

**CATALYTIC EMISSION CONTROL WITH RESPECT TO CH₄ AND CO
FOR HIGHLY EFFICIENT GAS FUELED DECENTRALISED
HEAT AND POWER PRODUCTION**

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ABSTRACT

A new Rhodium (Rh) based monolithic catalyst has been developed for oxidation of carbon-monoxide (CO), methane and other hydrocarbons in the exhaust from lean-burn gas engines for decentralised heat and power production plants. The cleaning efficiency of this catalyst has been monitored over 5000 hours in a field test at constant inlet temperature. The methane conversion as a function of temperature has been determined in a separate test and the results are used in an evaluation of practical process design for exhaust gas cleaning in full-scale lean-burn gas engines. The design includes supplementary firing as well as recuperative and regenerative heat exchange for increasing the inlet temperature of the exhaust gas.

KEYWORDS

Lean-Burn Gas Engine, Oxidation Catalyst, Carbon Monoxide (CO), Methane (CH₄), Unburned Hydrocarbons (UHC), Combined Heat and Power, Emissions Control.

INTRODUCTION

Combined heat and power production is an efficient tool to achieve the highest fuel utilisation and thus to reduce emission of the greenhouse gas carbon dioxide (CO_2). Also by substitution of fuels to a higher H/C ratio such as natural gas an even higher reduction of CO_2 is achieved. CO-generation, therefore, has been widely introduced in European countries in large-scale plants and as decentralised units, typically based on lean-burn gas engines or gas turbines. However, reciprocating engines have an emission of unburned fuel, UHC (Unburned HydroCarbons). For natural gas fuelled engines this UHC will to a large extent consist of methane, which is considered a serious greenhouse gas.

The latest versions of gas engines (lean-burn engines) for stationary purposes have reached shaft efficiencies above 40% (lower calorific value, LCV). For natural gas engines about 90% of the unburned fuel consists of methane and represents typically from 1-6% of the fuel input, equivalent to approx. 800-3000 ppm (vol.) in the exhaust. As methane has a Global Warming Potential (GWP) of 21 compared to CO_2 /1/, this problem outbalances greenhouse gas saving effects from cogeneration based on gas engines. The present work describes a novel Rh based oxidation catalyst that can solve this problem.

OXIDATION CATALYSTS

Oxidation catalysts for CO reduction are presently used for cleaning of the flue gas from lean-burn engines. At temperatures above 200°C these catalysts (often precious metal based) give a significant CO reduction throughout the catalyst lifetime, typically some 20.000 hours. The oxidation catalyst is often installed at flue gas temperatures in the range $400\text{-}500^\circ\text{C}$, upstream the heat recovery boiler.

For catalytic oxidation of methane in the temperature range $380\text{-}450^\circ\text{C}$, only precious metal types of catalysts have the sufficient activity. Therefore only palladium, rhodium and platinum based catalysts will be discussed in the following. In earlier field tests precious metal oxidation catalysts for oxidation of CH_4 (methane) have shown little or rapidly decreasing performance in the temperature range of $400 - 500^\circ\text{C}$ /2/. The catalysts often deactivated to an unacceptable level in less than 50 hours of operation.

Catalysts based on supported Pd are more active for methane oxidation than catalysts based on Rh and Pt. This is illustrated in Figure 1 /3/, where light off curves for three different catalysts are shown. However, several studies have shown that Pd based catalysts rapidly lose their activity when small amounts of SO_2 is present in the reactant gas. An example of this is shown in Figure 2 /4/. The sources of SO_2 in the exhaust gas for most natural gas engines are the odorant Tetra Hydro Thiophene (THT) added to the natural gas, and sulphur in the lubricating oil. The objective of the work presented here has been to develop a catalyst with an acceptable activity for methane oxidation in an exhaust gas with about 1 ppm SO_2 in the temperature interval $400\text{-}500^\circ\text{C}$.

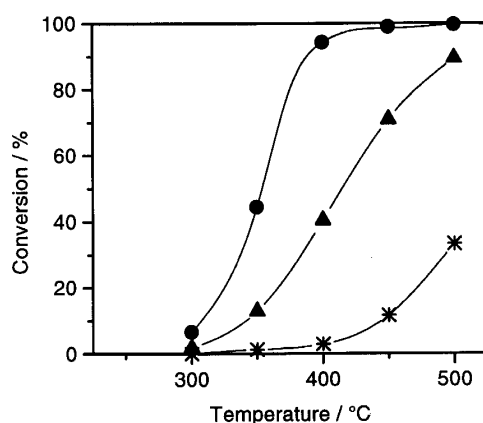


Figure 1 *CH₄ reduction efficiency for different precious metals versus temperature /3/.
 • 5% Pd/alumina, ▲ 2% Rh/alumina, * 2% Pt/alumina. Other conditions: CH₄ 1000 ppm, O₂ 10%, H₂O 10%, Space Velocity (SV): 40.000 h⁻¹*

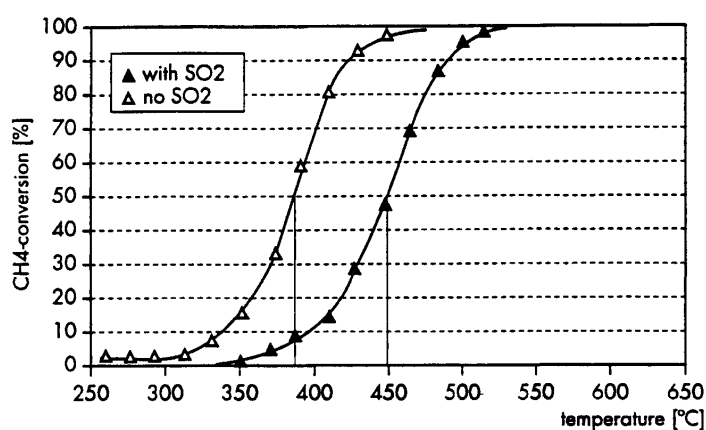


Figure 2 *CH₄ reduction efficiency with and without the presence of 4 ppm SO₂ for a precious metal oxidation catalyst /4/*

Experimental

Several lab-scale tests led to the production of a monolith with a hydraulic diameter of 1.1 mm, a washcoat layer of Al₂O₃ promoted with base metal and a Rh loading of about 2 wt % for the long term test /5/.

The catalyst was installed in the exhaust gas from a 1 MW_e natural gas fuelled Caterpillar lean-burn gas engine (CAT3516). The temperature of the exhaust gas at the catalyst inlet side was 425-430 °C and the amounts of catalyst installed corresponded to a normal hourly space velocity (NHSV) of about 17,000 Nm³/(m³ · h). The conversion of hydrocarbons and CO was measured using a flame ionisation detector (FID) for hydrocarbons and an infra-red absorption detector for CO.

Results and discussion

Figure 3 shows the conversion of hydrocarbons as a function of time in a 5000 h field test. The temperature of the exhaust gas at the inlet to the catalyst was about 430°C.

The conversion of CO was higher than 95% during all 5000 h of the test. The conversion of methane, however, decreased rapidly from about 86% to about 60% in the first 1000 h of operation. Only a slow decrease in the conversion rate was observed in the last 4000 h of the test. The rapid decrease in methane conversion in the first 1000 h of the test is associated with uptake of Sulphur on the catalyst. The slow decrease over the last 4000 h of the test may be due to a reaction of Rh with the support material. Fresh and spent catalyst material was analysed by transmission electron microscopy and no increase in Rh particle size could be observed.

Figure 4 shows the measured conversion of methane measured at 3 different temperatures at an NHSV of $10.000 \text{ Nm}^3/(\text{m}^3 \cdot \text{h}) /6/$. Notice how the conversion of methane increases with temperature from about 24% at 418°C to about 87% at 492°C . The catalyst used for this test was a part cut out of the catalyst which had been used for the long term test (5000 h).

From the data in Figure 4 an apparent activation energy can be determined. Assuming simple first order kinetics for the oxidation of hydrocarbons under the given experimental conditions, the activation energy has been used to estimate the hydrocarbon conversion for inlet temperatures of 450, 470 and 490°C in the long term test. These estimates are shown in Figure 3. If a hydrocarbon conversion of more than 90% is needed, the inlet temperature of the exhaust gas should be about 490°C .

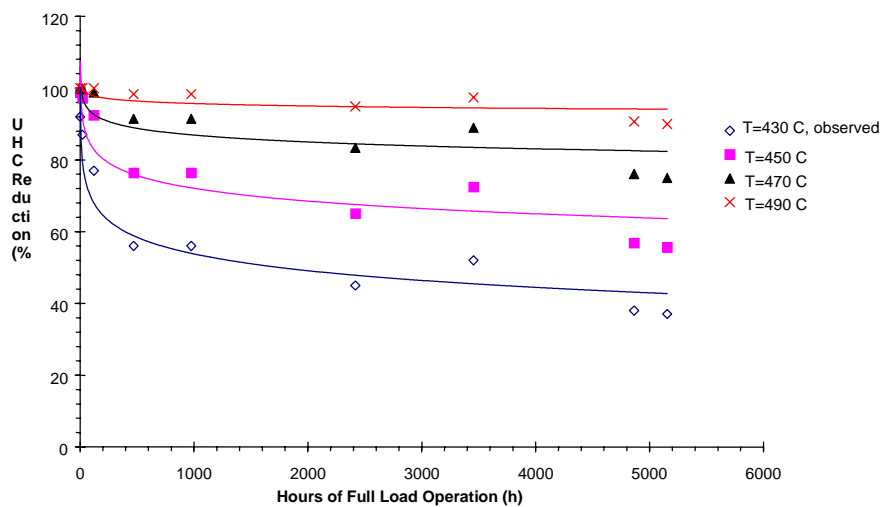


Figure 3 Novel rhodium based oxidation catalyst - Field-test results, Space Velocity approx $17.000 \text{ nm}^3/(\text{m}^3 \cdot \text{h})$. Tests were performed at 430°C . Performance at other temperatures is calculated based on results presented in Figure 4 /7/.

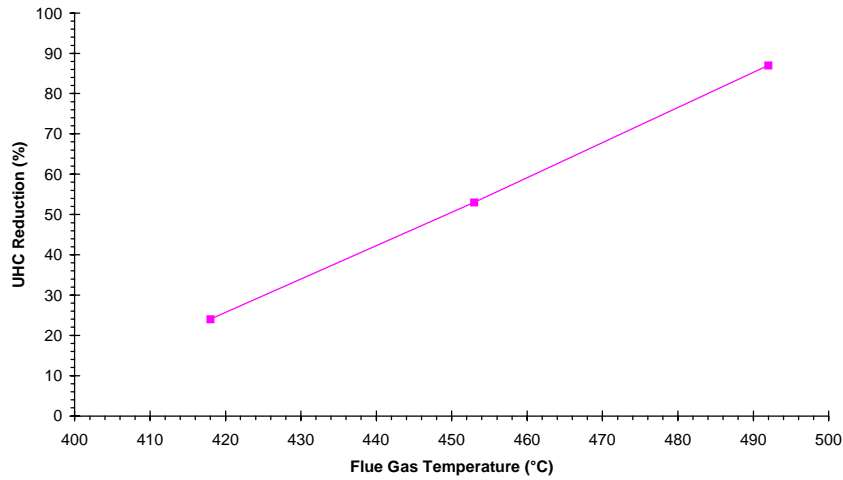


Figure 4 Novel rhodium based oxidation catalyst - Short-term testings at various temperatures performed after 5000 hours of operation /6/, /7/, Space Velocity 10.000 Nm³/(m³ · h)

SUPPLEMENTARY THERMAL PROCESSES FOR INCREASED CATALYST EFFICIENCY

Afterburner

An increase of the flue gas temperature of approx. 25°C will reduce the cost of the CH₄ reducing catalyst to approx. 50% and therefore an afterburner can be used upstream the catalyst. This afterburner will to a certain extent also reduce the incomplete combustion products including CH₄.

Some 90% of the extra heat produced will typically be recovered in the heat recovery boiler. Figure 5 shows the required fuel input to the afterburner depending on the desired temperature rise and the actual oxygen content in the exhaust. The fuel input is expressed relative to the fuel input for the cogeneration unit.

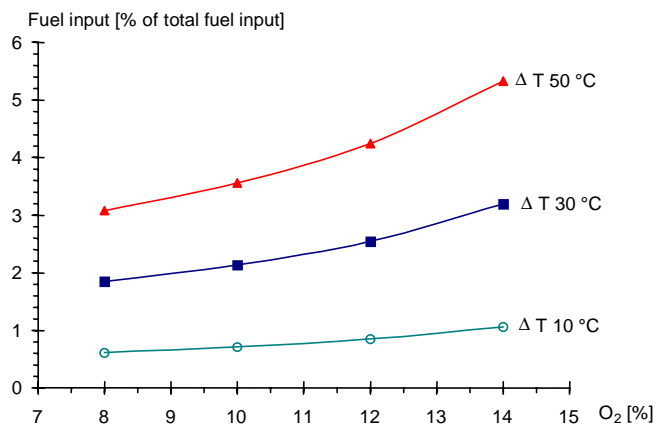


Figure 5 Afterburner fuel input required for a certain increase in flue gas temperature. Fuel input expressed relative to fuel input to the cogeneration unit as a whole /7/.

The investment cost for oxidation catalyst and afterburner for a 1 MW_e plant is estimated at approx. 50.000 Euro, of which the afterburner accounts for approx. 15.000 Euro.

Regenerative Oxidation Process

A regenerative process can be used for achieving an increase in flue gas temperature. As shown in Figure 6, a burner is used to increase the flue gas temperature to improve operation conditions for the oxidation catalyst. After the catalyst the hot flue gasses are led through a heat-absorbing layer to increase the temperature of the layer. After some minutes of operation the valves are activated and the flow direction in the system is changed. The heat-absorbing layer now serves as preheating of the incoming non-cleaned flue gasses. Due to the actual content of CH₄ in the flue gasses from gas engine based cogeneration units the burner is only needed in the start-up phase. Later, the heat released through oxidation in the catalyst is sufficient to keep the process running.

Such regenerative systems are being used for cleaning of volatile organic compounds from other processes than cogeneration systems.

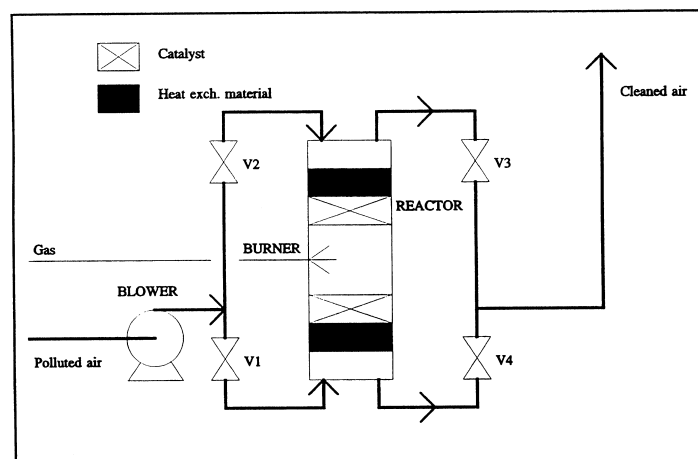


Figure 6 Regenerative oxidation catalyst system (REGENOX[®])

A small fraction of exhaust gasses will pass unreacted at each valve shift. This can be avoided by using a more complicated valve system, see Figure 7.

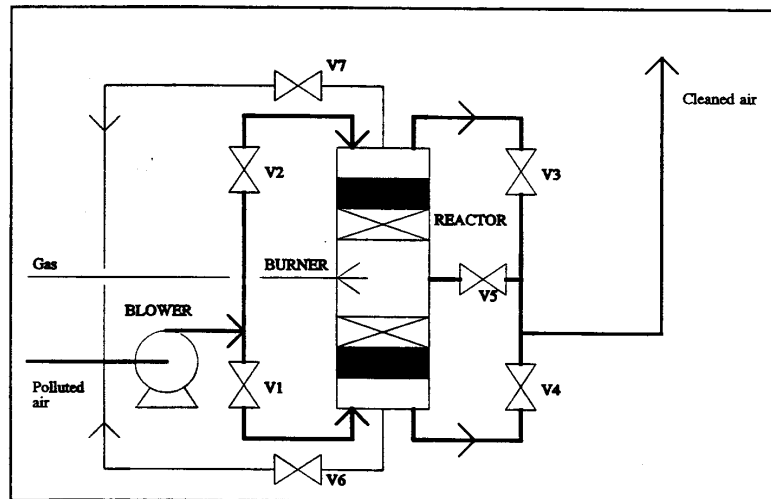


Figure 7 Regenerative oxidation catalyst system (REGENOX[®]) with HAPS[®] anti-pulse system (patented)

The regenerative system will have lower fuel cost compared to the afterburner solution, but will demand more space for installation and require higher initial investments. The initial cost for the system presented in Figure 6 is estimated to approx. 270.000 Euro for a 1 MW_e plant.

Recuperative heat exchange

The heat released as a result of the oxidation in the catalyst can be used as a basis for continuous heat exchange. With flue gasses from typical gas engine exhaust a temperature increase of 30-50°C can be expected with oxidation of CO and UHC. As shown in Figure 8, this can be utilised through recuperative heat exchange with supplementary firing in the start-up phase.

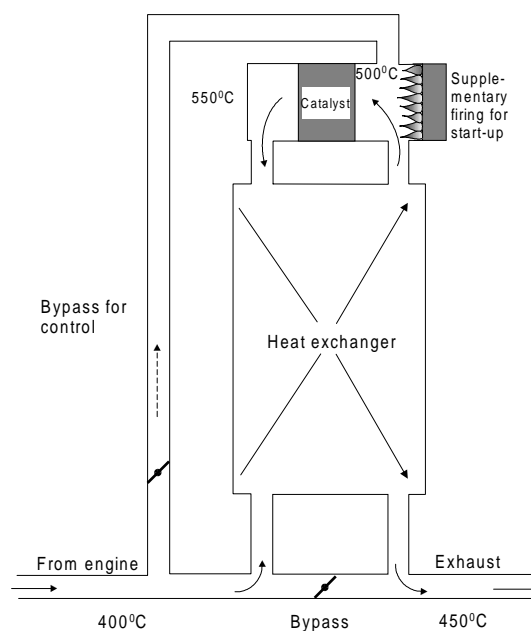


Figure 8 Recuperative heat exchange and start-up supplementary firing to achieve better operation conditions for the oxidation catalyst

The start-up phase from cold conditions has been estimated to be in the order of 15 minutes. Temporary stop of the plant (up to 12-18 hours) will not necessitate the use of supplementary firing because of the heat capacity of the heat exchanger.

Cost-effective plate heat exchangers with low pressure drop have been identified and a demo plant is planned to demonstrate the recuperative technology in combination with the oxidation catalyst. Heat exchangers with efficiencies in the order of 70% have been estimated to be able to increase the inlet temperature to the catalyst by 60-100°C. This will raise the temperature in the catalyst to a level (about 500°C), where the CH₄ reduction efficiency of the catalyst will be much higher. The result will be cheaper catalysts with higher UHC conversion efficiencies.

However, in this concept heat exchangers are necessary, which will reduce the economic benefit. The initial costs are estimated to approx. 70.000 Euro for a 1 MW_e plant. The cost per MW, of course, will be reduced for higher power output.

CONCLUSION

A new oxidation catalyst formula has been developed and successfully tested at a commercially operating field-test unit up to 5000 hours. The CO reduction has been higher than 90% and the UHC/CH₄ reduction has been higher than 50% at flue gas temperatures above 440°C. The formula has proved more resistant to poisoning processes than previously seen for oxidation catalyst performance under practical operation.

The CH₄ oxidation process is very dependent on flue gas temperature. The exhaust temperatures for highly efficient gas-engine based cogeneration units are sometimes as low as 400°C and this is too low for obtaining the desired methane conversion. Therefore technologies that give a temperature increase in the range of 25 - 50°C will lower the cost of the precious metal catalyst.

Installation of an afterburner has the lowest investment cost but has a continuous need for fuel during operation.

Due to the UHC content of the exhaust gas regenerative or recuperative systems will only need external fuel input during start and stop phases of the engine. These systems will require investments five times higher than the sole oxidation catalyst or the combination oxidation catalyst/afterburner. Regenerative systems include cyclic operation of valves/dampers. Such systems are in commercial use for VOC reduction in other industrial areas.

The recuperative system presented in this paper has no cyclic operation of valves and dampers. This system has not yet been tested during practical operation.

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