessment by an independent odor panel. Five samples were pre-diluted prior to the assessment by the odor panel because the dilution range of the olfactometer was found to be insufficient.

All odor samples as presented, except for one, had relatively high odor concentrations, greater than 10,000 ou_E/m^3. Due to concerned comments from the panelist regarding the character of the odor they perceived and the specific demand for a hedonic assessment at a standard dilution of 1:100 (actual dilution 1:156), the hedonic assessment was performed by a single series of upper threshold odor concentrations.

It can be concluded for 11 samples that the odors can already be classified as slightly annoying (H = -1) when observed or just above threshold. In addition, a standard dilution (= 156 times) of all samples was assessed by the panel, which showed that the odor concentrations were rated as "very" to "extremely unpleasant". Of the 12 samples, 7 samples were recognized, 5 of which were directly associated with (natural) gas.

The pre-diluted samples presented to the panel all have an extremely high odor concentration, greater than 200,000 ou_E/m^3. From previous research [lit. 2] it has been found that the odor concentration of odorized natural gas in the Netherlands has a concentration between 11,000 - 42,000 ou_E/m^3. It is therefore questionable whether the prediluted samples have realistic odor concentrations in relation to the other findings.

THT is well recognized by most panelists as (natural) gas in all mixing ratios between natural gas and hydrogen. For Spotleak 1001 and Gasodor S-Free, the odor is less known and is less often associated with natural gas. A common recognition/description was respectively "chemical" and "(burnt) rubber/plastic". The odor thresholds for Spotleak 1001 and Gasodor S-Free are lower than those for THT.

For all three odorants, a slight trend can be observed that the odor concentration increases with an increase in the hydrogen concentration in the assessed mixtures. It is possible that the decrease of natural gas concentration masks the odorant less, which increases the odor perception.

The main components of Gasodor S-Free, methyl acrylate and ethyl acrylate, can be detected with a gas chromatograph. However, in mixtures of natural gas and hydrogen, these components coelute with natural gas components, as a result detection is insufficiently with conventional techniques in laboratories.

Overall, it can be concluded that mixtures of natural gas and hydrogen and pure hydrogen can be sufficiently odorized with existing odorants. Adding THT results in the best recognition and association with (natural) gas, which is to be expected with a Dutch odor panel, because in The Netherlands only THT is used as an odorant for natural gas.

LITERATURE

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APPENDIX 1 COMPOSITION OF "PSEUDO G-GAS"

Nr.#	Component		mol%		Nr.#	Component		mol%
1	Methane	CH4	78.668		30	Methylcyclopentane	C6H12	0.000
2	Ethane	C2H6	4.858		31	Ethylcyclopentane	C7H14	0.000
3	Propane	C3H8	0.967		32	Cyclohexane	C6H12	0.011
4	n-Butane	C4H10	0.171		33	Methylcyclohexane	C7H14	0.006
5	2-Methylpropane	C4H10	0.152		34	Ethylcyclohexane	C8H16	0.000
6	n-Pentane	C5H12	0.039		35	Benzene	C6H6	0.020
7	2-Methylbutane	C5H12	0.047		36	Toluene	C7H8	0.003
8	2,2-Dimethylpropane	C5H12	0.003		37	Ethylbenzene	C8H10	0.000
9	n-Hexane	C6H14	0.011		38	o-Xylene	C8H10	0.000
10	2-Methylpentane	C6H14	0.000		39	Methanol	CH3OH	0.000
11	3-Methylpentane	C6H14	0.006		40	Methanethiol	CH3SH	0.000
12	2,2-Dimethylbutane	C6H14	0.003		41	Hydrogen	H2	0.000
13	2,3-Dimethylbutane	C6H14	0.015		42	Water	H2O	0.000
14	n-Heptane	C7H16	0.012		43	Hydrogen sulfide	H2S	0.000
15	n-Octane	C8H18	0.002		44	Ammonia	NH3	0.000
16	n-Nonane	C9H20	0.000		45	Hydrogen cyanide	HCN	0.000
17	n-Decane	C10H22	0.000		46	Carbon monoxide	CO	0.000
18	Ethylene	C2H4	0.000		47	Carbonyl sulfide	COS	0.000
19	Propylene	C3H6	0.000		48	Carbon disulfide	CS2	0.000
20	1-Butene	C4H8	0.000		49	Helium	He	0.030
21	cis-2-Butene	C4H8	0.000		50	Neon	Ne	0.000
22	trans-2-Butene	C4H8	0.000		51	Argon	Ar	0.000
23	2-Methylpropene	C4H8	0.000		52	Nitrogen	N2	12.181
24	1-Pentene	C5H10	0.000		53	Oxygen	O2	0.000
25	Propadiene	C3H4	0.000		54	Carbon dioxide	CO2	2.795
26	1,2-Butadiene	C4H6	0.000		55	Sulfur dioxide	SO2	0.000
27	1,3-Butadiene	C4H6	0.000		56	Dinitrogen monoxide	N2O	0.000
28	Acetylene	C2H2	0.000		57	Krypton	Kr	0.000
29	Cyclopentane	C5H10	0.000		58	Xenon	Xe	0.000

	Physical properties					Total amount		100.000
	ISO 6976 (1995, table 3)							
	Superior (gross) calorific value	36.411	MJ/m3					
	Inferior (net) calorific value	32.897	MJ/m3					
	Relative density	0.674	-					
	Density	0.871	kg/m3					
	Wobbe index	44.351	MJ/m3					
	PE getal	4.294	-					
	Summation factor	0.051	-					
	Compression factor	0.997	-					
	Mean molecular weight	19.482	kg/kmol					
	Sum ESTD	99.999	mol%					

APPENDIX 2 HEDONIC TONE

Odor intensities of the mixtures (ou_E/m^3) @ 3 standard hedonic tones.

Cylinder	Odorant	[Odorant] $mg/m^3_{(n)}$	SampleID	H = -0.5 ou_E/m^3	H = -1.0 ou_E/m^3	H = -2.0 ou_E/m^3
D566189	THT	18.6	199	0.8	1.3	3.3
D248062		17.6	103	<0.6	0.8	6.6
D566116		18.6	022	0.8	1.3	3.2
D566212		22.2	036	<0.7	0.8	3.8
D566154	Spotleak 1001	4.9	192	<0.8	<0.8	>11.1
D247462		4.4	141	<0.6	0.9	10.3
D247597		5.0	084	0.8	1.7	7.1
D566217		3.8	029	<0.7	1.1	6.8
D566122	Gasodor S-Free	13.4*	050	2.1	4.6	>12.2
D247606		11.7*	002	<1.0	2.3	>7.2
D215952		11.7*	010	0.7	1.8	>6.2
D247561		9.3	014	<0.7	<0.7	>21.9

** gravimetric concentration*

APPENDIX 3 ORDER OF ODOR TESTS

Odor test series 1, oktober 28 2019.

SampleID	Cylinder	Odorant	Analysis time
2019LO-105-036	D566212	THT	08:34/13:25
2019LO-105-199	D566189	THT	09:01/13:44
2019LO-105-010	D215952	Gasodor S-Free	09:22/14:01
2019LO-105-022	D566116	THT	09:46/14:26
2019LO-105-002	D247606	Gasodor S-Free	10:13/14:41
2019LO-105-050	D566122	Gasodor S-Free	10:57/15:42
2019LO-105-103	D248062	THT	13:09
2019LO-105-192	D566154	Spotleak 1001	15:56

Odor test series 2, oktober 29 2019.

SampleID	Cylinder	Odorant	Analysis time
2019LO-105-014	D247561	Gasodor S-Free	08:35/13:28
2019LO-105-141	D247462	Spotleak 1001	09:02/15:25
2019LO-105-029	D566217	Spotleak 1001	09:23/14:02
2019LO-105-084	D247597	Spotleak 1001	09:43/13:48
2019LO-105-192	D566154	Spotleak 1001	10:03/13:10
2019LO-105-103	D248062	THT	10:48/16:47
2019LO-105-199	D566189	THT	15:50
2019LO-105-036	D566212	THT	16:03
2019LO-105-022	D566116	THT	16:14
2019LO-105-002	D247606	Gasodor S-Free	16:26
2019LO-105-010	D215952	Gasodor S-Free	16:37
2019LO-105-050	D566122	Gasodor S-Free	17:01

About DNV GL

DNV GL is a global quality assurance and risk management company. Driven by our purpose of safeguarding life, property and the environment, we enable our customers to advance the safety and sustainability of their business. We provide classification, technical assurance, software and independent expert advisory services to the maritime, oil & gas, power and renewables industries. We also provide certification, supply chain and data management services to customers across a wide range of industries. Operating in more than 100 countries, our experts are dedicated to helping customers make the world safer, smarter and greener.