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CATALYTICALLY STABILIZED COMBUSTION OF CH_4 IN ZERO EMISSION PROCESSES

Markus Wolf, Timothy Griffin, Richard Carroni, Dieter Winkler, Christoph Appel*, John Mantzaras*

ALSTOM Switzerland /Technology Center, Segelhof 1, CH-5405 Baden-Dättwil, Switzerland
** Paul Scherrer Institute (PSI), Combustion Research, CH-5232 Villigen-PSI, Switzerland*

ABSTRACT

A number of Zero Emission Power (ZEP) concepts for gas turbines mitigate NO_x and CO_2 emissions by combusting natural gas/oxygen mixtures with large quantities of recycled exhaust gas (CO_2 and H_2O). The resultant high degree of dilution narrows considerably the stable combustion operation window, which can again be extended by the addition of an upstream catalytic combustion stage. Therefore, we have chosen a concept consisting of an upstream heterogeneous followed by a subsequent homogeneous combustion zone. The catalytic stage is fed with a fuel-rich methane oxygen mixture and stabilizes the highly-diluted downstream gaseous flame by producing syngas. The goal is to maximize the hydrogen yield in the catalyst. Kinetic modeling can help to develop such a catalyst by analyzing which system and operational parameters have the greatest impact on syngas selectivity.

Key Words: Partial Catalytic Oxidation, Exhaust Gas Recycle, Zero Emission Power, Water reforming, Catalyst loading, Gas Turbine Power

INTRODUCTION

Due to the increasingly stringent emission regulations, including future restrictions on CO_2 emissions for power plants, new combustion processes must consider further reduction or – even better– nearly zero emission strategies. A number of zero emissions gas turbine concepts [1] are based on near stoichiometric natural gas combustion in a pure oxygen stream produced by the continuous separation of air in a metal-oxide-based membrane. In this way the exhaust stream contains primarily CO_2 and H_2O, which eases CO_2 capture. Dilution of the fuel/oxygen mixture by recycled exhaust gas (ZEP mixtures: up to ~27% CO_2 and ~55% H_2O per vol.) is performed to control temperatures within the combustion chamber. Another positive side effect of combustion in oxygen rather than air is the avoidance of NOx formation at high temperatures. Although ZEP concepts do not necessarily require catalytic combustion, this approach has been shown to extend the operating window significantly, given the inhibitory effect of the large amounts of water (> 50% per vol.) on homogeneous ignition [1].

The choice of the catalyst depends on the operating conditions. While in fuel-lean or stoichiometric ZEP combustion Pd and Pt catalysts are preferred, in fuel-rich ZEP combustion other catalysts, such as Rh or Ru are widely considered to be most active. The unsuitability of Pd and Pt under stoichiometric ZEP conditions ($\lambda \sim 1$) has been documented previously [2]. The dominant reaction pathway at fuel-rich/air conditions is the partial oxidation (POX) of methane (main component of natural gas). Under ZEP conditions the contributions of the water-gas-shift (WGS) and reforming reactions become more dominant due to the high water content. Both the POX and reforming reaction form syngas (CO and H_2). While the complete and partial oxidation of methane (POX) are exothermic reactions leading to a strong and rapid increase of the catalyst surface temperature, the reforming reaction, due to its endothermicity, can limit the surface temperature rise. Under ZEP conditions, the endothermic reforming reaction that kicks off above a certain temperature prevents overheating and damage of the catalyst. In order to stabilize the downstream gaseous combustion, a catalytic system and optimized operation conditions must be found that guarantee a low catalytic light-off temperature and a large syngas yield with high hydrogen selectivity. Numerical studies are presented that analyze the optimum boundary conditions for the catalyst and help to design a catalytic monolith, which demonstrates high hydrogen selectivities. Details on ZEP processes, accompanied with experimental and numerical investigations can be found in [2] and [1].

METHOD OF APPROACH

The reactor configuration used in experiments and simulations [1,2] has a monolithic structure, which comprises a multitude of channels (length 75 mm, diameter of the monoliths used 35 mm) each coated with a technical catalyst. Simulations were carried out under gas-turbine relevant conditions. Further information on the reactor configuration and on high-pressure test rig can be found in [3].