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METHANE SLIP ABATEMENT BY HYDROGEN ADDITION

Master´s thesis for the degree of Master of Science in Technology submitted for inspection in Vaasa 7.11.2017.

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FOREWORD

The special thank you goes to my family, my husband Jarno and our sons Jero and Sasu, and to my parents, who all have supported me during my studies.

Vaasa, 7.11.2017

Sonja Heikkilä

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SYMBOLS AND ABBREVIATIONS

Ag_2O	Silver (II) oxide
Al_2O_3	Aluminium (III) oxide
CeO_2	Cerium oxide
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
ECU	Engine control unit
F.S.	Full scale
H_2	Hydrogen
HC	Hydrocarbon
IR	Infrared
LNG	Liquefied natural gas
N_2	Nitrogen
NG	Natural gas
NiO	Nickel (II) oxide
NMHC	Non-methane hydrocarbons
NO_x	Nitrogen oxides
O_2	Oxygen
OH	Hydroxyl
n.a.	Not available
Pd	Palladium
PdO	Palladium monoxide
PdO_2	Palladium dioxide
PdS	Palladium sulphide
PM	Particulate matter
ppm	parts per million

Pt	Platinum
Rh	Rhodium
SiO_2	Silicon dioxide
SnO_2	Tin (IV) dioxide
SO_x	Sulphur oxides
SO_4^{2-}	Sulphate
S-poisoned	Poisoned by sulphur
THC	Total hydrocarbons
ZrO_2	Zirconium dioxide
XPS	X-ray photoelectron spectroscopy

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ABSTRACT:

The gas engines are a good alternative for peaking power, when the production of renewable energy is increasing. In the combustion of gas, unburned fuel, especially methane, tends to remain in the exhaust gas. The Pd-Pt/Al_2O_3 catalytic converters are proven to be the best for methane conversion but they are easily poisoned by sulphur and water from the exhaust. A poisoned catalyst is inactive and methane conversion is low. By regeneration it might be possible to revive the catalyst. According to the literature hydrogen injections are the most effective regeneration method.

In the experiments, two temperatures and multiple H_2 injection concentrations (1 % to 2.5 %) and periods (10 minutes to 1 hour) were used for regeneration. The lower temperature of 380 °C was too low for the catalyst to activate. Experiments at 500 °C where more successful, but no long-lasting effect was achieved with the regenerations. In both experiments, sharp peaks of SO_2 were registered in the exhaust gas just after the start of the regeneration. It could be assumed that H_2 reacts in the catalyst and releases SO_2. Before this method is taken into everyday use, this topic needs to be studied further.

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TIIVISTELMÄ:

Kasvava uusiutuvan energian tuotanto edellyttää säätövoiman lisäämistä, johon kaasumoottorit sopivat hyvin. Kaasun poltossa pieni määrä palamatonta polttoainetta, erityisesti metaania, saattaa kuitenkin vapautua pakokaasun mukana.

Pd-Pt/Al_2O_3-katalysaattori on tutkimusten mukaan paras vaihtoehto metaanipäästöjen konvertointiin, mutta se myrkyttyy hyvin helposti pakokaasussa olevien rikin ja veden vaikutuksesta. Myrkyttynyt katalyytti on toimimaton, ja metaanin konversio on heikkoa. Katalyytin toimintaa voidaan yrittää parantaa regeneroinnilla. Kirjallisuuslähteiden mukaan vetysyöttö toimii tehokkaimmin katalyytin regenerointiin.

Regenerointikoeajoissa käytettiin kahta lämpötilaa, useita erilaisia vetypitoisuuksia (1 % - 2,5 %) sekä erimittaisia vedyn syöttöaikoja (10 min – 1 h). Lämpötila 380 °C oli liian matala katalyytin aktivoitumiseen. Koeajo 500 °C:ssa oli onnistuneempi, mutta katalyyttiä ei saatu elvytettyä pysyvästi. Molemmissa lämpötiloissa vetysyöttö vapautti SO_2:ta katalyytistä. Vety siis reagoi katalyytissä ja vapautti SO_2:ta. Menetelmä vaatii kuitenkin lisätutkimuksia ennen käyttöönottoa.

AVAINSANAT: kaasumoottori, pakokaasupäästöt, metaani, katalysaattori, regenerointi

1. INTRODUCTION

While the production of renewable energy, wind and photovoltaic, is increasing, the need for energy sources for peaking power to keep the electricity network stable is also increasing. Although the hydropower would be the primary solution, it is not available everywhere. In that case the gas engine power plants could offer very flexible peaking power. They can be in stand-by mode and started rapidly in response to high power demand. Gas engines can also be stopped in only one minute.

During the very rapid transient loading situations and at low loads, methane (CH_4) emissions of gas-driven power can grow. The unburned CH_4 becomes a challenge, as it is a significant greenhouse gas and has proved to have a stronger impact on global atmosphere warming than carbon dioxide (CO_2) when their emission rates are equivalent. Oxidative catalytic converters can be used to block these CH_4 emissions, but they are easily poisoned by sulphur. Exhaust gas contains always small amounts (~1-5 ppm) of sulphur compounds, which originate from the lubricating oil and the fuel gas itself.

Catalysts play an increasing role in achieving a cleaner environment, through the destruction of pollutants in the catalytic converters of the exhaust treatment systems of vehicles. The requirements for a successful catalytic process are (Atkins et al. 2006: 680-686)

1. The catalysed reaction must be thermodynamically favourable and fast enough.
2. The catalyst must have an appropriate selectivity towards the desired product.

3. A lifetime long enough to be economical.

Supported palladium (Pd) catalysts have shown to have good activity toward CH_4 conversion. Although platinum (Pt) based catalysts are commonly used for the elimination of non-methane hydrocarbons (NMHC), they are not reported to have good activity for oxidizing CH_4. Palladium oxide (PdO) is assumed to be the active species for CH_4 conversion, which is then usually higher than 80 %. Pt/Pd mixtures are also used. Alumina has been reported to be the most active catalyst support for CH_4 combustion, although it is not very durable. (Bank at al. 2015. Arosio et al. 2006. Gélin et al. 2002.)

The oxidation catalyst oxidizes hydrocarbon (HC) and carbon monoxide (CO) by using the oxygen present in the exhaust gas flow, and converts them to CO_2 and water vapour. The catalyst is activated at a certain temperature. Longer hydrocarbons start to oxidize at lower temperatures. Once the longer hydrocarbon chains start to oxidize, the heat release heats up the system and initiates the oxidation of CH_4. Catalyst performance can be up to 90 % and it is dependent on the exhaust gas temperature. It increases linearly with the exhaust temperature until the temperature level is high enough. The catalyst activity decreases by thermal ageing over time and by sulphur poisoning. (Lee et al. 1995)

The aim of this work was to research the regeneration of sulphur poisoned catalyst by hydrogen (H_2) in conjunction with a natural gas (NG) engine. The first part of the work consisted of a literature review of CH_4 catalysts. In the second part, the experimental setup is explained with the results, conclusions, and recommendations.

A bimetallic palladium-platinum catalyst with alumina support was used in the experiments at two different temperatures. The catalyst was poisoned by adding extra SO_2 into the exhaust. After poisoning, the catalyst was regenerated by H_2 using different concentrations and durations.

2. HYDROCARBON EMISSIONS

Throughout the world, the concern of increasing HC emissions has arisen. NMHC, total hydrocarbon (THC), and combined nitrogen oxides (NO_x) and HC limits are proposed or are already set for different engine operations. In this chapter, HC emissions are covered shortly.

2.1 Methane in atmosphere

CH_4 concentrations in atmosphere stabilized in the early 2000s but began increase again in 2007. Since 1850 the concentration of CH_4 in the atmosphere has more than doubled. Atmospheric CH_4 reacts with hydroxyl (OH) radicals and eventually after sequence of reactions CH_4 transforms to CO_2 and H_2O. (Turner et al. 2017)

The model of CH_4 emissions isotopic analyses from 1985 to 2013 Figure 1 shows that global CH_4 emissions from fossil fuels are about 200 Tg/year (black line), the previous estimates form the literature are shown in blue. Microbial sources are the biggest source of global CH_4 emissions (about 350 Tg/year in 2013). These emissions were previously estimated to be higher (blue line). (Schwietzke et al. 2016: 88-91)

Figure 1. CH$_4$ emissions by source in the period of 1985-2013.

The Intergovernmental Panel on Climate Change has made the 5th Assessment Report of climate change in 2014. In the report they have recalculated the Global Warming Potential for CH$_4$ among few other significant greenhouse gases. In the new calculations the warming impact of CH$_4$ is 84 times bigger compared to CO$_2$ in the timescale of 20 years (previously the value was 63). In the time scale of 100 years the cumulative impact is 28 years, because of CH$_4$'s shorter lifetime.

2.2. Hydrocarbon emission standards

The HC emissions are usually addressed as THC or as NMHC. CH$_4$ is often disregarded due its different reactivity from longer chain HCs, although in gas engine operation the CH$_4$ emissions have a quite significant impact due to the possible slip from the engine. Now, standards limiting HC are found for example in the EU, USA and China.

In Europe, the EU has set new limits for inland waterway vessels emissions. The stage V emission limits will be effective for engines below 56 kW and over 130 kW in 2019, and for engines 56–130 kW from 2020 on. For the propulsion and auxiliary engines of over 130 kW the HC limits will be 0.19 g/kWh and 1.0 g/kWh (depending on the power range). (Dieselnet)

In the USA, the US-EPA Tier 4 regulation has now been implemented. For the marine diesel category of 1/2 engines the HC emission limit is 0.19 g/kWh. (Dieselnet)

China has adopted the I/II regulations in 2016 and they will become effective in 2018 (China I) and 2021 (China II). The standards do not apply to ocean going vessels. In China I CH_4 limits will vary from 1.5 g/kWh to 2.0 g/kWh depending on the power and displacement volume of the engine. Later the limits of China II will be tightened up from 1.0 g/kWh to 2.0 g/kWh depending on the engine. The CH_4 limits apply only for natural gas and dual fuel engines. (Dieselnet)

3. CATALYST DEACTIVATION AND REGENERATION

3.1. Catalyst deactivation

Harmful conditions may cause catalyst converter to deactivate. When the converter is deactivated, it doesn't remove the targeted emissions from the exhaust. The catalyst can be deactivated by different ways. In this section some of the causes of catalyst deactivation are reported.

A catalysed reaction is faster than an uncatalysed version of the same reaction because the catalyst provides a different reaction pathway with lower activation energy. Some substances retard catalyst reactions and they are called catalyst poisons. They cause catalyst deactivation by blocking one or more elementary steps in a catalytic reaction. (Atkins et al. 2006: 680-686)

Deactivation can have physical and chemical causes. Most common mechanisms are poisoning, coking or fouling, sintering and phase transformation. Masking and loss of the active elements via volatilization, erosion or attrition are also possible mechanisms. In the CH_4 catalysts, sulphur poisoning is the most harmful and probable option. Sintering due to too high temperatures can also occur, which might be a problem when either thermal regeneration or reduction by H_2 are used. (Forzatti et al. 1999: 165-181)

3.1.1. Poisoning

Poisoning occurs when feed stream includes impurities and those adsorb on the active sites of the catalyst, which then loses its activity. This active site blocking is called a geometric effect. The poison may also alter the adsorption of other species or modify the chemical structure of the active sites and result in the formation of new compounds. The most common poisoning components are sulphur oxides and water vapour. (Forzatti et al. 1999: 165-181)

Palladium based catalysts are sensitive to sulphur poisoning and the activity toward CH_4 oxidation deteriorates quickly if sulphur dioxide (SO_2) or sulphur trioxide (SO_3) is present. The exhaust of gas engines contains 1-5 ppm sulphur which can originate from the NG itself, it can be added to gas as an odorant for safety reasons or it can come from the lubricating oil. (Leprince et al. 1993: 125-138) have identified the poisoning species to be sulphate groups which have been adsorbed on the Pd particles .

Mechanisms for deactivation in the presence of SO_2 are related to operating temperatures. The rate of deactivation is a function of the exhaust temperature. The composition of the gas does not affect the deactivation as much as temperatures. The deactivation is occurring through adsorption of SO_2 onto Pd particles. When it happens, sulphur spillovers onto the alumina support. At low temperatures, 240 °C, the adsorption rate of SO_2 and SO_3 is at maximum and deactivation of the catalyst is rapid. The deactivation is much less at 500 °C because SO_2 adsorption on the Pd particles is lower and SO_2 adsorbed into alumina wash coat begins to desorb. The upper temperature limit for bad deactivation to occur is about 400 °C. Above 500 °C, deactivation appears to be slower.

Temperatures lower than 500 °C are not reported to be practical when it comes to regeneration of the catalyst. Regeneration should occur periodically, often and rapidly. (Leprince et al. 2004)

Kinnunen et al. (2017: 117) have though proposed a new hypothesis

> "Sulfur does not poison the methane oxidation catalyst, instead it makes the catalyst more sensitive to water vapor poisoning."

During their laboratory experiences they have compared the effect of water vapours for CH_4 conversion. Catalyst poisoned by SO_2 was more active at low temperature when the exhaust did not contain water vapour. When the water was added to the exhaust, the conversion was notably decreased. Sulphur poisoning is claimed to reduce oxygen mobility and prevents water desorption.

In some cases, poisoned catalysts may be impossible or very hard to regenerate and then the only option is to decrease the levels of the poison content. (Forzatti et al. 1999: 165-181)

3.1.2. Sintering

Catalyst sintering degrades catalyst performance due to the loss of the active surface area. The area is bigger when a support is used and the catalysts thermal stability is greatly dependent on the support. Sintering is usually irreversible and in case it occurs, the catalyst needs to be removed. Sintering is a complicated process accelerated by high temperatures and it can usually not be avoided.

Forzatti et al. (1999: 165-181) have proposed two models for sintering, the atomic migration and the crystallite migration. In the first case, metal atoms escape from a crystallite. Then atoms move around the surface of the support or in the gas phase, and collide with other metal crystallite. In the second model crystallites migrate along the support surface and sintering occurs via collision and coalescence of two crystallites.

3.1.3. Agglomeration

It has been proposed that palladium catalyst deactivation is caused by Pd^0 agglomerating. This is because Pd^0 will not efficiently re-oxidize to PdO or palladium dioxide (PdO_2) as it has a limited oxygen storage capacity. The oxygen transferring can be promoted by adding zirconium dioxide (ZrO_2). This will increase the rate of Pd^0 oxidation and defuses the deactivation of the catalyst. (Yin et al. 2008: 108-116)

3.2.   Regeneration of poisoned catalyst

Hoyos et al. (1993:136) have discovered that during thermal treatment in vacuum and in flowing nitrogen the $PdSO_4$ decomposes according to Reaction 1.

$$\mathbf{PdSO_4 \rightarrow PdO + SO_2 + 0.5\ O_2} \tag{1}$$

Respectively Kinnunen et al. (2017:118) stated palladium regeneration to follow the Reaction 2.

$$\textbf{PdSO}_2 \rightarrow \textbf{PdSO}_3 + \textbf{0.5}\, O_2 \rightarrow \textbf{Pd} + \textbf{SO}_2 + \textbf{0.5}\, O_2 \tag{2}$$

As it can be seen, Reaction 2 results to metallic Pd, which is inactive to convert CH_4, and it can expose the catalyst for sintering, if the temperature is high. In lower temperatures it causes permanent decrease in CH_4 conversion.

In the study of Leprince et al. (2004) it was approximated that Pd catalyst would need regeneration at least every 2000 hours. Most practical would be in-situ catalyst regeneration, in which there is no need to remove the catalyst. H_2 based regeneration was assumed to be the best for CH_4 oxidation catalysts.

3.3.   Catalyst regeneration with H_2 treatment

Results from various studies indicate that H_2 gas recovers the catalyst activity by removing the sulphite and sulphate groups. The H_2 treatments from the previous studies are compared in Table 1. In the table, there are two references, Hoyos et al. (1993: 125-1389) and Jones et al. (2003: 589-601), which do not include as specific details from the H_2 treatment as the others. All the compared studies were performed in a laboratory scale, but Leprince et al. (2004) and Lampert et al. (1996) also included catalyst experiments on engines.

Table 1. Literature review of the hydrogen addition.

Reference	Catalyst materials	Temperatures	H_2 volume	H_2 reaction time
Ordónes et al. (2004)	0.5% Pd/Al_2O_3	350 and 550 °C	10 % H_2 in Ar	not available (n.a.)
Leprince et al. (2004)	10 g/l 3:1 $Pd/Pt/Al_2O_3$	250 to 550 °C	1. 1%, balance N_2. 2. 0.25% H_2, 0.75% CO, balance N_2, 3. 70 ppm H_2, 200 ppm CH_4, 3ppm SO_2, 500 ppm CO, 6 % H_2O, balance N_2	30 min
Arosio et al. (2006)	2% PdO/γ-Al_2O_3	400 to 700 °C	2% H_2, 2% H_2O, balance He-Ar	30-60 min
Yu et al. (1998)	3 % $Pd/CeO_2/\gamma$-Al_2O_3	600 °C	5 %	56 min temperature program and 30 min hold
Lampert et al. (1996)	Pd/Al_2O_3	600 °C	10 %	n.a.
Jones et al. (2003)	Pd/Al_2O_3	400 °C	n.a.	0.5 h
Hoyos et al. (1993)	Pd/Al_2O_3 Pd/SiO_2	350 and 600 °C	n.a.	overnight
Xi et al. (2016)	$Pd/Pt/\gamma$-Al_2O_3	500 °C	10 % H_2O, 7 % CO_2, 5000 ppm O_2 in balance Ar with 5000 ppm CH_4, 2500 ppm CO and 5000 ppm H_2	5 min

Ordonés et al. (2004: 27-34) had the highest H_2 concentration, 10 %. They compared regeneration by H_2, vacuum, nitrogen, wet air and dry air. The H_2 was the most efficient treatment in terms of the activity of recovery. The regeneration and deactivation process was easier in samples deactivated at 350 °C than

at 550 °C. As the regeneration temperature increased, the regeneration efficiency, however, also increased.

Leprince et al. (2004: 1-5) studied three different H_2 concentrations and gas compositions. The mixture one, which contained the highest H_2 concentration, was the most efficient in catalyst regeneration. However, the H_2 concentration was not the only changing component of the tested gas mixtures, therefore the effect of H_2 concentration was not confirmed. For all gas mixtures, the regeneration at 600 °C showed better CH_4 conversion than regeneration at 500 °C.

Arosio et al. (2006: 569-576) compared H_2 treatment to CH_4 reducing pulses and they stated that the CH_4 was more effective for palladium catalyst regeneration than H_2. They suggest, that this is due to the formation of surface sulphite species associated with the stronger reducing action of H_2, which was in evidence by notable H_2S production.

Results of Yu et al. (1998: 105-114) indicated that the activity of the catalyst regenerated by H_2 was mostly recovered. They claimed that reduction with 5 % H_2 from room temperature to 600 °C can remove most of the surface sulphide and sulphate groups.

Lampert et al. (1996:15-20) compared the regeneration of engine aged catalyst by H_2 reduction at 600 °C and thermal regeneration at 750 °C. With the H_2 inclusion, the catalyst activity was restored to some level, but not completely. No detectable changes in the catalyst sulphur content were acknowledged by X-ray photoelectron spectroscopy (XPS) or microprobe. The effects to improve the

activity were subtle. However, they proposed that poisoning may be prevented by periodical reduction of the catalyst at a relatively high temperature.

Jones et al. (2003: 589-601) did not give specific information on the use of H_2. One part of the experiment was to compare poisoning and regeneration of Pd, Pt and rhodium (Rh) catalysts. In their studies, they had the catalysts in flowing H_2 at 400 °C for 0.5 hours, but the concentrations remain unclear. All of the catalyst materials showed some regeneration, but the rhodium was little better than palladium. Pt showed very slight recovery. They also studied the effect on particle sizes and discovered very large areas of agglomerated palladium particles after the regeneration.

Hoyos et al. (1993:125-138) treated the catalysts overnight in flowing H_2 at various temperatures between 350 and 600 °C. Pd on alumina was compared to Pd on silica, the latter having a higher poisoning rate. Independent of the support material the number of active sites decreased in the same proportion. Regeneration after poisoning was performed only for silica supported palladium catalyst and the effect of H_2 and nitrogen were compared. Nitrogen was proven to be more effective in reactivating the conversion of CH_4 after poisoning. Infrared spectroscopy (IR) showed a band at 1435 cm^{-1}, which is associated to sulphate species linked to Pd. After regeneration with H_2 at 600 °C this band had disappeared. However, it did not have any effect on the catalytic activity. There are two hypotheses proposed what could cause the disappearing of sulphate groups and the lack of catalytic recovery. The first one is that the H_2 could induce a secondary reaction between palladium and the support at high temperatures. The second proposal is that the sulphate group could be reduced into a sulphide species linked to Pd, according to Reaction 3:

PdSO$_4$ + 4H$_2$ → PdS + 4H$_2$O (3)

Palladium sulphide (PdS) is then oxidized into a sulphate group, which leads to a loss in the catalytic activity. Only a small portion of sulphide was removed by flowing H$_2$. Because the surface PdS coincides with the silica supports absorption range, it cannot be detected by IR spectroscopy.

In the most recent research, Xi et al. (2016) tested the CH$_4$ light-off and extinction after regeneration with two different reductive gas environments at 500 °C. The regeneration mixture which contained H$_2$ was simulating rich combustion exhaust, and it contained 5000 ppm CH$_4$, 2500 ppm CO and 5000 ppm H$_2$. The other regeneration gas contained 5000 ppm CH$_4$. In the study they noticed that the regeneration mixture containing H$_2$ improved the light-off performance, but the effect was noticed only right after the regeneration. The regeneration mixture containing only CH$_4$ did not have the same effect. They also noted that sulphur species started to release at about 500 °C under the regeneration mixture containing H$_2$, while the other regeneration mixture didn't have any effect below 600 °C. They proposed that more effective sulphur removal could be achieved by using the regeneration mixture containing H$_2$ and increasing the regeneration temperature.

Based on the H$_2$ regeneration results from the literature, it seems thus that the effect has a lot of variation and it is very dependent on the conditions. In the reviewed articles, the concentrations, temperatures and reaction times varied very much, and not to mention the effect of the catalyst and support materials. The most successful results were obtained with high H$_2$ concentrations (5-10 %)

and higher temperatures (500-600 °C). Both of these should cause little caution, because the catalyst is sensitive to too high temperatures and H_2 can self-ignite in concentrations above 4 %. The injected H_2 could heat up the catalyst in certain higher than the calculations expect because it might react with noble metal dust. For example in the marine applications, the high H_2 concentration could cause very serious safety concerns.

Nevertheless, there were more positive results than negative, although none of the studies researched were able to proof H_2 to solve the catalyst regeneration issues. There is still a lot to research under this topic.

4. CATALYST CONDITIONS

4.1. Catalyst materials

The complete oxidation of CH_4 can be performed over both noble metals and transition metal oxides. Pt, Rh and Pd have been used the most as noble metals show higher activity than metal oxides. Pd catalysts are found to be the most active for CH_4 conversion. Metals can be used with or without supports. In Figure 2 the structure of CH_4 oxidation catalyst is presented. The metal loading on the support has a positive effect on the CH_4 oxidation because then metal is spread out over a bigger surface area. An optimal concentration of Pd is 0.5-2 %. (Lee et al. 1995: 339-359)
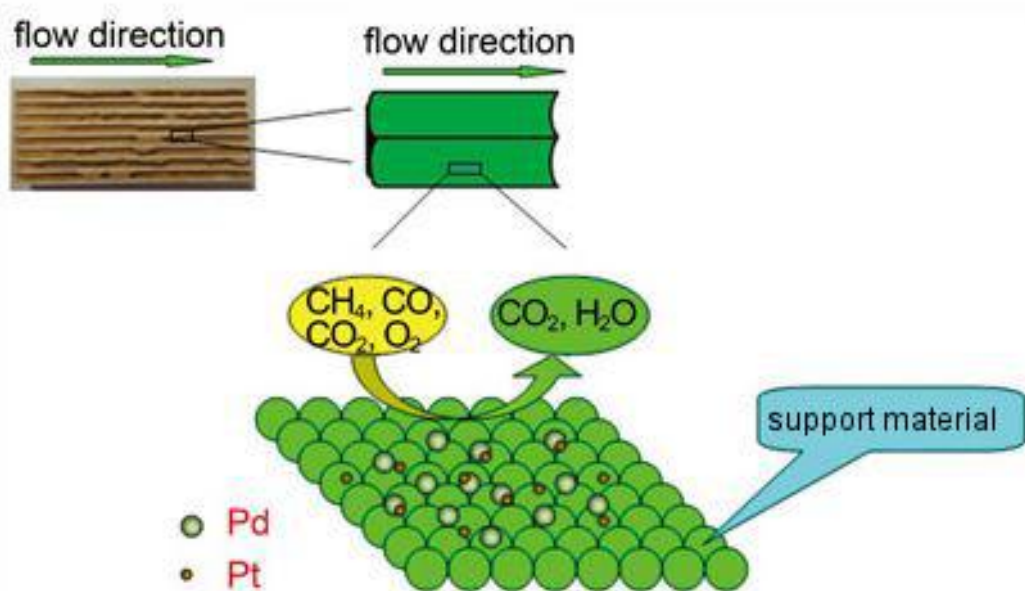

Figure 2. CH_4 oxidation catalyst structure. (Wei et al. 2015: 1771-1779)

Bimetallic catalysts with support are also in use. By combining two different noble metals, they can improve and protect each other. Pd and Pt are commonly used together.

Catalyst promoters and additives to catalyst support can be used to enhance the catalyst operation. Promoters can have a physical or chemical function. For example physical promoter can reduce the Pd catalysts tendency to agglomerate or sinter. Nickel (II) oxide (NiO), Tin (IV) dioxide (SnO_2) and silver (II) oxide (Ag_2O) are found to be effective to improve the oxidation activity. Metal oxides can be added to alumina supports as an additive to increase the temperature where phase transformation occurs, which also retains higher surface area at the normal transition temperature. (Hayes et al. 1997: 46)

4.1.1. Noble metals

PdO is more active catalytically than Pd as a metal. At a pressure of 101.325 kPa and a temperature of over 800 °C PdO starts to decompose to metallic Pd and O_2. When the temperature is decreased to below 800 °C the PdO will start to re-form.

4.1.2. Support materials

The support plays a very important role in the catalyst poisoning. The supports suitable for CH_4 oxidation are for example alumina, silica, zirconia, titanium and ceria. Sulphating support acts as a sulphate sink, adsorbing the sulphate

content, and therefore catalysts poisoning is decreased. Difference between sulphating support and non-sulphating support is shown is Figure 3.
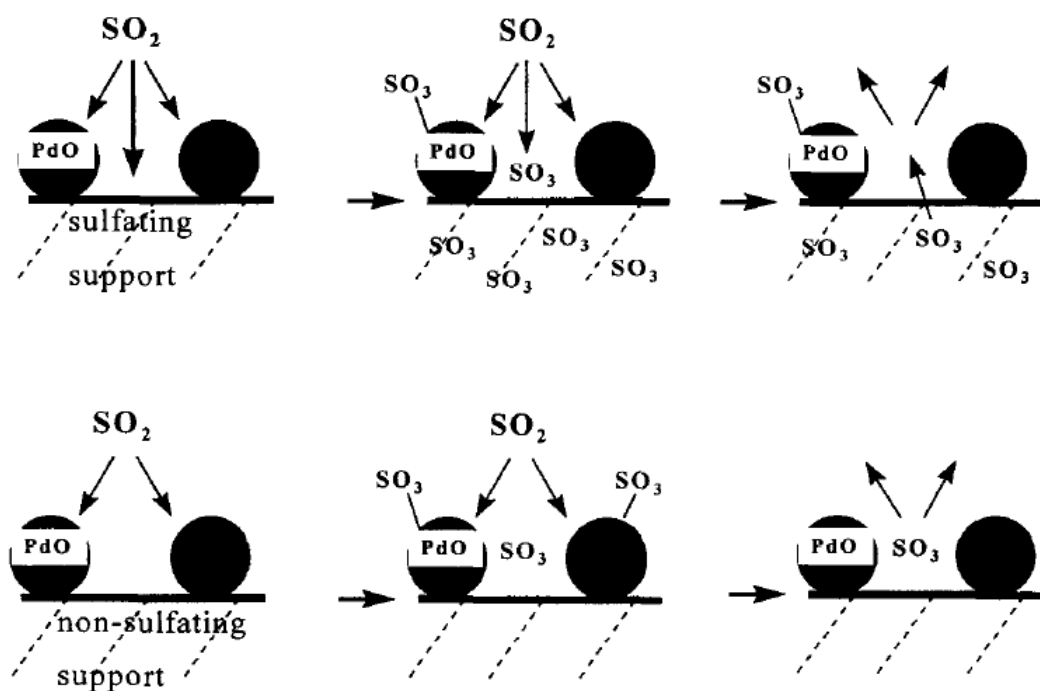

Figure 3. Proposed differences between sulphating support and non-sulphating support. (Lampert et al. 1997: 211-223)

γ-alumina is the most common as the support material for PdO catalysts, because it affects to maintain dispersion of active PdO_x to accomplish valid utilization of noble metal. High temperature is harmful for alumina-supported PdO, because it becomes unstable due to a significant decrease in the surface area of alumina and it can transform PdO_x to Pd^0. (Zhou et al. 2008: 4701-4707)

At 623 K the poisoning rate of sulphur is smaller for palladium on alumina than for palladium on silica. Under oxidizing conditions alumina is able to store sulphur as surface sulphate species. With an excess of oxygen the silica support is not sulphated in the presence of hydrogen sulphide or sulphur dioxide. The

chemical analysis of poisoned solids shows that the sulphur content on alumina support is higher than in the silica support. (Hoyos et al. 1993, 125-138)

4.2.   Catalyst temperatures

CH_4 conversion improves at higher temperatures. The oxidation initiates at quite high temperatures and after initiation the reaction is rapid and heat release is considerable. The temperature is difficult to control below the desired maximum. The selectivity towards the conversion product CO increases at higher temperatures.

Sulphur poisoning is especially rapid at lower temperatures (240 °C) and it decreases considerably when temperature is higher (500 °C). The temperature affects the adsorption rate of the SO_2 and SO_3 on the Pd particle and into the alumina support. At lower temperatures, the adsorption rate is maximized and the deactivation is very rapid. (Leprince et al. 2004)

4.3.   Other conditions

CH_4 conversion is strongly dependent on the feed ratio of O_2 and CH_4. If the amount of oxygen is high, the CH_4 will oxidize to CO_2, if not, then to CO. Both products are possible in the same catalysts, Pt and Pd supported on alumina. CO in the feed should not have any effect on the CH_4 conversion. (Lee et al. 1995: 339-359)

CH_4 oxidation has said to be structure-sensitive reaction when the catalyst material is platinum or palladium. It means that the metal may be in dispersed or

crystallized particles, on the surface of the catalyst support. The crystallites of both Pt and Pd are said to be more active than dispersed versions. (Lee et al. 1995: 339-359)

5. EXPERIMENTAL SETUP

Engine experiments to study H_2 injections impact on catalyst regeneration were implemented at VTT in Espoo from March to April 2016. Two experiment temperatures, 380 °C and 500 °C, were selected. The experiment was first run at 380 °C and later at 500 °C. Each experiment had its own $Pd/Pt-Al_2O_3$ catalyst both of which were studied under the same conditions.

5.1. Experiment plans

The experiment matrixes are presented in Tables 2 and 3. First, the catalyst converters were conditioned at 400 °C for 48 h in both experiments. During the implementation, the catalysts were cleaned by the flowing exhaust gas. The starting point was an operational control of the catalyst and the test bench. Also, the H_2 addition was tested in concentrations of 0 %, 1 % and 2 %. Emissions were controlled constantly and they were CH_4, C_2H_6, C_2H_4, SO_2, CO, CO_2, NO, NO_2, N_2O, ethane, propane, i-butane, n-butane, and some noble gases.

The actual experiment consisted of 7 regeneration cycles. Each of them lasted 24 hours. The catalyst was first poisoned by sulphur for 20 hours while the regeneration and emissions measurements took the remaining 4 hours.
The regeneration durations and concentrations were altered according to the results from the first experiment.

Table 2. Experimental matrix in experiment 1, exhaust temperature 380 °C.

	Duration (h)	Test bench temperature (°C)	H_2 addition	Test bench flow (kg/h)	Emissions measured	SO_2 (ppm)
Catalyst implementation	50	400	-	80	-	-
Starting point	4	380	1 h 1 % - 2 %	80	x	-
Sulphur poisoning	20 (24)	380	-	80	x	1-2
Regeneration 1	4	380	0.5 h 1 %	80	x	-
Sulphur poisoning	20 (48)	380	-	80	x	1-2
Regeneration 2	4	380	0.5 h 1 %	80	x	-
Sulphur poisoning	20 (72)	380	-	80	x	1-2
Regeneration 3	4	380	0.5 h 2 %	80	x	-
Sulphur poisoning	20 (96)	380	-	80	x	1-2
Regeneration 4	4	380	0.5 h 2 %	80	x	-
Sulphur poisoning	60 (168)	380	-	80	x	1-2
Regeneration 5	4	380	1 h 2 %	80	x	-
Sulphur poisoning	20 (192)	380	-	80	x	1-2
Regeneration 6	4	380	1 h 2.5 %	80	x	-
Sulphur poisoning	20 (218)	380	-	80	x	1-2
Regeneration 7	4	380	1 h 2.5 %	80	x	-
Ending point	1	400	1 h 1 % - 2 %	80	x	-
Sulphur poisoning†	20 (243)	380	-	80	x	1-2
Thermal regeneration†	1	520	-	80	x	-

† Additional experiment to see the effect of heating

Table 3. Experimental matrix in experiment 2, exhaust temperature 500 °C.

	Duration (h)	Test bench temperature (°C)	H_2 addition	Test bench flow (kg/h)	Emissions measured	SO_2 (ppm)
Catalyst implementation	50	400	-	80	-	-
Starting point	4	400	1 h 1 % - 2 %	80	x	-
Sulphur poisoning	20 (24)	500	-	80	x	1-2
Regeneration 1	4	500	0.25 h 2 %	80	x	-
Sulphur poisoning	20 (48)	500	-	80	x	1-2
Regeneration 2	4	500	0.25 h 2 %	80	x	-
Sulphur poisoning	20 (72)	500	-	80	x	1-2
Regeneration 3	4	500	0.25 h 2 %	80	x	-
Sulphur poisoning	20 (96)	500	-	80	x	1-2
Regeneration 4	4	500	0.25 h 2.5 %	80	x	-
Sulphur poisoning	60 (168)	500	-	80	x	1-2
Regeneration 5	4	500	0.5 h 2.5 %	80	x	-
Sulphur poisoning	20 (192)	500	-	80	x	1-2
Regeneration 6	4	500	0.5 h 2.5 %	80	x	-
Sulphur poisoning	20 (218)	500	-	80	x	~0.5
Regeneration 7	4	500	0.5 h 2.5 %	80	x	-
Ending point	1	400	1 h 1 % - 2 %	80	x	-

The regenerations were started by emission measurements before the actual regeneration was conducted. After the regeneration, the emissions were controlled for 3 to 4 hours, before the SO_2 aging was restarted.

5.2. Experimental engine

The experimental engine was a Mercedes Benz (model MB111) 2.0 litre naturally aspirated gasoline engine which had been converted to run on NG. A Zöllner B-300 AD eddy-current brake was used as the dynamometer. The original en-

gine control unit was replaced with an aftermarket Engine Control Unit (ECU) (Hestec 32) which was used to control the engine parameters such as injection and ignition timing and air-to-fuel ratio. A parallel fuel injection system was installed for the NG usage. It included four fuel injectors installed in the cylinder specific ducts of the intake manifold. The injectors were operated sequentially in pairs as the original fuel injectors. The constant pressure at the fuel injectors was maintained with a fuel gas pressure regulator. The original ignition system was also replaced with a more powerful system to operate at a lean air-to-fuel mixture. Table 4 shows the engine specification. (Murtonen et al. 2016)

Table 4. Experimental engine specification.

Engine model	111.940
Engine type	In-line, 4-cylinder, naturally aspired
Displacement	1998 cm^3
Power	100 kW / 5500 min^{-1}
Torque	190 Nm / 4000 min^{-1}
Fuel injection	Multi-point injection
Ignition	Bosch Double-Fire Coil
ECU	Hestec 32

5.3.   Catalyst setup

The catalyst experiment bench was built up by VTT's engine laboratory personnel. The exhaust after treatment system is presented in Figure 4. The catalyst bench consisted of temperature and flow control sections. The exhaust gas first

entered to the heating section, where it was heated to 380 °C or 500 °C depending on the experiment. The bench had four independent heating units for heating and maintaining the exhaust gas temperature at the desired level. By the heating section it was possible to influence the temperature without changing the engine operation mode. The heating system had the total electrical power of approx. 840 kW, and the flow range was 80 kg/h.
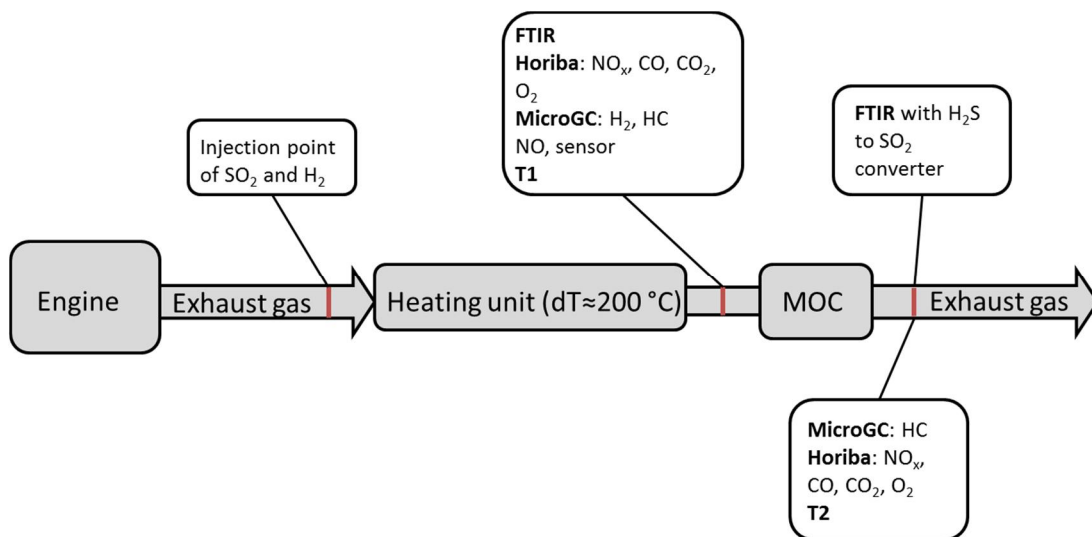

Figure 4. Exhaust gas after treatment installation.

The catalyst was located downstream the heating section and the emission measuring instruments were located before and after the catalyst. The flow control section was located at the end of the bench.

The flow control section consisted of a flowmeter and a pump for creating and maintaining the necessary flow through the experiment bench. The flow meter was located after the emission measuring system/point and the temperature was decreased to 80-150 °C before the exhaust gas entered to the flow meter. An internal compensation was used for varying the gas temperature.

The H_2 was injected to the exhaust gas between the heating units to ensure it was fully mixed into the exhaust gas. The concentration of the H_2 was controlled before the catalyst.

5.4. Emission measurements

During the experiments CH_4, C_2H_6, C_2H_4, SO_2, CO, CO_2, NO, NO_2, N_2O, ethane, propane, i-butane, n-butane, and some noble gases were controlled to detect the effect of H_2 injection.

Horiba PG-250 analyser was used to measure NOx, CO, CO_2, and O_2. CO and CO_2 were measured by non-dispersive infrared, NO_x by chemiluminescence and O_2 by paramagnetic measurement cell. Exhaust gas was dried with gas-cooler before it was measured by Horiba. The measurement range for NO_x was from 0 ppm to 25/50/100/250/500/1000/2500 ppm, for CO from 0 ppm to 200/500/1000/2000/5000 ppm, for CO_2 from 0 vol-% to 5/10/20 vol-%, and for O_2 from 0 vol-% to 5/10/25 vol-%. The repeatability of PG-250 is ±0.5 % full scale (F.S.) for NO_x > 100 ppm and CO > 1000 ppm, for other components and ranges it is ±1.0 % F.S.

Online SO_2 emissions were detected by Rowaco 2030 1 Hz FTIR Spectrometer with Automated MEGA-1 (miniMEGA) sampling system. Detection limit for SO_2 was 2.5 ppm.

Agilent 490 MicroGC was used with the following three columns:
1. Molsieve, 10 m, Backflush, for H_2, CO, CH_4, N_2, O_2, and some noble gases

2. PoraPlot (PPU), 10 m, Backflush, for ethane, propane, i-butane, and n-butane

3. Al_2O_3/KCl, Backflush, for ethane, propane, i-butane, and n-butane

Detection limits for ethane, ethene, and propane were approximately 2 ppm, 10 ppm for methane, and 100 ppm for hydrogen.

Multiple gaseous components were measured by two Gasmet DX-4000 Fourier transformation infrared spectrometers. One Gasmet was connected to Total Reduced Sulphur Thermal Converter 891 to convert H_2S emissions to SO_2, which was possible to measure with FTIR.

The uncertainties in measurements in this study were not available. Only the repeatability of Horiba PG-250 analyser was given.

6. RESULTS

In this chapter, the results from the experiments at 380 °C and at 500 °C are presented in charts and tables. The results from the first experiments at 380 °C are presented first and then followed by the results from experiments at 500 °C.

6.1. Experiments at 380 °C

The first catalyst experiment was conducted using an exhaust temperature of 380 °C. During the experiment, the temperature in the catalyst was too low for CH_4 conversion. The measurements indicated that the catalyst was only working when the H_2 addition affected the temperature in the catalyst. In Figure 4, it can be seen, that during the H_2 injection the temperature rose only after the catalyst. From this it can be concluded that H_2 did not react before the catalyst, but only at the catalyst. The temperatures increased by 65 °C, 134 °C, and 171 °C, depending on the amount of the injected H_2.

The CH_4 conversion of the catalyst was very low at 380 °C (Figure 5) because the temperature was below the catalysts operational temperature. During H_2 addition the temperature was high enough for the catalyst to start converting the CH_4, which can be seen in Figure 6. Nevertheless, the conversion was very low after the H_2 injections, ranging from 0 to 2 %. As expected, the ethane conversion (Figure 6) was higher than CH_4 conversion at this temperature, but still only 10 to 20 %.
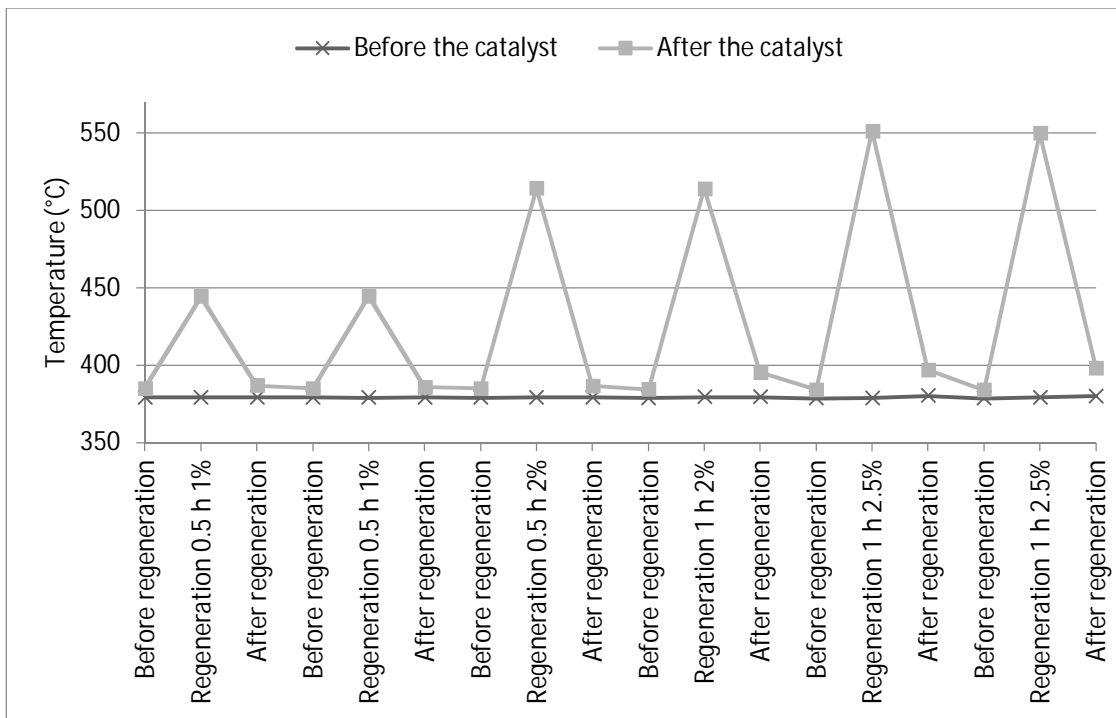
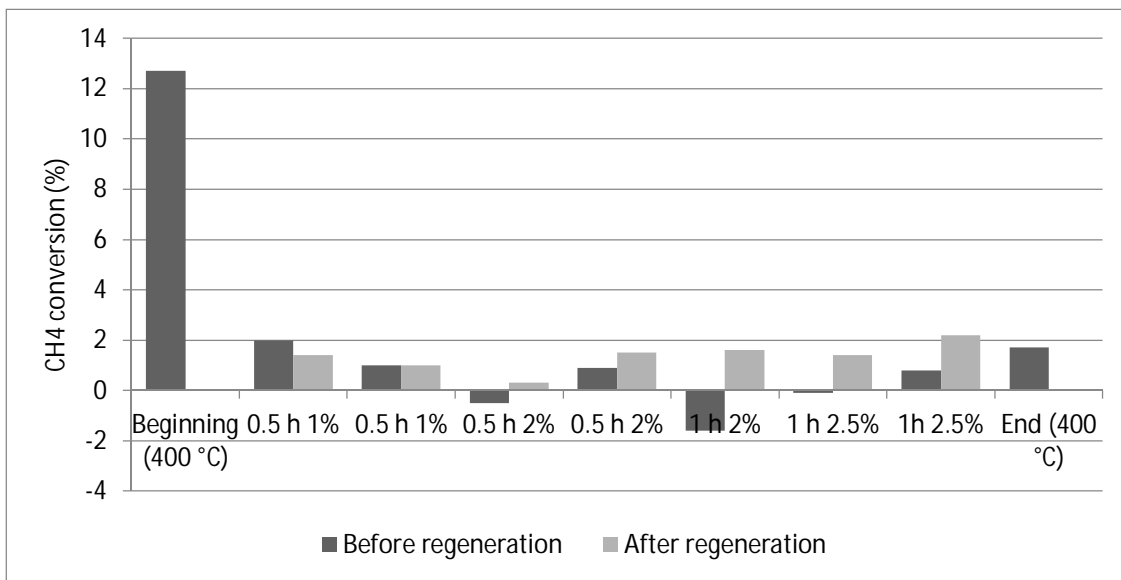Figure 4. Average temperatures before and after the catalyst.

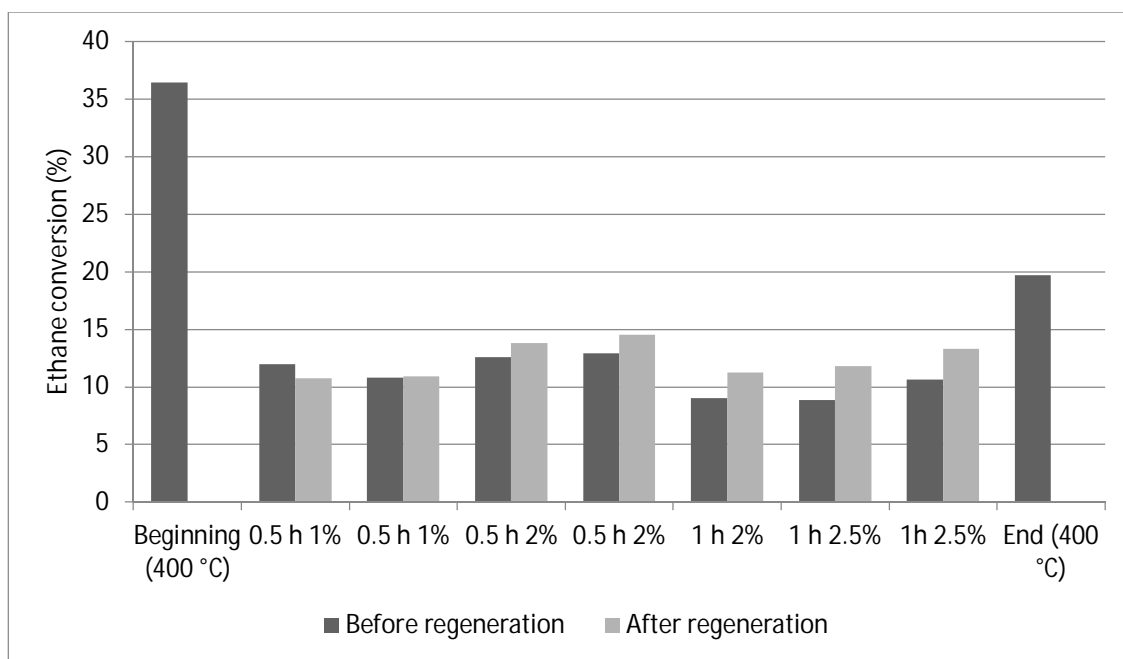Figure 5. Average CH$_4$ conversions during the experiment at 380 °C.

Figure 6. Average ethane conversions during the experiment at 380 °C.

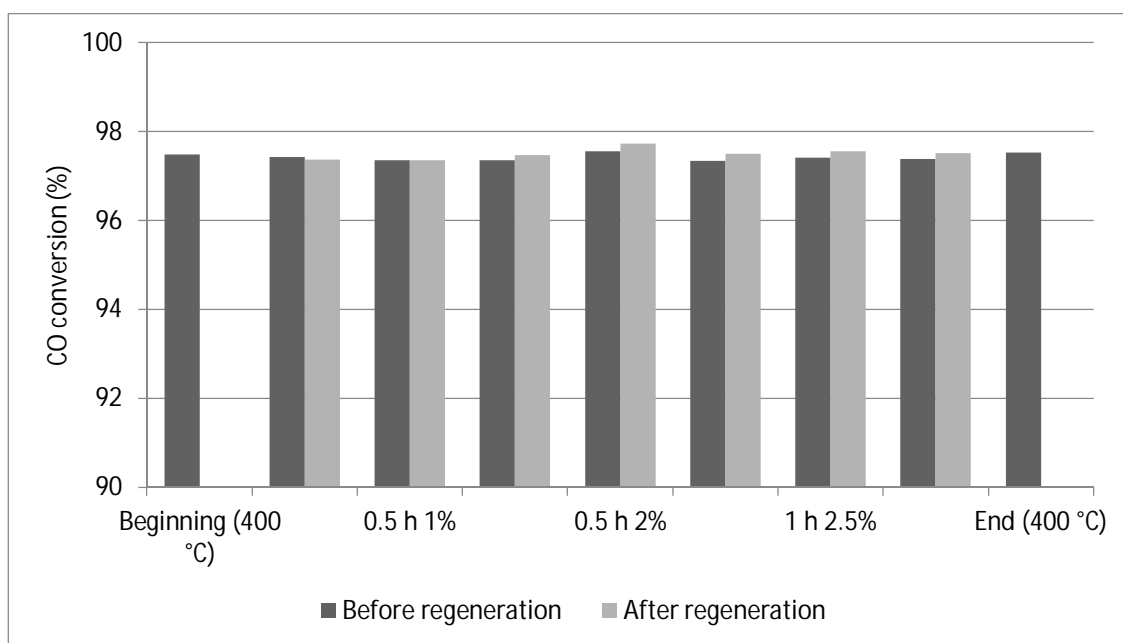CO conversion at 380 °C (Figure 7.) was controlled to follow the catalyst operation.

Figure 7. Average CO conversions during the experiment at 380 °C.

In Figure 8, it can be seen that the catalyst is only working when the H_2 is inject-ed and the temperature is increased. Each of the charts presents different regen-erations; the H_2 concentration and the injection duration are on top of the charts. The thermal regeneration did not increase conversion after the regenera-tion; the change is due to higher temperature at the end.
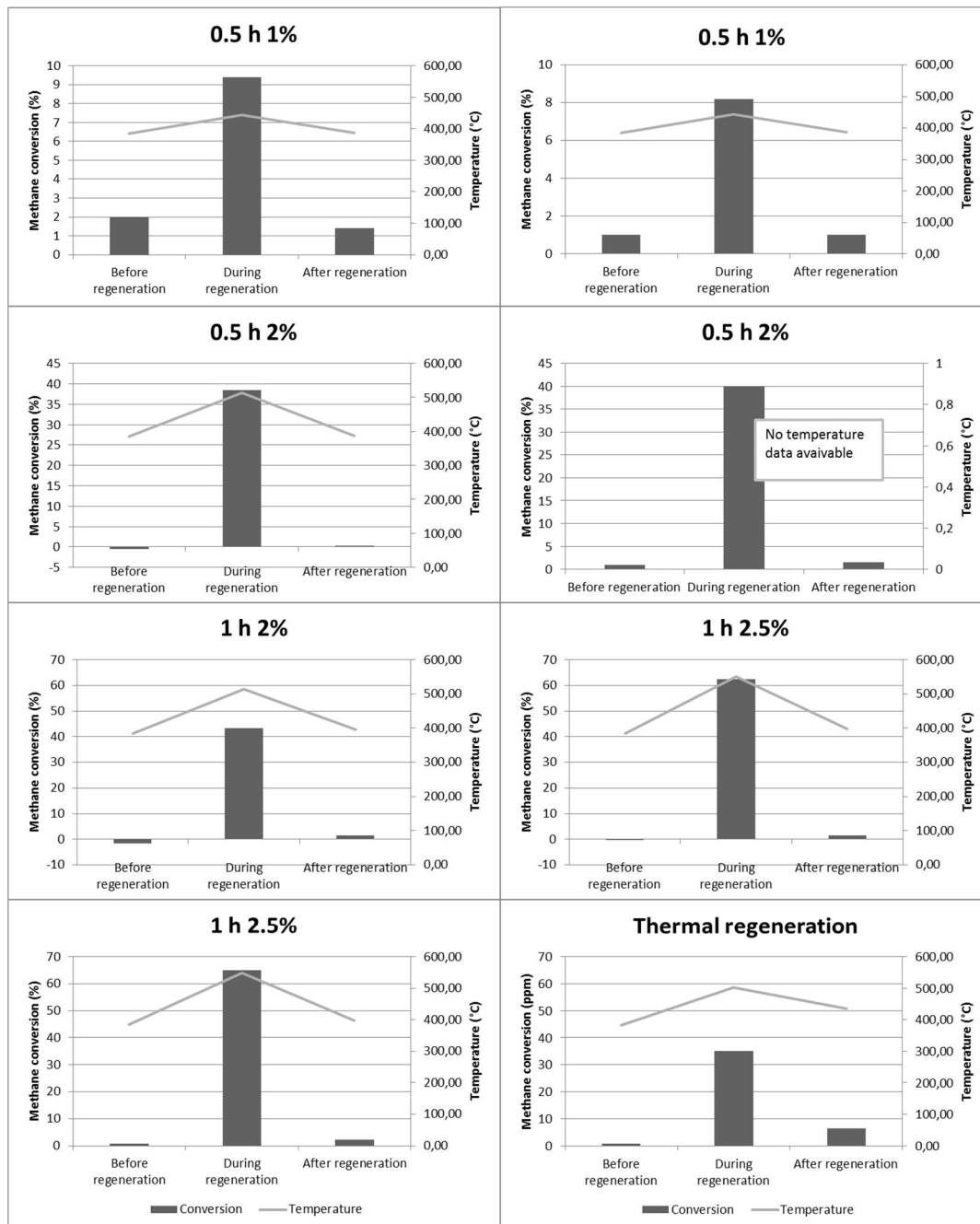

Figure 8. Correlation between the temperature and the CH_4 conversion. – Note the different y-scales.

The highest SO_2 peak was gained from regeneration with one hour of 2 % H_2 (Figure 9). Before this regeneration the catalyst was poisoned for 60 hours in contrast to the other regenerations which had the poisoning time of 20 hours. The effect of thermal regeneration was at the same level as the 1 % feed of H_2.
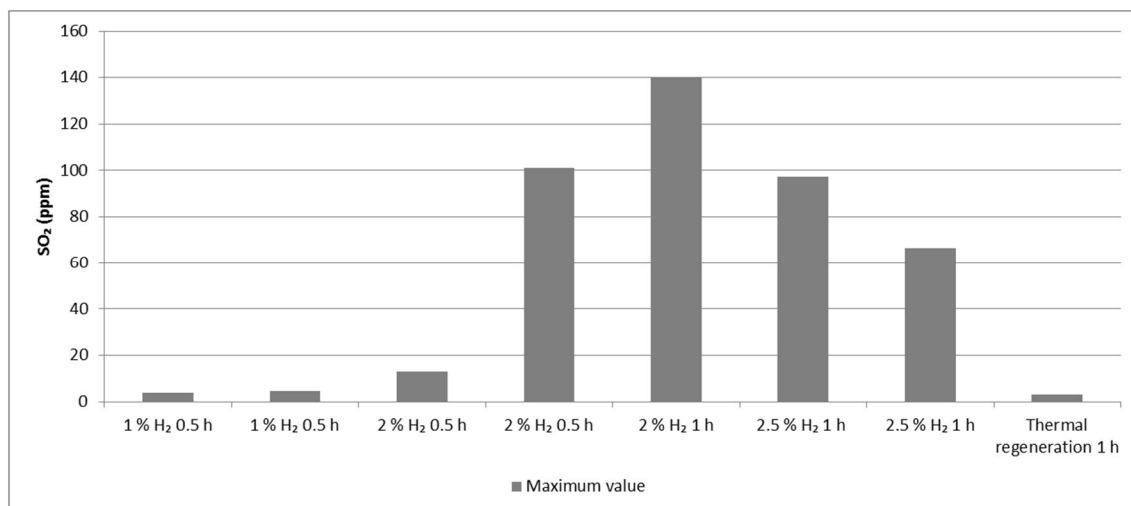

Figure 9. Measured maximum values of SO_2 released during the regeneration stages.

During the regeneration by H_2, removal of SO_2 from the catalyst was noticed in some cases. This is presented in Figure 10. SO_2 was released as a sharp peak very rapidly after the H_2 injection had been started. Each of the charts presents different regenerations; the H_2 concentration and the injection time are on top of the charts. With higher H_2 concentrations the SO_2 release seems to continue for about 5 minutes, but with 1% H_2 concentration the release is very short and low peak.
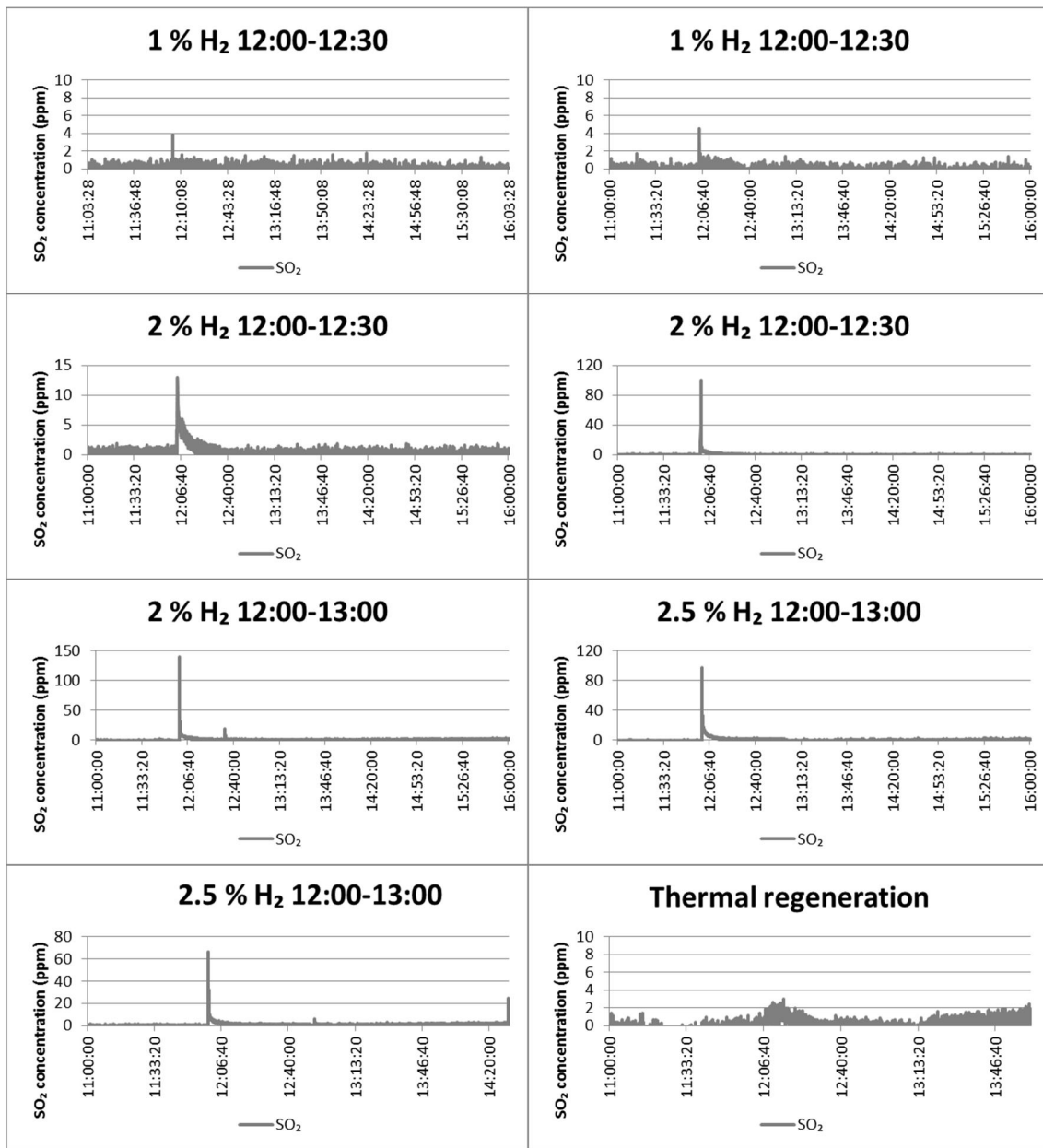
Figure 10. SO₂ concentrations after the catalyst during the regenerations. The H₂ concentration and the injection time are on top of the charts. – Note the different y-scales.

6.2. Experiments at 500 °C

The second set of experiments was conducted at 500 °C. The experimental matrix was modified based on the results from the experiments at 380 °C, the modified matrix can be seen in chapter 5.

Figure 11 illustrates the temperatures before and after the catalyst. After the catalyst, the temperature increased by 140 °C and 165 °C, depending on the concentration of injected H_2. The temperatures before the catalyst stayed in the same level regardless of hydrogen injection.
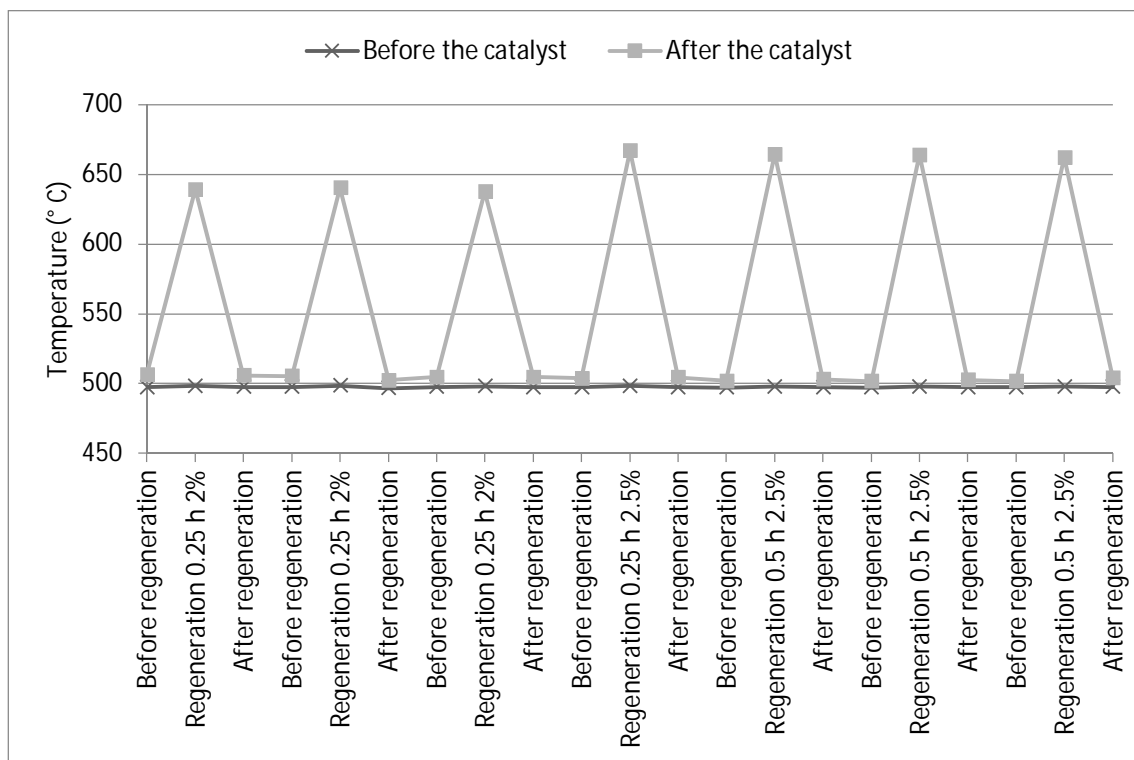

Figure 11. Average temperatures before and after the catalyst.

Throughout the second experiment the CH_4 conversion was higher than in the first experiment. The CH_4 conversion (in Figure 12) decreased steadily after the

first three sulphur poisonings, from 37 to 27 %, and the effect of the regeneration (15 minutes with 2 % of H_2) was almost the same in these three cycles. When H_2 concentration was increased to 2.5 %, the effect of regeneration also increased slightly. The last poisoning was performed without sulphur addition which may affect the result.

Figure 12 shows the CH_4 conversions before and after each of the regenerations. After the fourth regeneration, the CH_4 conversion was slightly increased. Before the fifth regeneration, the catalyst was poisoned for 60 hours, which seems to have stabilised the conversion levels for the rest of the experiment.
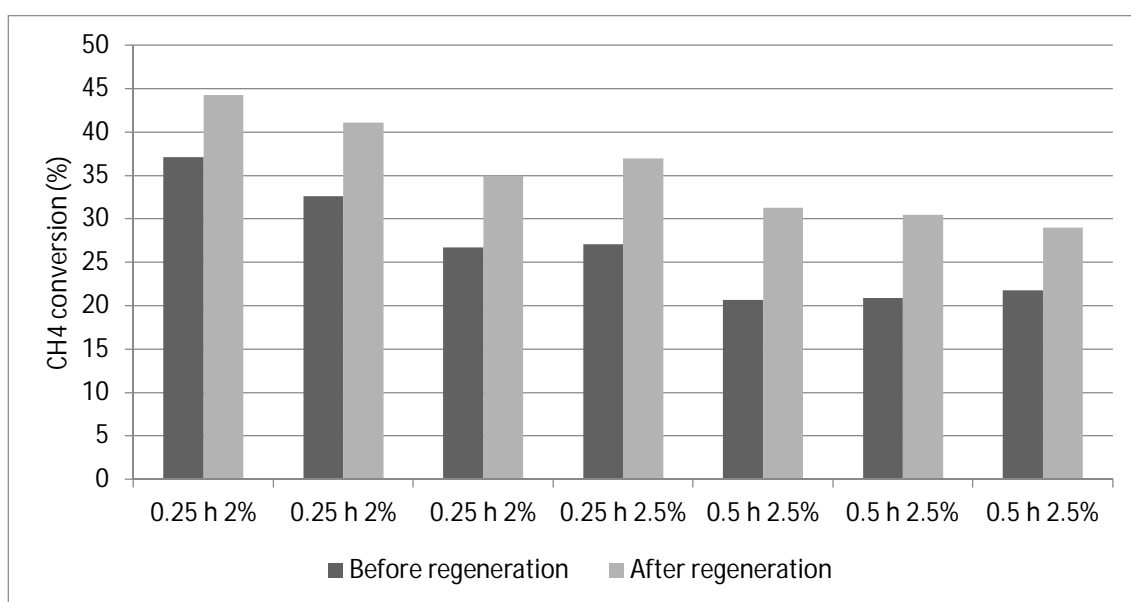

Figure 12. Average CH_4 conversions during the experiment at 500 °C.

Ethane conversion is shown in Figure 13. The effect of increased temperature is also visible here by the higher conversions. The regeneration had the best effect in the same regeneration as in case of CH_4.
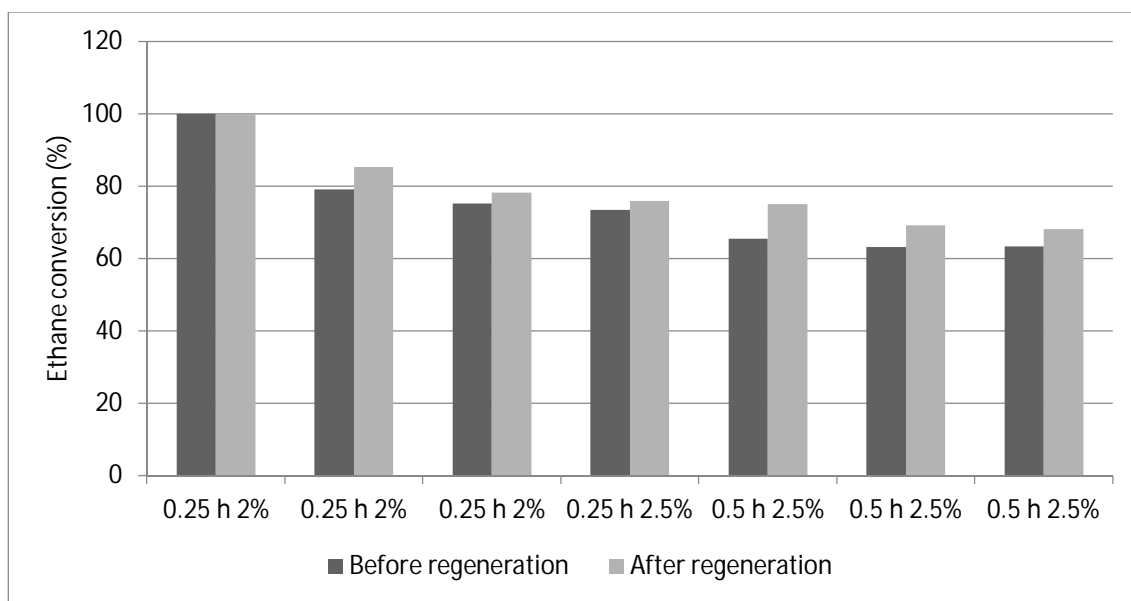
Figure 13. Average ethane conversions during the experiment at 500 °C.

The carbon monoxide conversion is shown in Figure 14. The conversion was almost 100 % throughout the experiment. Only before the sixth regeneration, the conversion was low. This could be due to a malfunction of the catalyst or measurement instruments.
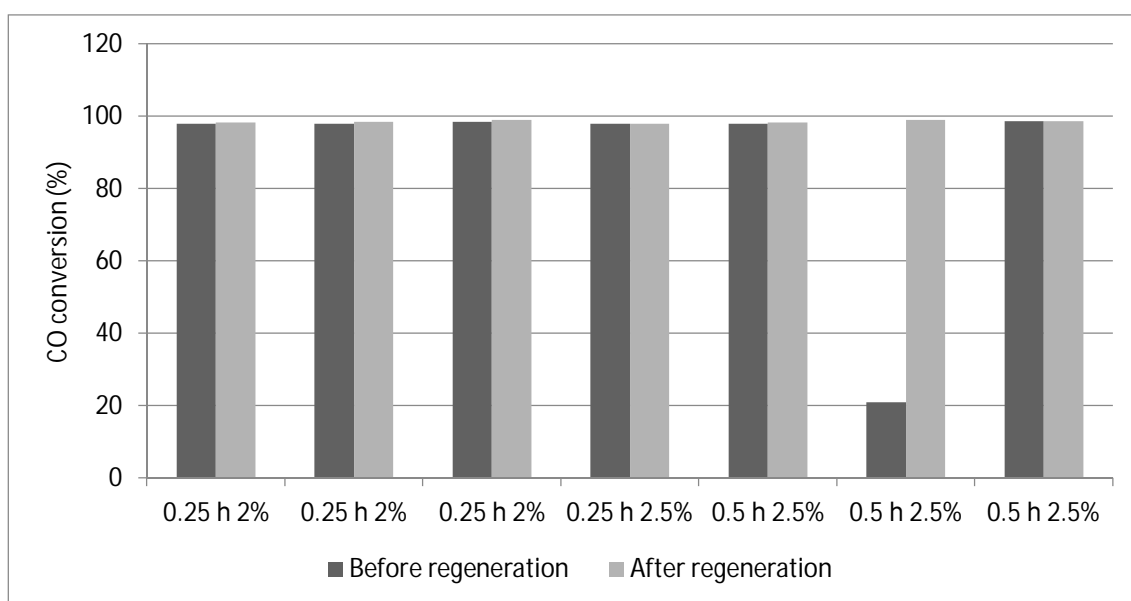

Figure 14. Average CO conversions during the experiment at 500 °C.

The maximum values of released SO_2 are presented in Figure 15. The highest peak was detected from the fourth regeneration with 2.5 % of H_2 for 15 minutes. However the peaks were overall lower compared to the regenerations at 380 °C.
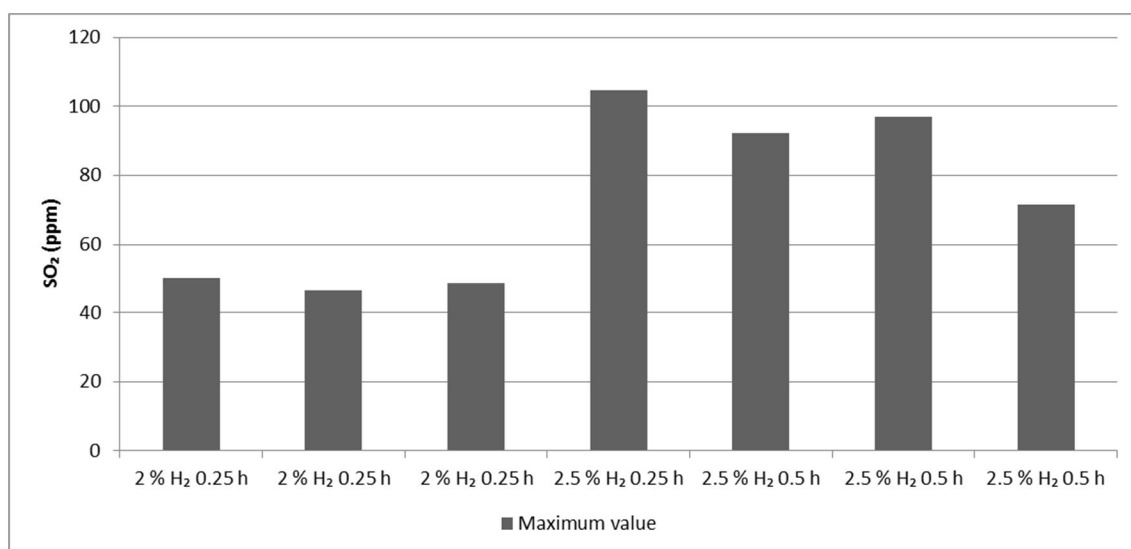

Figure 15. Measured maximum values of SO_2 released during the regeneration stages in the experiments at 500 °C.

Figure 16 shows that the SO_2 release from the catalyst was quite rapid during the regeneration. Each of the charts presents different regenerations; the H_2 concentration and the injection time are on top of the charts. Compared to the experiment at 380 °C, the release time was continuing longer. In first 4 regenerations the SO_2 continued to release whole 15 minutes when the H_2 was injected to exhaust. In the last 3 regenerations the H_2 injection was 30 minutes long. In Figure 16 it seems that the SO_2 release was kept on the whole regeneration, but in reality the values were far below the limit of detection (2.5 ppm) of the instrument.
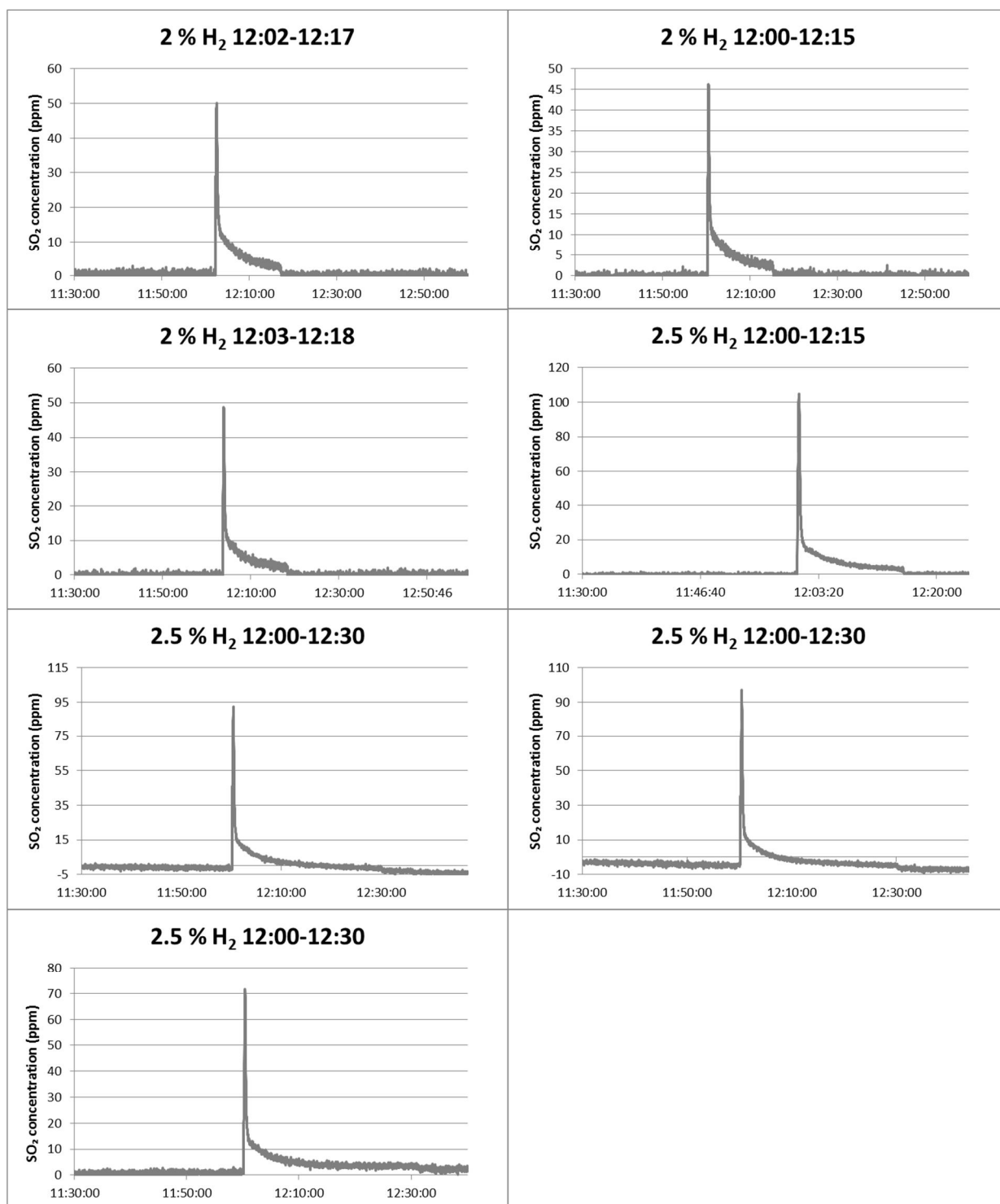
Figure 16. SO₂ concentrations after the catalyst during the regenerations in the experiments at 500 °C. The H₂ concentration and the injection time are on top of the charts. – Note the different y-scales.

7. DISCUSSION

To exclude the differences between the catalytic converters they were pretreated the same way before both of the experiments. The uncertainty of measurements came largely from the measuring instruments. Additionally, the engine, gas injections, and surroundings may have caused some uncertainties. The instruments were checked and calibrated daily to control their accuracy. The measured emissions were mainly within the detection limits. In the last three regenerations of the second experiments, however, the SO_2 concentrations during regeneration were below the detection limit. It was assumed that it could be caused by impurities in the instrument.

The first catalyst experiment was conducted at an exhaust temperature of 380 °C. During the experiment, the temperature in the catalyst was too low for CH_4 conversion. The measurements indicated that the catalyst was only working when the H_2 addition increased the temperature in the catalyst. Even though the experiment at 380 °C was not as successful as hoped, it gave new ideas to continue the experiment at 500 °C. The experimental matrix was modified based on the results from the first experiment. In the second experiment, shorter H_2 injections were used, because in the first experiment most of the SO_2 was discharged from the catalyst immediately after the H_2 injection. In both experiments SO_2 was released from the catalyst during the H_2 injections, although the CH_4 conversion did not improve during the experiment, i.e. regeneration did not produce the desired result. Hoyos et al. (1993: 125-138) had similar results. With IR spectroscopy they observed that the sulphate species linked to palladium disappeared by H_2 treatment without improving the catalyst activity.

When comparing the SO_2 release between the regenerations at different temperatures, it could be noted that the SO_2 release peaks at 500 °C did not reach as high values as measured in the regenerations at 380 °C, although the release was continuing longer at 500 °C. This finding could be in line with the study of Ordóñez et al. (2004: 31), where they stated that the catalyst was deactivated stronger and regenerated more efficiently at 350 °C compared to samples deactivated and regenerated at 550 °C.

H_2 injections raised the catalyst temperatures. At 380 °C, the increase was between 65 °C and 170 °C and at 500 °C the increase ranged from 140 °C to 165 °C. This needs to be taken into account when the exhaust initial temperature is still higher, because too high a maximum temperature can cause permanent damage to the catalyst due sintering.

Jones et al. (2003: 589-601) discovered very large areas of agglomerated palladium particles after the regeneration with H_2 at 400 °C for 0.5 hours. Palladium agglomeration could also be the cause of the lack of recovery in the present study.

In the end of the second experiment, it could be observed that the CH_4 conversions seemed to have stabilised. Gélin et al. (2002: 1-37) have proven that the complete deactivation was achieved far below the saturation of alumina by sulphates, and the time of poisoning stream does not have significant difference once the catalyst is deactivated. By IR, they had measured almost the same sulphur volumes from the catalyst after it had been poisoned for 30 hours and for 2.5 hours. It could be assumed that in the current experiments, the saturation point of the poisoning was achieved during the long 60 hours poisoning, when

the whole poisoning time had been 168 hours. Although, the number of results is so low that it is impossible to draw any conclusions.

The hypothesis of Kinnunen et al. (2017:117) of the effect of water vapour on S-poisoned catalyst should be studied further. Also their model of regeneration model could explain why no increase in the activity was noticed after regenerations.

Before taking H_2 regeneration into everyday operation, the current topic needs to be studied further. Regeneration times and H_2 concentrations need to be studied further. When the optimal parameters have been found it would still need some estimations to see if the method is profitable. Before commercialisation it needs to be taken into account that H_2 is a very flammable gas and it can cause danger if safety is neglected.

8. CONCLUSIONS

Based on the performed literature review, the following conclusions could be drawn:

- Pd/Pt on γ-alumina is the most efficient catalyst material. γ-alumina is a sulphating support and protects the noble metals from sulphur poisoning.

- Optimal catalyst temperatures are from 500 °C to 700 °C. At lower temperatures the catalyst is inactive and higher temperatures can cause sintering which is irreversible.

- H_2 regenerates the sulphur poisoned catalyst by removing sulphite and sulphate groups. Effective concentrations are between 70 ppm to 10 %, and the durations of the treatments vary. H_2 injections were the most effective regeneration method.

- Sulphur can make the catalyst more sensitive to water vapour poisoning.

Based on the received experimental results, the following conclusions could be drawn:

- The temperature of 380 °C was too low for catalyst operation, and no CH_4 conversion was achieved at that temperature. Ethane conversion was also quite low during the experiment.

- At 500 °C, the catalyst worked well, but even with the H_2 regenerations, the poisoning could not be inhibited.

- The temperature measurements showed that the H_2 reacts in the catalyst. The increase in the temperature needs to be taken account when the exhaust gas is hotter.

- At both experiments, the H_2 injections released SO_2 from the catalyst. After the regenerations, when the SO_2 was again added to the exhaust gas, the CH_4 conversion started to decrease slowly.

- Short H_2 injections seemed to be sufficient, because most of the SO_2 was released immediately after the injection. At 380 °C, the SO_2 peaks were higher, but at 500 °C, the SO_2 release lasted longer.

- The most effective regenerations were achieved with 2 to 2.5 % H_2 concentrations.

- Removing sulphur compounds from the exhaust gas would be the most effective method to prevent poisoning of the catalyst.

9. SUMMARY

The need for peaking power is increasing while the production of renewable energy, wind and photovoltaic, is increasing. Gas engines offer a very flexible alternative for more traditional hydropower. Yet the very rapid transient loading situations and low loads can cause increase of the CH_4 emissions. Emissions can be blocked by catalytic converters, but the sulphur compounds from the fuel and lubricating oil are very poisonous for the catalyst.

The target of this thesis was to find out how the CH_4 conversion of an oxidation catalyst could be regenerated by reducing the poisoning sulphur compounds by H_2 injected directly into the catalyst. Scientific articles were first reviewed. Thereafter, the engine experiments were performed by incorporating a Pd-Pt/Al_2O_3 catalytic converter into the exhaust pipe of a NG driven engine to evaluate the effect of the H_2 regenerations on the catalyst performance.

The literature review gave positive results about the regeneration of CH_4 catalysts by H_2 addition, which indicated that poisoned catalysts might be regenerated. Among the reviewed studies, however, only few results were found concerning engine experiments for the CH_4 catalyst improvement.

In the experiments, two temperatures and multiple H_2 injection concentrations (1 % to 2.5 %) and periods (10 minutes to 1 hour) were used. The lower temperature of 380 °C in the first experiment was too low for catalyst to activate and hence the CH_4 conversion stayed very low regardless of regenerations. Experiments at 500 °C where more successful, but still, the conversion of the aged catalyst did not reach the targeted conversion of a fresh catalyst.

In both experiments, in the beginning of the regenerations, sharp peaks of SO_2 were registered in the exhaust gas after the catalyst. It could be assumed that H_2 reacts in the catalyst and releases SO_2.

The current work could not find straightforward answers to CH_4 catalyst regeneration problems. H_2 injections concentrations and durations should be optimised. More importantly, more studies are needed about the effects of SO_2 and water vapour on the catalyst deactivation.

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