



# Influence of Real CNG Engine Emissions On PdO/Al<sub>2</sub>O<sub>3</sub> Methane Oxidation Catalysts



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## Abstract

Natural gas engines play an important role in stationary energy generation, but also in mobile applications, especially in the maritime sector. However, this form of natural gas use produces methane emissions due to incomplete combustion, which must be removed because of the high greenhouse effect. This is done by means of oxidation catalysts. The PdO/Al<sub>2</sub>O<sub>3</sub> investigated in this publication has emerged as an efficient catalyst material. Nonetheless, the water and sulphur present in real engine exhaust gas can lead to deactivation of the catalyst. Nitrogen oxides on the other hand can even be beneficial under certain circumstances. However, these findings are largely based on investigations with synthesis gas, which differs from real exhaust gas. In addition, various influencing variables such as temperature and space velocity are coupled with each other through engine control. For this reason, the investigation of the influences of real engine emissions and conditions on methane conversion discussed here is necessary as a supplement to laboratory investigations. Thus, a natural gas engine modified for lean-burn operation is connected to an innovative exhaust system in order to thereby measure catalyst samples on a laboratory scale under real conditions. The engine's operating ranges analysed here extend from rich conditions required for the regeneration of deactivated catalytic converters to lean conditions such as are standard for combined heat and power plants. In addition, the influence of exhaust gas recirculation was considered. As a result, a noticeable minimum of methane conversion was observed in slightly lean conditions. Therefore, the influences of water, sulphur and nitrogen oxide emissions in particular are examined using exhaust gas measurement technology such as Fourier-Transform Infrared Spectroscopy.

**Keywords:** Methane Oxidation Catalyst (MOC); PdO/Al<sub>2</sub>O<sub>3</sub>; Water Inhibition; Sulfatization; CNG Engine; Regeneration; Lean Burn Gas Engine

**Abbreviations:** AMA: Abgasmessanlage (Exhaust Gas Measuring System); bef. Cat.: Before Catalyst; CNG: Compressed Natural Gas; DFG: Deutsche Forschungsgemeinschaft (German Research Foundation); EGR: Exhaust Gas Recirculation; FTIR: Fourier-Transform Infrared Spectroscopy; GC: Gas Chromatograph; GHSV: Gas Hourly Space Velocity; MFB50: Mass Fraction Burned 50 %; T: Temperature; URAS: Ultrarot-Absorptions-Schreiber (Nondispersive Infrared Sensor)

## Introduction

Despite the tight supply situation, natural gas is an important energy carrier that will remain relevant especially in the transition phase to climate neutrality. One form of using natural gas in this context is combustion in an engine. Natural gas engines play an important role above all in the area of stationary energy generation (combined heat and power plants) but also in mobile applications such as maritime transportation. Against the backdrop of supply difficulties and increasingly stringent exhaust gas standards, the further optimisation of engine processes and the associated exhaust gas aftertreatment is thus moving further into the focus of research activities. However, due to incomplete combustion,

methane slip always occurs [1], which is very problematic due to the high influence of methane on the greenhouse effect [2] and thus requires the use of methane oxidation catalysts. Palladium-based catalysts with aluminium oxide as a carrier material have been shown to be effective, especially in lean-burn gas engines [3,4]. For reasons of efficiency, natural gas engines are often operated lean. This also has positive effects on nitrogen oxide formation. Another measure to reduce nitrogen oxides is the use of Exhaust Gas Recirculation (EGR). Despite the abovementioned control measures, nitrogen oxide is still emitted. Although being harmful to the environment, they can have a positive influence

on catalysis under certain circumstances [5-7]. An exhaust gas species that has a negative (inhibitory) effect on a methane oxidation catalyst is water. This results from competition between water and methane for the active sites on the catalyst surface [8] and hydroxyl adsorption on the support material and the active sites [9]. Besides inhibition effects, deactivation in the form of sulphur poisoning (sulphatisation) [8,9,11] occurs particularly in natural gas applications. Two sources of sulphur can be identified in the engine context. The first is sulphur-containing engine oil, which enters the cylinder during combustion, and sulphur-containing odorants, which are added to natural gas for safety reasons. Regeneration takes place via rich operation, as the resulting reducing conditions favour the removal of the sulphur on the catalytic converter surface [12]. Nevertheless, the findings of the literature cited so far were only obtained under laboratory conditions. In contrast to experiments with synthetic gases, real engine operation has a greater variety of exhaust gas species. In addition, important state variables that define the boundary conditions at the catalytic converter are coupled with each other. For example, lean-burn at constant engine load causes a change in exhaust gas temperature, exhaust gas composition and space velocity. Therefore, an investigation under real conditions is necessary as a supplement to laboratory tests. The aim of the tests discussed in this paper is thus to find out what influence real engine exhaust gas and conditions have on a palladium-based catalytic converter, especially with regard to NO, H<sub>2</sub>O and SO<sub>2</sub> as well as the coupling of the state variables.

Materials and Methods

Engine Test Bench

First, a stoichiometrically operated 2.2l-gas engine originally used in commercial and industrial applications was modified to

enable lean-burn operation and exhaust gas recirculation (EGR). The modifications included a redesign of the intake manifold and the integration of an EGR section including cooler. In order to be able to handle higher engine loads, a connection to an external charge air supply is also necessary. The engine is coupled with an exhaust system whose integral component is a bypass line that enables catalytic converter samples to be measured. A backpressure flap simulates the flow resistance that a turbocharger would generate in reality. The mass flow through the bypass and thus the space velocity at the catalytic converter are controlled with the aid of a flow divider flap. Cooling of the exhaust gases up to the sample is prevented by using an adjustable heating band. The reference position, which is defined in such a way that it corresponds to the typical installation location (after the turbocharger) of a catalytic converter in series applications, serves as the basis for the setpoint values of the two aforementioned controls. The mass flow at the reference corresponds to the sum of the flows entering the engine (natural gas and air), both of which are measured using Coriolis scales. To determine the space velocities of the sample as well as the reference, the exhaust gas composition, pressures, temperatures as well as the catalyst volumes are missing. The exhaust gas composition is measured using Fourier transform infrared spectrosopes (FTIR) and an exhaust gas measurement system (AMA) and is the same at both locations. Pressure and temperature are recorded via thermocouples and pressure cells, respectively. The catalyst volume results from the geometry of the sample, which at the reference is defined as the volume of the series catalyst from the original engine (retrofit). The mass flow through the sample is recorded by a mass meter based on the differential pressure. In addition, the composition of the natural gas is measured using a gas chromatograph (GC). The EGR rate is determined by comparing the measured CO<sub>2</sub> concentrations (URAS) in the exhaust gas and in the intake manifold (Figure 1).

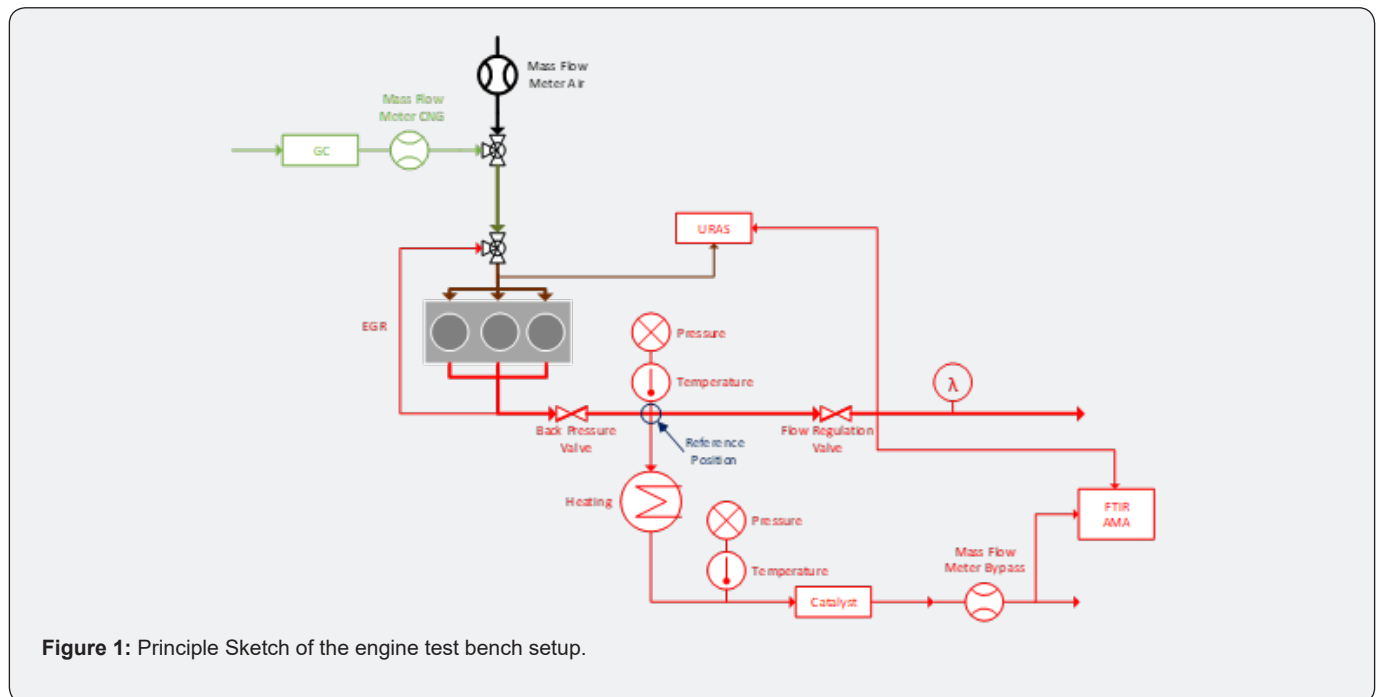


Figure 1: Principle Sketch of the engine test bench setup.

### Catalyst Probe

The catalyst material considered here is PdO on Al<sub>2</sub>O<sub>3</sub> (Table 1), which, as explained at the beginning, is particularly well suited for methane oxidation. The catalyst diameter is 1", the length 5 cm since a coating of near-series geometries is not feasible on a laboratory scale.

**Table 1:** Properties of the used catalyst probe.

Properties	Values
Catalyst Material	2 wt% PdO on Al <sub>2</sub> O <sub>3</sub>
Loading	80 g/ft <sup>3</sup>
Monolith Material	Cordierite
Length	5 cm
Diameter	1"
Cell Density	600 cpsi

### Measuring Program

(Table 2) lists the operating points investigated. The tests were carried out with almost constant added fuel mass. A change in the operating parameters results in a change in efficiency, which causes the torque changes. The fuel-air-equivalence ratio  $\lambda$  was varied from rich (0.8) to lean (1.4). The rich operating points here represent regeneration, the remaining points normal operation in maritime or stationary applications. The oxygen content at stoichiometric conditions is slightly above zero due to incomplete combustion and the lambda control. The exhaust gas temperature is influenced by the position of the combustion phasing (MFB50). If it is shifted to later, the exhaust gas temperatures rise. Since, with an almost constant fuel mass, leaning can only occur through an increased air supply, therefore the exhaust gas mass flow also increases, which leads to an increase in the space velocity.

**Table 2:** Measurement program, main operating and exhaust state conditions.

Air-fuel equivalence ratio $\lambda$	EGR	MFB50	T bef. Cat.	GHSV	Torque	O <sub>2</sub>
-	%	°CA	°C	1/h	Nm	g/h
0.8	0	8	565	134043	128	0
0.8	0	12	576	133419	128	0
0.8	5	8	558	131629	128	0
0.8	5	8	569	130226	129	0
0.8	10	12	549	126977	128	0
0.8	10	8	559	128937	123	0
1	0	12	635	155785	164	19
1	0	8	646	158776	160	20
1	5	12	630	153015	163	19
1	5	8	639	155979	152	19
1	10	12	621	152292	157	19
1	10	8	634	156391	163	19
1.1	0	12	624	168858	160	44
1.1	0	8	635	168219	163	43
1.1	5	12	617	167419	167	43
1.1	10	8	605	164264	163	43
1.1	10	12	617	169561	162	44
1.4	0	8	546	166519	150	137
1.4	0	13	552	169601	144	140
1.4	0	19	576	173223	151	139

### Results and Discussion

(Figure 2) shows the methane conversion as a function of lambda and EGR rate. Under lean conditions, the conversion rate is predictably poor due to the lack of oxygen for oxidation of methane. However, it is noticeable that a minimum seems to

form in the lean range at  $\lambda = 1.1$ . This raises the question of where this can come from. Do the deactivation mechanisms mentioned in the introduction have an influence? What role does NO play? After all, it is known that raw nitrogen oxide emissions reach their maximum in slightly lean operation. These issues are discussed in more detail below.

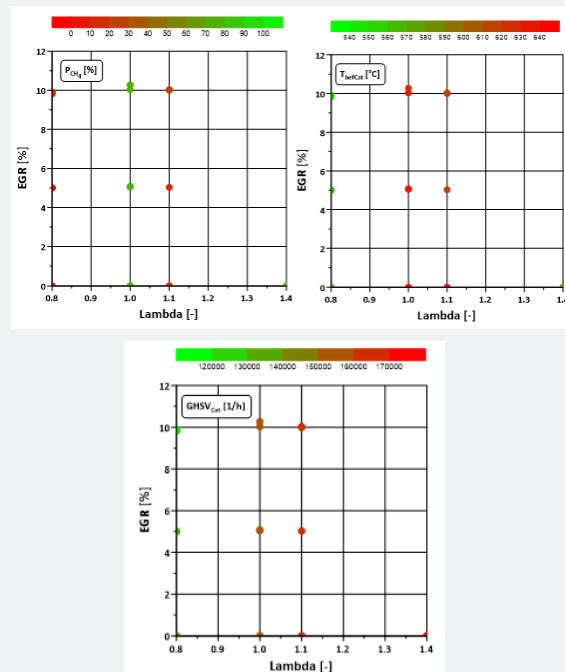


Figure 2: Configuration of 4-in HMAc and subgrade.

## Catalyst Deactivation

In order to shed more light on the issue of catalyst deactivation, it is necessary to take a look at the typical influencing variables known from the literature. As mentioned in the introduction, nitrogen monoxide influences catalysis. If the methane conversion is plotted against the NO mass flow, it can be seen that the decrease in  $CH_4$  conversion in the lean seems to be accompanied by an increased proportion of nitrogen monoxide (Figure 3 a-d). Another species known for its influencing (inhibitory) effect is water. A higher mass flow of both species is accompanied by a deterioration of the catalytic activity, which is clearly shown in (Figure 3d). In a comparison of  $H_2O$  and NO (Figure 3e,3f), an influence of both temperature and space velocity is visible for water quantities above approx. 190 g/h and for  $O_2$  quantities between 0 and 50 g/h. The effect of water on the catalytic activity is also visible in the comparison of NO and  $H_2O$ . A higher temperature in combination with a lower space velocity (and thus a higher residence time) has a positive effect on methane conversion (Figure 2b, c, Figure 3 d-f).

The interaction of water with temperature and space velocity is shown separately in (Figure 4). The range of  $\lambda = 1.1$  tends to show higher temperatures, whereby there is no clear limit as with the space velocity. This suggests that the influence of the GHSV weighs more heavily here. Following the findings from the literature ([5], [7]), this deterioration means that the positive effects of NO (despite the high amounts) are overcompensated by water. The emissions occurring here in engine operation range from 500 to

4400ppm for  $\lambda \geq 1$  and thus significantly exceed the proportions (up to 500ppm) studied in Auvinen et al. [5]; Gremminger et al. [6]; Sadokhina et al. [7]. Since the deterioration of methane conversion is accompanied by a more significant change in nitrogen oxide amounts compared to the changes in water, temperature and space velocity, and the nitrogen oxide fractions differ significantly from those in the literature cited here, the exact influence of NO in real exhaust gas might need further investigation.

Another form of deactivation is sulphation, which can occur even with small amounts Lott et al. [11]. Since sulphur as well as nitrogen oxide and water raw emissions occur simultaneously, their effects on catalysis must also overlap. To assess which of the deactivation or promotional mechanisms dominate, the methane conversion is plotted against the  $SO_2$  mass flow (Figure 5). The first two plots in (Figure 5) indicate that sulphur poisoning has a lower effect on the methane conversion than water in the experimental period (10h in total), since the conversion rate in the range  $\lambda \geq 1$  shows high as well as low values at approximately equal amounts of  $SO_2$  (< 4mg/h). This is possibly due to the different nature of inhibition as opposed to poisoning. The latter needs more time to unfold its effect, whereas inhibition effects are characterised by a more abrupt occurrence. For example, in Lott et al. [11], a noticeable deterioration occurred at a temperature of 500°C from about 3h, whereas the test run time here per operating point is significantly lower at a higher temperature. Besides the temporal component, the amount of sulphur dioxide also plays a role. The  $SO_2$  concentrations measured in this publication are on average

2ppm and thus below the detection limit of the FTIR (4ppm) and below the concentration of 5ppm investigated by Lott et al. [11].

So, in order to investigate the influence of sulphur under real engine conditions more time is required.

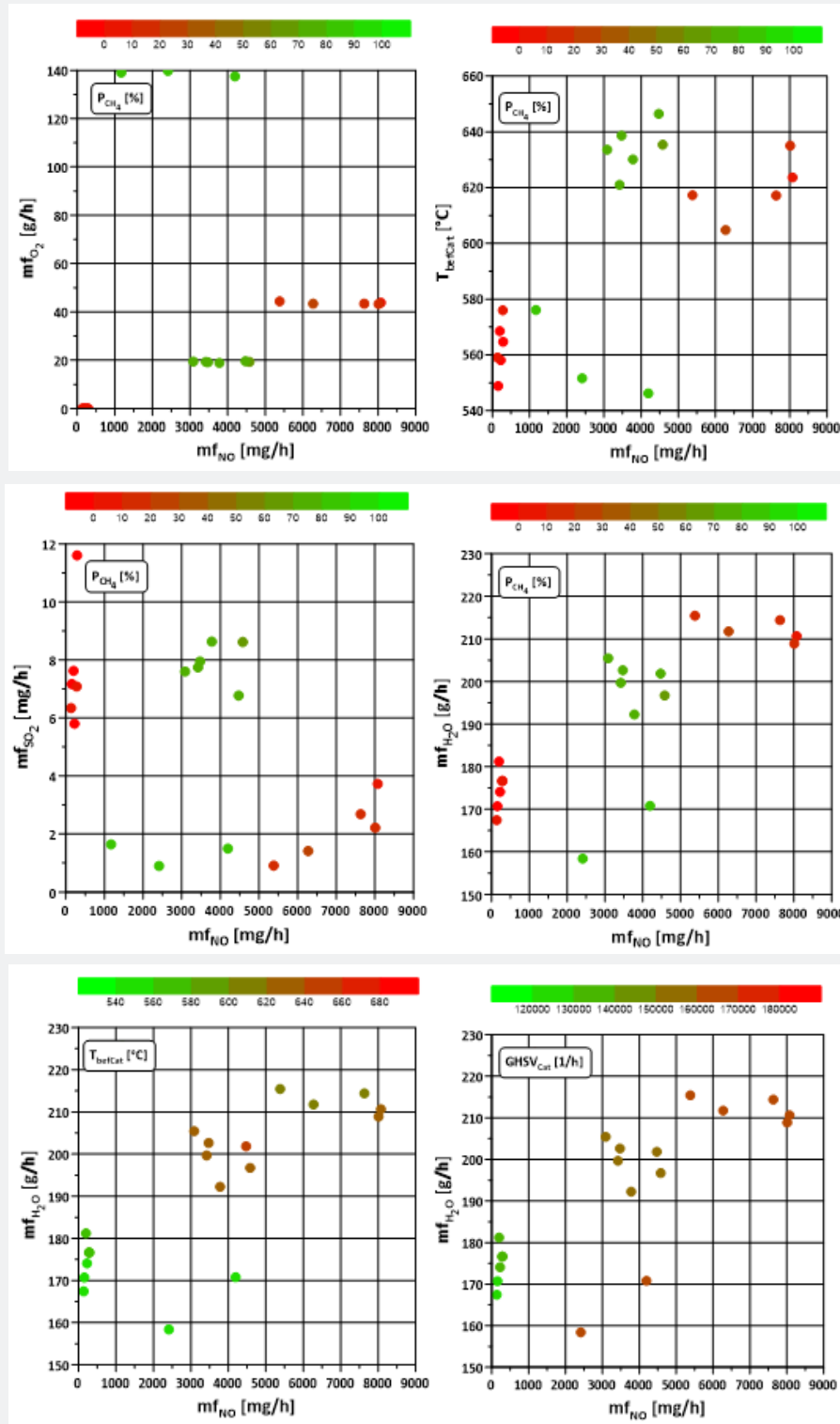


Figure 3: Methane conversion in % (a-d), temperature at catalyst in °C (e) and space velocity in 1/h (f) as a function of NO.

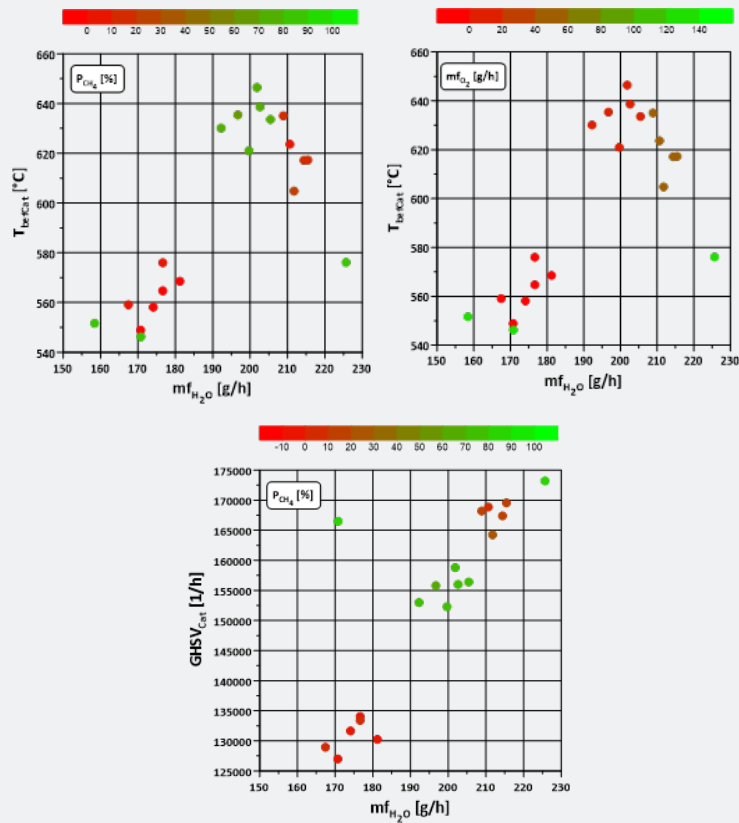


Figure 4: Oxygen content (a) and methane conversion (b,c) as a function of H2O.

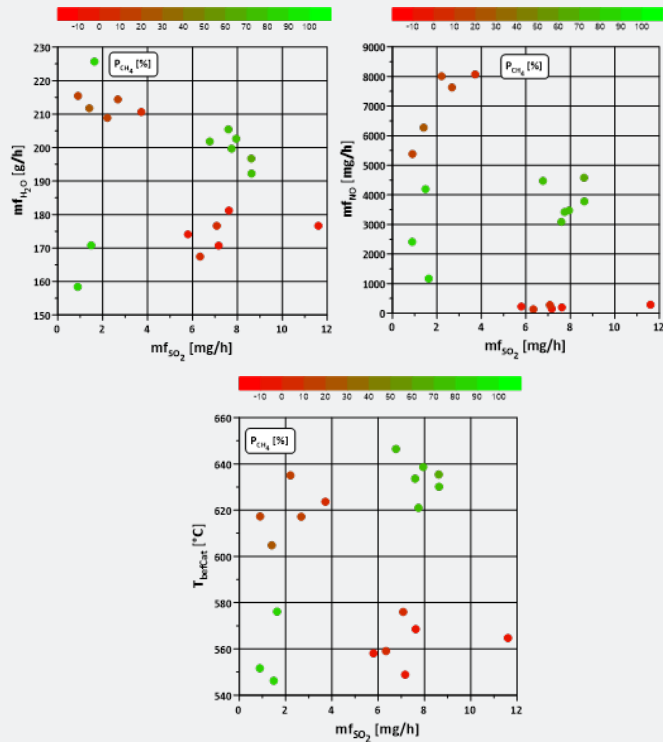


Figure 5: Methane conversion as a function of SO2.

**SO<sub>2</sub> Desorption or Post-Oxidation**

If deactivation phenomena occur, the question also arises as to which measures can be used to at least partially reverse them. One way of assessing the effectiveness of regeneration measures is the desorption of sulphur-containing species from the catalytic surface [11] which results in an increase in SO<sub>2</sub> emissions downstream of the catalyst. Lott et al. [11] found that such desorption is enhanced in the presence of water and under rich conditions. (Figure 6) a seems to partially confirm this. In this diagram, the SO<sub>2</sub> formation rate is shown as a function of the amount of O<sub>2</sub> and H<sub>2</sub>O. The highest increase rates occur - except for one outlier - at higher water quantities, but under lean conditions, which is why

it is still unclear whether and to what extent the SO<sub>2</sub> formation in the catalyst is not due to post-oxidation of other sulphur species not detected here. There does not seem to be a clear influence of both temperature and space velocity, since in both cases both high and low formation rates occur in a similar range of values (Figure 6b,6c). Interesting could be a possible influence of NO, which is shown in (Figure 6d). It can be seen that higher NO emissions lead to higher rates of increase, whereby a maximum seems to be formed in the range between 5000 and 7000 mg/h. However, since increased water and nitrogen monoxide emissions occur simultaneously, as described above, it is also not entirely certain here whether the desorption-promoting effect can be attributed to only one of the two species.

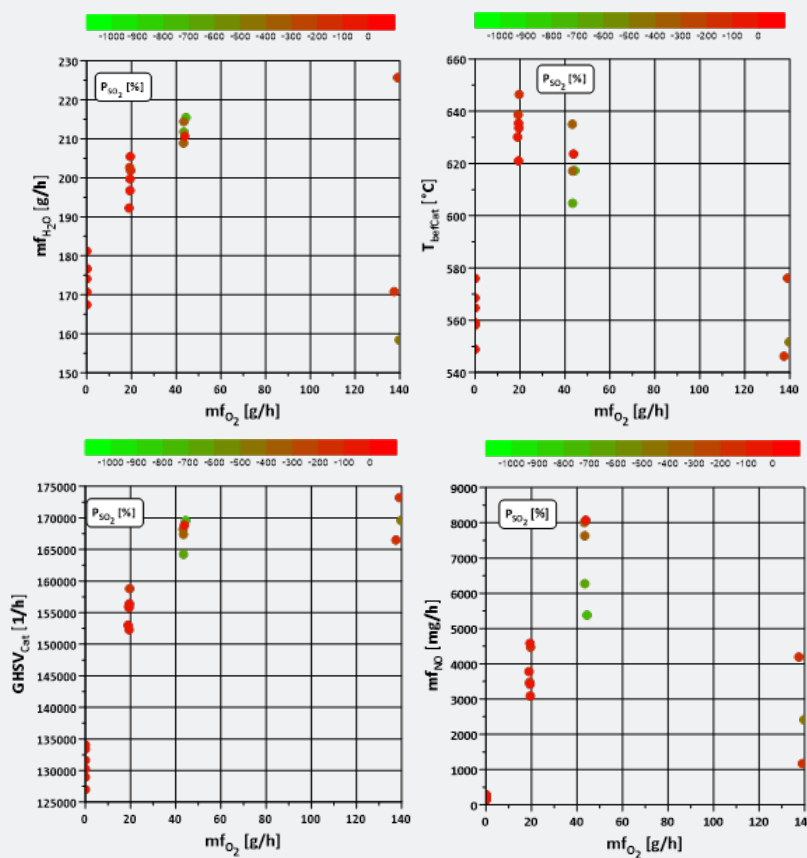


Figure 5: Methane conversion as a function of SO<sub>2</sub>.

**Conclusion**

The minimum in methane conversion in the range of λ = 1.1 could be due to several effects:

i. The results seen in this paper together with the findings from Sadokhina et al. [7] and Auvinen et al. [5] suggest that water inhibition is more powerful than the promoting effect of NO on methane conversion in the presence of H<sub>2</sub>O and SO<sub>2</sub>. So, following the discoveries from the literature, this deterioration

means that the positive effects of NO (despite the high amounts) are overcompensated by water. The emissions occurring here in engine operation range from 500 to 4400 ppm for λ ≥ 1 and thus significantly exceed the proportions (up to 500 ppm) studied in Auvinen et al. [5], Gremminger et al. [6]; Sadokhina et al. [7].

ii. The influence of SO<sub>2</sub> on methane conversion is minimal, as the measurement period may be too short to achieve a strong effect.

iii. One way of assessing the effectiveness of regeneration measures is the desorption of sulphur-containing species from the catalytic surface Lott et al. [11], which results in an increase in SO<sub>2</sub> emissions downstream of the catalyst. The highest rates of increase occur - apart from one outlier - at higher water amount, but under lean conditions, which is why it is still unclear whether and to what extent the SO<sub>2</sub> formation in the catalyst is not due to post-oxidation of other sulphur species not detected here.

The results show a strong influence of the operating strategy on PdO/Al<sub>2</sub>O<sub>3</sub> catalysts. In order to avoid too high methane emissions, the slightly lean range would thus have to be left out and the engine would have to be operated outside of it.

## Acknowledgements

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## Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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