

Performance Characterisation of Catalytic Combustion with Liquid Hydrocarbons based on Temperature Measurements and Emission Analysis

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Abstract

Catalytic combustion of liquid hydrocarbons like diesel fuel shows a significant potential for the reduction of pollutant and acoustic emissions in several applications such as passenger cars, mobile homes and portable heating devices.

The present work shows the catalytic burner setup and the results of measurements using ShellSol D100 as a liquid fuel. The variation of combustion parameters like air-fuel ratio, thermal power, recirculation ratio and mixing temperature was used to determine the factors that significantly affect carbon monoxide emissions at reaction temperatures up to 950 °C on a noble metal catalyst. It was found that the residence time has the strongest effect on carbon monoxide emissions whereas the variation of the mixing temperature had a weak influence.

Introduction

The increasing public awareness about the interaction of air pollution and health demands low exhaust emissions as well as high combustion efficiency when consuming fossil and renewable fuels. One method for reduction of emissions is by applying catalytic combustion.

This paper analyses the effects of the heterogeneous catalytic combustion on carbon monoxide emissions. In the following section the experimental setup is described. Furthermore, the measurement procedure and conditions as well as the experimental results are analysed.

Experimental setup

Previously a catalytic burner concept has been developed [1] [3] and applied in the present research. This experimental setup is shown in Figure 1. A mass flow controller is used to regulate the amount of combustion air. Hot recirculated flue gas and air are mixed in front of an evaporator. This stream is fed with its mixing temperature (ϑ_{Mix}) to the evaporator and heats up the porous medium before it enters the reactor (mixing zone and catalyst).

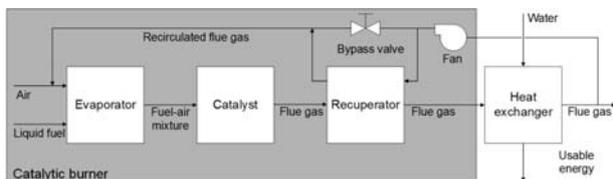


Figure 1: Schematic layout of the catalytic burner system

A piston pump supplies the liquid fuel to the evaporator and changes the fuel quantity by its pulse width. The fuel is converted from liquid to gas phase by using direct fuel evaporation in the porous medium. There heat can be transferred more easily to the liquid fuel which is supported by the huge surface area of the internal pore structure. Consequently, the evaporation energy of the liquid fuel can be provided by two heat

sources. Most of the evaporation heat is recuperated from the entire stream (combustion air and recirculated flue gas) and the other part is given by thermal radiation from the front side of the catalyst.

The gaseous hydrocarbons are homogenous premixed with combustion air and hot recirculated flue gas in the mixing zone of the reactor. This mixture enters the catalyst cross section with an evenly distributed mass flux to provide a uniform residence time. The mixture reacts on the catalytic active surface of noble metals. The reaction inside the ceramic monolith (honeycomb structure with $d = 2.5$ inch, $l = 10$ cm, cell density of 400 cps) is strongly exothermic. The temperature of the burner system is limited by the boiling point of the fuel on the one hand and by the maximum catalyst material temperature of 950 °C on the other hand. Therefore, it is inevitable to reduce the combustion temperature. Two ways are generally applicable to reduce the combustion temperature (reaction temperature) in this experimental setup: lean combustion or external flue gas recirculation. The latter one decreases the reaction temperature more efficient because of the 3-atomic gas (CO_2) in the recirculation flow. The recirculation rate is defined as follows:

$$\text{Recirculation ratio} = \frac{\text{Volume flow of recirculated gas}}{\text{Volume flow of flue gas}}$$

The catalyst is equipped with thermocouples placed inside small channels of the catalytic monolith. The flue gas flows through a cross-flow heat exchanger (recuperator) downstream of the catalyst, in which it is cooled down. Behind the recuperator the flue gas is finally cooled down to ~ 25 °C while condensing the water of the flue gas in the heat exchanger. One part of the flue gas flows to the chimney and leaves the system. The other part flows through the recuperator where it is heated up to temperatures between 550 °C and 750 °C. The independent variation of the recirculated flue gas temperature and mass flow rate are possible due to the use of an external variable bypass as well as a fan that is operating with variable speed.

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The catalytic oxidation operates at gas hourly space velocity (GHSV) of up to 84000 h^{-1} . The GHSV is calculated by the volume flow through the catalyst at standard conditions ($T = 273.15 \text{ K}$, $p = 1.013 \text{ bar}$) divided by the volume of the catalyst.

Measurement procedure, calculation and conditions

Temperatures of the reaction flow are measured on five different positions (Figure 2) along the flow direction of a small channel inside the catalytic monolith with honeycomb structure. These temperature measurements give information about the axial profile of the temperature caused by the local chemical reactions. The temperature is measured with 0.5 mm thermocouples (Type K). The measured gas phase temperature does not have to be corrected of radiation effects due to a high heat transfer coefficient inside the small catalyst channels. The temperature correction value is smaller than the accuracy of the thermocouple at the corresponding temperature. At the beginning of the measurement the thermocouples were positioned at the catalyst inlet. The burner was conditioned at the reference operating point ($P_{th} = 3 \text{ kW}$, $\lambda = 1.1$, $R = 0.8$, $\vartheta_{Mix} = 400 \text{ }^\circ\text{C}$) and the different stationary operating points were measured subsequently. After that the five thermocouples were moved 1 cm downstream during operation. The measurement starts again for each stationary operating point. This procedure was repeated until the thermocouples have reached the outlet of the catalyst.

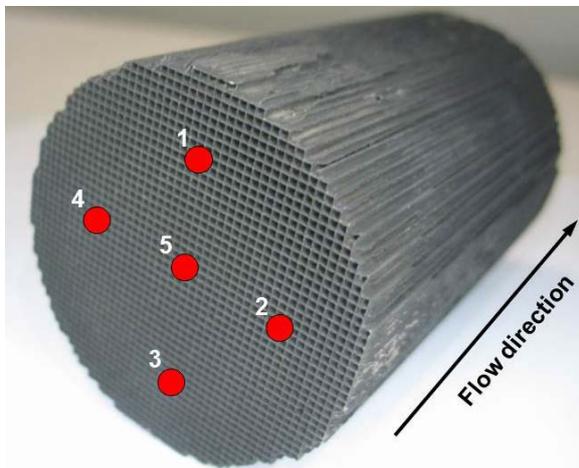


Figure 2: Position of temperature and exhaust gas measurements

The residence time inside a channel is calculated with the help of the measured temperatures and volume flows: combustion air and recirculated flue gas. A homogeneous mass flux distribution to the catalyst was assumed. The measurement error caused by the resistance of the thermocouple, that influences the mass flow and the velocity inside the channel, was neglected. The coated catalyst with a cell density of 400 cpsi has an average porosity of 0.66 [4]. Only a laminar flow is formed inside the small channels of the 400 cpsi

catalyst, because the Reynolds number is always lower than 200 .

The used liquid fuel ShellSol D100 [5] consists predominantly of C13 - C15 paraffins and naphthenes. The deep hydrogenation produces a solvent with very low aromatic and low fuel bond nitrogen content of 3.8 mg/kg . The fuel has a boiling point of around $264 \text{ }^\circ\text{C}$ [5].

Next, local exhaust gas emissions at the catalyst outlet and the reference point (RP) in the chimney were analysed. The probe positions (P1 - P5) of the exhaust gas analysis correspond to the radial position of temperature measurements. This exhaust gas analysis was performed for the same stationary operating points.

Experimental Results and Discussion

Figure 3 shows the temperature measurements inside the five catalyst channels for the reference operating point with a GHSV of 50000 h^{-1} . The catalyst inlet corresponds with the axial position 0 cm . On this axial position the temperatures have the smallest radial variation. Since the radial heat transfer is negligible the measured temperature at P5 along the flow direction is generally the highest.

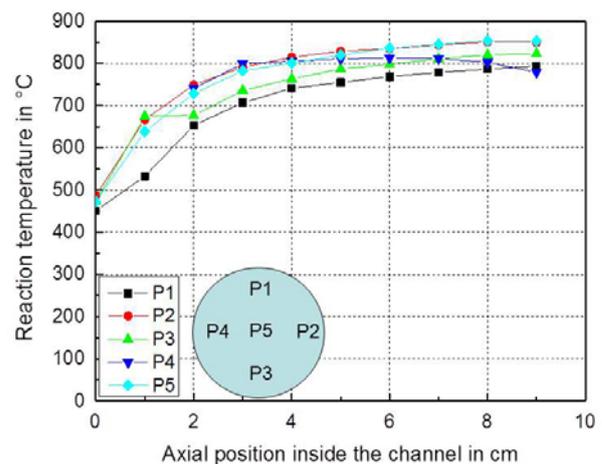


Figure 3: Reaction temperature at different radial and axial positions inside the catalyst channel for $P_{th} = 3 \text{ kW}$, $\lambda = 1.1$, $R = 0.8$, $\vartheta_{Mix} = 400 \text{ }^\circ\text{C}$

Figure 4 shows the measured carbon monoxide emissions according to DIN EN 267 [2] as a function of the air-fuel ratio for the reference operating point. Carbon monoxide emissions increase rapidly close to stoichiometry ($\lambda < 1.03$) because the oxygen amount is locally too small. As it can be seen in Figure 4, carbon monoxide emissions increase, since the residence time and the reaction temperature inside the catalyst fall, in connection to higher air-fuel ratio.

Figure 5 represents the averaged reaction temperature of the five measurement points along the flow direction inside the catalyst as a function of the thermal power. The first 2 cm behind the catalyst entrance a large positive temperature gradient is measured which flattens further downstream for the smallest thermal power. The temperatures at the catalyst

entrance are low, so that the reactions are limited by the kinetics [6]. Within the entrance length no influence on the mass transfer coefficient was found [7]. At high temperature laminar flows the mass transfer becomes rate-limiting to an increasing extent. In a hydrodynamic fully developed laminar velocity profile the transversal convective mass transport is insignificant [6]. At low thermal power very low carbon monoxide emissions exists, because the mass transport is ensured due to the high residence time at relatively high temperatures by diffusion.

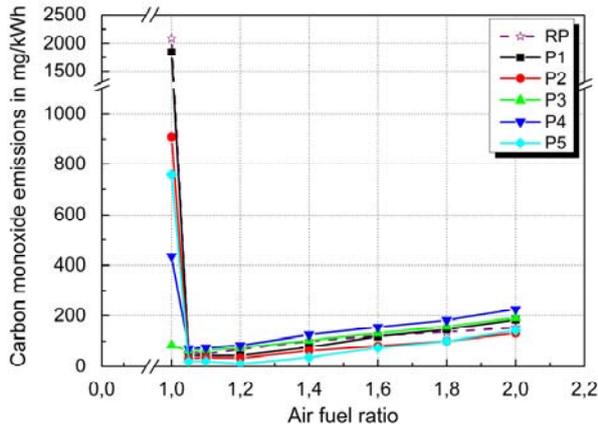


Figure 4: Carbon monoxide emissions as a function of the air fuel ratio for $P_{th} = 3 \text{ kW}$, $R = 0.8$, $G_{Mix} = 400 \text{ }^\circ\text{C}$

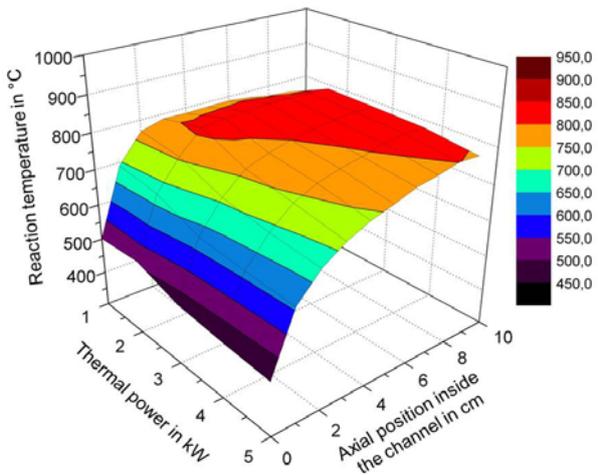


Figure 5: Average reaction temperature at different axial positions inside the catalyst channel as a function of the thermal power for $\lambda = 1.1$, $R = 0.8$, $G_{Mix} = 400 \text{ }^\circ\text{C}$

Increasing thermal power moves the maximum temperature level in flow direction (Figure 5) leading to higher carbon monoxide emissions (Figure 6). At these conditions the entrance length is approximately 13 mm. Despite of high reaction temperatures the carbon monoxide oxidation is incomplete due to the limited transversal mass transport caused by the laminar flow and short residence time inside the channel. However, at high reaction temperatures homogeneous post reactions (e. g. carbon monoxide oxidation) between the catalyst outlet and the recuperator inlet are possible because this

area is almost adiabatic. For thermal powers above 3 kW a significant increase in carbon monoxide emissions is found.

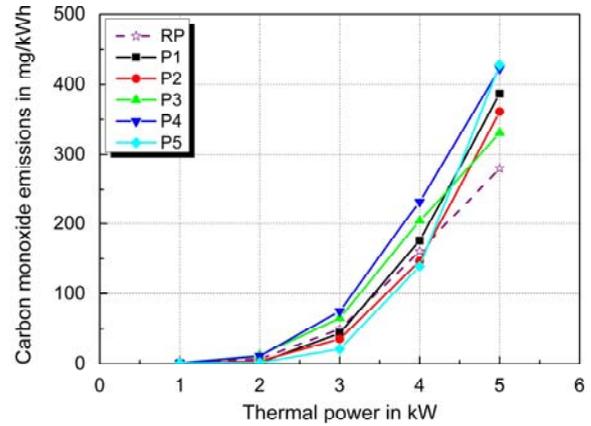


Figure 6: Carbon monoxide emissions as a function of the thermal power for $\lambda = 1.1$, $R = 0.8$, $G_{Mix} = 400 \text{ }^\circ\text{C}$

Figure 7 visualises the averaged reaction temperature along the flow direction inside the catalyst as a function of the mixing temperature. The rising mixing temperature increases the enthalpy of the constant inlet mass flow and therefore the maximum reaction temperature. In contrast, the influence of the temperature gradient ($\Delta T/\Delta x$) behind the catalyst entrance is negligible solely because the light-off temperature inside the catalyst is already exceeded.

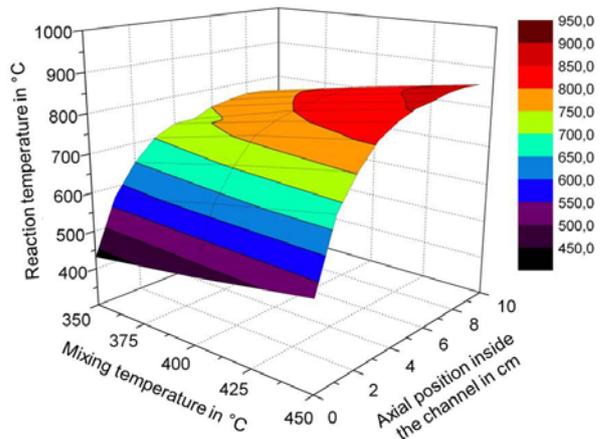


Figure 7: Average reaction temperature at different axial positions inside the catalyst channel as a function of the mixing temperature for $P_{th} = 3 \text{ kW}$, $\lambda = 1.1$, $R = 0.8$

As depicted in Figure 8, a higher mixing temperature tends to result in smaller amounts of carbon monoxide emissions because the reaction rate increases with higher reaction temperatures.

Figure 9 illustrates the averaged reaction temperature along the flow direction inside the catalyst as a function of the recirculation ratio. The temperature has already reached its maximum 4 cm behind the catalyst entrance with the smallest recirculation ratio of 0.75. This operating point has also very low carbon

monoxide emissions due to the high residence time at high temperatures.

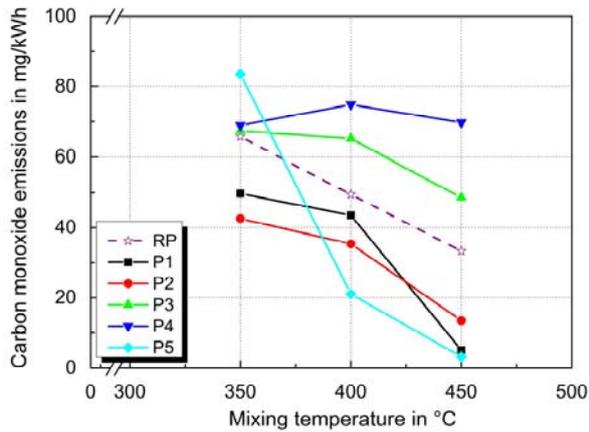


Figure 8: Carbon monoxide emissions as a function of the mixing temperature for $P_{th} = 3 \text{ kW}$, $\lambda = 1.1$, $R = 0.8$

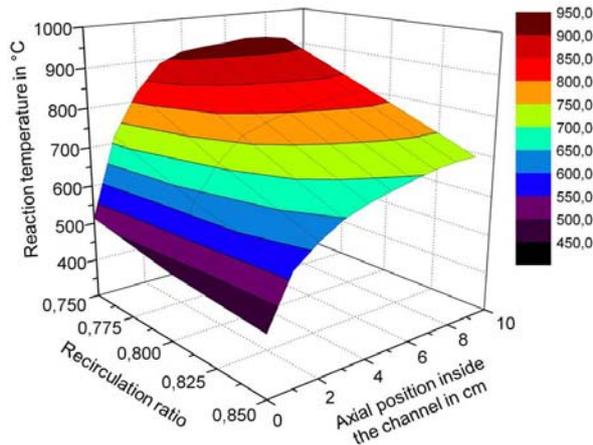


Figure 9: Average reaction temperature on different axial positions inside the catalyst channel as a function of the recirculation ratio for $P_{th} = 3 \text{ kW}$, $\lambda = 1.1$, $\vartheta_{Mix} = 400 \text{ °C}$

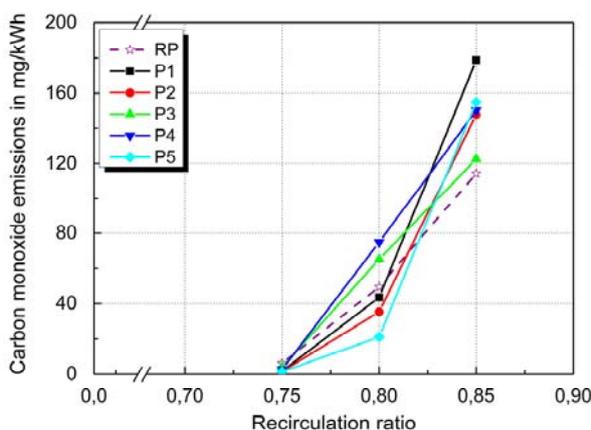


Figure 10: Carbon monoxide emissions as a function of the recirculation ratio for $P_{th} = 3 \text{ kW}$, $\lambda = 1.1$, $\vartheta_{Mix} = 400 \text{ °C}$

The variation of the recirculation ratio from 0.75 to 0.85 (Figure 10) results in a temperature drop of 200 K and a shorter residence time of around 28 %. Hence, low temperatures in the catalyst result in higher carbon monoxide emissions due to small reaction rates.

Figure 11 shows the carbon monoxide emissions at the catalyst outlet without homogeneous post reactions as a function of the averaged axial reaction temperature and the corresponding residence time of the channel.

The influence of the averaged reaction temperature on the carbon monoxide emissions of the heterogeneous catalysis is quasi linear. In contrast, the calculated residence time exhibits an exponential behaviour on carbon monoxide emissions.

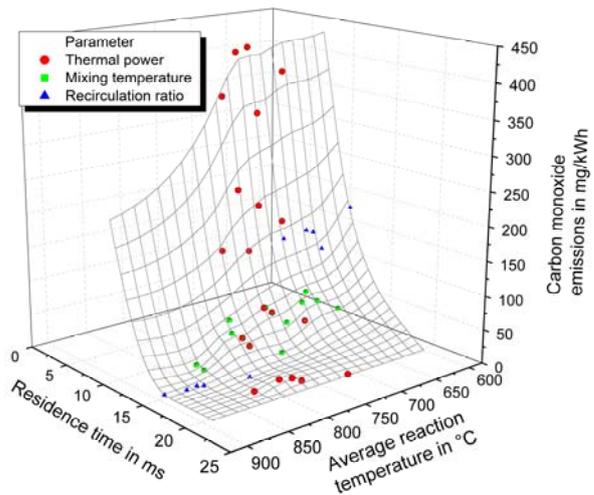


Figure 11: Carbon monoxide emissions as a function of the average axial reaction temperature and the residence time

Summary and Conclusion

The paper describes the performance of the catalytic combustion on the basis of heterogeneous reactions with the liquid hydrocarbon ShellSol D100. Therefore, temperature measurements inside the channel of the catalytic honeycomb monolith and emission analysis at the catalyst outlet were performed. A wide operational range in terms of air-fuel ratio, mixing temperature, recirculation ratio and thermal power was investigated.

The carbon monoxide emissions increase exponential with respect to the residence time since heterogeneous catalysis is limited by the mass transport at the high temperature laminar flow. At high catalyst outlet temperatures homogeneous post reactions are possible. The effect of the catalyst inlet temperature with regard to carbon monoxide emissions is small because the temperature of the air fuel mixture has exceeded the ignition temperature.

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