

ROLE OF CATALYTIC STAGE IN A LOW NO_x HYBRID GAS BURNER

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Abstract

An extensive experimental campaign was carried out on a prototype hybrid radiant burner with ultra low emissions based on the novel concept of fuel-rich catalytic + homogeneous flame combustion with interstage heat transfer. Special attention was paid to the impact of two alternative active formulations for the catalytic partial oxidation stage (0.5% Rh and 0.25-0.25% Rh-Pt on γ -Al₂O₃) on the general performance of the burner, and particularly on its NO_x emissions. Experimental evidence of the reduction of both thermal and prompt NO_x is presented.

Introduction

Due to the increasing use of natural gas (NG) to meet the world's energy demand, large research efforts are devoted to the reduction of NO_x emissions and increase of safety and efficiency in NG combustion appliances at both industrial and domestic level [1]. Currently, both industrial and utility gas turbine manufacturers prefer lean-premixed combustion technology which has demonstrated the ability to achieve an impressive reduction in NO_x emissions during operation on natural gas [1]. A similar picture is also valid for non-adiabatic burners for domestic and industrial applications. As flame temperatures are reduced to achieve low levels of emissions, flame stability and safety issues may arise [1]. Recently we have adapted the concept of fuel-rich catalytic combustion [1] proposing a novel staged hybrid catalytic gas burner, with integrated interstage heat removal by IR radiation from the hot catalytic reactor/radiator [2]. In this work we set out to study the impact of two catalytic formulations (namely 0.5 % Rh and 0.25-0.25% Rh-Pt on γ -Al₂O₃) on the main features and NO_x emissions performance of the prototype hybrid burner in its simplest configuration with a purely diffusive secondary flame.

Experimental

Structured catalytic elements were prepared starting from a metallic gauze made of a high temperature FeCrAlloy knitted wire ($d \approx 120 \mu\text{m}$) in the form of flexible cylindrical sockets (external diameter $D=80\text{mm}$, effective height $H=80\text{mm}$, thickness 2mm, apparent density 0.38 g/cm^2). The substrates were washcoated with La₂O₃-stabilised γ -Al₂O₃ (SCFa140-L3 Sasol, $140\text{m}^2/\text{g}$.) applied by a dip-coating procedure (loading of $\sim 7\%$ wt.) [2]. SEM observation of the coated FeCrAlloy gauze revealed the presence of a well adhering porous layer on the metallic wire

with an average thickness in the range 7-14 μm . Monometallic Rh and bimetallic Rh-Pt catalysts were prepared via incipient wetness impregnation onto washcoated FeCrAlloy gauzes using aqueous solutions of Rh $(\text{NO}_3)_3$ and H_2PtCl_6 to achieve a total PM loading of 0.5 %wt. (metallic wire excluded).

The hybrid catalytic burner under typical operation together with a rendering of its longitudinal section are presented in Figure 1: the fresh gas mixture flowed radially through a distributor, the CPO gauze reactor and then into the flame [2]. The hybrid burner was tested in upward position and secondary air for flame combustion was withdrawn by natural convection from the surroundings. The burner was operated at atmospheric pressure on methane in the 4 – 30 kW^{th} power (P) range, at varying the feed equivalence ratio ϕ from 2.0 to 3.6.

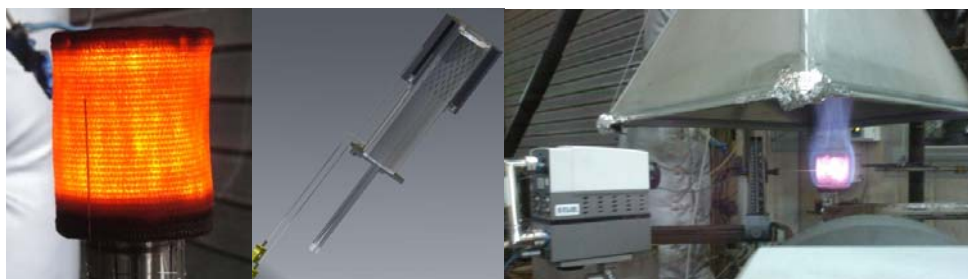


Figure 1. Picture of the catalytic combustion head under typical operation (left), rendering of its longitudinal section (centre), and view of experimental set-up for IR thermography (right).

Two FLIR thermocameras were employed to investigate the hybrid burner: a Phoenix with digital acquisition system, and a SC500, respectively with spectral sensitivities in the range 1.5-5 μm and 7.5-12 μm . Optical spectral filters centred at 3.4 or 3.9 μm were applied on the Phoenix camera in order to eliminate flame (gas) emissivity when measuring the surface temperature of the catalyst; a further filter at 4.25 μm was used to estimate CO_2 (flame) temperature. The temperature of the syn-gas emerging from the catalytic stage was measured with a shielded K-type thermocouple placed 1 mm downstream from the catalyst surface and parallel to it. Gas analysis was performed in real time with ABB instruments equipped with ND-IR/-UV, TC and paramagnetic detectors (respectively for CH_4 , CO , CO_2 ; NO , NO_2 ; H_2 ; O_2). The effluent gas from the catalytic partial oxidation stage was sampled with a cooled stainless steel probe in close contact with the surface of the catalytic gauze. Exhaust gases from the burner were collected by a hood and the emissions of CO , NO_x and CH_4 were corrected to 0% O_2 conditions.

Results and Discussion

IR analysis of the hybrid burner (Fig. 2) showed the presence of an axial-symmetric laminar diffusive flame structure surrounding the hot radiating catalytic

reactor, which had a very uniform temperature distribution on the whole outer surface. The flame itself, which appeared blue and had a low-luminosity, was found to be non-sooting, as confirmed by careful inspection of IR images collected at $F=3.9\mu\text{m}$ in the gas phase surrounding the burner (Fig.2 b). Hot gas leaving the combustion head through the catalytic gauze were slightly colder than the catalyst itself. This was also confirmed by the thermocouple measurements [2] and implies that, inside the structured catalytic layer, heat generation occurs through surface oxidation reactions and the flowing gases are only heated by convection. Thereafter T_{gas} raised to a maximum in correspondence of a symmetric laminar diffusion flame front developed around the burner and above it, which was well captured by CO_2 profiles ($F4.25\mu\text{m}$). The laminar flame envelope expanded at higher power (and lower ϕ), due to the corresponding higher flow rate and exit velocity of the gas leaving the catalytic head in the radial direction. It is also clear that the flame front extended well above the catalytic head, due to the poor mixing effectiveness with secondary air achieved by natural convection.

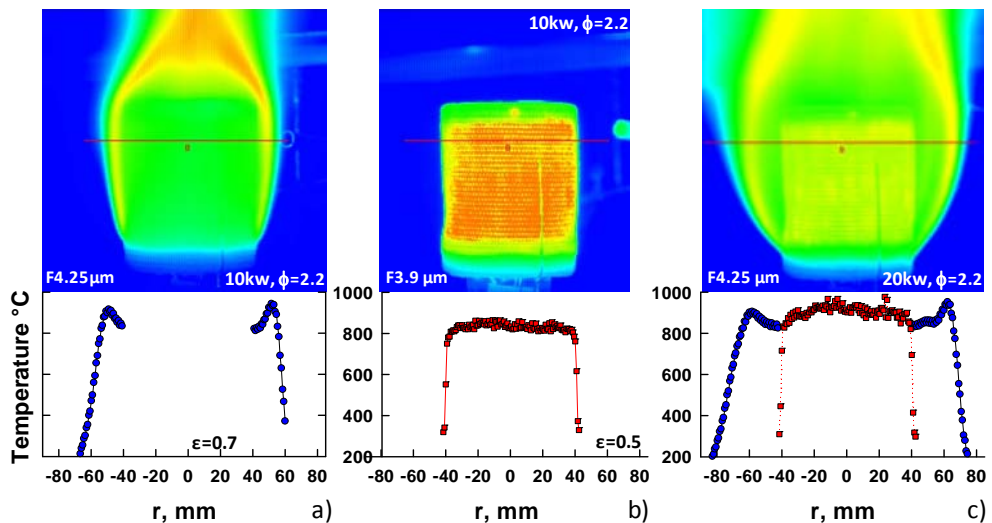


Figure 2. InfraRed images of the flame structure (CO_2) and of the catalytic surface collected at $4.25\mu\text{m}$ and $3.9\mu\text{m}$ respectively, together with the corresponding temperature profile at fixed height along the line. Rh catalyst operated at $\phi=2.2$: a) $P=9.6\text{kW}$, $F=4.25\mu\text{m}$; b) $P=9.6\text{kW}$, $F=3.9\mu\text{m}$; c) $P=19.2\text{kW}$, $F=4.25\mu\text{m}$.

The hybrid catalytic burner performs a staged combustion, and is characterized by interstage heat transfer by IR radiation from the hot catalytic head to a heat sink. By this way the peak temperature reached at the diffusion flame front can be strongly reduced. This is shown in Figure 3 a-b which reports the temperatures measured on the outer surface of the two catalytic gauzes as a function of ϕ and for 3 nominal power levels, together with the corresponding adiabatic flame

temperatures calculated from the measured composition of the syn-gas leaving the catalytic stage. For both catalysts the outer surface temperatures were comprised in the range 650°C - 1050°C, strongly increasing with decreasing ϕ , due to a larger availability of the limiting reactant (oxygen) for the heterogeneous oxidation reactions. Higher temperatures were also measured at constant ϕ for a higher nominal power (i.e. flow rate) to the burner: this is a well recognized feature of non-adiabatic CPO reactors, because heat loss does not scale with flow rate as long as the contact times are adequately long to maintain full O₂ conversion [3].

From Figure 3 it appears that the bimetallic catalyst always ran 50-100°C hotter than its monometallic Rh counterpart at any fixed P level. It was already reported that substitution of half of the Rh loading with same weight amount of Pt entails a significant increase in the operating temperatures of methane CPO monoliths, since reactions leading to total oxidation products become more important on Pt [4].

The adiabatic flame temperature of the syn-gas follows an opposite trend with respect to the catalyst temperature (Fig. 3a,b), progressively decreasing for lower ϕ values, as a consequence of the larger quantity of heat transferred by radiation from the hotter catalytic surfaces. However, at fixed ϕ , the adiabatic flame temperature increases with the nominal input power due to a reduction in the percentage of heat loss from the CPO reactor.

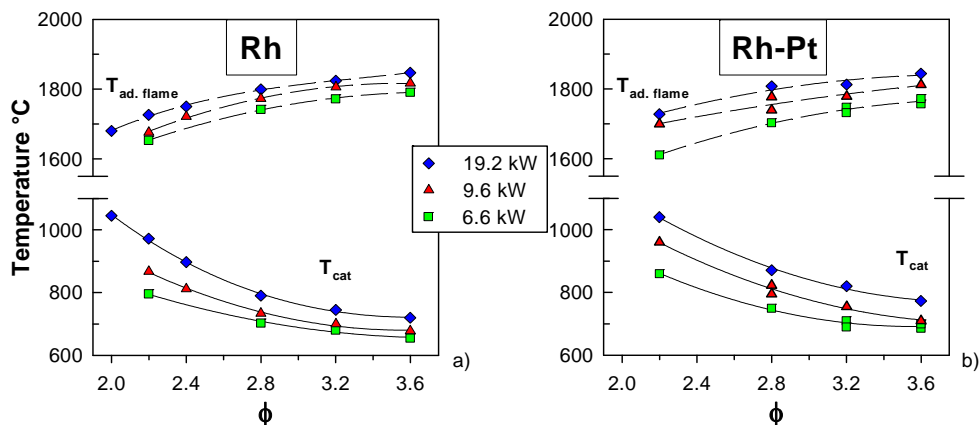


Figure 3. Temperature of the outer catalytic surface and corresponding adiabatic flame temperature of the emerging syn-gas for Rh (a) and Rh-Pt (b) catalysts as a function of ϕ at different power levels.

Since no evidence of NO_x formation could be detected at the exit of the catalytic partial oxidation stage, NO_x emissions from the hybrid burner are only due to the homogeneous flame combustion stage: in the simple current configuration, syn-gases emerging from the catalytic gauze were burned under purely diffusive and laminar conditions. For both catalysts NO_x emissions (Figure 4a,b) decreased almost linearly with decreasing ϕ , following the same trend of the adiabatic flame temperature of the syn-gas. Moreover, along with the general increase in the flame

temperature levels with the nominal power, also NO_x emissions increased, ranging from 10 to 60 ppm and from 10 to 80 ppm for Rh and Rh-Pt catalysts respectively. In fact, at any fixed power level, monometallic Rh catalyst guaranteed a significant reduction in NO_x emissions over its bimetallic counterpart. As a general figure, the emissions of NO measured at the exhaust of two commercial burners, a fully premixed lean surface stabilized device and a blue-diffusive turbulent flame one, ranged respectively between 20 to 60 ppm and 80 to 120 ppm, when operated with their optimal excess of air between 20 and 30% [2].

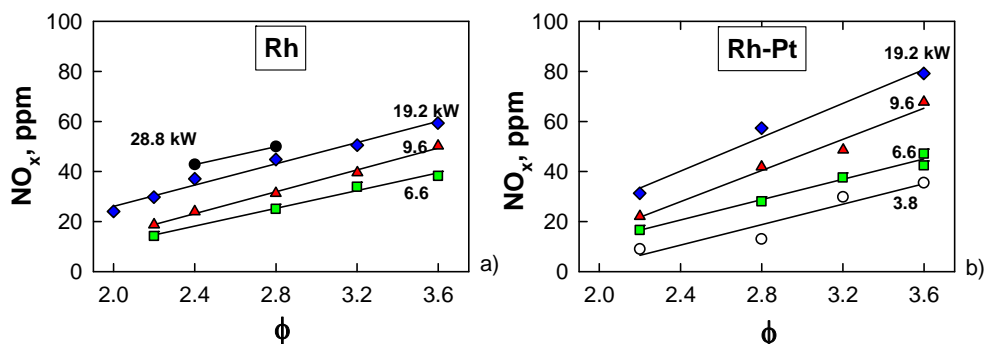


Figure 4. Total NO_x emissions corrected @0% O_2 from hybrid burner with Rh (a) and Rh-Pt (b) catalyst as a function of ϕ at different power levels.

Previous studies on syn-gas combustion in non premixed flames reported that the contributions of thermal and prompt mechanisms to total NO_x are comparable while that of N_2O -intermediate and NNH mechanisms were found to be relatively small and negligible [5 and ref. therein]. In line with those findings, we showed that the strong NO_x reduction achieved by the hybrid burner with integrated heat removal from the catalytic head is largely due to the reduction of the peak flame temperatures responsible for thermal NO_x formation. However, NO_x formation through the prompt mechanism is less affected by temperature due to the relatively low activation energy of the initiation reaction step involving CH radical ($\text{CH} + \text{N}_2 \leftrightarrow \text{HCN} + \text{N}$) [5]. In order to separate the thermal and chemical effects, the NO_x mole fractions in the exhaust from the two catalytic burners are presented in Figure 5a as a function of the stoichiometric adiabatic flame temperature of the syn-gas from the CPO stage. In fact all of the scattered emission data reported in Fig. 4 collapse in single curves for each catalyst formulation, showing a relatively weak exponential growth with T_{ad} , suggesting a minor role played under such conditions by thermal NO_x with respect to prompt mechanism.

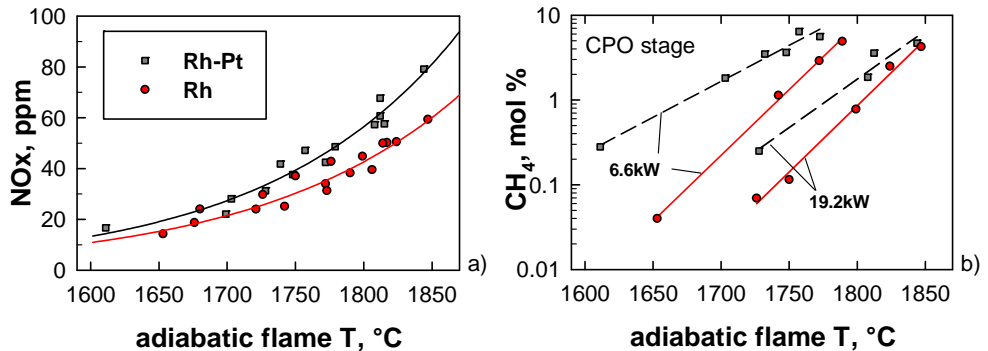


Figure 5. a) Total NO_x emissions corrected @0% O₂ produced by the hybrid burner with Rh and Rh-Pt catalysts as a function of the adiabatic flame temperature of the syn-gas produced. b) Comparison of the residual methane mol fractions in the syn-gas from the two catalysts for two nominal power levels.

For the same T_{ad} of the syn-gas, monometallic Rh catalyst constantly guaranteed a further 20-25% NO_x reduction with respect to its bimetallic counterpart. In order to explain this behaviour Figure 5b compares the residual CH₄ mole fractions in the syn-gas produced on each of the two catalysts as a function of T_{ad} at two power levels. It appears that the superior performance of Rh catalyst in terms of lower unconverted CH₄ reflects in a lower formation of prompt NO_x in the flame. In fact it was demonstrated [5] that the presence of relatively small amounts of methane in CO-H₂ mixtures increases the formation of acetylene considerably, which causes a significant increase in CH concentration and thereby in prompt NO_x.

References

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