

ICE2003-568

DEVELOPMENT OF PRE-TURBO CATALYST FOR NATURAL GAS ENGINES

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ABSTRACT

Distributed power generation is an efficient method for reducing CO₂ emissions through the elimination of transmission losses. Co-generation has similar benefits with higher thermal efficiency. Natural gas engines are very popular for these applications. Unfortunately, these engines emit significant levels of methane, which is a greenhouse gas. Reduction of methane emissions would greatly improve the environment and provide greenhouse gas emissions credits.

The exhaust temperature downstream of the turbocharger in a natural gas engine is typically below 500°C. At these temperatures, methane is difficult to oxidize with current oxidation catalysts. It would be a much better option to install the oxidation catalyst before the turbocharger where temperatures are 100-150°C higher. Pressures upstream of the turbocharger are higher than downstream and also affect catalyst conversion efficiencies.

Misfiring events are common in natural gas engines. During misfiring events, the catalyst will see a sudden increase in hydrocarbon (methane). When this pulse of hydrocarbon hits the catalyst, it will be oxidized and generate a large exotherm which could lead to catalyst failure (mechanical and/or chemical). This issue is critical for a pre-turbo catalyst:

- 1) Mechanical failure of the catalyst could lead to catastrophic turbocharger failure, a result of the turbine blades being damaged.
- 2) Misfiring with catalyst installed before the turbocharger is more likely to ignite the methane pulse because of the higher temperatures in this location. High exotherms from ignition could negatively affect catalyst performance.

Through careful catalyst design, one can minimize this risk and this paper will address these issues.

INTRODUCTION

Lean-burn natural gas engines are very popular for applications involving power generation and co-generation. On-site power generation reduces power transmission losses and in the case of co-generation also supplies heat. Unfortunately, due to incomplete combustion within these engines the exhaust contains trace amount of hydrocarbons with up to 1000 ppm of methane. Since methane has a greenhouse warming potential of about 20 to 50 times that of carbon dioxide, its emissions are becoming an area of concern. Although Denmark is the only jurisdiction with methane regulations today, it is likely that other jurisdictions will follow. Regulatory agencies are continually lowering emissions requirements on engines and methane emission standards are the next logical progression. Reliable cost-effective technology to combat methane emissions is not yet available but is highly desirable.

The most common technology for exhaust gas cleanup is a catalytic converter. In most applications, the converter would be installed downstream of the turbocharger where temperatures are typically below 500°C. These temperatures are too low for achieving significant methane conversions with current oxidation catalyst technology. This paper will discuss a novel approach where the catalyst is installed upstream of the turbocharger where temperatures are 100 – 150°C higher. However, installing a catalyst upstream of a turbo presents other complications that will be addressed in this paper.

The literature reports many catalyst formulations that can be used for methane reduction [1-16]. Unfortunately there are none that can maintain their performance for more than a few hours of operation. Palladium based catalysts have been shown to give modest conversions (~30%) in the temperature region of typical natural gas exhaust (~400°C) [1,2,6,12,14]. These catalysts show rapid performance deterioration caused by the small amount of sulphur present in the exhaust [1,2,6,7,12-15]. This performance loss is further aggravated by other

components in the exhaust (i.e. water) [2,5,6,12,14,15]. Up to 50 to 80% reduction in performance have been reported.

Lean burn spark ignited engines can experience misfires due to ignition failure, flame quenching, and incomplete flame propagation [17]. This can lead to the catalyst being exposed to large concentrations of hydrocarbon during the misfiring event. In the pre-turbo position, temperatures are expected to be well above the catalyst light off temperature causing ignition of the excess fuel mixture. This could cause a rapid temperature rise across the catalyst leading to catalyst deactivation and/or catastrophic failure. This paper will discuss design issues and give suggestions for minimizing those risks.

NOMENCLATURE

$C_{g,i}$	Gas concentration (mole fraction) of component i
C_{pg}	Specific heat at constant pressure of gas (J/kg/K)
C_{ps}	Specific heat of solid (J/kg/K)
C_{o_2}	Mole fraction of oxygen on catalyst surface
$C_{p_i}^{\gamma}$	Dimensionless empirical coefficient representing catalyst loading and activity
CPSI	Cells per square inch
Ga	Geometric surface area per unit substrate volume (m^2/m^3).
h	Heat transfer coefficient ($J/m^2/s/K$)
ΔH	Heat of reaction (J/mol)
k^i	Overall reaction rate term for component i (m/s)
k_c^i	Mass transfer rate term for component i (m/s)
k_r^i	Kinetic reaction rate term (m/s)
\dot{m}_g	Exhaust mass flow (kg/s)
M_g	Molecular weight of exhaust (kg/kmol)
$N_{species}$	Number of species
R	Radius (m)
S_{BET}	Effective BET surface area (m^2/g)
t	Time (s)

T_g	Gas temperature (K)
T_s	Solid temperature (K)
v	Superficial velocity (m/s)
z	Axial distance (m).

Greek symbols

\mathcal{E}	Void volume fraction
ρ_g	Gas density (kg/m^3)
ρ_s	Solid density (kg/m^3)
ρ_{wc}	Washcoat density (kg/m^3)
λ_s	Thermal conductivity of solid (W/mK)
η	Internal effectiveness factor

Superscript

n	Index of time step
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Subscript

i	Species index
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EXPERIMENTAL METHODOLOGY:

This study consists of two methods; first is the model gas reactor testing which simulates the actual conditions in the exhaust gas, and the second is computer simulations.

1. Model Gas Reactor Testing

Various catalysts were tested for their ability to completely oxidize methane to carbon dioxide and water under pseudo real life exhaust gas conditions. Exhaust gas conditions upstream of the turbocharger were simulated using a model gas reactor (Figure 1). Exhaust gas conditions and catalyst dimensions are presented in Table 1. A thermocouple was placed 1 mm away from the outlet of the catalyst. The temperature recorded by this thermocouple was taken as the reaction temperature. Four gases (CH_4 , O_2 , SO_2 and balance N_2) were introduced to the reactor from four separate mass flow controllers. Prior to entering the reactor, the bulk-premixed gases were preheated to 130°C. Water was added using a peristaltic pump after the pre-heater. The length of tube from the pre-heater to the reactor

was heated to 130°C using heating tape to prevent condensation of the water. The tubing from the reactor to the gas chromatograph was heated to prevent water condensation. Gas pressure over the catalyst was controlled by restricting the flow through a valve installed downstream of the catalyst.

- No interactions among pollutants
- Adiabatic conditions for the catalytic converter

As a simplifying assumption, surface reactions were not explicitly modeled, i.e. no surface reaction and no adsorption/desorption mechanisms were used. Instead surface reactions were bulked into a first order reaction kinetic term for each species. Laboratory experiments conducted by DCL indicated that kinetic rates could be adequately expressed as first order rates for the operating range studied.

The basic equations for the model consist of a mass balance for the gas phase (Equation 1), an energy balance for the gas phase (Equation 2), an energy balance for the solid phase (Equation 3), and a mass balance for the solid phase [18]. If first order reaction rates are assumed, then the explicit equation for mass balance in the solid phase can be eliminated and replaced with an overall reaction rate term (k^i) (Equation 4). For a given species the overall reaction rate term is determined from the bulked reaction rate taking place at the catalyst surface (the middle term of Equation 4) and the mass transfer rate of species from the bulk gas to the catalyst surface (the right-hand term of Equation 4). With oxygen in excess, the mole fraction of oxygen at the surface can be assumed the same as in the bulk gas. The heat transfer, mass transfer and kinetic rate expressions were developed by DCL from model gas reactor and engine test cell data.

To obtain the numerical solution, the length along the catalytic converter is divided into a number of longitude computational elements and the corresponding finite difference relations are approximated. As the first step the gas temperature is solved iteratively until convergence with the solution is achieved. Next the reaction rates are solved for each species using a fourth order Runge-Kutta method, and finally solid temperature is solved. This method normally achieves a solution in several minutes using a recent model desktop PC, allowing a number of design variations to be quickly assessed.

$$\varepsilon \frac{\partial C_{g,i}}{\partial t} = -v \frac{\partial C_{g,i}}{\partial z} - k^i Ga C_{g,i}, \quad i = 1, 2, \dots, N_{\text{species}} \quad (\text{Equation 1})$$

$$\varepsilon \rho_g C_{pg} \frac{\partial T_g}{\partial t} = -v \rho_g C_{pg} \frac{\partial T_g}{\partial z} + h Ga (T_s - T_g) \quad (\text{Equation 2})$$

$$(1 - \varepsilon) \rho_s C_{ps} \frac{\partial T_s}{\partial t} = \lambda_s (1 - \varepsilon) \frac{\partial^2 T_s}{\partial z^2} + h Ga (T_g - T_s) + \sum_{i=1}^{N_{\text{species}}} (-\Delta H)_i \frac{\dot{m}_g}{\pi R^2 M_g} \frac{\partial C_{g,i}}{\partial z} \quad (\text{Equation 3})$$

The subscript i refers to the species CO, NO, H₂, CH₄, C₂H₄, C₃H₈ and C₄H₁₀. The overall reaction rate constant k is calculated by Equation 4.

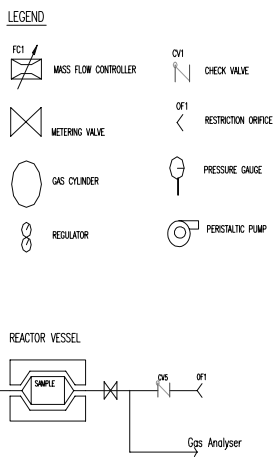


Figure 1: Flow Diagram of Model Gas Reactor

Table 1: Test conditions

Catalyst Dimensions	1 cm O.D. x 5 cm long	
Space Velocity	110,000 1/h	
Gas composition	CH ₄	112 ppm
	H ₂ O	6%
	O ₂	10.8%
	SO ₂	5 ppm
	N ₂	Balance
Temperature Range	500°C to 560°C	

Analysis was performed using a Varian CP-3800 Gas chromatograph (GC) equipped with an FID and TCD. The columns used on the GC for the separation are a CP-Sil 5CB, Hayesep T, Hayesep R and Molsieve 13X.

The catalyst formulations used in this study are listed in Table 2. Detailed preparation and composition information is not provided due to its confidential nature.

Table 2: Catalyst Compositions

Catalyst A	10 g/l Pd/Pt 3:1 on Al ₂ O ₃
Catalyst B	10g/l Pd on Al ₂ O ₃

2. Computer Simulation

A transient catalyst model is used based on the following assumptions:

- One dimensional “plug flow” monolith catalytic converter model
- Axial diffusion of mass and heat in the gas phase is neglected
- First order reaction rate (one step reaction)

$$\frac{1}{k^i} = \frac{1}{\eta C_{Pt}^\gamma k_r^i \rho_{wc} S_{BET} C_{o_2}} + \frac{1}{Ga k_c^i}. \quad (\text{Equation 4})$$

RESULTS AND DISCUSSION

1. Model Gas Reactor

Catalysts described above were tested for their methane conversion efficiency in the pre and post-turbo position. These catalysts were aged using SO₂ and water to deactivate the catalyst. In the pre-turbo position (550°C, 2.6 bar), it was found that the aged Pd catalyst reproduced results consistent with those in the literature [2,6,14]. Methane conversions of about 50% were achieved at the pre-turbo position (Figure 2). The Pd catalyst was then exposed to post-turbo conditions (350°C, 1 bar) under the same mass flow conditions. The methane conversion decreased from 50% to approximately 5% in the post-turbo position. From these results, installing the catalyst upstream of the turbo is beneficial because of higher pressure and temperature.

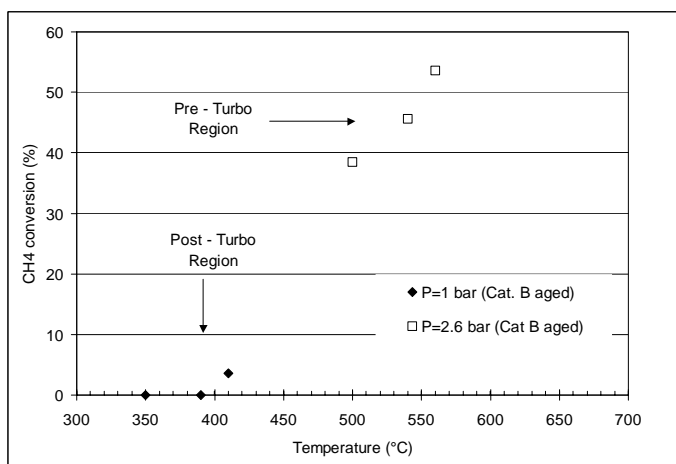


Figure 2: Influence of catalyst position on methane conversion (aged catalyst B)

Published results of McCormick and others [2,6,7,12-15] show that sulphur present in the exhaust stream in low concentrations of 1 ppm or less causes deactivation of Pd based catalysts. Our results confirm this finding. Figure 3 shows rapid deactivation of the Pd catalysts in this study after exposures of 12 hours to 5 ppm S in the gas stream. Methane conversions on catalyst A decrease from 90% to 55% and appear to plateau after 10 hours sulphur exposure. This is a result of S reacting with the surface of the PdO catalyst to form PdSO₄ (2,6,12).

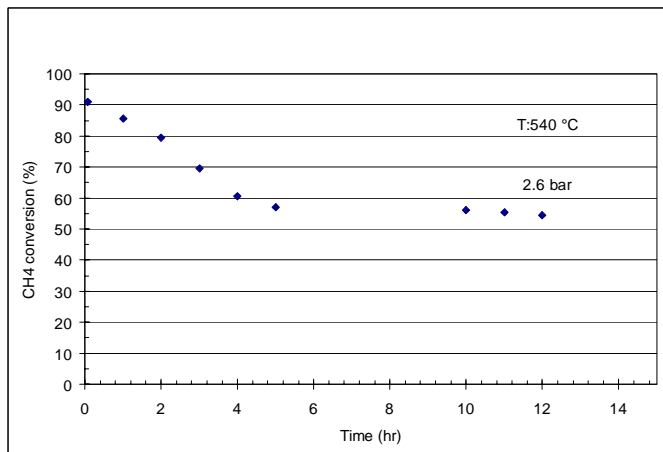


Figure 3: Aging of methane catalyst A with sulphur exposure

Misfiring events in natural gas engines are known to be frequent. During misfiring events, a pulse of a fuel rich mixture comes in contact with the catalyst. If sufficient energy is available this fuel mixture can ignite resulting in a large exotherm inside the catalyst. This exotherm can cause considerable amounts of damage to the catalyst. A rapid local temperature rise results from the hydrocarbon combustion may damage the catalyst through sintering of precious metal and the washcoat carrier. In extreme cases, the substrate can begin to melt or fracture and pieces can break off. In engines without a turbocharger this is not a significant problem since the fragments of the substrate would exit through the muffler or tail pipe. This is not the case with a catalyst installed upstream of the turbocharger. Dislodged fragments of the catalyst would encounter the precisely balanced blades of the turbocharger causing major failure.

2. Computer Modeling

In order to prevent the likelihood of this failure mode, a series of computer simulations were performed. These simulations helped to investigate different catalyst configurations to minimize the exotherm. The transient computer simulation is designed to mimic a misfiring event. During the first five seconds, the catalyst is exposed to normal operating conditions (550°C, 2.5 bar, 1000ppm CH₄) where methane conversion is approximately 80% for a fresh, non-poisoned catalyst. At time equals five seconds, a pulse of 5% methane is entered in the model as illustrated in Figure 4. At time equals ten seconds, normal operation resumes. The length of misfiring event and methane conversion has been chosen arbitrarily as a reference case. As illustrated in Figure 4, the lower the cell density, the lower the maximum temperature will be, a result of lower conversions.

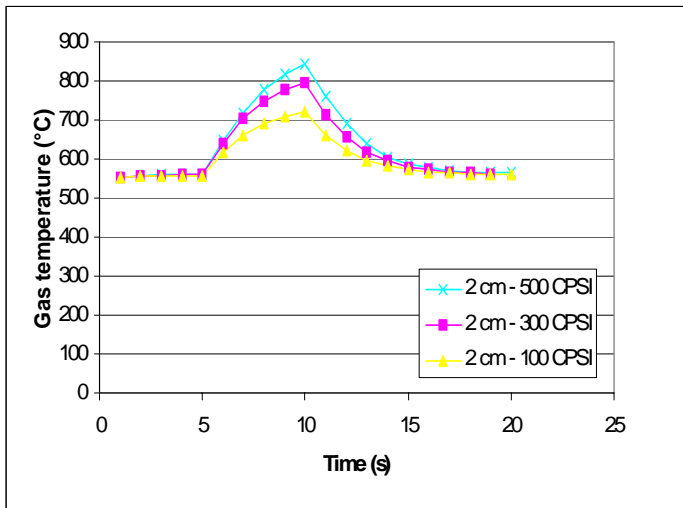


Figure 4: Influence of cell density on maximum temperature during misfiring event

Figure 5 shows the influence of catalyst length. In this case, the shorter the catalyst, the lower the maximum conversion will be. Since a shorter catalyst has a lower thermal mass, it warms up and cools down faster as illustrated in Figure 5. The benefit with a short catalyst is that it would be exposed to high temperatures for shorter periods of time. As a result, it is suggested to use a very short catalyst with a low cell density.

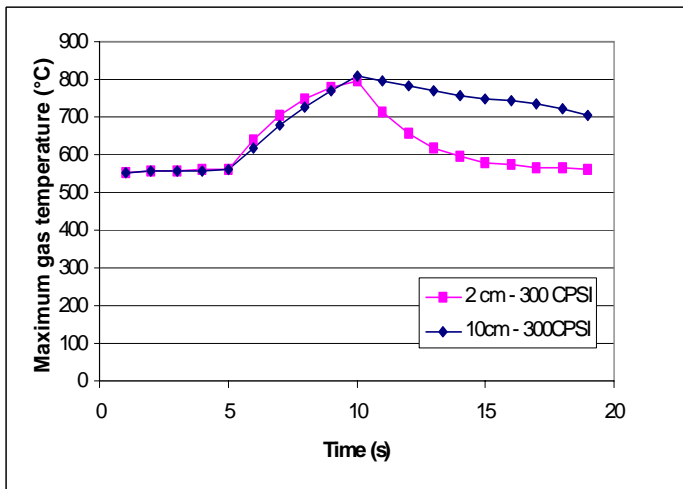


Figure 5: Influence of catalyst length on maximum temperature during misfiring event

The thermal management of catalyst outlet gas temperature can be optimized with the use of a cascade of catalysts instead of one single catalyst. For example, Figure 6 compares two scenarios, a single catalyst and a cascade of 3 catalysts in series representing the same total volume of catalyst. The catalysts are assembled together with an air gap between them so that there is no heat transfer by conduction between the catalysts. As illustrated in Figure 6, this yields a lowering of 25°C of maximum gas temperature before the turbo in this example.

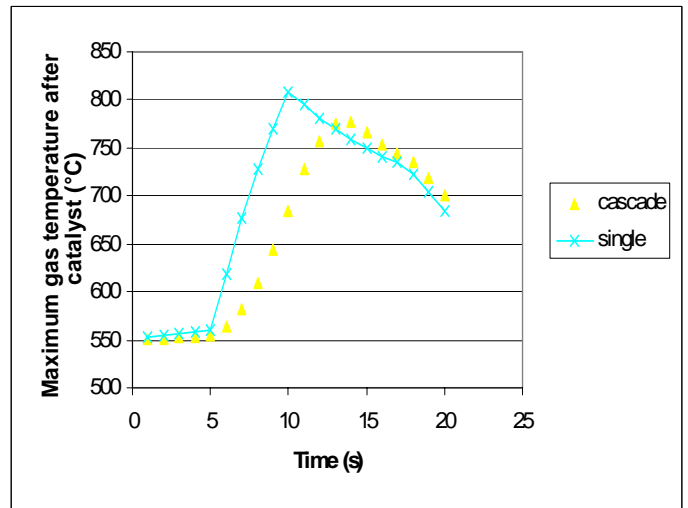


Figure 6: Thermal management through catalyst design

Figure 7 below shows the influence of the length of the misfiring event. As the duration of the misfiring event increases, the maximum temperature may reach unacceptable limits. Clearly, this demonstrates the need for controlling the misfiring events and stopping the engine after a certain period of time. By failing to control the misfiring, the engine manufacturer runs the risk of damaging the turbine blades because of excessive exhaust gas temperatures.

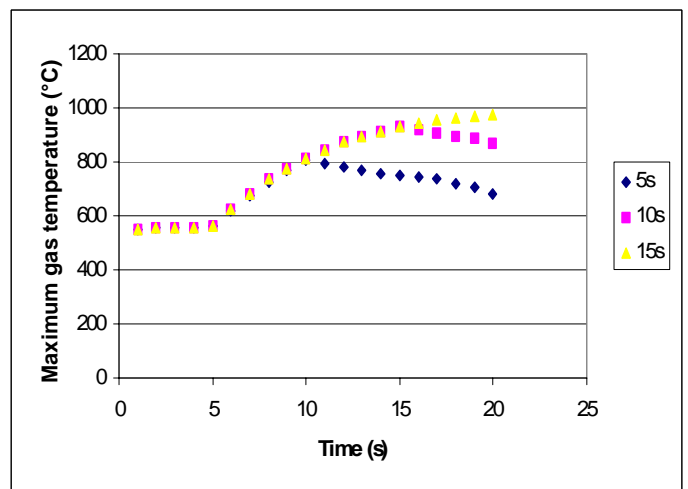


Figure 7: Influence of length of misfiring event

CONCLUSION

It has been shown in this paper that installing a catalyst upstream of a turbo is desirable for methane abatement. Overall methane conversion is significantly improved and can provide a greenhouse benefit with an appropriate catalyst. However, this creates additional design challenges of potential damages to the turbo. We have shown that through catalyst design; selecting a series of low cell density and short catalysts in series, the risk can be minimized. The final optimization of the catalyst system will depend on external factors such as turbine maximum

operating temperatures, probable length of misfiring events, space constraint and catalyst technology.

ACKNOWLEDGMENTS

The authors would like to thank the following DCL employees. Darek Bialasz and Michal Huzij for their help during engine testing and catalyst preparation. We acknowledge the helpful advice of Karen Schrimmer and John Muter.

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