Influence of H2S Poisoned Biomethane on Catalyst Performance

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Summary

The influence of the level of H_2S in the fuel on catalyst performance was investigated. The main conclusion is that at H_2S levels of 30ppm and above, it is probable that the exhaust gas emissions of NGV's are negatively influenced. Further research is suggested to:

1) Determine the effect of different H_2S concentrations on tailpipe emissions.

And, if it is found that there is an influence on tailpipe emissions:

2) Determine a maximum fuel H_2S content to limit this influence.

1. Introduction

In subtask 5.2.3 TNO studied both biogas (biomethane) composition and NGV fuel specifications. Based on this information a vehicle selection for the heavy-duty 13-mode emission testing was planned to be carried out. At the time of the definition of the BiogasMax project, it was assumed that both LD as well as HD-NGV's might have difficulties with performance and emissions when using biogas instead off natural gas. Since HD vehicles were expected to be more sensitive then LD-NGV's, it was originally proposed to carry out HD emissions test, using different biogas (biomethane) qualities.

However, after the BiogasMax program started and while working on this subtask, it proved to be the case that biomethane will be upgraded to such a specification, that both grid injection and use in NGV's is possible. In order to correctly compare different (natural) gases like biomethane for use in NGV's first a new gas parameter (sonic Bievo index) needed to be developed. This because the current index (lambda shift factor) as used in the EC type approval regulations R49 and R83, can lead to erratic results.

After studying both the fuel specifications and regulations of both light-duty as heavy-duty vehicles, it became clear that the originally proposed heavy-duty 13 mode emission tests will not contribute to the overall objective of the Work package 5 "use of biogas in vehicles".

As a result a useful alternative for this activity is proposed, in which the effect of biomethane related impurities like H2S on the performance of the after treatment system will be quantified. Both the activities related to the original objectives as the revised objectives are described in this report (D5.3).

Some remarks regarding differences between heavy-duty and light-duty NGV's:

From an engine and after-treatment point of view, today's' HD and LD vehicles show great similarity, since almost all HD natural gas engines use stoichiometric engines with three-way catalysts, also the standard concept for LD-NGV's. This means that all research carried out in subtask 5.2.3, as described in this report, applies to both HD and LD-NGV's. Vise-versa this also means that all research carried out in subtask 5.2.4, durability of three-way catalyst in combination with biogas (biomethane), can be applied in HD-vehicles.

However, there is a big difference in emission testing regulations. Light-duty NGV's are tested on the MVEG test cycle. The MVEG cycle includes a cold start at 20°C, together with a fairly low load regime. It's a general rule of thumb that more the 90% of the emissions are made directly after the cold start, prior to the light-off of the catalyst, and for this reason for LD vehicles light-off performance is crucial. Heavy-duty vehicles however, are tested under fully warmed up conditions, like the ESC or ETC and relatively high loads compared to light-duty MVEG testing. The steady-state conversion efficiency is the dominant parameter for Heavy-duty NGV's.

2. Objectives

The general objective Task 5.2 "Engine performance", part of Work Package 5 "Use in vehicles", is to study and quantify the effect of operating NGV's designed for natural gas on biomethane (upgraded biogas) focusing on energy-efficiency, performance and emissions.

In one of TNO's other Subtasks (5.2.4.) the long term emission effects of the use of biomethane in NGV's are quantified, by means of (light-duty) catalyst ageing testing. The results are presented in the belonging D5.4 report.

While working on subtask 5.2.3 (HD vehicle testing, described in this report) it became clear that the originally defined objectives proved to be not effective in the BiogasMax program, see below.

2.1. Original objectives subtask 5.2.3

The original objective of subtask 5.2.3, resulting in deliverable 5.3, was to study the short term effect of different biomethane gas qualities on vehicle emissions, *by means of a number of 13-mode heavy-duty (HD) emissions tests on four different biogas qualities.* However, at the end of the first year more detailed information of the composition of some biomethane qualities became available. It proves to be the case that biomethane for use in vehicles as in the BiogasMax program, will be upgraded to specifications that allow e.g. grid injection. It was proved that these biomethane qualities can be matched with NGV's, with fuel specification following R83 (light-duty) and R49 (heavy-duty) UN-ECE vehicle type approval regulations as well.

Furthermore it proves to be the case that operation of NGV's outside the specified fuel quality range, could not only lead to emission and performance problems but even to engine damage; a risk TNO can't take. For reasons mentioned above, the proposed HD emission tests will not contribute to the overall objective of the Work package 5 "use of biogas in vehicles" and subsequently alternative emission measurements are defined.

2.2. Revised objectives

2.2.a. Motivation

As mentioned in the abstract and in the section "Introduction" it became clear that after upgrading, only little differences between natural gas and biomethane occur. These differences are mainly 1) dust (particles) that will have negative influence on fuel system components, or 2) pollutants like siloxane that has negative influence on engine durability, and 3) pollutants like H_2S that might have influence on vehicle emission. This last issue is proposed to be studied by means of an extensive test bed measurement program, as an alternative for the originally proposed HD vehicle testing. The polluting component H_2S was selected, because this is a potential pollutant of biomethane, in case of failures in the production or upgrading process. Furthermore sulphur is considered to be a known polluting component in after-treatment systems.

2.2.b. Revised objectives

For subtask 5.2.3 we now have the following combination of old and new objectives:

- Overview biomethane qualities and national regulations within BiogasMax
- Summary UN-ECE regulations regarding both heavy-duty NGV's as well as light-duty NGV's in combination with fuel specification, in relation to biomethane

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- Study combination fuel and vehicle and develop new gas parameter to predict vehicle performance and emission, especially for biomethane

- HD-vehicle selection and HD vehicle test preparation (not continued)

- Study influence of biomethane specific impurities like H_2S on the conversion efficiency of three-way catalysts (TBD) by means of extensive emission testing with various H_2S concentrations.

The last bullet defines the alternative research, planned to be carried out in stead of the originally planned HD vehicle emission testing.

2.2.c. Rejected alternative test work

Before proposing the alternative H_2S test work as described above, another suggestion was made. It was suggested to carry out emission test activities to study the emission (durability) differences of NGV's running on biogas (biomethane) in comparison with the emission performance of gasoline vehicles.

Although most of the gasoline vehicles use stoichiometric engines with 3-way catalyst after-treatment systems, as used by most of the NGV's, it makes no sense to compare NGV after-treatment components with gasoline vehicle after-treatment components regarding (durability of) emissions. This because NGV's use special (more expensive) catalyst formulations, in order to comply with the regulated emission standards. The chemical stability of the methane molecule requires these dedicated methane catalysts.

Since BiogasMax WP 5.2 (use in vehicles) focuses on implications of using biogas (biomethane) in NGV's designed for natural gas, it makes no sense to compare the (durability of) the emissions of NGV's operated on biomethane with gasoline vehicles, as suggested for alternative tests, replacing the HD 13-mode emission testing.

3. Activities related to HD 13-mode emission testing

The following activities were carried out in subtask 5.2.3, heavy-duty natural gas vehicle 13-mode testing:

3.1. Overview biomethane quality and national biomethane fuel regulations

In order to study the combination of biomethane and HD NGV's, the following (preliminary) overview of the biomethane qualities, as used or expected by the cities, and regulated in the national regulations are presented.

3.1.a. Preliminary biomethane analysis data

Biogas (biomethane) analysis data was gathered through various channels within the BiogasMax community. This analysis data together with national biomethane quality regulations (see section 3.1.b and table 2) clearly shows that upgraded biogas (biomethane) has a relative high methane content compared to average natural gas CH_4 content of 83% – 93% (98%).

Table 1 Biomethane quality

Site or City	Gothenburg	Stockholm	Lille	Roma	Torun Zielena Gora
In production?	Expected Feb 2007	Yes, since 1996	expected		
Analysis date	-	2001			
CH_4 %	96 – 98	> 97		99	
CO_2 %	< 4	< 2	< 2.5	1 – 2	
CO %			< 2		
H_2 %	< 0.5		< 6		
O_2 %	< 1	0.2	< 0.01		
N_2 %		< 0.8			
H_2O [mg/m_n^3]	< 32				
H_2S [mg/m_n^3]	< 23	< 0.5	< 0.5 - 10	1 – 5 (ppm)	
NH_3 [mg/m_n^{33}]			< 3		
CL, Fl [mg/m_n^3]			< 0.1		
THT [mg/m_n^3]		< 4 - 23	15 – 40		
Particles [mg/m_n^3]			< 5		
LHV [MJ/m_n^3]		35	37.8		
Density [kg/m_n^3]		0.7075	0.555 – 0.7		
Wobbe (upper) [MJ/m_n^3]					
Wobbe (lower) [MJ/m_n^3]	45.5 – 48.2	> 44.7			

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3.1.b. Biomethane national regulations

The regulations as presented in table 2 below generally don't have any specific limits for dust or siloxane. Dust could interfere with the NGV fuel system equipment, and components like siloxane have a negative influence on engine durability.

Table 2

Country	Switzerland[1]	Germany	Sweden	France	Italy	Poland
Regulation		G262	SS 15 54 38	2004		
CH_4 %	≥ 96		> 97			
CO_2 %	≤ 6	< 6	< 3	< 2		
H_2 %	≤ 5		< 0.5			
O_2 %	≤ 0.5	< 3	<1			
H_2O [mg/mn^3]						
H_2S [mg/m_n^3][2]	≤ 5		< 23			
Total S [mg/m_n^3]						
THT [mg/m_n^3]						
CL, Fl [mg/m_n^3]						
LHV [MJ/m_n^3]						
HHV [MJ/m_n^3]				H: 38.5 - 46.1 L: 34.2 - 37.8		
Wobbe (upper) [MJ/m_n^3]		H: 46.1 - 56.5 L: 37.8 - 46.8		H: 48.2 - 56.5 L: 42.5 - 46.8		
Wobbe (lower) [MJ/m_n^3]			43.9 – 47.3			

[1] Switzerland regulations for unlimited grid injection

[2] 1 ppm H_2S equals 1.52 mg/m_n^3

3.2. NGV fuel specifications and regulations

NGV's have to comply to UN-ECE legislation, as can be found in ECE regulations. For light-duty R83 applies; for heavy-duty vehicles UN-ECE R49 should be used.

3.2.a. Light-Duty reference fuels of R83

LD NGV's have to be emission tested on both reference fuels G20 and G25, a relatively wide range. As a result it should be possible to operate these NGV's in all countries of the EU, even when traveling from one country to the other.

LD reference gas specification (G20 and G25) can be found in Annex 10A of R83 Rev3; see copy of the relevant text in figure 1 below:

E/ECE/324 ⎫ Rev.1/Add.82/Rev.3
E/ECE/TRANS/505 ⎬
Regulation No. 83
page 228
Annex 10a

1.2.   TECHNICAL DATA OF THE NG REFERENCE FUELS

Characteristics	Units	Basis	Limits min.	Limits max.	Test Method
Reference fuel G$_{20}$					
Composition:					
Methane	per cent mole	100	99	100	ISO 6974
Balance 1/	per cent mole	-	-	1	ISO 6974
N$_2$	per cent mole				ISO 6974
Sulphur content	mg/m^3 2/	-	-	10	ISO 6326-5
Wobbe Index (net)	MJ/m^3 3/	48.2	47.2	49.2	
Reference fuel G$_{25}$					
Composition:					
Methane	per cent mole	86	84	88	ISO 6974
Balance 1/	per cent mole	-	-	1	ISO 6974
N$_2$	per cent mole	14	12	16	ISO 6974
Sulphur content	mg/m^3 2/	-	-	10	ISO 6326-5
Wobbe Index (net)	MJ/m^3 3/	39.4	38.2	40.6	

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1/   Inerts (different from N$_2$) + C$_2$ +C$_{2+}$

2/   Value to be determined at 293.2 K (20 °C) and 101.3 kPa

3/   Value to be determined at 273.2 K (0 °C) and 101.3 kPa

Figure 1

Since biomethane will be expected to be upgraded to specifications between G20 and G25, light-duty NGV's will have no specific emission or performance problems when using biomethane with an average a methane content of > 97%.

3.2.b. Heavy-Duty reference fuels of R49

HD NGV's can be approved for a wide gas quality range, similar to the light-duty range, see below. However, it is also allowed in R49 to specify a certain limited gas quality range, e.g. L-gas or H-gas or even only one specific fuel composition.

Earlier UN-ECE R49 specified G20 - G23 for the H-gas range and G23 - G25 for the L-range. However, in UN-ECE R49 regulations ammend1 the G20 is replaced by GR. Today's heavy-duty NGV reference gas specification (GR, G23 and G25) can be found in "Annex 6 of R49 ammend-1" see copies of the relevant data in figure 2 below:

Reference fuel GR

Characteristics	Units	Basis	Limits		Test Method
			Min.	Max.	
Composition:					
Methane	% mole	87	84	89	
Ethane	% mole	13	11	15	
Balance (*)	% mole	-	-	1	ISO 6974
Sulphur content	mg/m^3 (**)	-	-	10	ISO 6326-5

(*)   Inerts +C_{2+}
(**) Value to be determined at standard conditions (293.2 K (20°C) and 101.3 kPa)

Reference fuel G23

Characteristics	Units	Basis	Limits		Test Method
			Min.	Max.	
Composition:					
Methane	% mole	92.5	91.5	93.5	
Balance (*)	% mole	-	-	1	ISO 6974
N_2	% mole	7.5	6.5	8.5	
Sulphur content	mg/m^3 (**)	-	-	10	ISO 6326-5

(*)   Inerts (different from N_2) +C_2/C_{2+}
(**) Value to be determined at standard conditions (293.2 K (20°C) and 101.3 kPa).

Reference fuel G25

Characteristics	Units	Basis	Limits		Test Method
			Min.	Max.	
Composition:					
Methane	% mole	86	84	88	
Balance (*)	% mole	-	-	1	ISO 6974
N_2	% mole	14	12	16	
Sulphur content	mg/m^3 (**)	-	-	10	ISO 6326-5

(*)   Inerts (different from N_2) +C_2/C_{2+}
(**) Value to be determined at standard conditions (293.2 K (20°C) and 101.3 kPa).

Figure 2

Remark: Standard conditions conform ISO 10780 are: 273.15 K (0°C) and 101.325 kPa.

3.2.c. Heavy-Duty vehicle R49 certification classes:

Due to the regional operation of HD NGV's, see also previous section 3.2.b, HD NGV's are allowed to be designed for the "whole" natural gas quality range (GR – G25) or to a limited fuel quality range, conform R49/03 amend-2; see table 3 below:

Table 3: R49/03 HD vehicle classifications

"Class"	Reference fuel	Manufacturers' request and/or (COP) reference fuel *	Approval mark
Universal	GR and G25	Market fuel with $0.89 < S_\lambda < 1.19$	HL
"Universal" plus switch	both H: GR and G23 and L: 25 and G23	Market fuel with $0.89 < S_\lambda < 1.19$	HL
Restricted L- or H-gas	H: GR and G23 or L: 25 and G23	Market fuel with $0.89 < S_\lambda < 1.19$	H or L
Restricted: one specific gas	GR and G25 fine tuning allowed	H: GR and G23 or L: 25 and G23	H_t or L_t or HL_t

* The gas quality parameter S_λ will be explained in section 3.3.b.

To what extend various biomethane (upgraded biogas) qualities fall within the vehicle specifications, and the type approval category (not necessarily the same!) requires detailed information from the NGV manufacturers. In-depth studies in section 3.3 will help to compare biomethane quality with various natural gas qualities.

3.2.d. Vehicle selection

Based on the original objective, a HD vehicle should be selected and these NGV's should be 13-mode tested on both biomethane qualities inside, as well as outside its natural gas specification range. The original idea was to select a HD vehicle that would be suspicious from an engine and engine management conceptual point, with reference to the class (table-3) in the previous section. As explained before, this original objective proved to be not effective for the BiogasMax general objectives.

Table 4 below, shows an overview of the HD-NGV information gathered in the BiogasMax project:

Table 4

Manufacturer	Daimler Chrysler	Iveco	Volvo	IRISBUS RVI	IRISBUS IVECO	MAN	Scania
Engine code	M906 LAG	M 8469.41 CNG	G9A	MGDR 062045 A / B / C	Cursor 8 F2G	E 2866 DUH3	
Displacement	6.88 liter	9.5 liter	9.36 liter	9.83 liter	7.79 liter	11.97 liter	9 liter
NA or TC	TC & waste gate	TC & waste gate	TC & waste gate		TC & waste gate	NA	
Max. torque	1100 Nm @ 1200 rpm	1000 Nm @ 1100 rpm	1200 / 1400 Nm	850 / 1000 Nm @ 1400 rpm		880 Nm @ 1000 – 1200	
Max. power	205 kW @ 2300 rpm	190 kW @ 2100 rpm	191 / 223 kW	186/168/190 kW @ 2100 rpm	154 /228 kW	180 kW @ 2200 rpm	195 kW
Fuel system	MPFI	MPFI sequential	Single point injection		MPFI	Venturi & A/F control	
Combustion concept	Lean-burn	Lambda=1 & EGR	Lambda=1 & EGR	Lean-burn	Lambda=1	Lambda=1	
After treatment	Oxidation catalyst	3-way catalyst	3-way catalyst	Oxidation catalyst	3-way catalyst	3-way catalyst	
Fuel specs.		G20 – G25	G25		L/H/G25		
Emission specification		Euro-3	EEV and Euro-5	Euro-2 / 3 / 3	EEV	EEV	Euro-3

For reasons mentioned above and in section 2 "Objectives", actual vehicle selection became obsolete.

3.3. Combination biomethane and NGV's

In this section a comparison between the vehicle specifications and the biomethane quality will be made, by means of the characteristic fuel parameters: Wobbe index, "lambda shift factor" S_λ and "Bievo" indices.

A calculation sheet "Wobbe_Lambda-shift_Sonic-Bievo.xls" is developed in order to calculate all above mentioned characteristic fuel parameters, required to check if the specific biomethane will match with the vehicle specifications.

3.3.a. Wobbe index

The Wobbe index can be based on the lower caloric heat value (Wobbe lower of Wobbe inferior) or based on the higher caloric heat value (Wobbe higher or Wobbe superior); see formula's below:

$$Wobbe_{l,i} = LHV / \sqrt{\frac{density_{gas}}{density_{air}}}$$

$$Wobbe_{h,s} = HHV / \sqrt{\frac{density_{gas}}{density_{air}}}$$

The Wobbe index was defined to ensure constant A/F-ratio in fuel systems using *venturi based, zero pressure type, mixture formation* as used in gas burners or venturi type engine carburetor systems.

The Wobbe index is becoming slightly old-fashioned, because all light-duty NGV's and almost all heavy-duty NGV's use fuel injection equipment working with over pressure. In that case the Wobbe index can not be used to achieve a constant A/F-ratio. For over pressure fuel systems the Bievo index [6] and the Sonic Bievo index was developed at TNO; see section 3.3.c and 3.3.d.

3.3.b. Lambda shift factor S_λ (as in R49)

In R49 a number of reference gases i.e. G20, G23, G25 and GR are defined, as well as the so called "lambda shift factor" or "S_λ". This factor should indicate how much the A/F-ratio (lambda) will shift when any NGV is operated not on pure methane, but on a specific natural gas composition. The calculation of the "lambda shift factor" is quite complex, however not very accurate or correct. The calculation of the "S_λ" will be explained by means or the original "R49 rev3 ammend1" text below.

Conform R49/03 ammend-2 paragraph 4.1.2, L-range natural gas has a lambda shift factor $1.08 < S_\lambda < 1.19$ and natural gas within the H-range has a lambda shift factor $0.89 < S_\lambda < 1.08$. However in the same document, paragraph 8.3.2.4, related to COP testing, the L-range is defined by $1.00 < S_\lambda < 1.19$ and the H-range by $0.89 < S_\lambda < 1.00$.

In figure 3 below the actual R49/03 ammend-1 text is presented:

2.26.   "λ-shift factor (S$_\lambda$)" means an expression that describes the required
flexibility of the engine management system regarding a change of the
excess-air ratio λ if the engine is fuelled with a gas composition
different from pure methane (see annex 8 for the calculation of S$_\lambda$).

Figure 3: definition S$_\lambda$

In figure 4 and 5 below relevant parts for the "lambda shift" calculation as found in R49 Annex 8 is presented:

$$S_\lambda = \frac{2}{\left(1 - \dfrac{inert\%}{100}\right)\left(n + \dfrac{m}{4}\right) - \dfrac{O_2*}{100}}$$

Figure 4: calculation S$_\lambda$

In the formula above "inert %" is defined as volume% of inert components like N_2, CO_2, He etc. Furthermore the parameters "n" and "m" refer to the average C_nH_m of the fuel. The "n" and "m" can be calculated using the following formula's, copied from in R49 Annex 8 as well, see figure 5 below:

$$n = \frac{1 * \left[\dfrac{CH_4\%}{100}\right] + 2 * \left[\dfrac{C_2\%}{100}\right] + 3 * \left[\dfrac{C_3\%}{100}\right] + 4 * \left[\dfrac{C_4\%}{100}\right] + 5 * \left[\dfrac{C_5\%}{100}\right] + ..}{1 - \dfrac{diluent\%}{100}}$$

$$m = \frac{4 * \left[\dfrac{CH_4\%}{100}\right] + 4 * \left[\dfrac{C_2H_4\%}{100}\right] + 6 * \left[\dfrac{C_2H_6\%}{100}\right] + 8 * \left[\dfrac{C_3H_8\%}{100}\right] + ..}{1 - \dfrac{diluent\%}{100}}$$

where:

CH_4 = % by volume of methane in the fuel;
C_2 = % by volume of all C_2 hydrocarbons (e.g.: C_2H_6, C_2H_4, etc.) in the fuel;
C_3 = % by volume of all C_3 hydrocarbons (e.g.: C_3H_8, C_3H_6, etc.) in the fuel;
C_4 = % by volume of all C_4 hydrocarbons (e.g.: C_4H_{10}, C_4H_8, etc.) in the fuel;
C_5 = % by volume of all C_5 hydrocarbons (e.g.: C_5H_{12}, C_5H_{10}, etc.) in the fuel;
diluent = % by volume of dilution gases in the fuel (i.e.: O_2*, N_2, CO_2, He, etc.).

Figure 5: calculation S$_\lambda$

3.3.c. Bievo index [6]

To compare various natural gas compositions when used in NGV's *with subsonic over-pressure fuel metering* systems (like Volvo V70 bi-fuel, using Teleflex-GFI MEGA metering hardware) the Wobbe index as well as the lambda-shift factor, will give incorrect results, and a new index was developed by TNO. This Bievo index [6] should be used to calculate the A/F-ratio error, in case the NGV with subsonic metering equipment is operated on a (natural) gas mixture like biomethane, in stead of on pure methane.

The absolute pressure ratio (PR$_{critical}$) across the metering device (e.g. injector) defines if the flow is subsonic or sonic (choked flow). For natural gas (kappa approx 1.3) the critical pressure ratio is calculated below:

$$PR_{critical} = \frac{p_{abs,downstream}}{p_{abs,upstream}} = \frac{p_2}{p_1} = \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa}{\kappa-1}} = 0.546$$

For pressure ratios $0.546 \leq PR \leq 1.00$ the flow is sub-sonic, and the Bievo index can be used; for a $PR \leq 0.546$ the flow is sonic (choked) and subsequently the newly developed Sonic Bievo should be used; see section 3.3.d.

The (subsonic) Bievo index is defined as the required metering area, or injector opening duration, compared to the 100% methane situation. Validation measurements on engines with sub-sonic equipment proved that the Bievo index performs as expected.

By definition the Bievo index of pure methane is 100%. [6]. The Bievo index can be calculated using the following formula:

$$Bievo\_index = \frac{14.231}{(1 + AF_{stoich})} * \sqrt{\frac{density}{kappa}} * 100\%$$

Notes:

- The AF$_{stioch}$ in the formula above is the volumetric (or molar) A/F-ratio, not the mass A/F-ratio.

- The kappa in the formula above is the polytropic exponent c_p/c_v for gaseous fuels between 1.1 and 1.4 are to be expected.

- When using a mixture of gases, like biomethane or natural gas, the Bievo of the mixture can be calculated. One should note that quantities like density, LHV, and AF$_{stoich}$ can be calculated proportional to the individual components. However, for calculation of the kappa of the mixture it is required to calculate the proportional c_p of the mixture, and from this c_p the kappa of the mixture can be calculated.

- When calculating the Bievo index of methane, the results differ slightly depending on the data source of gas properties like: kappa, AF$_{stoich}$ and density.

- When dealing with gas analysis, one should note that such an analysis can be presented using vol% units or mol% units. Due to non-ideal gas properties, in reality molar volume is not constant (~22.4 l/mol) but differs slightly per component. The error made when using mol% instead of vol% is negligible.

- The spread-sheet "Wobbe_Lambda-shift_Sonic-Bievo.xls" is provided, in order to calculate the Bievo index and all other relevant gas mixture properties.

The Bievo index is based on the following formula for sub-sonic, un-choked flow: [6] [7]

$$\dot{m}_{gas} = C_d * A * \sqrt{\frac{2 * \kappa * p_1 * \rho}{\kappa - 1} * \left(PR^{\frac{2}{\kappa}} - PR^{\frac{\kappa+1}{\kappa}}\right)}$$

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Where PR equals the pressure ratio (p2/p1), downstream and upstream of the metering device, e.g. the injector.

3.3.d. Sonic Bievo index

Most of today's OEM NGV's, both light-duty as well as heavy-duty, are using multi point (or single point) natural gas injectors, operated under a (relative) gas pressure of approx. 0.1 – 1 MPa and the manifold pressure varies between absolute pressures of 30 – 200 kPa, depending on engine load and engine type, natural aspirated (NA) or turbo charged (TC). Subsequently most of the NGV's metering hardware is based on sonic (choked) metering devices i.e. injectors.

For a correct prediction of the effect of biomethane compared to reference fuels like G20, G23, G25 and GR it is strongly advised to use the Sonic Bievo index. The development of the new Sonic Bievo index is explained below.

For choked (sonic) flow the mass flow is defined [7] as follows:

$$ \dot{m}_{gas} = \frac{C_D * A * p_1}{\sqrt{R*T}} * \kappa^{1/2} * \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa+1}{2*(\kappa-1)}} = C_D * A * \sqrt{p_1 * \rho * \kappa} * \left(\frac{2}{\kappa+1}\right)^{\frac{\kappa+1}{2*(\kappa-1)}} $$

Furthermore the gas flow of a given gas engine can be related to the mixture flow as follows, where λ_{stoich} equals the volumetric stoichiometric A/F-ratio.:

$$ Q_{gas} = \frac{Q_{mix}}{1 + \lambda * \lambda_{stoich}} \qquad \text{or} \qquad \dot{m}_{gas} = \frac{Q_{mix} * \rho_{gas}}{1 + \lambda * \lambda_{stoich}} $$

For a given engine and operation point, the ratio of the mass flow of "gas x" and the mass flow "methane" can be represented as follows:

$$ \frac{\dot{m}_{gas\_x}}{\dot{m}_{methane}} = \frac{\rho_{gas\_x} * \left(1 + \lambda_{stoich\_methane}\right)}{\rho_{methane} * \left(1 + \lambda_{stoich\_gas\_x}\right)} $$

Combining the above mass flow ratio with the sonic flow formula, the ratio of the required area (or injection time) can be calculated, see formula below:

$$ \frac{A_x}{A_m} = \frac{\rho_x * \left(1 + \lambda_{stoich\_m}\right) * \sqrt{\rho_m * \kappa_m} * \left(\frac{2}{\kappa_m+1}\right)^{\frac{\kappa_m+1}{2*(\kappa_m-1)}}}{\rho_m * \left(1 + \lambda_{stoich\_x}\right) * \sqrt{\rho_x * \kappa_x} * \left(\frac{2}{\kappa_x+1}\right)^{\frac{\kappa_x+1}{2*(\kappa_x-1)}}} $$

Where indices "x" and "m" represent "gas_x" and "methane".

Influence of H2S poisoned biomethane on catalyst performance

In order to define the "Sonic Bievo index" the following methane data [4] [5] is used:

$$\lambda_{stoich} = 9.675$$

$$\kappa \text{ (kappa)} = 1.306$$

$$\rho \text{ (density)} = 0.718$$

$$Sonic\_Bievo = \frac{\rho * 8.4202}{(1 + \lambda_{stoich}) * \sqrt{\rho * \kappa} * \left(\frac{2}{\kappa + 1}\right)^{\frac{\kappa + 1}{2*(\kappa - 1)}}} * 100\%$$

The Sonic Bievo index is, representing the correction of the metering area, or the injection duration for sonic (choked) conditions like present with injectors. With pure methane the Sonic Bievo should be 100% by definition; see Excel calculation sheet "Wobbe_Lambda-shift_Sonic-Bievo.xls" including many other interesting characteristic gas properties.

The "Sonic Bievo index" is the correct index to compare biomethane fuels with (reference) fuels for today's sonic injected NGV's.

In next section some characteristic gas parameters of biomethane and reference gases will be compared.

3.3.e. Characteristic gas parameters: examples

Below a number of gases are compared regarding S_λ and Sonic Bievo. The Excel sheet "Wobbe_Lambda shift_Bievo.xls" contains the calculations of the characteristic gas parameters, and will available within the BiogasMax project.

Table 5

	H-gas max	H-gas min	L-gas max	L-gas min	Methane	Dutch NG dd 05-01-07
HD reference fuel	GR	G23	G23	G25	G20	
Lambda shift factor (S_λ)	0.911	1.081	1.081	1.163	1.00	1.123
Sonic Bievo index	0.975	1.101	1.101	1.200	1.00	1.199!

Table 5 above clearly shows the difference between the lambda shift factor (S_λ) and the Sonic Bievo index, although both characterizing gas parameters are defined as 1.00 with pure methane. As explained in previous sections, for use in modern NGV's, equipped with engines with sonic (choked flow) metering devices (e.g. injectors) the Sonic Bievo index should be used.

For comparison reasons the Dutch natural gas, from a recent analysis, was added in table 5. It becomes clear that for a (sonic) injection type NGV, the quality of Dutch natural gas is on the edge of the vehicle regulations, although the lambda shift factor (S_λ) does not have an alarming value! This means that the performance of any NGV on Dutch natural gas, depends on the amount of extra margin between the actual manufacturer's vehicle fuel specifications, and the regulated fuel specifications. Using the Sonic Bievo index when comparing Dutch natural gas with G25 (representing the lowest possible gas quality) proves that the G25 reference gas is not "low enough" to be used as reference fuel for NGV's, if Dutch natural gas quality should be covered by the reference gases. This applies for both light-duty as heavy-duty NGV's. This important conclusions however is not directly related to the use of biogas. To avoid future problems with NGV's on Dutch natural gas, or gas with similar Sonic Bievo index the G25 reference gas should be replaced with a reference gas with a somewhat lower quality (higher Sonic Bievo index) reference gas.

In table 6 on the next page, the situation for a number of estimated biomethane compositions is presented.

The following can be concluded:

- NGV's with "H" certification can use biomethane with 0.975 < Sonic Bievo < 1.101

- NGV's with "L" certification can use biomethane with 1.101 < Sonic Bievo < 1.200

- NGV's with "HL" certification can use biomethane with 0.975 < Sonic Bievo < 1.200

Below a number of estimated biomethane qualities are compared regarding Sonic Bievo:

Table 6 Biomethane examples

	Normal Biomethane-1	Normal Biomethane-2	Normal Biomethane-3	Normal Biomethane-4	Methane	Exceptionally low quality biomethane
CH_4	94 vol%	97	95.5	98	100	89.8
N_2	2	0.8	2	0	0	0
CO_2	2	2	2	2	0	10.2
H_2	1.5	0	0	0	0	0
O_2	0.5	0.2	0.5	0	0	0
Sonic Bievo	1.077	1.050	1.073	1.036	1.00	1.196

Table 6 shows, that if biogas will be upgraded to above presented estimated "normal" biomethane qualities, all of these biomethane fuels can be used in NGV's with H approval, as well as in HL type approved NGV's. Exceptional low biomethane qualities, as presented in the last column, can be used in L approved, or HL approved NGV's.

3.3.f. Conclusions biomethane quality for NGV's

The Sonic Bievo index is developed by TNO to compare various biomethane qualities with the heavy-duty R49/03 reference gases, i.e. GR, G23 and G25 for vehicles using sonic injection equipment. When applying this calculation methodology, together with nationally regulated biomethane qualities, the following can be concluded:

Conclusion 1:

Since the highest biomethane quality is comparable with pure methane, because of the fact that no other hydrocarbons like ethane, ethene, propane and butane are present in biomethane, the Sonic Bievo index of biomethane will never be lower than 1.00. *For this reason the highest possible biomethane quality will never exceed the H-range*, that covers Sonic Bievo index values from 1.101 – 0.975.

Conclusion 2:

Assuming that the two dominant components of biomethane are methane (CH_4) and carbon dioxide (CO_2), which might not 100% be true for landfill derived biomethane, an exceptional low biomethane quality is defined;

see table 6 above. It can be calculated that even this exceptional biomethane with a CO_2 content of approx. 10%, can be used in L-gas approved NGV's. However, various national regulations limit the CO_2 content up to values like 2% up to 6% which means that *even the lowest biomethane qualities (up to 6% CO_2) can be used in L or HL approved NGV's.*

This all means that expected biomethane qualities can be used in both heavy-duty as well as light-duty NGV's conform R49 and R83, without negative influence on performance and emissions.

Therefore we had to decide to not carry out actual HD emissions tests on various biomethane qualities. For these activities an alternative research topic is proposed; see section 4.

4. Influence of H₂S pollution on catalyst conversion efficiency

4.1. Objectives H₂S measurement program

Biomethane can contain various polluting components that can be divided in two groups. One group is formed by components like dust, moisture (acid formation together with Cl_2 Br_2 etc.) and e.g. siloxane's from landfill gas origin, that all can have negative influence on the durability or the reliability of the fuels system or engine of the specific NGV.

The second group is formed by components that are known for their influence on three-way catalyst performance. H_2S is one of them, and furthermore this is the most likely biomethane polluting component that might appear in the biomethane incase some production process problem has occurred.

The following objectives are defined:

- study the influence of various H_2S concentration on catalyst light-off
- influence of various H_2S concentration on steady-state catalyst performance

4.2. Definition H₂S measurement program

4.2.a. Research platform specification

The research engine used in this project is the same engine as used at the subtask 5.2.4 catalyst ageing program. The research engine is a Volvo B5234T engine, in natural aspirated version, with increased compression ratio from 8.5 : 1 to 11.5 : 1. Maximum torque approx. 170 Nm; maximum power approx. 95 kW.

The engine was equipped with both MPFI sequential fuel injectors as well as equipped with a single point injection device, using 5 sequential injectors as well. By using a single point mixing device, high and constant mixture homogeneity can be achieved. Furthermore, in this way it is guaranteed that (varying) inaccuracies in fuel injectors will not be of any influence on the raw emission of the engine, and the subsequent conversion efficiency. The engine is controlled by means of TNO's rapid control prototyping system "MACS", using software generated in MatLab/Simulink the A/F-ratio can be controlled e.g. by a PID control or any other control algorithm. More detailed information regarding engine control can be found in the section "measurements".

Tests will be carried out using G20 reference fuel in pure form and using G20 contaminated with different H_2S concentrations.

Influence of H2S poisoned biomethane on catalyst performance

See figure 8 below for an overview of the research platform and after-treatment components, undergoing emission tests in TNO's engine and emission test laboratory.
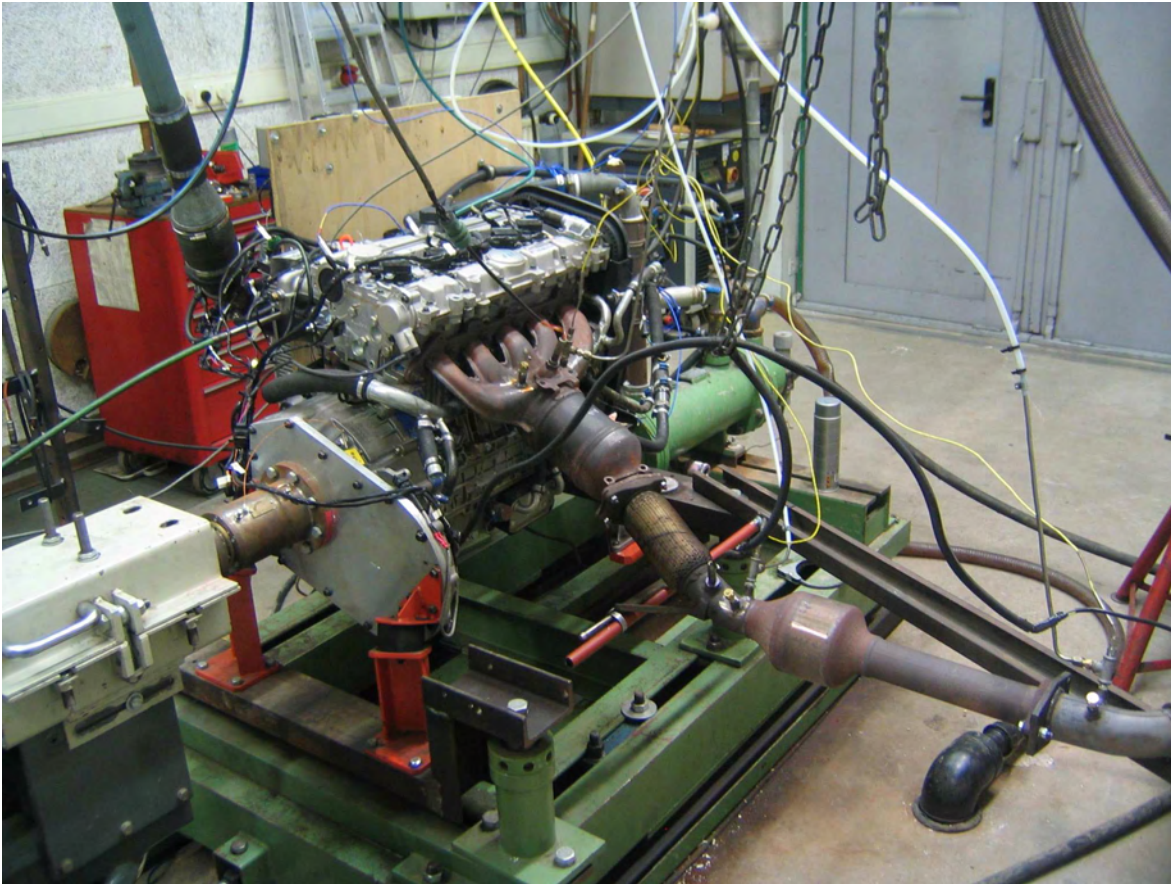

Figure 6

4.2.b. Catalyst selection for H₂S testing

The effect of H_2S on the catalyst conversion efficiency will be measured using the "short aged" catalysts aged on biomethane, as used during the catalyst ageing measurement program. This catalyst was operated on biomethane for approx. 160.000 km; see table 1 below.

The Volvo part number for the manifold including pre-catalyst is 8603493 and the under floor catalyst is part number 8603058.

See table 1 below for an overview of the available catalysts:

Table 7

Identification	mileage	referred as	origin	fuel
1 mark	269.803 and 276.639 km*	medium aged	Stockholm delivery service	Stockholm biomethane
2 marks	365.578 km	long aged	Stockholm taxi	Stockholm biomethane
3 marks	**161.599 and 166.501 km***	**short aged**	**Stockholm taxi**	**Stockholm biomethane**
no marks	126.000? km	reference catalyst	Dutch private/business	natural gas**
4 marks	0 km	100% new	Volvo dealer	X

Influence of H2S poisoned biomethane on catalyst performance

* Under floor (UF) catalyst was replaced previously to pre-catalyst replacement
** Mostly operated on Dutch natural gas, but the vehicle was operated incidentally in Germany as well.

4.3. Measured quantities and equipment used

In next sections the test bed equipment and the measured quantities are described. All test data is filed under a unique TNO engine and emissions laboratory project number.

4.3.a. Measured quantities

Engine:	speed, torque, p-manifold, air flow, T-oil, T-water-in, T-water-out, p-oil
Emissions:	before pre-catalyst (raw) and after pre-catalyst
Lambda:	calculated from emissions as well as Horiba/NTK lambda-scan
H_2S flow:	by means of pre-mixed test gases
After-treatment:	p and T before pre-catalyst (raw), after pre-catalyst and after UF-catalyst (tail pipe)

See figure 7 below for an overview of the operating desk of the test bed and measurement equipment: in the control room of TNO's engine and emission laboratory:
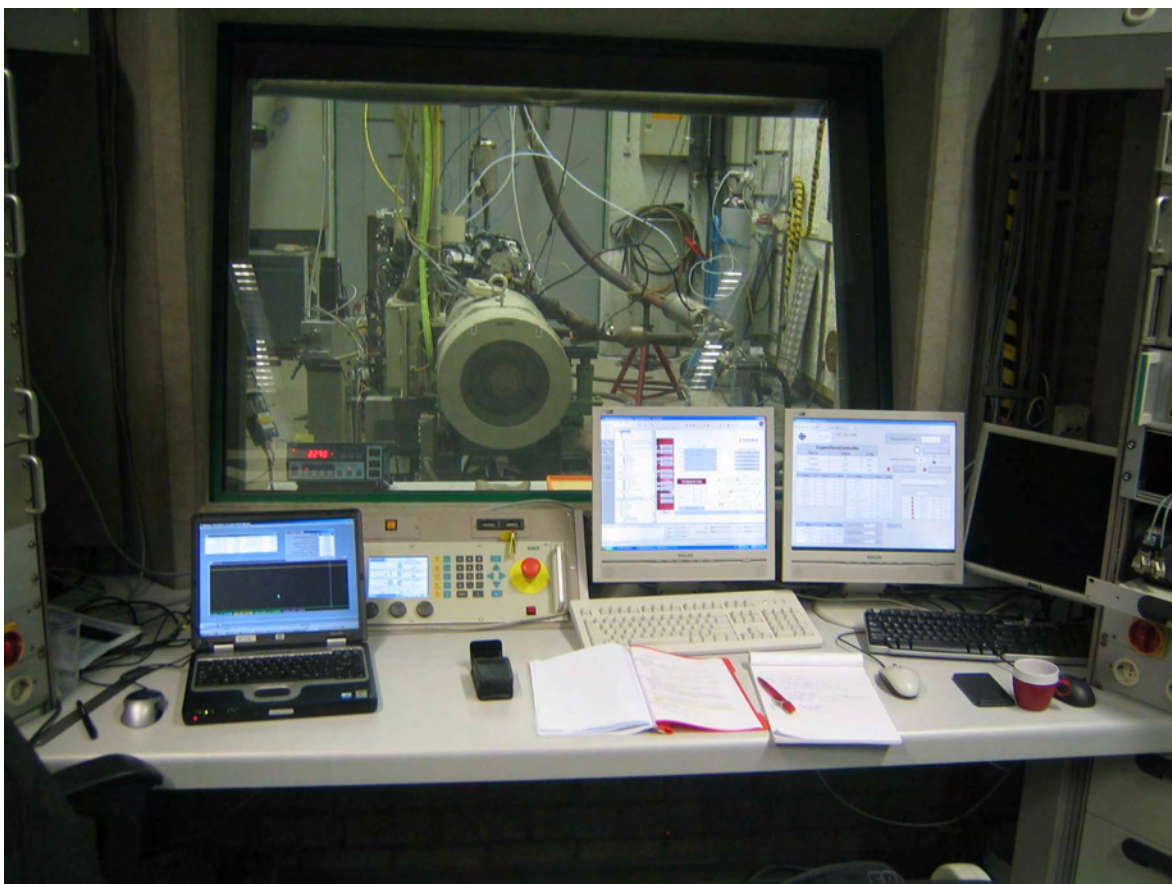

Figure 7

Influence of H2S poisoned biomethane on catalyst performance

4.3.b. Test bed equipment

Dynamometer: Test cell P2: Schenk transient brake type DYNAS$_2$ - 220

Dynamometer control: X-act Dynamo control

Data acquisition: Schenk STARS Automation Software Platform

Test control: Schenk STARS Automation Software Platform

Pressure transmitters: Keller 0-1000kPa (Oil pressure)

Keller 20-120kPa (Intake manifold pressure)

3x Keller 0-300kPa (Exhaust pressures)

Temperature measurement: Thermo couples type-K for exhaust gas; type T for ambient temperatures

Humidity: Testo 33

Air flow: Laminar flow element type LFE-2 max 170 mn^3/hr

Lambda sensor wide-band: Horiba/NTK lambda-scan before pre-catalyst

Lambda sensor binary: NTK TiO2 after pre-catalyst and after UF-catalyst

Emission unit 7A: Horiba MEXA: CO, CO$_2$, NO, NO$_x$, O$_2$, THC and CH$_4$

Emission unit 7B: Horiba MEXA: CO, CO$_2$, NO, NO$_x$, O$_2$, THC

4.4. H$_2$S Measurement program

4.4.a. Definition H$_2$S concentrations

From public sources [8] we learnt that the H$_2$S concentration of raw biogas can vary between 1500 – 2300 ppm. Based on this data and on data collected from the BiogasMax partners, the following three-H$_2$S levels are selected, assuming that these mixtures are available.

- 30 ppm
- 300 ppm
- 3000 ppm

Volume concentration in [ppm] can be converted to [mg/m$_n^3$] by using: 1 ppm H$_2$S equals 1.52 mg/m$_n^3$

It should be noted that using H$_2$S poisoned (bio)methane as an engine fuel, will cause severe corrosion in engine and after-treatment components. For this reason the engine will run only limited time on this corrosive gas.

4.4.b. Engine operation points

For the "lambda sweep" conversion efficiency program three-different H$_2$S contents will be tested, with the engine on operating point "A" the dominant point in the NDEC test cycle. The light-off test and the buffering capacity measurement will be carried out at point "A" as well.

A: 2000 rpm @ 2 bar BMEP (equals 37 Nm and 7.7 kW)

4.4.c. Catalyst preparation

To ensure that the catalyst is in a pre-defined state before actual H₂S catalyst performance testing will start, the catalysts will be prepared by running a conditioning cycle. This conditioning cycle will be conducted using engine operation point "A" as defined above. The fuel used for the following measurements will also be used to conduct this preparation cycle. The preparation cycle will be run with a fully warmed up exhaust system at lambda 1.02 for 5 minutes.

4.4.d. Light-off measurement

Catalyst light-off performance is crucial for complying to light-duty emission standards; since approx. 90% of the vehicle emissions are produced before the light-off temperature has been reached. For this reason the light-off performance is measured for both new and aged catalysts. Light-off time per component, CO, (T)HC and NOₓ is defined as the time required reaching 50% conversion. Light-off tests are carried out at lambda 1.02 because our focus is on HC light off, which is crucial because the relative low methane conversion compared to gasoline after-treatment, requires expensive catalyst formulation. Because the light-off measurement is carried out using a lean A/F-ratio, the NOₓ light-off cannot be measured correctly.

General remark: the engine was started and immediately brought to 2000 rpm and 2 bar BMEP. In contrary to a production NGV engine, the ignition angle was not retarded to reduce the time required for light-off. Furthermore no specific light-off fueling strategies were applied; the engine was operated on lambda = 1.02 and because of this lean conditions during light-off testing, only the light-off curves of CO and THC are presented. Both total hydro carbons (THC) as methane (CH₄) was measured, but because the regulations require THC measurements, the THC emission is presented in the result section.

Since light-off performance is dominated by the light-off performance of the CC-catalyst, the light-off conversion of the pre-catalyst is used to compare the catalysts aged on biomethane versus the catalyst aged on natural gas. Light-off time is defined as the time required reaching 50% of the steady-state conversion rate.

Note: some incorrect efficiencies are calculated, e.g. right after engine start, due to in-simultaneous range-switching of the analyzing equipment upstream and downstream of the two catalytic converters.

Procedure:

- Catalyst is "prepared" and cooled down, prior to catalyst light-off testing
- Engine and catalyst temperature between 10 - 20 °C
- Start emission measurement both engine-out and in between catalysts
- Engine start and immediately set to operating point "A" (2000 @ 2 bar BMEP)
- Run emission test for 10 min. using 2 Hz sample interval.
- After test is finished, warm up for steady state conversion tests at lambda 0.95 to ensure proper catalyst preparation

4.4.e. Steady-state conversion efficiency

With the selected catalyst, the "lambda sweep" program will be executed using three-levels of H₂S poisoning of the natural gas. Engine and after-treatment should be fully warmed up; using criteria "dT/dt" below 2°C / min.

The following 15 lambda steps are commanded by STARS to the MACS engine controller, using a relative slow PID lambda control algorithm, to ensure stable and accurate raw emissions:

> 0.950, 0.960, 0.970, 0.975, 0.980, 0.985, 0.990, 0.995,

Influence of H2S poisoned biomethane on catalyst performance

1.000, 1.005, 1.010, 1.015, 1.020, 1.030, 1.040.

The time delay between the lambda steps (especially around lambda 0.99 – 1.00) should be large enough to ensure stable emissions (due to catalyst oxygen buffering). Measurements will be carried out from rich to lean, i.e. starting at lambda 0.950.

At each operation point the three-levels of H_2S contamination plus a zero measurement using G20 reference fuel will be carried out.

Since steady state conversion is dominated (see BiogasMax deliverable 5.4:"Report on emission test results on (aged) biogas catalyst performance compared to natural gas", section 5.2) by the CC-catalyst, the steady state conversion in the pre-catalyst is used to asses the influence of H_2S on the after treatment system.

The conversion efficiency will be calculated from the measured emissions and represented as function of fuel H_2S content.

4.4.f. Buffering capacity

The buffering capacity will be carried out using the H_2S contaminated methane, and will be compared with buffering capacity on Dutch G20 reference fuel.

After steady state emissions are measured, the PID control algorithm is changed to a switching algorithm around $\lambda = 1.00$ with fixed lambda steps, with which it will be possible to quantify the buffering capacity.

The buffering capacity of both catalysts is measured using the switching (binary) lambda sensors after the individual catalysts. The time between an A/F-ratio change to lean A/F-ratio and the switching of the binary sensor after the catalyst is measured, and compared with the new catalyst, and the catalyst aged on natural gas. Please be aware the TiO_2 binary HEGO oxygen sensors used give a high voltage (~ 4.5 VDC) under lean conditions (O_2 is present) and a low voltage (~ 0.5 VDC) in rich conditions (absence O_2 in the exhaust gas). This is the other way around, compared to conventional binary ZrO_2 sensors.

Because the buffering capacity of the under floor catalyst does play an important role in the emission control system of the vehicle, it is included in the buffering capacity measurements.

The measurements are conducted as follows: The research engine is run at engine setting "A" at lambda 0,95. After 15 seconds, the target lambda is switched to 1,05. The buffering capacity of both catalysts is measured using switching (binary) lambda sensors after the individual catalysts. The time between an A/F-ratio change to lean A/F-ratio and the switching of the binary sensor after the catalyst is measured, and compared with the new catalyst, and the catalyst aged on natural gas. Please be aware the TiO_2 binary HEGO oxygen sensors used give a high voltage (~ 4.5 VDC) under lean conditions (O_2 is present) and a low voltage (~ 0.5 VDC) in rich conditions (absence O_2 in the exhaust gas). This is the other way around, compared to conventional binary ZrO_2 sensors.

Delay-1 is the delay in seconds between the setpoint A/F ratio step and the A/F ratio step before the CC-catalyst. It is a measure for the reaction time of the fuelling system and the engine and should remain constant.

Delay-2 is the delay seconds between the setpoint A/F ratio step and the A/F ratio step between CC and UF catalyst. It is a measure for the oxygen buffering capacity of the CC catalyst.

Delay-3 is the delay seconds between the setpoint A/F ratio step and the A/F ratio step after the UF catalyst. It is a measure for the oxygen buffering capacity of the UF and CC catalyst.

5. Results

In the sections below, the results from the measurements (see Annex 1) are presented. Please note that all catalyst performance data will be compared to the performance of the catalyst when using G20 reference fuel.

5.1. Influence of H₂S on light-off performance

Because of the lean conditions during light-off testing, only the light-off curves of CO and THC and CH₄ are presented:
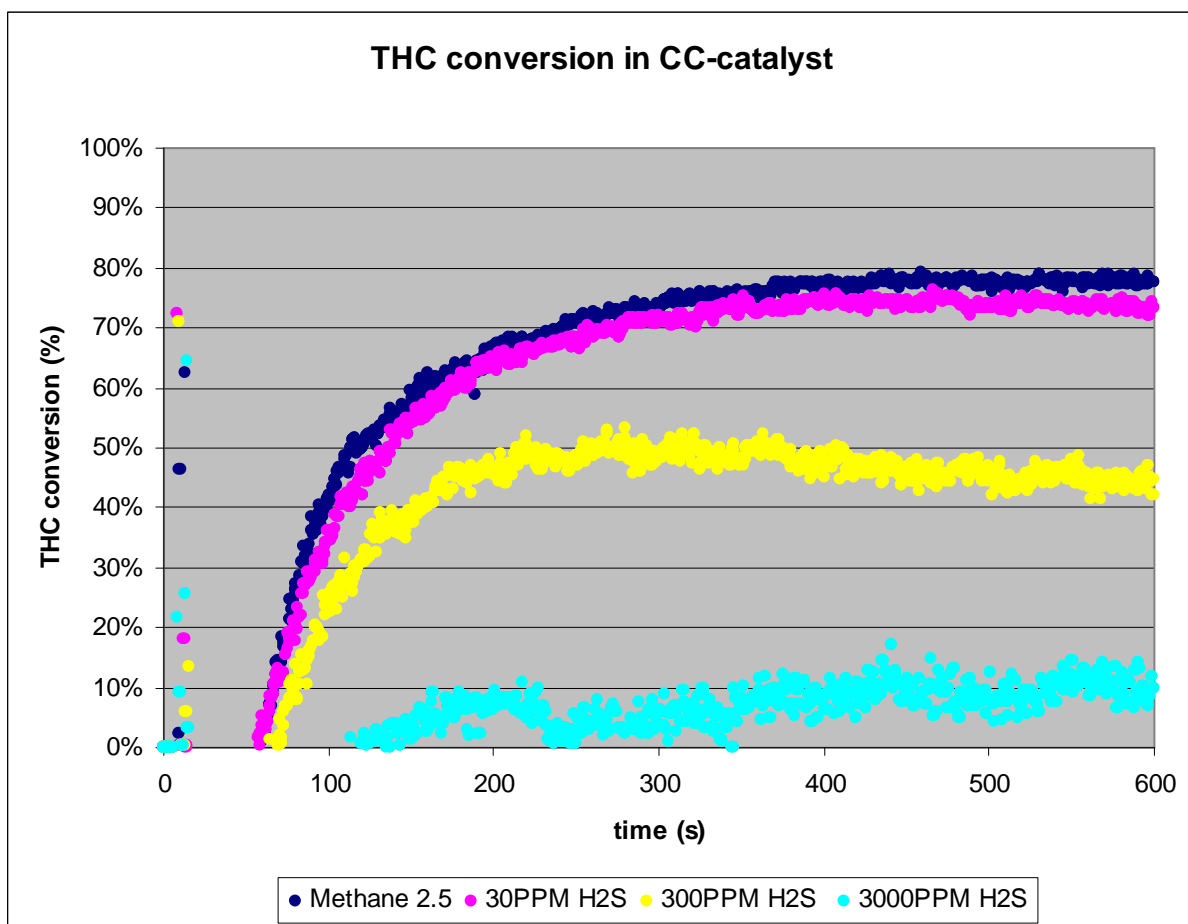

Figure 8

It is immediately clear that H₂S concentrations of 300ppm and above significantly influence the conversion of THC's during light-off conditions. A smalll effect can also be seen at the 30ppm H₂S concentration. If the H₂S concentration is increased to 3000ppm, the conversion efficiency remains below 15% and the catalyst is almost rendered useless. These results imply that it is very probable that H₂S concentrations above 30ppm can have a significant influence on vehicle cold-start emissions.
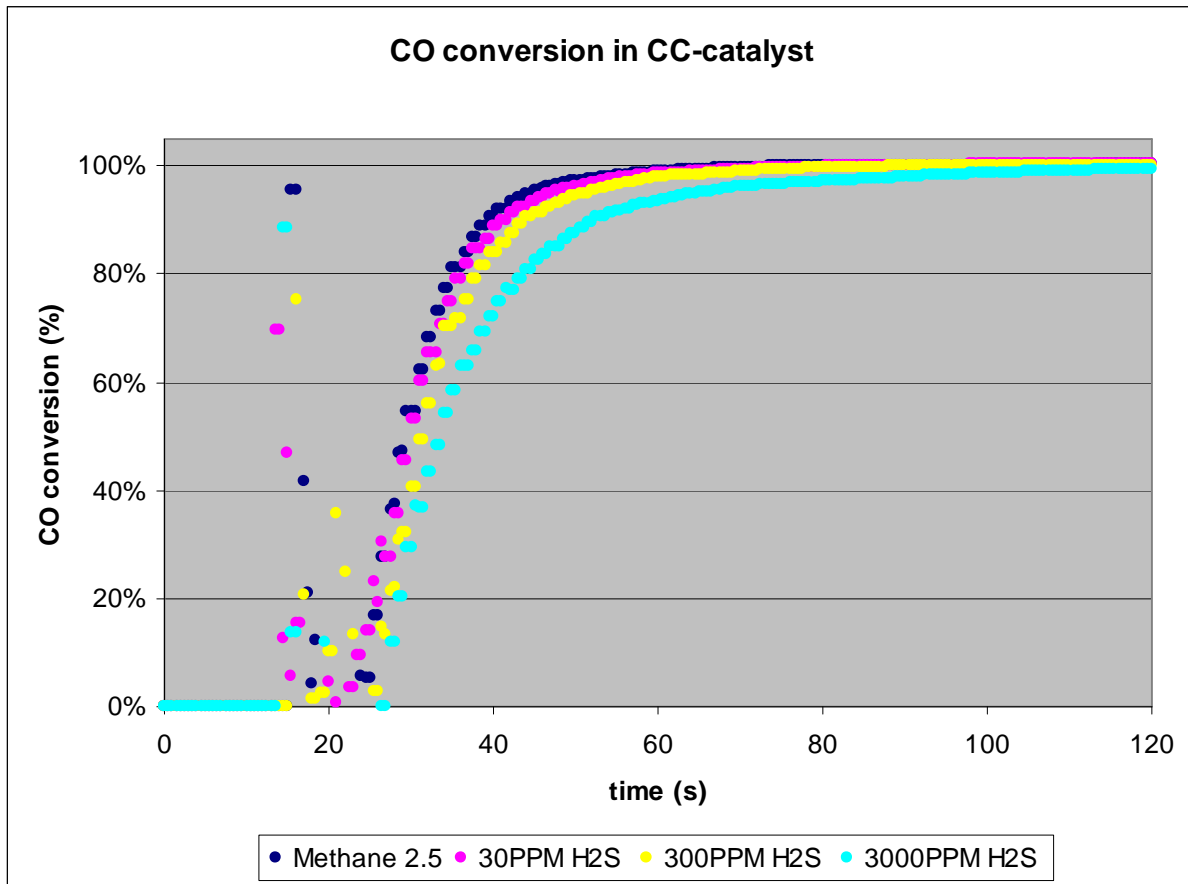
Figure 9

The influence of fuel containing H_2S on the conversion efficiency of CO during light-off conditions is a lot smaller. The final conversion efficiency remains uninfluenced. The light-off time (the time needed to get to 50% conversion efficiency) does increase from 30 to 34 seconds for the fuel containing 3000ppm H_2S when compared to G20 reference fuel.

5.2. Influence of H₂S on steady-state conversion efficiency

During the steady state conversion efficiency tests, conversion of THC, CO and NOx was measured as a function of lambda at engine setting "A". The measurement sweeps were conducted from rich to lean. In this section, the results are presented and a number of preliminary conclusions are drawn.

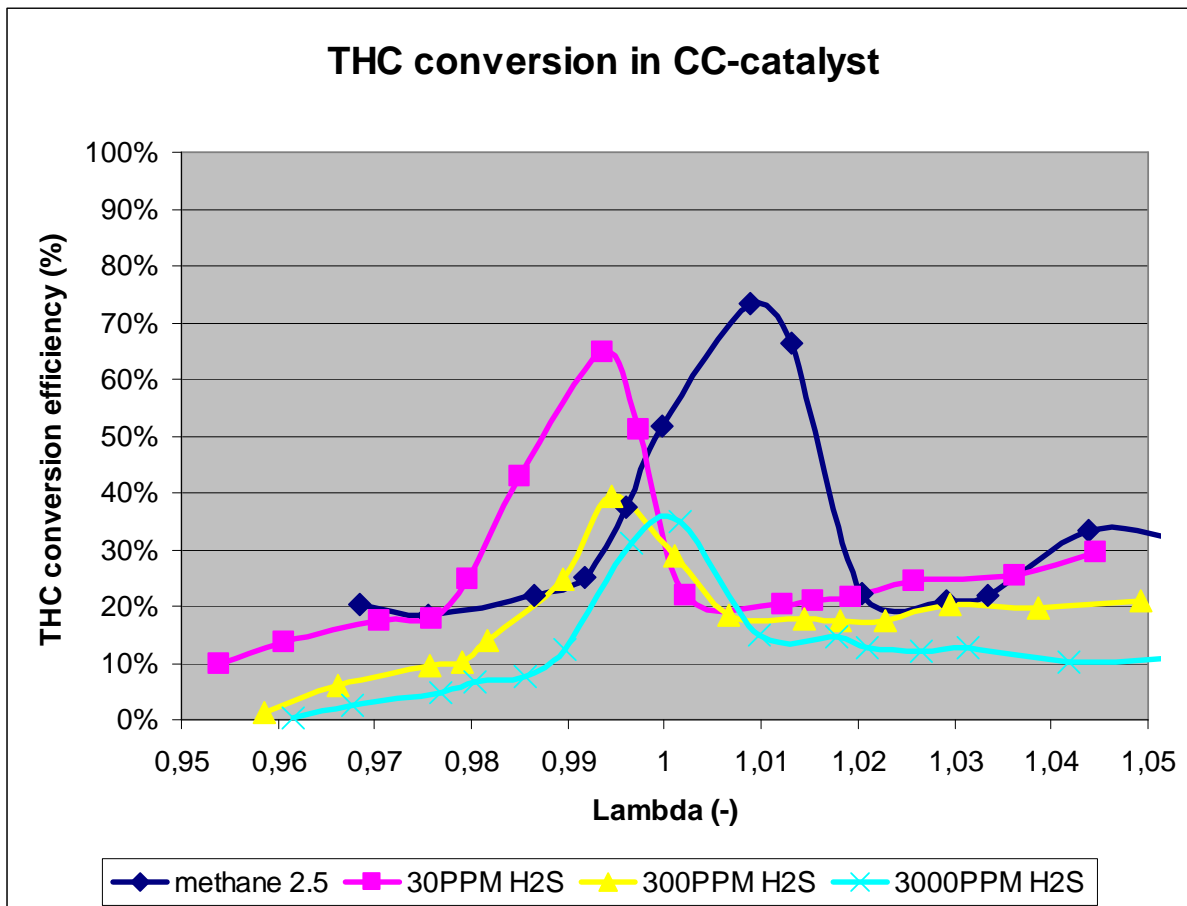The steady state conversion of THC in the CC-catalyst is shown in the next graph.

Figure 10

The results for THC indicate that the peak conversion efficiency gets lower with increasing H₂S concentration and that it also shifts towards richer mixtures. In practice this means that the steady state THC emissions will increase significantly with increasing H₂S concentration.

The results for CO conversion (see the next graph) show an opposite effect. At lambda values above 1.02, the conversion efficiency remains at near 100%. If H₂S is introduced into the fuel, the oxidation process of CO to CO_2 at lower lambda values is improved. No significant difference between the different H₂S concentrations (30, 300 and 3000ppm) was measured.
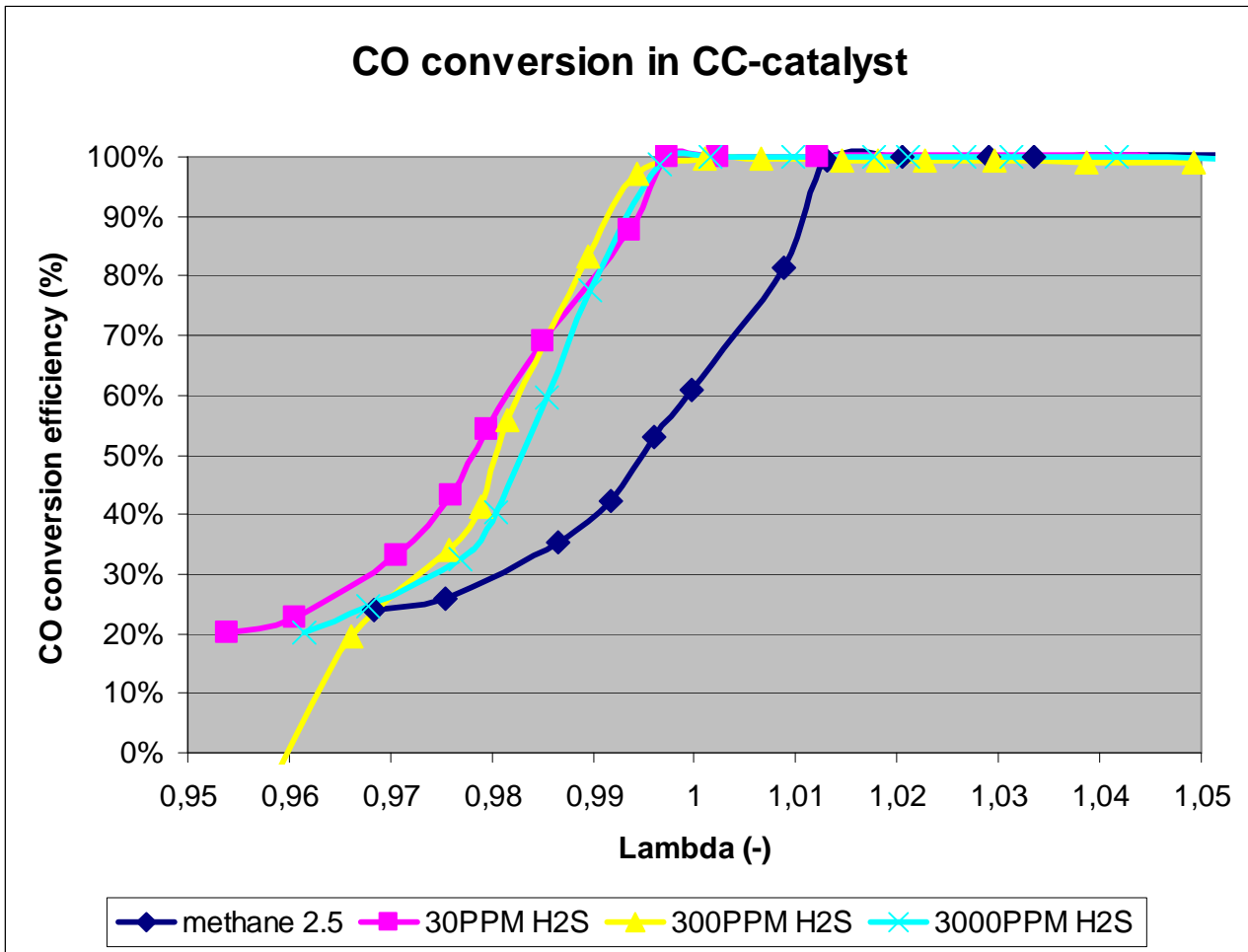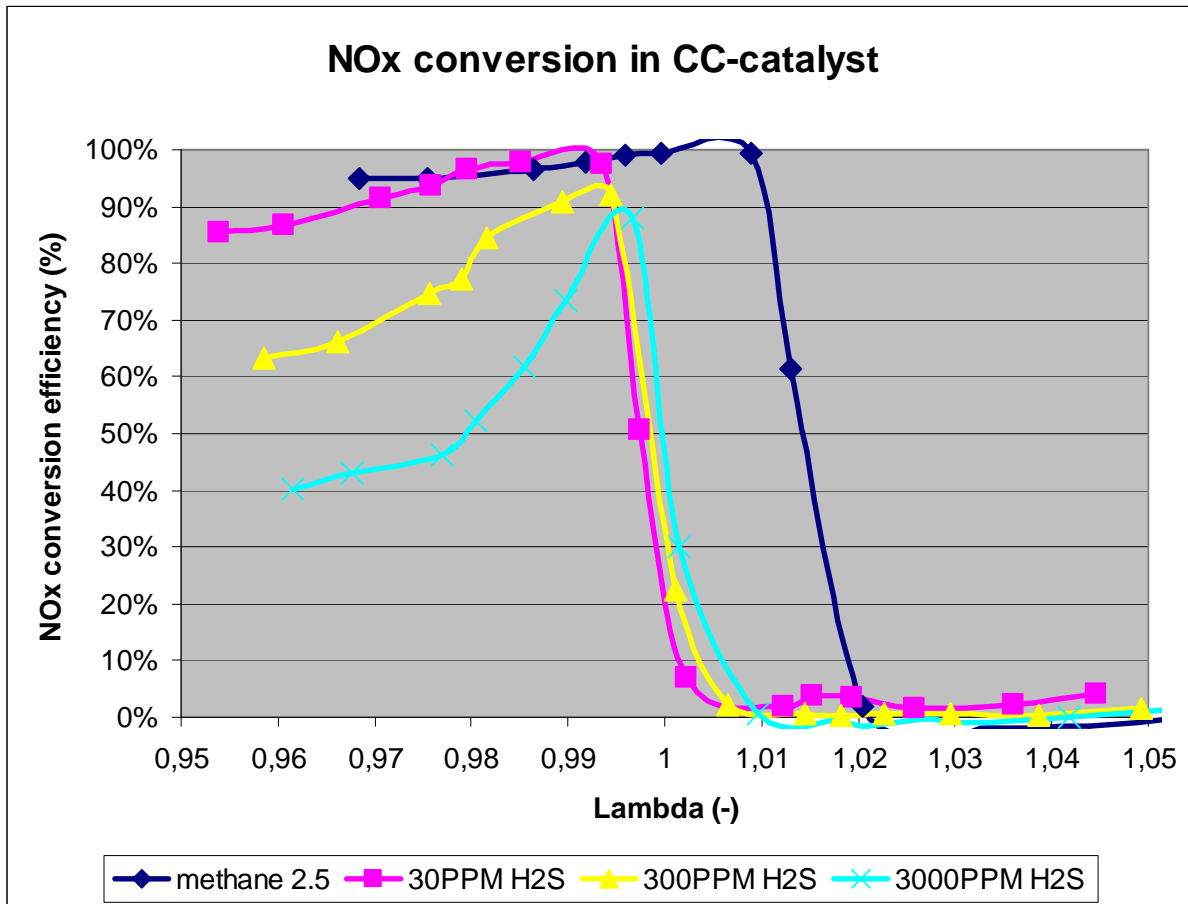
Figure 11

NOx conversion in CC-catalyst

Figure 12

The location of peak NOx conversion efficiency shifts to lower lambda values at 30ppm H_2S. At higher H_2S concentrations the peak efficiency drops to lower values and the efficiency ability of the catalyst to reduce NOx emissions at low lambda values (<0.99) is also lowered.

The impact of these changes in steady state conversion efficiency become clear if we plot the conversion efficiency of THC, CO and NOx in one graph for G20 reference fuel and for 30ppm H_2S fuel.
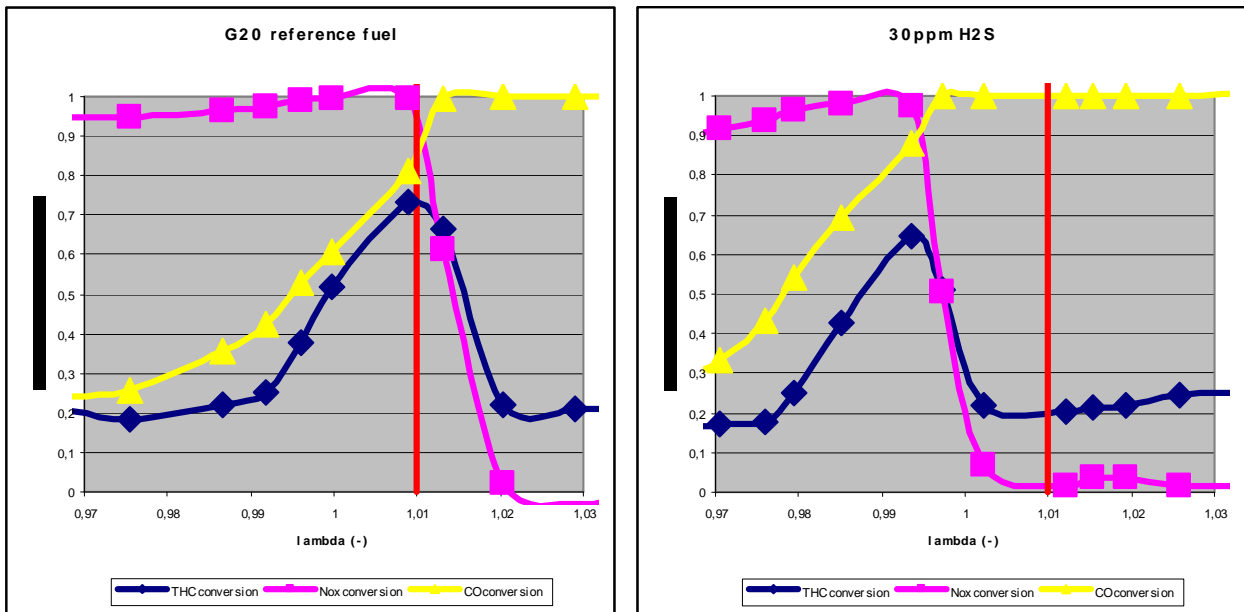
Figure 13 conversion with G20 and 30ppm H2S fuel compared

In these graphs, the lambda value at which maximum combined conversion efficiency occurs when using G20 (at lambda = 1.01) is marked with a vertical red stripe. If we mark the same lambda value in the 30ppm H_2S graph it becomes apparent that the conversion of both NOx and THC is already greatly reduced at these low values of H_2S content. From this, it can be concluded that the steady state tailpipe emissions of a NGV running on fuel containing 30ppm of H_2S will be higher then those of a NGV running on G20 reference fuel.

5.3. Influence of H$_2$S on catalyst buffering results

In this section, the results of the catalyst buffer capacity measurements will be discussed. For a description of the values presented here, see section 4.4.f of this report.
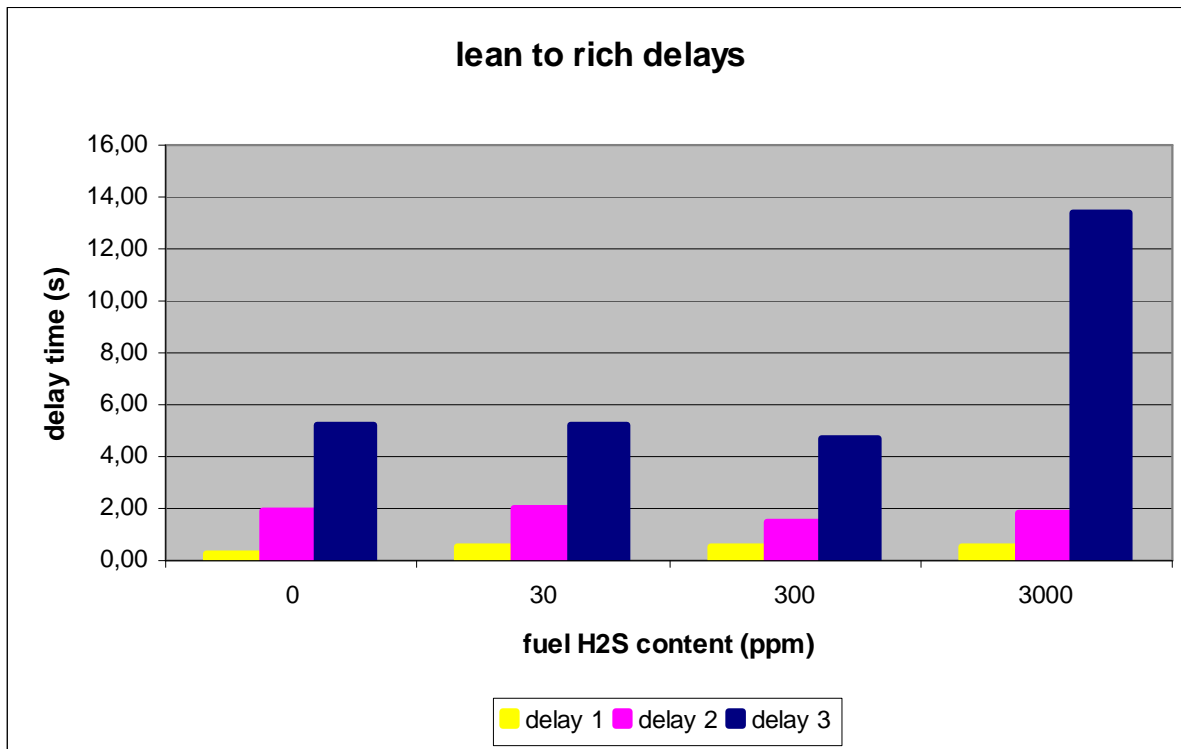

Figure 14

The above graph shows the different delay times when the A/F ratio is swiched from lean to rich. The "delay-1" and "delay-2" times prove to be relatively insensitive to the different H$_2$S concentrations. This means that:

  a) the measurement principle is OK to use, since delay-1 is constant

  b) the time it takes to purge the buffered oxygen from the CC-catalyst is not influenced by the different H$_2$S concentrations.

The "delay-3" time is influenced by the 3000ppm H$_2$S fuel. This delay time is increased from around 5 seconds to more then 13 seconds at this H$_2$S concentration. This could mean two things:

  a) There is more oxgygen stored in the UF catalyst at 3000ppm H$_2$S.

  b) It takes longer to purge the stored oxygen from the UF catalyst.

A combination of these two factors is of course also possible.

The next graph shows the different delay times when the A/F ratio is swiched from rich to lean. Again, the "delay-1" and "delay-2" times are largely unaffected by the different H$_2$S concentrations. The influence on "delay-3" is again much more pronounced. At 3000ppm H$_2$S, the delay is almost halved when compared to the reference situation. This could mean two things:

  a) the UF catalyst is able to store less oxygen at 3000ppm H$_2$S

  b) the oxygen storage occurs faster at 3000ppm H$_2$S

Again, a combination of these two factors is also possible.

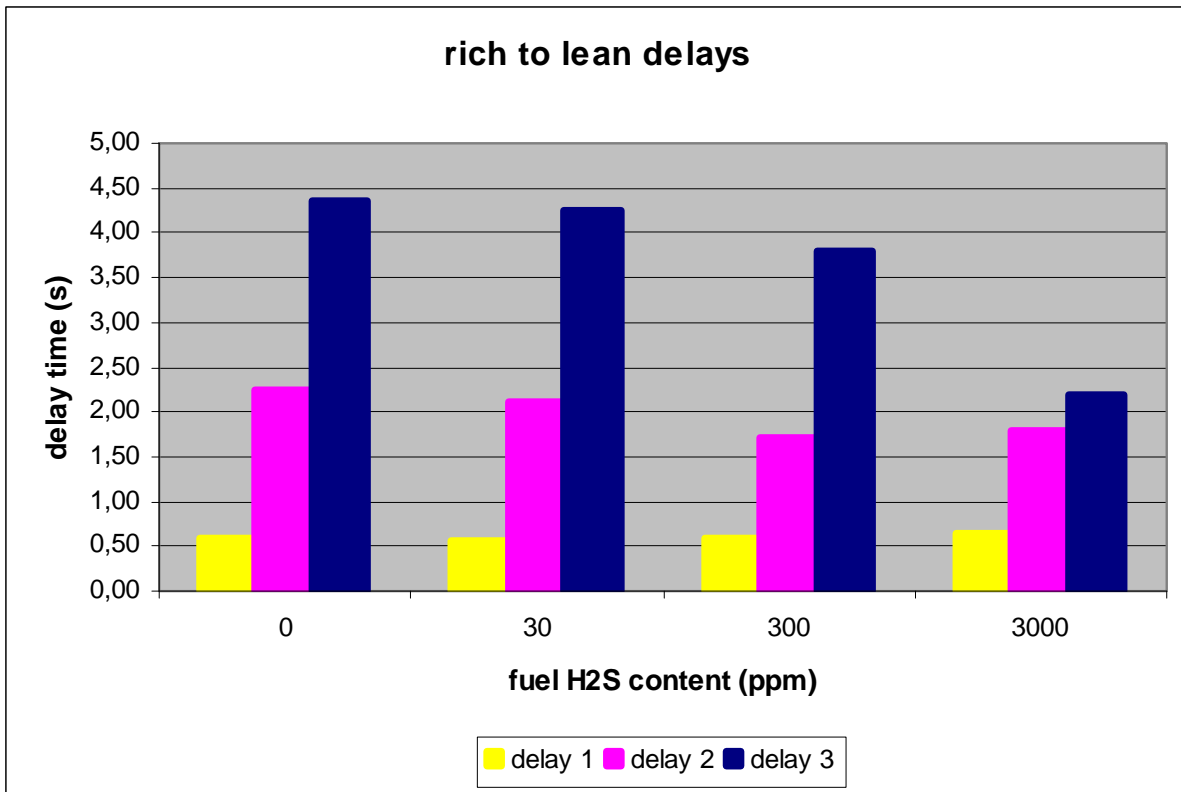Influence of H2S poisoned biomethane on catalyst performance

Figure 15

Without further research, it is not possible to draw solid conclusions regarding the tailpipe emissiosn resulting from the difference in delay-times measured in this way.

6. Conclusions

Regarding biogas (biomethane) gas quality, in relation to light-duty and heavy-duty NGVs' fuel specifications, we can conclude that:

- Raw biogas will be upgraded to so called biomethane gas quality, following regional regulations. By doing so, biomethane can be used in vehicles, designed to run on natural gas (NGV's).

- Even the highest possible biomethane (upgraded biogas) gas quality will never exceed both light-duty as well as heavy-duty NGV fuel specifications.

- "Normal" biomethane qualities (with e.g. CH_4 content of approx. 95% or higher) can be used in all LD-NGV's as well as all HD-NGV's specified for the HL or H fuel range.

- Exceptional low biomethane quality (e.g. with a CO_2 content of approx. 10%) can still be used in all LD-NGV's, but also in HD-NGV's if designed for the L or HL fuel quality range.

- In order to compare various (bio)methane gas qualities with NGV fuel specifications, a new gas quality key parameter (Sonic Bievo index) had to be developed, since today's NGV's are mainly using sonic fuel injection equipment. Using the current R49 lambda-shift factor will lead to erratic conclusions.

- Using the new "Sonic Bievo index" it became clear that Dutch natural gas has exactly the same Sonic Bievo index as the lowest NGV reference fuel specification (G25). This means that in case the vehicle manufacturer has not designed sufficient extra margin in the fuel injection system, both in the hardware and the software, problems with NGV performance and/or emissions will occur.

Regarding the use of fuel contaminated with various levels of H_2S, we can conclude that:

- The cold start THC emissions of NGV's operating on H_2S poisoned gas will be increased due to lower light-off conversion efficiency at H_2S levels of 300ppm and above.

- The steady state conversion of THC and NOx is reduced by fuel containing 30ppm of H_2S and more. This could lead to increased vehicle exhaust gas emissions. Further research is necessary to confirm this.

- To limit the effect of H_2S on vehicle exhaust gas emissions, it would be wise to limit the maximum concentration of H_2S in the processed biogas to a value below 30ppm. To determine the H_2S limit value, further research is needed.

- If this further research is conducted, it would be wise to measure the tailpipe emissions of a number of different NGV's from different manufacturers operating at a number of H_2S levels.

  Although the research engine used in the BiogsMax project has proven to be suitable for drawing these first conclusions, it cannot be used to determine the maximum allowed H_2S concentration in biogas fuel. In practice, it is very likely that catalysts used by different manufacturers have differing precious metal loads and are thus deferently influenced by H_2S.

7. References

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