

Determination of Ignition Temperature in Micro Reactors

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Explosion protection of oxidation reactions in micro reactors was investigated. Lange et al. (2014) reported on the possibilities of operating oxidation reactions in catalyst coated micro reactors within the explosion regime, but also warned about hotspot induced thermal runaway and detonation ignition at certain conditions. Methane and ethene, representing the explosion groups IIA1 and IIB (DIN EN ISO 16852), were used in stoichiometric oxygen mixtures with respect to total oxidation, which represents the worst case scenario in terms of safety assessment. Using laser radiation on a ceramic target inside of the micro channel, an artificial, controllable hotspot was generated. The ignition temperatures of fuel gas/oxygen mixtures inside a micro reactor were measured and their dependencies on initial pressure, initial temperature, volumetric flow rate, and micro channel height were examined. Deflagration reactions prior to the detonation were observed for the first time inside a micro reactor.

1. Introduction

Heterogeneously catalyzed gas phase partial oxidations are characterized by high rates of heat production and are typically operated outside of the explosion region. Since micro structured reactors are known to narrow the explosion region and to reduce the effectiveness of ignition sources (Gödde et al., 2009), it is promising for process intensification purposes to operate such reactions inside the conventional explosion region (Klais et al., 2010). Therefore micro reaction technology may open novel process windows (Hessel et al., 2011), however their safety margins (Hieronymus et al., 2011 and Liebner et al., 2012) need to be investigated further. The ignition of an explosion induced by a hot surface represents a potential safety hazard. Heinrich et al. (2012) reported on a hotspot emerging on a catalyst's surface and acting as an ignition source inside a micro reactor. In the present work the ignition temperatures of stoichiometric fuel gas/oxygen mixtures at elevated initial pressures are investigated. Parallel to the safety investigations in Berlin, aspects of reaction technology such as selectivity and space-time yield are investigated in Stuttgart. The combination of safety engineering and reaction technology, aims to evaluate the potential of micro reactors operated within the explosion region.

2. Experimental

Mixtures of fuel gas and oxygen are ignited inside a micro reactor using a laser induced hotspot. Ignition experiments are performed with methane and ethene as fuel gases at reactor temperatures of 20 °C and 100 °C. Initial pressure is varied between 1 bar and 20 bar and for each initial pressure three experiments with different volumetric flow rates (200 mL min⁻¹, 350 mL min⁻¹, and 500 mL min⁻¹) are performed. A stoichiometric composition with respect to total oxidation of the fuel gas/oxygen mixtures (33 mol% methane and 25 mol% ethene respectively) is chosen, which represents the worst case scenario in terms of safety assessment. The mixtures are prepared using individual mass flow controllers (500 mL min⁻¹ maximum volumetric flow rate) for each gas. As illustrated in Figure 1, the separate feeds are led into a micro mixer and the resulting mixture run through the primary chamber into the micro reactor and from there through the secondary chamber into the exhaust gas line. Both chambers have an inner diameter of 11 mm and a length of 0.5 m.

The experiments are performed using a custom-made high-pressure micro reactor consisting of two martensitic stainless steel plates (X39CrMo17-1). The top plate is mounted on the base plate forming a rectangular slit-like reactor channel (20 mm in width, 150 mm in length). Using different base plate designs, the height of the micro channel is variable from 0.25 mm to 1.00 mm. As displayed in Figure 2, the top plate contains a reactor window (borosilicate glass, 17 mm in thickness) and the base plate holds a flush-mounted circular ceramic element (96 % aluminum oxide, 10 mm in diameter) in contact with the gas flow running through the micro channel.

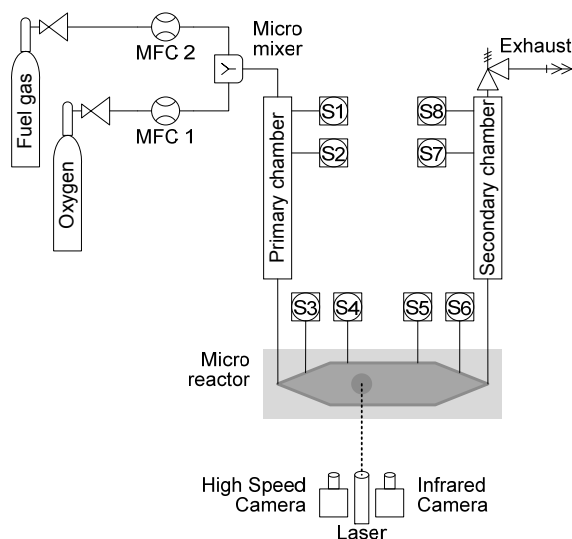


Figure 1: Schematic experimental setup diagram.

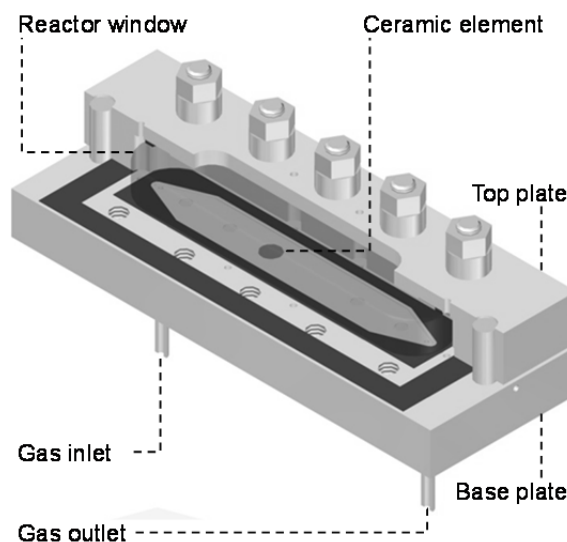


Figure 2: Model of the micro reactor assembly.

After preparing the gas mixture and setting the initial pressure using an overpressure relief valve, the mixture is run through the micro reactor and both chambers for 20 minutes to assure the exclusion of other gases and the pressure consistency. Then the local temperature on the ceramic surface is gradually increased by perpendicular laser radiation (940 nm wavelength) with variable output power (90 W maximum) until the gas mixture flowing through the micro channel is ignited. The rising ceramic surface temperature is measured using a near-infrared camera (900 nm to 1,700 nm spectral band) with a recording speed of 100 Hz and a spatial resolution of 0.5 mm. The explosion ignition and propagation inside the micro reactor is recorded with a high speed camera with a maximal recording speed of 1,000,000 fps. The explosion propagation through the micro reactor and into both adjacent chambers is detected by eight piezoelectric pressure sensors (690 bar maximum pressure, 500 kHz resonant frequency) positioned as shown in Figure 1. The experiments at elevated initial temperature are performed using 18 heating cartridges in six brazen heating plates, which encompassed the micro reactor.

3. Results and discussion

The first test series was performed with ethene as fuel gas in order to compare the results with previous investigations of Heinrich et al. (2012) on a catalyst coated micro channel. Thereafter methane was tested at 20 °C in a micro channel with a height of 0.50 mm. In order to examine the influences of the initial temperature and the micro channel height, the third test series was performed at a reactor temperature of 100 °C and in the last series a micro channel with a height of 1.00 mm was used. An overview of the operating parameters used for each series is shown in Table 1.

The temperature of the ceramic surface at the ignition moment is called micro ignition temperature in this contribution. The measured values are plotted as a function of the initial pressure in the Figures 3 and 4 using different symbols for each volumetric flow rate. If the artificial hotspot on the ceramic surface did not ignite the gas mixture, the highest measured hotspot temperature is plotted instead, using an unfilled symbol. Since the hotspot temperature was increased continuously, the region below the measured micro ignition temperatures can be considered as a safe operating region. In all experiments a decrease of the micro ignition temperature is observed at increasing initial pressure. At low initial pressures the explosive gas mixtures did not ignite even using the maximum laser power.

Table 1: Performed test series and used operating parameters.

Fuel gas	Initial temperature (T_0) in °C	Channel height (h) in mm	Initial pressure (p_0) in bar	Volumetric flow rate (\dot{V}) in mL min ⁻¹
Ethene	20	0.50	1.0; 3.0; 5.0; 10.0; 20.0	200; 350; 500
Methane	20	0.50	5.0; 6.0; 7.5; 10.0	200; 350; 500
Methane	100	0.50	3.0; 5.0; 6.0; 7.5; 10.0; 12.5	200; 350; 500
Methane	20	1.00	3.0; 5.0; 7.5; 10.0	200; 350; 500

The results show that the volumetric flow rate has little to no effect on the micro ignition temperatures. The error margin of the temperature measurement method is approximately ± 20 °C. All measurements show good reproducibility and the measured micro ignition temperatures of ethene/oxygen mixtures agree fairly with previous investigations of Heinrich et al. (2012) performed in a similar micro reactor with a total-combustion-catalyst coated channel with a height of 0.25 mm, at an initial pressure of 10 bar and an initial temperature of 320 °C. When the volumetric flow rate exceeded 500 mL min⁻¹ the temperature of a stationary hotspot on the catalyst surface began to increase rapidly until igniting the gas mixture at an absolute temperature of ca. 600 °C.

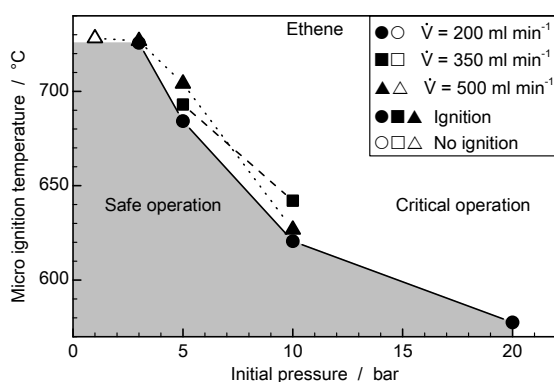


Figure 3: Measured micro ignition temperatures of 25 mol% ethene in oxygen at 20 °C reactor temperature and 0.50 mm channel height.

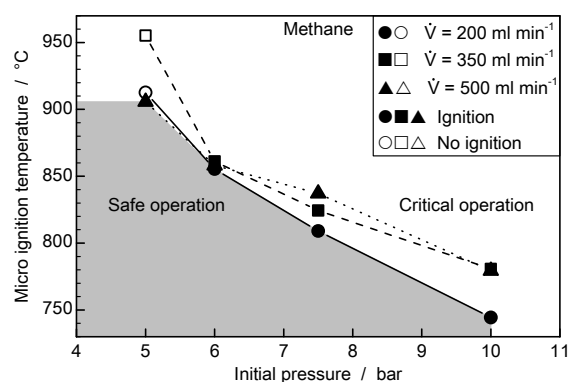


Figure 4: Measured micro ignition temperatures of 33 mol% methane in oxygen at 20 °C reactor temperature and 0.50 mm channel height.

The fact that the measured micro ignition temperatures of methane mixtures are distinctly higher than those of the ethene mixtures becomes clear by comparing the ordinates in the Figures 3 and 4. At 5 bar initial pressure the values differ from each other in about 200 °C. This difference decreases to a value of almost 100 °C at 10 bar. Since the experiment at an initial pressure of 20 bar provoked a detonation with pressure peaks greater than 1,000 bar and led to damaged measurement equipment and plant components, no further experiments at this pressure were conducted.

As shown in Figure 5, the initial reactor temperature has no measurable effect on the micro ignition temperatures in the investigated range. This was expected, since the hotspot temperature was generated almost exclusively by the laser energy, rather than the heat production of a chemical reaction. At 5 bar initial pressure and 100 °C initial temperature, the gas mixtures were ignited at all three volumetric flow rates. This was not the case at 20 °C initial temperature, where only the highest volumetric flow rate led to an ignition. The influence of the micro channel height is definitely larger than the measurement uncertainties. As illustrated in Figure 6, the micro ignition temperatures measured using a micro channel height of 1.00 mm are approximately 60 °C lower than those measured using a channel height of 0.50 mm.

Beside the ignition temperature, also the pressure development of the explosion propagation through the micro reactor and into both adjacent chambers was monitored. The eight piezoelectric pressure sensors were positioned in four pairs (see Figure 1) so that the explosion velocities in both sides of the micro reactor interior (inlet and outlet side) and in both chambers could be determined.

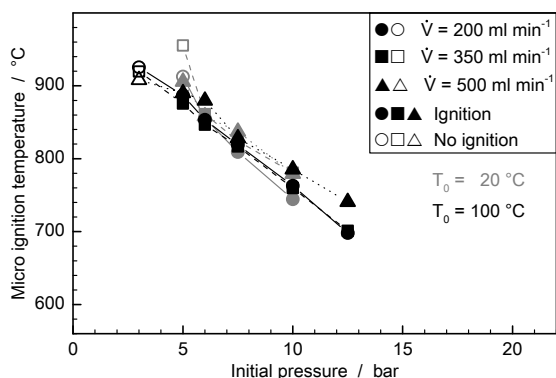


Figure 5: Measured micro ignition temperatures of 33 mol% methane in oxygen at different reactor temperatures and 0.50 mm channel height.

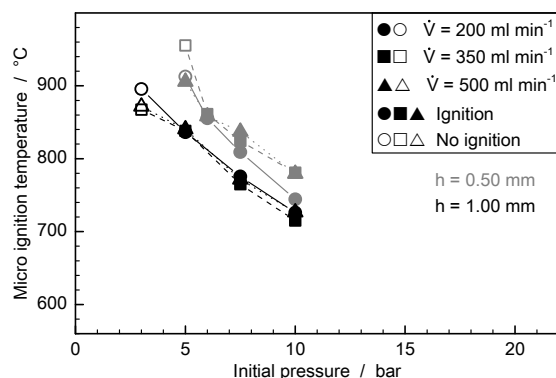


Figure 6: Measured micro ignition temperatures of 33 mol% methane in oxygen at 20 °C reactor temperature and different channel heights.

The results show an increase in explosion velocities with increasing initial pressure, as shown in Figure 7 and values about 100 m s^{-1} above the calculated Chapman-Jouguet velocities of a detonation under ideal conditions (dashed line), which is an indication for overdriven detonations. In the test series with ethene as fuel gas, the highest explosion velocities were always measured between the sensors 3 and 4, which is the sensor pair closest to the ceramic element. The measured velocities between the other three sensor pairs are very similar and move between $2,500 \text{ m s}^{-1}$ and $2,650 \text{ m s}^{-1}$. The influence of the volumetric flow rates on the measured explosion velocities is depicted in Figure 8. In the primary chamber a decrease of explosion velocity with increasing volumetric flow rate is observed.

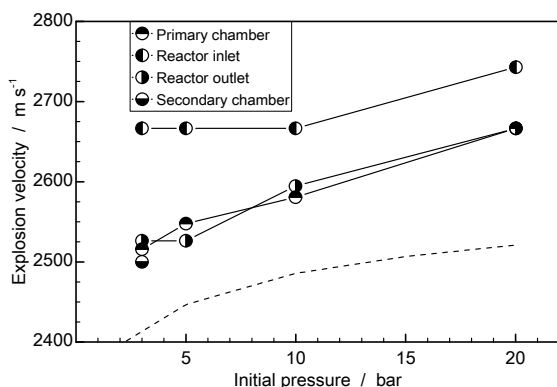


Figure 7: Explosion velocities of 25 mol% ethene in oxygen at 20 °C reactor temperature, 200 mL min^{-1} flow rate and 0.50 mm channel height.

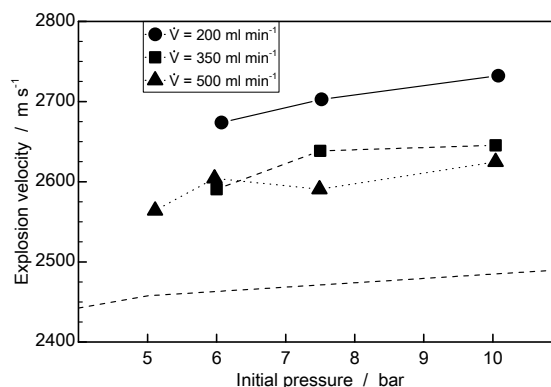


Figure 8: Explosion velocities of 33 mol% methane in oxygen at 20 °C reactor temperature and 0.50 mm channel height, measured in the primary chamber.

In the test series using methane as fuel gas, all four sensors inside the micro channel indicated a shock wave with overpressures of approximately 15 bar as shown in Figure 9, before the detonation started. This shock wave was always measured first at sensor 4, then almost simultaneously at the sensors 3 and 5 (which have similar distances to the ceramic element), and finally at sensor 6, where the transition to a detonation often occurred. The velocities of these shock waves were also determined and plotted in Figure 10. The results show an almost linear increase of the shock wave velocity with increasing initial pressure and a value of ca. 50 m s^{-1} higher at the reactor outlet side. The ignition of the gas mixture on the ceramic surface and the deflagration propagation starting from there and expanding in both directions, passing over the sensors 4 and 5 is illustrated in Figure 11.

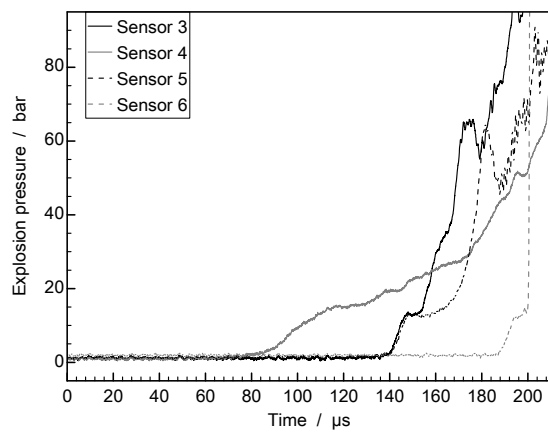


Figure 9: Pressure-time curves inside the micro reactor. (33 mol% methane, $p_0 = 10$ bar, $T_0 = 20$ °C, $\dot{V} = 200$ mL min^{-1} , $h = 1.00$ mm.)

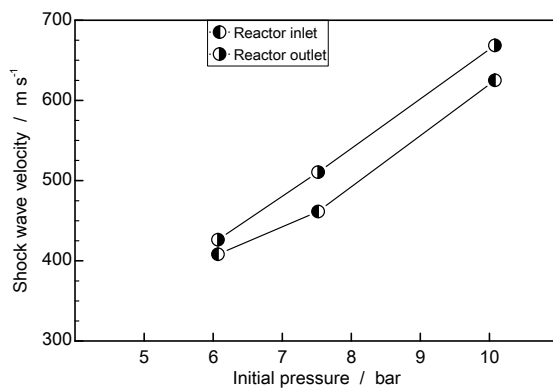


Figure 10: Shock wave velocities of 33 mol% methane in oxygen at 20 °C reactor temperature, 200 mL min^{-1} flow rate and 0.50 mm channel height.

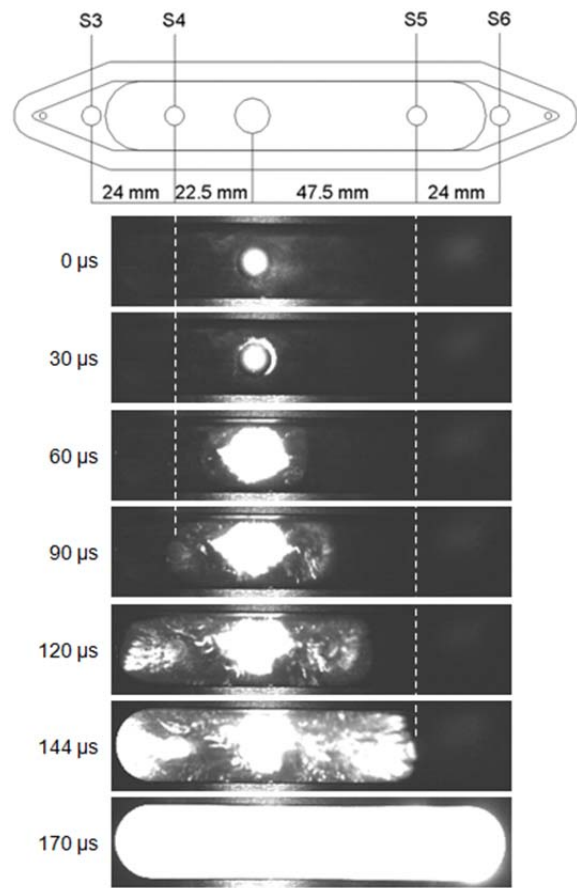


Figure 11: Explosion propagation inside the micro reactor. (33 mol% methane, $p_0 = 10$ bar, $T_0 = 20$ °C, $\dot{V} = 200$ mL min^{-1} , $h = 1.00$ mm.)

The temperature data from the recorded infrared images is plotted over the position on the reactor base plate in the Figures 12 and 13. Such plots show a constant increase of the hotspot temperature on the ceramic surface until an explosion is ignited. The data recorded moments after the explosion ignition is illustrated in Figure 13.

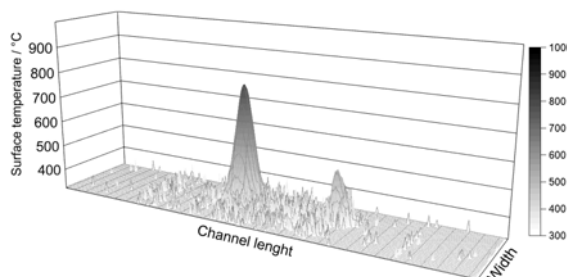


Figure 12: Micro channel temperature distribution 10 μs before ignition. (33 mol% methane, $p_0 = 10$ bar, $T_0 = 100$ °C, $\dot{V} = 500$ mL min^{-1} , $h = 0.50$ mm.)

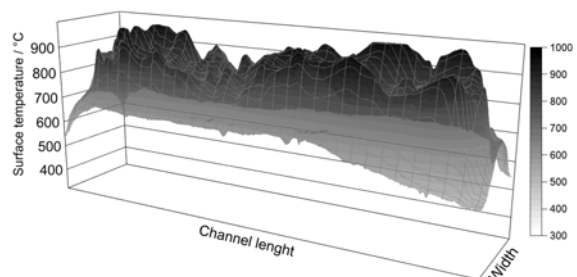


Figure 13: Micro channel temperature distribution at ignition. (33 mol% methane, $p_0 = 10$ bar, $T_0 = 100$ °C, $\dot{V} = 500$ mL min^{-1} , $h = 0.50$ mm.)

4. Conclusions

The safety of oxidation reactions operated within the conventional explosion region using micro reactors was investigated. An artificial hotspot was generated using laser radiation on a ceramic target inside of the micro channel. The ignition temperatures of stoichiometric fuel gas/oxygen mixtures with respect to total oxidation were measured and their dependencies on initial pressure, initial temperature, volumetric flow rate, and channel height were examined. The measured micro ignition temperatures are significantly higher than those determined in standard test procedures and show the conventional decrease with rising initial pressure. The results using ethene as fuel gas are fairly consistent with those of previous investigations (Heinrich et al., 2012) on a total-combustion catalyst. Using methane as fuel gas not only led to considerably higher micro ignition temperatures, but also to first-time recordings of the deflagration reactions inside a micro reactor prior to the detonation.

Acknowledgments

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