EMISSIONS FROM COMBUSTION OF H₂ AND CH₄ MIXTURES IN CATALYTIC BURNERS FOR SMALL-SCALE HEAT AND POWER APPLICATIONS

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Lean premixed fuel mixtures of hydrogen and methane are tested in two different burners developed at The Norwegian University of Science and Technology. The burners include a catalytic burner and a catalytically supported porous inert media burner, both using commercial catalysts. The thermal loads are varied up to 15 kW. Measurements performed of CO₂, O₂, NOₓ, and CO in the flue gases verify very low emission levels. The catalytic burner shows severe loss of activity during long-term testing, whereas the catalytically supported burner indicates long-term durability. Applications for such burners could be clean and efficient small-scale combined-heat-and-power systems, either in combination with fuel cells or in Stirling engines.

Keywords: NOₓ, Catalytic burner, Combustion, Methane, Hydrogen

INTRODUCTION

The commercial DO-6 and DO-12 catalysts (from Sued Chemie) are tested as catalytic burners. The DO-12 is also used as an inlet region in a porous inert media (PIM) burner. Both types are ceramic honeycomb monoliths with an alumina-based washcoat. The DO-6 with platinum (Pt) and the DO-12 with both platinum and palladium (Pd) have been used as 400 cells per square inch (cpsi) honeycombs.

Since oxidation of methane requires an initial catalyst temperature of at least 450°C, the approaches considered for ignition are preheating of the air, start up by hydrogen oxidation, or by both combined. The initial temperature requirement compares to the temperatures found in ignition curves of hydrogen-assisted catalytic combustion of methane (Deutschmann, 2000). When the methane is being completely oxidized, the amount of hydrogen or preheat may be lowered.

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EXPERIMENTS

The experimental setup of the catalytic burner (CB) is seen in Figure 1. The squared catalytic monoliths were placed at the inlet of an insulated combustion chamber. The catalytically supported PIM burner (CSB) is shown in Figure 2. The CSB has a catalytic inlet and is also compared to a PIM reference burner (RB), which does not have the catalytic inlet. Such PIM burners have been presented, i.e., by Trimis and Durst (1996) and Zepter and Hustad (2001). The CB and CSB are ignited by the use of lean hydrogen ignition (possibly preheated) on the catalyst, whereas the reference burner was ignited by a torch on top. The composite material in the squared 100-mm long main part of the burner is corrugated ceramic fibers (Al₂O₃/SiO₂), which provide enhanced heat transport. The 12-mm long inlet section for the CSB is the DO-12 catalyst, whereas the inlet section for the RB consists of a perforated ceramic tile. Some measurements are also performed for the CSB after a 600-mm long combustion chamber with inner diameter of 200 mm. This chamber is not insulated and is cooled by radiation and free convection only.

The thermocouples used for temperature measurements were both K (0.5 mm, encapsulated) and S [0.2 mm, coated as recommended by Kent (1970)] types. Because the thermocouples are enclosed within the burner, no radiation corrections are made. The gas sampling was done by two water-cooled steel probes in the centerline of the burners. The response time for gas sampling was on the order of seconds. NOₓ was measured with a chemiluminiscent analyzer (Signal NOₓ, Series 4000) on a wet basis with a heated sampling line, while the sampling line for CO (H&B Uras 3G), O₂ (Sybron, Series 500), and CO₂ (H&B Uras 10P) included a cooler and Drierite (CaSi) to remove the water. The calibra-

![Figure 1: Schematic illustration of the catalytic burner from The Norwegian University of Science and Technology (NTNU).](image-url)
tion gas used for the NO\(_x\) measurements was 29.8 ppm NO mixture in N\(_2\), whereas the calibration gas for the CO measurements was 83 ppm CO mixture in CO\(_2\) and N\(_2\). The concentrations of both CO and NO\(_x\) are given in ppm (dry) at 3\% O\(_2\) (dry) throughout.

**RESULTS AND DISCUSSIONS**

In the CB, both catalysts were found to completely oxidize pure hydrogen in air in the range of 1–8 vol.% H\(_2\) of the total flow. The Reynolds numbers based on the hydraulic diameter in the channels confirm laminar flow in the CB, and the measured temperatures were close to the adiabatic temperatures for the catalytic combustion of hydrogen. For the DO-6, it was found difficult to ignite and completely oxidize the methane, and a factor of about 3 is needed for a volume of H\(_2\) versus CH\(_4\). The DO-12 is found to be more flexible in terms of completely oxidizing various fuel compositions, and therefore the focus was placed on this catalyst. A new DO-12 was, after ignition, found to steadily oxidize, i.e., 4.6 vol.% CH\(_4\) in an air stream preheated to 350\(^\circ\)C, but is not found to be flexible in terms of steadily oxidizing while changing the flow rates. Preliminary testing indicates that whether the catalyst is heated by preheated air or by added hydrogen, it does not have a large impact on the CH\(_4\) conversion during ignition. At

![Schematic illustration of the catalytically supported PIM burner from NTNU. The inlet region consists of a catalytic honeycomb.](image)

**FIGURE 2** Schematic illustration of the catalytically supported PIM burner from NTNU. The inlet region consists of a catalytic honeycomb.
the low flow rates used (50 Nl/min) in the CB, the maximum preheat temperature was 450°C immediately before the catalyst. When CH₄ is flowing over the catalyst at these conditions, no conversion was observed. With the use of H₂, or combined H₂ and preheat, ignition of CH₄ was observed at about 550°C for the DO-12. At somewhat lower temperatures, initial CH₄ ignition could be observed by both CO₂ and temperature measurements, followed by extinction. For complete conversion of CH₄, the temperature in the flue gases immediately downstream of the catalyst was close to 1000°C. The actual maximum temperatures on the catalyst surface could, in these cases, be about 150°C higher than the measured flue-gas temperatures. These temperatures necessary for complete conversion of methane are, in general, higher than recommended for such catalysts (Ahlstrom-Silversand, 1996), which indicates a loss of activity. A long-term test of 8 h for pure CH₄ at an excess air ratio of 2.1, preheated to 350°C and with a thermal load of 1.3 kW, gave constant values of both $T_{\text{exhaust}}$ at 1040°C and $T_{\text{surface}}$ at 1210°C. However, severe loss of activity was indicated by resistance toward reignition afterward. Slightly lowered temperatures and emissions could have been obtained by reducing the preheat temperature after CH₄ ignition, but for consistency it was kept constant. In Figure 3 both the NOₓ and CO emissions are given for the long-term test. Low levels of emissions of NOₓ and CO both at about 8 ppm are verified. However, the CO concentration is slightly increasing up to 14 ppm with time. After the 8 h experiment a standard CO chemisorption test was performed for this catalyst, given that the dispersion was reduced to 1.95%, compared to 6.65% for a briefly ignited catalyst. For the chemisorption test, the weight percent of both metals was assumed to be 1% and the stoichiometric factor of CO on metal is set to 1. Complete conversion of CH₄ is verified through CO₂, O₂, and also unburned hydrocarbon measurements, while the measured tem-

![FIGURE 3](image)

FIGURE 3 Concentrations of CO and NOₓ during a long-term test over 8 h for the CB.
peratures are below adiabatic temperatures. Other fuels, such as methanol and propane, are both tested to ignite at far lower temperatures compared to methane in the CB burner.

Because of the large reduction of activity at these temperatures for the CB burner, the CSB burner was developed. The values at the two first positions in Figure 4 represent temperatures immediately before and after the catalytic inlet region. Although the maximum CSB temperatures will be higher, it is seen that the temperatures on the actual inlet catalyst is kept lower than the 1000°C recommended in (Ahlstrom-Silversand, 1996). The catalyst could also be reignited after the experiments. However, even for this configuration, this temperature should be monitored because lowering of the excess air ratio (see Fig. 4) and also the ther-
A further development of the CSB should thus include a flame arrestor or a heat shield downstream of the catalyst. One major advantage for the CSB versus the RB is the ignition procedure, where the H₂ in CSB may be used to heat the burner and light off the methane without need of further igniting. When comparing the emission of CO from the CSB to the RB in Figure 5, a small decrease in CO is observed at the three different thermal loads. The increased CO with increasing thermal load is caused by the reduced residence time. For the measured NOₓ concentrations at the three thermal loads given in Figure 6, only small deviations are found for these two burners. This is in agreement with Cerri et al. (2000), stating that the NOₓ is not significantly affected by the presence of the catalyst in their experiments on a catalytically supported PIM burner.
Another approach for lowering both NO\textsubscript{x} and CO emissions in the CSB can be hydrogen enrichment. Experiments with substitution of some CH\textsubscript{4} with H\textsubscript{2} at constant \(\lambda\) and thermal load were carried out. In these experiments both 10\% and 20\% of H\textsubscript{2} in the CH\textsubscript{4} were found to lower CO emissions slightly (as seen in Fig. 7). The subsequent oxidation in the combustion chamber, however, reduces the measured CO far more. The measured concentrations of NO\textsubscript{x} for the same cases in Figure 8 show no clear reduction for hydrogen enrichment. Increased NO\textsubscript{x} emissions in the combustion chamber are also shown in Fig. 8. Although no clear reduction in the NO\textsubscript{x} emissions is found for the CSB compared to the RB, the CSB is very flexible in terms of steady oxidizing of the fuel over a large thermal-load span, assuming that both H\textsubscript{2} and CH\textsubscript{4} are available. For very low thermal loads, sole H\textsubscript{2} may be burned at low temperatures, indicating zero emissions. For higher thermal loads, CH\textsubscript{4} could be oxidized with very low emission values. This flexibility could be favorable in CHP systems based on H\textsubscript{2} and CH\textsubscript{4} availability.

The emission values in Figs. 3–8 are comparable to the ones predicted by Forzatti and Groppi (1999) for pressurized catalytic combustors. These values are also in the lower end of the values presented by Cerri et al. (2000).

CONCLUSIONS

A low-emission catalytic burner for methane and hydrogen with the use of a commercial catalyst is presented. Because of the high temperatures required for complete conversion of the methane, severe loss of activity was found, and the burner is not flexible toward changes in the flow rates. A more promising cata-
lytically supported PIM burner shows low emission concentrations of both NO\textsubscript{x} and CO and is also more flexible toward changes in both excess air ratios and flow rates. The advantages of the catalytically supported burner compared to a reference PIM burner are (i) slightly reduced CO, (ii) much easier ignition, and (iii) increased flexibility toward thermal-load variations.

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**References**


