

Homogeneous oxidation of light alkanes in the exhaust of lean-burn gas engines

Bentolhoda Torkashvand, Patrick Lott, Deniz Zengel, Maria Casapu, Jan-Dierk Grunwaldt,
Olaf Deutschmann*

Karlsruhe Institute of Technology

*Corresponding author: deutschmann@kit.edu

Highlights

- Investigation of non-catalytic methane abatement of lean-burn gas engines exhaust gas.
- Investigation of the influence of the gas composition on the oxidation reactions.
- Modelling and experimental study of gas-phase reactions at high pressure.

1. Introduction

Beside engine measurements, catalytic systems have been widely used as a key part of the emission control system of different types of combustion engines over the last decades. Several studies discussed the application of Pd-based catalysts for lean-burn gas engines as they have shown superior catalytic performance for the total oxidation of methane under lean-burn conditions [1]. However, the inevitable exhaust gas component, water, inhibits the total oxidation of methane on Pd-based catalysts which leads to a continuous deactivation with time on stream. Thus, the light-off temperature of methane oxidation shifts to elevated temperatures (450 - 550 °C) [1, 2]. Furthermore, sulfate-/ sulfite-formation on both the noble metal and the support due to sulfur compounds present in the exhaust gas, remains a major challenge for the application of Pd-based methane oxidation catalysts [3]. Increased pressure typically present in case of pre-turbine positioning of the catalyst can only slightly decrease the inhibiting effect of water [4]. Nevertheless, in the exhaust of lean-burn turbocharged gas engines, the oxidation of hydrocarbons may also be possible in the gas phase due to the higher pressure and temperatures upstream of the turbo charger.

This study investigates experimentally and numerically the potential of homogenous gas-phase oxidation of hydrocarbons emitted from lean-burn gas engines at different temperatures and pressures for various gas compositions.

2. Methods

Kinetic measurements were performed in a counter-flow stainless steel reactor, which is dedicated for experiments at elevated pressure. As some experiments were conducted in the presence of SO₂, all setup parts were coated with a sulfur-inert layer (SilcoTek). A total gas flow of 5 l min⁻¹ and 20 l min⁻¹, respectively, was used at pressures of 1, 3, and 5 bar and a temperature range of 350 - 650 °C. Gas analysis was carried out using a MKS Multigas 2030 FT-IR spectrometer. The tested gas mixture matrix consisted of different gas compositions which are typical for lean-burn gas engines: either high methane or high NO_x slip. Additional gas mixtures with variation in NO_x and SO₂ concentrations were also tested. Furthermore, the effect of pressure and residence time on the gas phase reaction was studied numerically using the reaction mechanism developed by Konnov [5] and the DETCHEM^{BATCH} code [6], which simulates homogeneous gas-phase reactions in a batch reactor. For simulation, initial and boundary conditions are chosen according to the experiment.

3. Results and discussion

The obtained results demonstrate the potential of gas-phase oxidation of unburned hydrocarbons as shown in Figure 1a. Methane is converted above 500 °C under atmospheric conditions and a volume flow of 5 l min⁻¹ for gas mixture A (1000 ppm CH₄, 150 ppm C₂H₆, 25 ppm C₃H₆, 700 ppm CO, 800 ppm NO, 200 ppm NO₂, 10% O₂ and 12% H₂O, balance N₂), representing high level NO_x emissions. Increasing the pressure greatly decreases the initiation temperature and remarkably enhances the methane conversion. Thus, almost

complete conversion of methane is achieved at 550 °C and 5 bar, a feasible condition upstream of the turbo charger. A similar and more prominent trend is observed for the other hydrocarbons present. Comparison with the experimental data showed that the model predicts the conversion of methane and the effect of pressure with reasonable accuracy.

It is important to highlight that at temperatures above 450 °C, aside from the total oxidation products, CO and small amounts of HCHO and C₂H₄ were also detected (Figure 1b). Moreover, tests performed without NO_x revealed changes in methane conversion <5 % at 650 °C and 5 bar. This is in agreement with findings that NO_x is needed as a radical starter to promote the gas phase reaction playing the role of a homogenous catalyst [7, 8].

The presence of 3 ppm SO₂ in the gas mixture did not affect the oxidation rate of hydrocarbons in the gas-phase, which indicates that the gas-phase reaction is not sensitive to the presence of sulfur dioxide under the tested conditions.

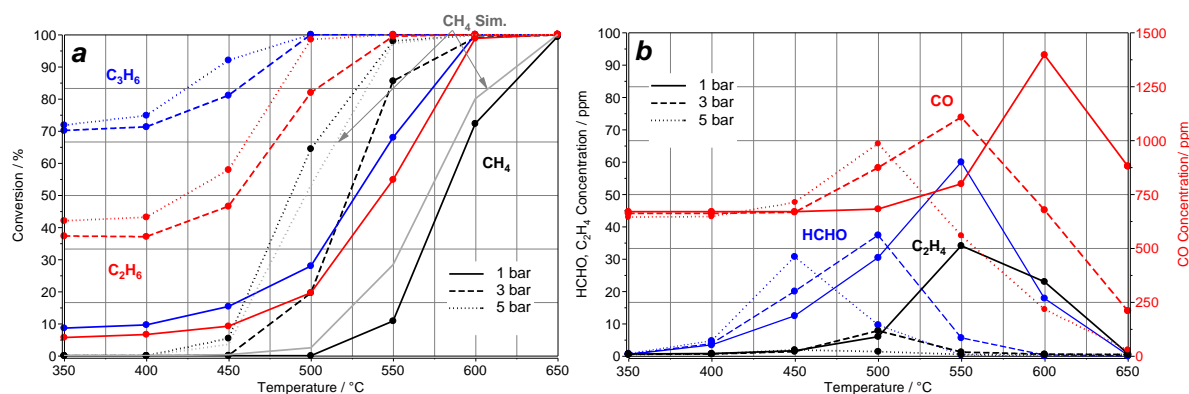


Figure 1: a) conversion of hydrocarbons and b) concentration of byproducts of partial oxidation of hydrocarbon vs. temperature at 1, 3 and 5 bar. Gas composition: 1000ppm CH₄, 150ppm C₂H₆, 25ppm C₃H₆, 700 ppm CO, 800ppm NO, 200ppm NO₂, 10% O₂ and 12% H₂O, balance N₂. For better visibility, only two curves out of many simulations are shown.

4. Conclusions

In this work it is shown that hydrocarbon emissions of lean-burn gas engines can be controlled solely by adjusting the pressure and residence time to accelerate the gas-phase reactions responsible for hydrocarbon oxidation. Hence, no oxidizing catalyst might be required for abatement of methane slip, which could decrease costs and efforts related to catalyst poisoning and deactivation significantly. However, further studies are needed to investigate operational issues and challenges, as gas-phase reaction times are not as short as catalytic ones. For stationary and large-bore gas engine applications, operated without fast load changes, the method introduced here might be of great interest.

References

- [1] D. Ciuparu, M.R. Lyubovsky, E. Altman, L.D. Pfefferle, A. Datye, *Catal. Rev. Sci. Eng.* 44 (2002) 593–649.
- [2] P. Gelin, M. Primet, *Appl. Catal. B: Environmental* 39 (2002) 1–37.
- [3] A. Gremminger, P. Lott, M. Merts, M. Casapu, J.-D. Grunwaldt, O. Deutschmann, *Appl. Catal. B: Environmental* 218 (2017) 833-843.
- [4] B. Torkashvand, A. Gremminger, S. Valchera, M. Casapu, M. Casapu, J.-D. Grunwaldt, O. Deutschmann, *SAE Technical Paper* 2017-01-1019.
- [5] A.A. Konnov, *Eurasian Chemico-Tech. J.* 2 (2000) 257-264.
- [6] O. Deutschmann, S. Tischer, S. Kleditzsch, V.M. Janardhanan, C. Correa, D. Chatterjee, N. Mladenov, H.D. Minh, *DETCHEM Software package*, version 2.3, www.detchem.com, 2013.
- [7] J. Zhang, V. Burklé-Vitzthum, P.M. Marquaire, *Chem. Eng. J.* 197 (2012) 123–134.
- [8] K. Otsuka, R. Takahashi, K. Amakawa, I. Yamanaka, *Catal. Today* 45 (1998) 23-28.

Keywords

Lean-burn gas engines; homogenous gas-phase reactions; oxidation of unburned hydrocarbons at high pressure; NO_x promoted oxidation