Hetero-/homogeneous combustion of hydrogen/air mixtures over platinum: Fuel-lean versus fuel-rich combustion modes

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Abstract
The catalytic combustion of hydrogen/air mixtures in platinum-coated channels was investigated by means of two-dimensional numerical simulations with detailed heterogeneous (catalytic) and homogeneous (gas-phase) chemical reaction schemes, detailed species transport, and heat transfer mechanisms in the solid wall. Three different combustion modes relevant to power generation were analyzed and their ranges of applicability were delineated. The investigated modes included the fuel-lean catalytically stabilized thermal combustion (CST), the inverse catalytically stabilized thermal combustion (i-CST), and the fuel-rich catalytic/gaseous-lean combustion. In the fuel-lean CST approach, the less-than-unity Lewis number of hydrogen led to superadiabatic surface temperatures. Even though the presence of homogeneous combustion moderated the wall temperature superadiabaticity, reactor and catalyst thermal stability considerations limited the CST mode to equivalence ratios less than 0.2. In the i-CST mode, the maximum attained wall temperatures strongly depended on the location of homogeneous ignition, as it directly affected the magnitude of the wall temperature superadiabaticity induced by heat recirculation inside the solid walls. The i-CST had advantages over CST in terms of reactor thermal management and extended the range of applicable equivalence ratios to 0.3. In the fuel-rich catalytic combustion mode, the larger-than-unity Lewis number of the deficient oxygen reactant and the cooling of the catalytic channel by the resulting bypass air led to surface temperatures below the adiabatic equilibrium value, even for those cases where homogeneous combustion was established in the channel. This mode facilitated safe reactor operation for overall equivalence ratios up to 0.5 and inlet temperatures up to 800 K, an operational range of particular interest for gas turbines.

1. Introduction

Combustion of hydrogen and hydrogen-rich fuels has attracted increased attention in large power plants and also in microreactors used for portable power generation [1]. In large-scale power generation, hydrogen-rich syngases can be produced via fossil fuel decarbonization, leading to pre-combustion capture of CO₂ [2,3]. Hydrogen-containing fuels are also intensively investigated in the latest post-combustion CO₂ capture concepts for natural-gas-fired
power plants [4,5]. Therein, the reactants are diluted with large exhaust gas recycle (EGR) so as to increase the CO₂ content in the flue gases and thus to facilitate its subsequent capture [6,7]. In such approaches, the addition of hydrogen in the natural gas fuel is highly advantageous as it increases the combustion stability of the heavily diluted reactive mixture [8]. Finally, hydrogen and hydrogen-rich fuels are also of interest in microreactors of small (∼100 Wₑ) power generation units [9–11]. In such systems, hydrogen can be produced from methane or higher hydrocarbons in suitable microreactors [12–16].

Catalytic combustion methodologies are of interest in power generation due to their enhanced combustion stability at very lean equivalence ratios and the ensuing ultra-low NOₓ emissions [17–19]. In the conventional catalytically stabilized thermal combustion (CST) mode [18,20] (see Fig. 1a), fractional fuel conversion is achieved in a heterogeneous (catalytic) reactor, which is typically Pd- or Pt-coated and is operated at fuel-lean stoichiometries, while the remaining fuel is combusted in a follow-up homogeneous (gas-phase) combustion zone, again at fuel-lean stoichiometries. However, for diffusionally imbalanced limiting reactants with Lewis numbers (Le) less than unity, such as H₂ whereby LeH₂ ≈ 0.3 at fuel-lean stoichiometries in air, CST is compounded by the attainment of superadiabatic surface temperatures [21–23] that endanger the catalyst and reactor integrity.

Alternative to the fuel-lean CST is the more recent catalytic-rich/gaseous-lean combustion (Fig. 1b), which was initially proposed for natural-gas-fueled power generation systems [24,25]. In this mode, part of the air and all of the natural gas are driven in a catalytic partial oxidation (CPO) reactor at fuel-rich stoichiometries to produce syngas (CO and H₂). Syngas and unconverted reactants are subsequently mixed with the bypass air, forming an overall fuel-lean homogeneous combustion zone. The fuel-rich catalytic combustion methodology has several advantages compared to the conventional fuel-lean CST, which include extended catalytic extinction limits [24–27], control of catalytic combustion by the availability of oxygen that in turn prevents complete fuel consumption inside the CPO module even in the event of accidental gas-phase ignition, and enhanced stability of the follow-up flame due to the presence of highly-reactive hydrogen in the syngas [8].

The catalytic-rich/gaseous-lean combustion mode in Fig. 1b is applicable not only to natural gas but also to pure hydrogen or syngas fuels. In this case the catalyst does not have a prime CPO function, but rather acts as a preheater and stabilizer for the subsequent homogeneous combustion zone. This method is suitable for a wide range of fuels that include low calorific value biofuels, whereby flame stability is an issue, and also for hydrogen-rich syngas fuels for which conventional lean-premixed gaseous combustion entails the risk of flame flashback. The aforementioned advantages have led to the development of integrated hetero-/homogeneous combustors based on the catalytic-rich/gaseous-lean approach for coal-derived syngas and also for pure hydrogen fuels [24,28]. Finally, in fuel-rich combustion of hydrogen or syngas, reactor thermal management is not an overriding issue as the catalyst temperature does not exceed the adiabatic equilibrium temperature. This is because the limiting reactant is oxygen, which has a Lewis number larger than unity (LeO₂ ≈ 2 at fuel-rich H₂/air stoichiometries).

The fundamentals of hydrogen hetero-/homogeneous combustion have been studied in the last years. Bui et al. [29] investigated numerically the combustion of fuel-lean and fuel-rich H₂/air mixtures at atmospheric pressure in a stagnation flow over a platinum surface. Appel et al. [22] applied in situ laser-based measurements over a Pt catalyst surface and, in conjunction with numerical predictions, provided validated hetero-/homogeneous chemical reaction schemes for non-preheated fuel-lean H₂/air mixtures at atmospheric pressure. More recently, Mantzaras et al. [30] and Ghermay et al. [31,32] extended the investigation in Ref. [22] to pressures up to 15 bar and mixture preheats up to 790 K, establishing the regimes where the competition between the two reaction pathways led to suppression of homogeneous combustion. The ignition propensity of lean hydrogen/air mixtures was investigated experimentally in stagnation flows over platinum surfaces [33]. Finally, Maestri et al. [34,35] studied experimentally and numerically the combustion of fuel-rich H₂/air mixtures at atmospheric pressure in a nearly isothermal Rh-coated catalytic annular reactor.

Of particular interest in the present work is a new fuel-lean hydrogen catalytic combustion mode proposed in Refs. [31], which is henceforth termed inverse CST or “i-CST”, wherein gaseous combustion precedes the catalytic one (see Fig. 1c).
Homogeneous combustion is initiated inside an inert porous burner, which is in turn ignited via heat conduction and radiation heat transfer from a downstream catalytic reactor. At steady operation, the catalytic module is exposed to the hot combustion products of the homogeneous combustion zone. As long as complete fuel conversion is achieved homogeneously, the maximum temperature encountered by the catalytic reactor may be limited by the adiabatic equilibrium temperature of the reactive mixture. As a matter of fact, superadiabatic surface temperatures can still be attained in i-CST due to heat recirculation in the solid structure of the gaseous burner, as will be shown in Section 3.3. Nevertheless, this type of superadiabaticity is generally smaller than the catalytic-combustion-induced one.

The present work undertakes a comparative study of the three modes in Fig. 1 for hydrogen/air combustion with an overall (based on the total air and hydrogen) fuel-lean stoichiometry. Detailed simulations are performed in a single plane channel catalytic reactor using a 2-D numerical model with elementary heterogeneous and homogeneous chemical reaction schemes, heat conduction in the solid wall, in-channel surface radiation heat transfer and detailed species transport. Main objective is the delineation of the operating regimes (in terms of fuel-to-air equivalence ratio, mixture preheat and catalyst maximum tolerable wall temperature) whereby each of the three examined modes exhibits a clear advantage. Additional objectives are to address the fundamental coupling of hetero-/homogeneous chemistry and transport in both fuel-lean and fuel-rich hydrogen/air mixtures.

This article is organized as follows. The numerical model and kinetic schemes are provided in Section 2, while the underlying physicochemical processes during fuel-lean and fuel-rich catalytic combustion of hydrogen/air mixtures are reviewed in Section 3.1. Results for the three different modes are presented in Sections 3.2–3.4, whereby the interactions of chemistry, transport and heat transfer mechanisms in the solid and their impact on the reactor thermal management are exposed and the safe operating regimes are identified. Comparisons between the investigated modes and implications for practical combustion systems are finally outlined in Section 3.5.

2. Numerical

2.1. Hetero-/homogeneous combustion channel model

For all modes, the catalytic reactor was modeled as a single planar channel with a length $L = 75$ mm, height $b = 1.2$ mm and a wall thickness $\delta = 50$ $\mu$m (see Fig. 2 – due to symmetry only half of the domain was considered). This geometry simulated an individual channel of practical honeycomb reactors [20,26] and also single-channel catalytic reactors with large cross-flow aspect ratios [9]. For Modes A (CST) and B (fuel rich combustion), the entire channel length was coated with platinum. However, for Mode C (i-CST), the initial channel length $L_i = 15$ mm was chemically inert (non-catalytic) while the remaining 60 mm was coated with platinum (Fig. 2c). This approach allowed for the establishment of an upstream homogeneous combustion zone in the inert channel section, as will be shown in Section 3.3. Thus, the same combustion mode as the one in Fig. 1c could be obtained, while avoiding the complex modeling of homogeneous combustion in a porous medium and its thermal coupling to the follow-up gas-phase combustion zone.

While the CST Mode A has appeared in many variants [20], here the conventional approach with adiabatic outer channel surfaces has been considered. The outer walls in Mode C were also adiabatic. In Mode B heat transfer occurred with the bypass air, which flowed in two adjacent channels (one above and the other below the catalytic channel), each having a height $H = 2b$. The gaseous combustion downstream of the catalyst in Modes A and B (Fig. 1a, b) is not addressed herein. Of prime interest in this work is the behavior of the catalytic reactor itself and not the subsequent homogeneous combustion; in any case, the post-catalyst flames involve intricate aerodynamic stabilization for Mode A and turbulent mixing of the two streams in Mode B.

To simulate the laminar flow in the catalytic channel, a full elliptic two-dimensional CFD code was used [31,36] for all combustion modes. It is stressed that the presence of gaseous combustion within the catalytic channel invalidates the use of common 1-D models with lumped heat and mass transfer coefficients. This is because the onset of homogeneous ignition inside the catalytic channels strongly depends on the boundary layer profiles of temperature and reactive species, as shown in analytical studies [37,38]. The governing equations for a steady reacting flow in Cartesian coordinates become:
continuity equation:
\[
\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0.
\] (1)

Momentum equations:
\[
\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho u v)}{\partial y} + \frac{\partial p}{\partial x} - \frac{\partial}{\partial y} \left[ \mu \left( \frac{\partial u}{\partial x} + \frac{\partial u}{\partial y} \right) \right] - \frac{\partial}{\partial y} \left[ \mu \left( \frac{\partial u}{\partial x} + \frac{\partial u}{\partial y} \right) \right] = 0.
\] (2)

Energy equation:
\[
\frac{\partial(\rho u h)}{\partial x} + \frac{\partial(\rho u Y_k)}{\partial y} + \frac{\partial}{\partial y} \left( \rho Y_k V_{k,xy} \right) - \frac{\partial}{\partial y} \left( \rho Y_k V_{k,y} \right) - \frac{\partial h_k}{\partial y} V_k = 0,
\] (3)
\[k = 1, \ldots, K_g.
\]

Gas phase species equation:
\[
\frac{\partial(\rho u Y_k)}{\partial x} + \frac{\partial(\rho u Y_k)}{\partial y} = \frac{\partial}{\partial y} \left( \frac{\partial (\rho Y_k V_{k,x})}{\partial y} \right) - \frac{\partial}{\partial y} \left( \frac{\partial \left( \rho Y_k V_{k,y} \right)}{\partial y} \right) - \frac{\partial}{\partial y} \left( \rho Y_k V_{k,y} \right) = 0.
\] (4)

Species diffusion velocities \( \vec{V}_k \) were computed using mixture average diffusion, including thermal diffusion for the light species H and H2 [39]:
\[
\vec{V}_k = -D_m \nabla \ln \left( Y_k \frac{\vec{W}}{W} \right) + \left[ \frac{D_{m,k}}{\rho} \frac{\vec{W}}{W} \right] \nabla \ln T.
\] (5)

Finally, the ideal gas and caloric state laws closed the system of equations:
\[
p = \frac{\rho R T}{W} \quad \text{and} \quad h_k = h_k^0(T) + \int_{T_k}^{T} c_{pk}dT.
\] (7)

At the channel inlet \((x = 0)\), uniform profiles were used for the temperature, axial velocity, and species mass fractions. No slip was applied at the gas–wall interface \((y = b)\) for both velocity components. At the outlet \((x = 75 \text{ mm})\) and the symmetry plane \((y = 0)\) the transverse velocity was zero \((v = 0)\), while zero-Neumann conditions were applied for all other variables. The interfacial boundary conditions for the gaseous species at the gas–wall interface \((y = b)\), were:
\[
(\rho Y_k V_{k,y})_{y=b} = W_k \delta_k, \quad k = 1, \ldots, K_g.
\] (8)

Whereby for Mode C \(\delta_k = 0\) over the non-catalytic length \(0 \leq x < L_t\). Implicit in Eq. (8) is the assumption that the ratio of the catalytically active area to the geometrical surface area is unity. Although in practical systems this ratio depended on the surface porosity and catalyst dispersion, its specific value was largely irrelevant for the present study as the catalytic conversion of the limiting reactant \((H_2 in fuel-lean and O_2 in the fuel-rich modes) was nearly transport limited. Finally, the surface species coverage equations over the catalytically-active sections of the channel were obtained by solving:
\[
\sigma_m \frac{\delta m}{\delta x} = 0, \quad m = 1, \ldots, M_s.
\] (9)

For the solid channel wall, a 2-D approach was also adopted for the steady heat conduction:
\[
\lambda_s \left( \frac{\partial^2 T_w}{\partial x^2} + \frac{\partial^2 T_w}{\partial y^2} \right) = 0.
\] (10)

With \(\lambda_s = 16 \text{ W m}^{-1} \text{ K}^{-1}\) referring to FeCr-alloy, a common material for catalytic honeycomb reactors in power generation [20,26].

The interfacial energy boundary condition at \(y = b\) was:
\[
\dot{q}_{\text{rad}} - \lambda_s \left( \frac{\partial T}{\partial y} \right)_{y=b} - \lambda_s \left( \frac{\partial T}{\partial y} \right)_{y=b} + \sum_{k=1}^{K_g} (\delta_k h_k W_k) = 0.
\] (11)

The term \(\dot{q}_{\text{rad}}\) accounted for radiation exchange of each channel surface element with all other channel surface elements and also with the channel inlet and outlet. The net radiation method for diffuse-gray areas [10,40] was employed to compute the radiation exchange between the discretized channel wall surface elements themselves and between each surface element and the inlet and outlet channel enclosures. For the \(t\)-th channel surface element, the radiation balance becomes:
\[
\frac{1}{T_w(t)} = \sum_{j=1}^{N_t} F_{t,j}(T_j^4 - T_{w(t)}^4) + \sum_{j=1}^{N_t} (1 - \varepsilon_j) F_{t,j}(T_j^4) - \varepsilon_j T_{w(t)}^4, \quad t = 1, \ldots, N_t
\] (12)

with the index \(j\) running over the \(N_t\) discretized wall surface elements as well as the inlet \((j = N_t + 1)\) and outlet \((j = N_t + 2)\). The emissivity of each channel surface element was \(\varepsilon = 0.6\), while the inlet and outlet sections were treated as black bodies \((\varepsilon_i = 1)\) and \((\varepsilon_o = 1)\). At the inlet and outlet solid wall vertical faces, radiative boundary conditions were applied:
\[
\lambda_{st} \frac{\partial T_{w(t)}(y = 0, x) - T_{w(t)}^4}{\partial x} = \varepsilon \sigma (T_{w(t)}^4 - T_{w(t)}^4 - T_{w(t)}^4) \quad \text{for} \quad b < y < b + \delta,
\]
\[
-\lambda_{st} \frac{\partial T_{w(t)}(y = L_t, x) - T_{w(t)}^4}{\partial x} = \varepsilon \sigma (T_{w(t)}^4 - T_{w(t)}^4 - T_{w(t)}^4) \quad \text{for} \quad b < y < b + \delta.
\] (13)

At the outer surface of the catalytic channel, adiabatic conditions were imposed for Modes A and C:
\[
\frac{\partial T_{w(t)}(y = b + \delta) - \delta y}{\partial x} = 0, \quad \text{for} \quad 0 < x < L_t.
\] (14)

For Mode B, the outer surface of the bypass channel \((y = b + \delta + H)\) was adiabatic (see Fig. 2b). Cooling of the catalytic channel with the bypass air was modeled with a lumped heat transfer coefficient. Local Nusselt numbers have been tabulated in Shah and London [41] for the combined hydrodynamically and thermally developing flow in a planar channel with one wall adiabatic and the other having constant heat flux. One-dimensional modeling was a reasonable simplification since the bypass flow was non-reacting. Using local Nusselt numbers, \(Nu_{w,b}\), from Ref. [41], the boundary condition at the outer surface of the catalytic channel \((y = b + \delta)\) in Mode B becomes:
\[
\dot{q}(x) = (Nu_{w,b} \delta / \bar{h}_b) [T_w(x, y = b + \delta) - T_m(x)],
\] (15)

with
\[
\dot{m}_{\text{in}} c_p(x) dT_m(x) / dx = \dot{q}(x).
\] (16)
In Eqs. (15) and (16) $d_h$ is the hydraulic diameter of the bypass channel, which is twice the full channel height $2H$ [41]. $T_{in}(x)$ is the mean temperature of the bypass air flow, $\lambda_h$ the thermal conductivity of the air evaluated at a temperature $0.2T_{in} + 0.8T_{wall}$, and $c_p(x)$ the local mixture heat capacity evaluated at $T_{in}(x)$ and $m_{air}$ the air mass flow rate in one bypass channel per unit channel width. The above 1-D heat transfer model for the inert channel gave good agreement with full 2-D simulations, as will be shown in Section 3.4.

An orthogonal staggered grid with $280 \times 60$ points (in $x$ and $y$, respectively), over the channel half-domain produced a grid-independent solution for the flow. Finer spacing towards the channel wall and entry section was used. Furthermore, a $280 \times 20$ grid resolution (in $x$ and $y$, respectively) discretized the solid wall. Details of the solution algorithm have been provided elsewhere [22,23].

### 2.2. Chemical kinetics

Detailed surface reaction mechanisms [42–44] as well as reduced ones [45] have been reported for the catalytic oxidation of hydrogen on platinum. The detailed heterogeneous reaction scheme from Deutschmann et al. [42] (11 irreversible and three reversible reactions, 5 surface and 6 gaseous species, see Table 1) was employed, with a platinum surface site density $g = 2.7 \times 10^3 \text{ mol/cm}^2$. Surface thermodynamic data for the three reversible reactions in Table 1 were taken from Ref. [46].

For homogeneous chemistry, the $\text{H}_2/\text{O}_2$ mechanism of Li et al. [47] (see Table 2) was employed (21 reversible reactions and 9 species, including the carrier $\text{N}_2$) with its accompanying gas-phase thermodynamic data. This mechanism has been validated against shock tube, flow-reactor, and laminar flame speed measurements at pressures up to 87 bar. Moreover, its aptness for combined hetero-/homogeneous hydrogen combustion over Pt was assessed with in-situ OH-LIF and Raman measurements for lean stoichiometries in Refs. [31,32] and more recently for rich stoichiometries in Ref. [48].

Gas-phase and surface reaction rates were evaluated with CHEMKIN Ref. [49] and Surface-CHEMKIN Refs. [50], respectively, while transport properties were calculated from the CHEMKIN transport database [39].

### 3. Results and discussion

The investigated parameter ranges for each mode are summarized in Table 3. The inlet pressure was $p = 1$ bar, the preheat temperature ranged from $T_{in} = 300$ K–800 K, while the total equivalence ratio $\phi_{TOTAL}$, based on the total amount of air) was fuel-lean and varied from 0.1 to 0.5. For Mode B, the equivalence ratios inside the catalytic channel ranged from 1.0 to 5.0, while $T_{in}$ was the same for both reacting and bypass-air flows. Two total inflow velocities $U_{IN}$ were considered, 10 m/s and 20 m/s. In Modes A and C, the total $U_{in}$ was the same with the inflow velocity in the catalytic channel. For
Table 3 — Operating conditions for the three modes in Fig. 2.a

<table>
<thead>
<tr>
<th>Mode</th>
<th>φTOT</th>
<th>UIN (m/s)</th>
<th>TIN (K)</th>
<th>φCAT</th>
<th>Bypass air (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (CST)</td>
<td>0.1–0.3</td>
<td>10, 20</td>
<td>300–800</td>
<td>0.1–0.3</td>
<td>0</td>
</tr>
<tr>
<td>B (fuel-rich)</td>
<td>0.2–0.5</td>
<td>(2.2–7.8)</td>
<td>300–800</td>
<td>1–5.0</td>
<td>32.7–91.3</td>
</tr>
<tr>
<td>C (I-CST)</td>
<td>0.1–0.3</td>
<td>10, 20</td>
<td>300–800</td>
<td>0.1–0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

a) Total equivalence ratio (φTOT), inlet velocity in the catalytic channel (UIN), inlet temperature (TIN), equivalence ratio in the catalytic channel (φCAT), different than φTOT for Mode B, and bypass air (% of the total mass flux).

Mode B, however, the inflow velocities in the catalytic channel and the bypass air were adjusted to yield a total mass flux \(\rho_{IN,CAT}U_{IN,CAT} + \rho_{IN,bypass}U_{IN,bypass}\) equal to that of the corresponding cases in Modes A and C (\(U_{IN}\)) that shared the same \(\phi_{TOT}, T_{IN}\) and total \(U_{IN}\). This resulted for Mode C in bypass air accounting for 32.7%–91.3% of the total incoming air flow (see Table 3).

3.1. Impact of Lewis number of deficient reactant on surface temperature

The attained catalyst surface temperatures crucially depended on the Lewis number of the limiting reactant. The nature of this dependence, which apart from transport also involved hetero-/homogeneous chemistry coupling and heat transfer mechanisms in the solid, is firstly clarified in this section.

Computed axial temperature profiles at the gas–wall interface \((y = b)\) are shown in Fig. 3 for cases with lean (\(\phi = 0.3\)) and rich (\(\phi = 6.9\)) equivalence ratios; these plots were also representative of the temperatures inside the solid since, under the present steady-state conditions, solid temperature differences in the transverse direction \((b < y < b + L)\) were less than 1.5 K. In fuel-lean H2/air combustion, superadiabatic surface temperatures were attained as illustrated by three computations in Fig. 3 (Cases 1–3) pertaining to a \(\phi = 0.3\) mixture in the channel geometry of Fig. 2a with \(U_{IN} = 10\) m/s and \(T_{IN} = 300\) K. Case 1 (curve marked \(T_{W,1}\)) was computed with an infinitely fast catalytic step \(H_2 + \frac{1}{2}O_2 \rightarrow H_2O\) (i.e., transport-limited catalytic hydrogen conversion), without gas-phase chemistry and without the inclusion of heat conduction in the solid or surface radiation heat transfer. Appropriate transport-limited interfacial boundary conditions for the gas-phase species were imposed (see also [38]) which, with \(H_2\) being the limiting reactant, become:

\[Y_{H_2} = 0,\]

and

\[
(\rho_y V_{y,b})_{y=b} - \frac{(\phi_y - \phi_y^*)}{W_{H_2}^*}W_{y,b} = 0, \quad k = O_2; H_2O, N_2.
\] (17)

with \(\phi_y^*\) and \(\phi_y\) the stoichiometric coefficients of species \(k\) in the reactants and products, respectively, for the reaction \(H_2 + \frac{1}{2}O_2 \rightarrow H_2O\). The corresponding interfacial energy boundary condition for the simulation of Case 1 was a local balance between surface heat generation and convection to the gas:

\[-\lambda_y \left(\frac{T_{W}}{W_{y,b}}\right)_{y=b} + \sum_{k=1}^{n} \frac{k}{(\phi_y^* - \phi_y^*)}W_{k,b} = 0.\] (18)

The boundary condition Eq. (18) was the limiting case of Eq. (11) for an infinitely-thin wall \((\delta \rightarrow 0)\) without surface radiation. The maximum temperature for Case 1 occurred at the channel entry \((x \rightarrow 0)\) and was \(T_{W,1,max} = 2143\) K, i.e. 954 K above the adiabatic equilibrium temperature \(T_{ad} = 1189\) K. As the transport-limited catalytic channel solution at \(x \rightarrow 0\) was equivalent to the corresponding transport-limited solution over a catalytic flat plate [37], the maximum computed temperature \(T_{W,1,max}\) could be compared against theoretical results. The computed \(T_{W,1,max} = 2144\) K was in excellent agreement with the theoretical transport-limited solution, \(T_{W,max} = 2143\) K, obtained over a catalytic flat plate by the formula [22,29]:

\[T_{W,max} = T_{IN} + (\Delta T)_c L_{H_2O}^{-2/3}.\] (19)

or equivalently,

\[T_{W,max} = T_{ad} - (\Delta T)_c \left(L_{H_2O}^{-2/3} - 1\right).\] (20)

where \((\Delta T)_c\) is the adiabatic combustion temperature rise, \((\Delta T)_c = T_{ad} - T_{IN} = 889\) K, and \(L_{H_2O} = 0.335\). The Lewis number
of the limiting hydrogen reactant, $L_{E_h}$, was computed for a $\varphi = 0.3$ H$_2$/air mixture using mixture-average diffusion [39] with transport properties evaluated at $(T_{w,1,\text{max}} + T_{ad})/2$. The computed wall temperature $T_{w,1}$ dropped monotonically with increasing axial distance to the adiabatic equilibrium temperature $T_{ad} = 1189$ K (see Fig. 3) upon complete conversion of hydrogen.

Additional results are shown in Fig. 3 for the $\varphi = 0.3$ H$_2$/air mixture, using finite-rate chemistry, and the full model of Section 2.1 with solid heat conduction and surface radiation heat transfer: Case 2 ($T_{w,2}$) referred to predictions using only the detailed catalytic reaction mechanism (C) and Case 3 ($T_{w,3}$) to simulations with both the catalytic and gaseous (C-G) reaction mechanisms of Section 2.2. Simulations with only catalytic chemistry, $T_{w,2}$, yielded a maximum wall temperature of 1756 K, i.e. 567 K above the adiabatic equilibrium temperature. Although these values were appreciably lower than those obtained for the transport-limited adiabatic solution $T_{w,1}$, they were still high and posed great concerns for the reactor thermal management and catalyst stability. The reduced degree of superadiabaticity in Case 2 was a combined result of radiation heat losses towards the cold entry, redistribution of energy in the wall via solid heat conduction and finite-rate surface chemistry. Moreover, the shift of the peak temperature location from $x = 0$ ($T_{w,1}$) to $x = 5.3$ mm ($T_{w,2}$) was a result of increased radiation heat losses at the channel entry due to the corresponding higher view-factors ($F_{j,j+1}$ in Eq. (12)) and also due to the increased finite-rate surface chemistry effects at the leading edge ($x \to 0$). Finally, it could be shown that for Case 2 at axial locations $x > 2$ mm catalytic reactions were largely transport-controlled since $Y_{H_2}(y = b)/Y_{H_2}(y = 0) < 0.08$.

Simulations with combined catalytic and gas-phase chemistry (C–G) at $\varphi = 0.3$ (Case 3 in Fig. 3) yielded a lower superadiabaticity compared to the transport-limited Case 1 and the only-catalytic-chemistry (C) Case 2, with a maximum wall temperature of 1698 K. Reason for this quite interesting behavior was the presence of gaseous combustion, which partially shielded the catalyst from the hydrogen-rich channel core and hence reduced the heterogeneously-driven superadiabaticity. For Case 3, axial profiles are given in Fig. 4 of the catalytic ($C_3$) and gas-phase ($G_3$) conversion rates of hydrogen as well as the % total conversion of hydrogen; superposed are also the catalytic conversion rate ($C_2$) and the % hydrogen conversion for Case 2. The C rates in Fig. 4 accounted for the catalytic conversion on one catalytic surface ($y = b$), while the $G_3$ rate was calculated by integrating the volumetric gaseous H$_2$ conversion over the 0.6 mm channel half-height. The C and G rates are herein considered positive when referring to consumption of hydrogen. Homogeneous ignition for Case 3 was achieved close to the channel entry, at $x_{ig} = 2$ mm; the ignition distance $x_{ig}$ was defined as the far-upstream position whereby OH reached 5% of its maximum value in the channel and this location closely corresponded to the sharp rise in the $G_3$ conversion of hydrogen in Fig. 4. It is stressed that although all modes in Fig. 1 presumed only heterogeneous combustion inside the catalytic module, in reality gaseous combustion could not be neglected under realistic operating conditions either for hydrogen and syngas [23,32,51] or for lower hydrocarbon fuels [10,52,53].

For Case 3 in Fig. 3, over the extent of appreciable gaseous hydrogen conversion (2 mm < $x$ < 22 mm), catalytic conversion ($C_3$) occurred in parallel with $G_3$, albeit with decreasing magnitude at increasing axial distances (Fig. 4). Hydrogen could still leak through the gaseous combustion zone to be subsequently converted catalytically at the channel wall, although at diminished magnitudes when compared to the only catalytic combustion Case 2. Therefore, the presence of gaseous combustion limited the amount catalytic conversion which was responsible for the superadiabatic wall temperatures, as further seen by comparing the $C_3$ and $C_2$ curves in Fig. 4. As in matter of fact, the proposed i-CST Mode C in Figs. 1c and 2c could be envisioned as a limiting process for Case 3 in Fig. 4 whereby $G_3$ completely dominated over $C_3$, hence lowering the wall temperature down to $T_{ad}$. Apart from the moderation of the wall temperature, the presence of gaseous combustion had the additional advantage of allowing complete conversion of hydrogen at shorter reactor lengths; this was because the gas-phase reaction pathway did not exhibit the strong transport limitations of the heterogeneous pathway. Characteristically, 99.9% of hydrogen conversion was attained at $x = 40.2$ mm for Case 3 and at $x = 65.5$ mm for Case 2 (see Fig. 4).

Additional simulations are provided in Fig. 3 for the fuel-rich stoichiometry $\varphi = 6.9$ (Cases 4–5), which had the same adiabatic equilibrium temperature as $\varphi = 0.3$ ($T_{ad} = 1189$ K). To make a direct comparison with the forgoing $\varphi = 0.3$ results, simulations were performed in the channel geometry of Fig. 2a. Predictions in Fig. 3 referred to adiabatic, transport-limited conditions (Case 4, $T_{w,4}$) and to finite-rate chemistry with detailed hetero-/homogeneous reaction mechanisms and the full model of Section 2.1 (Case 5, $T_{w,5}$). With increasing axial distance, the transport-limited solution $T_{w,4}$ approached the adiabatic equilibrium temperature $T_{ad} = 1189$ K from underadiabatic values. The Lewis number of the deficient reactant, calculated using a mixture-average transport model as in the previous lean case, was $L_{E_O} = 2.268$. Substituting $L_{E_O}$ to Eq. (19), the resulting theoretical minimum temperature...
The confinement of the gaseous flame near the wall had profound implications for the underlying combustion processes and the reactor thermal management. The maximum wall temperature in Fig. 6b was $T_{w,max} = 1717$ K, i.e. 484 K higher than the mean gas temperature $T_{m,gas}$. This was a direct consequence of the Lewis number $L_{H_2} \approx 2$, which led to the formation of a closed V-shaped flame extending over the entire channel height.

3.2. Catalytically stabilized combustion (CST)

Fundamental processes involving the coupling of hetero-/homogeneous kinetics, transport and heat loss mechanisms are outlined, and the parameter space of suitability for the CST mode is delineated. Fig. 6 provides the OH distributions, the catalytic and gas-phase hydrogen conversions, and also the wall and mean gas temperatures for CST (and i-CST as well, for later comparison) at $\varphi = 0.3$, $U_{IN} = 10$ m/s and $T_{IN} = 350$ K. Concentrating on the CST results (Fig. 6a, b), the 2-D OH map in Fig. 6a illustrates the creation of two separate flame branches near the catalytic channel walls. This was a direct consequence of the Lewis number $L_{H_2} < 1$: fuel was transported towards the hot wall more efficiently than heat was transported away from it, leading to the confinement of the ensuing flames at the wall vicinity. It has been shown [22] that an artificial increase of the hydrogen Lewis number to unity led to the formation of a closed V-shaped flame extending over the entire channel height.

The confinement of the gaseous flame near the wall had profound implications for the underlying combustion processes and the reactor thermal management. The maximum wall temperature in Fig. 6b was $T_{w,max} = 1717$ K, i.e. 484 K higher than the mean gas temperature $T_{m,gas}$.
above the adiabatic equilibrium temperature $T_{\text{ad}} = 1233$ K. Simulations without the inclusion of gaseous chemistry (not shown in Fig. 6b) yielded $T_{w, \text{max}} = 1784$ K, signifying that the flame provided a modest thermal shielding of 67 K. However, the lower wall temperature in the presence of gaseous chemistry, the surface temperature moderation in Fig. 6b was constrained by two facts; the presence of a short gaseous induction zone ($0 \leq x \leq x_{\text{ig}}$, where $x_{\text{ig}} \sim 0.7$ mm, see Fig. 6a, b) with pure catalytic conversion, and the inability of the flame to fully suppress catalytic conversion downstream of the homogeneous ignition position, $x > x_{\text{ig}}$. Characteristically, over the extent $x_{\text{ig}} \leq x \leq x_{\text{TW, max}}$, where $x_{\text{TW, max}} = 3.3$ mm denotes the location of maximum wall temperature, the ratio of the catalytic to gaseous hydrogen conversion $C/G$ ranged from 54 to 0.24 (Fig. 6b). The transverse plots of $H_2$ mass fraction and temperature in Fig. 7 (pertaining to the CST case in Fig. 6) further attested the leakage of hydrogen through the gaseous flame, as the gradients $(dY_{H_2}/dy)_{-b}$ were clearly non-zero over the length $x_{\text{ig}} \leq x \leq x_{\text{TW, max}}$. Moreover, as seen in Fig. 7, the maximum temperatures in the reactor occurred at the wall and not in the gas. This was also the case for all examined CST cases.

The behavior in Figs. 6b and 7 was consistent with asymptotic studies of gaseous combustion over stagnation flow catalytic surfaces having deficient reactants with Lewis numbers less than unity [54]. It was therein shown that a continuous increase of the strain rate pushed the flame towards the wall, leading to incomplete gaseous conversion of the fuel (deficient reactant) and consequently to catalytic conversion of the fuel that leaked through the flame. A further increase of the strain rate pushed the flame against the stagnation surface and eventually extinguished it [54]. In the present channel-flow geometry, the aerodynamic strain (characterized by the transverse mass flux towards the channel walls) was imposed by the incoming mass flux ($\sim \rho_U \nu_U$) whereas the gaseous reactivity was largely controlled by the equivalence ratio and the inlet temperature. Reducing the equivalence ratio to $\phi = 0.2$, while keeping all other parameters the same as in Fig. 6, led to a drastic reduction of the $G$ hydrogen conversion as shown in Fig. 8a, b. The OH levels in Fig. 8a and the $G$ magnitude in Fig. 8b manifested a hydrogen $G$ conversion that was insignificant when compared to the corresponding $C$ conversion. The maximum wall temperature in Fig. 8b was $T_{w, \text{max}} = 1431$ K, i.e. 460 K above the adiabatic equilibrium temperature $T_{\text{ad}} = 971$ K. Although the maximum superadiabaticity, $T_{w, \text{max}} - T_{\text{ad}}$ for the $\phi = 0.2$ case in Fig. 8b was comparable to that of the $\phi = 0.3$ case in Fig. 6b ($T_{w, \text{max}} - T_{\text{ad}} = 484$ K), the suppression of superadiabaticity was much more pronounced in the latter case due to the appreciable gaseous combustion. This was

![Fig. 7 – Transverse profiles of hydrogen mass fraction and temperature at three axial locations within the extent of appreciable gas-phase $G$ hydrogen conversion for the CST case in Fig. 9(a, b). The gas–wall interface is located at $y = 0.6$ mm.](image)

![Fig. 8 – Predictions at $\phi = 0.2$, $U_{IN} = 10$ m/s, $T_{IN} = 350$ K for the CST (a, b) and the i-CST (c, d) modes; (a, c) 2-D maps of OH concentration (in ppm mass), (b, d) axial profiles of wall temperature ($T_w$), mean gas temperature ($T_{m, \text{gas}}$), catalytic ($C$) and gas-phase ($G$) hydrogen conversion. The horizontal lines marked $T_{\text{ad}}$ provide the adiabatic equilibrium temperature of the incoming mixture.](image)
Finally, as seen in Figs. 6, 8 and 9, the attained temperatures in turn endangered the catalyst and reactor thermal stability. It was actually desirable in lean catalytic combustion of hydrogen to have an 80% gaseous conversion. This is further demonstrated in Fig. 9a, b, pertaining to a case with \( \varphi = 0.3 \) and a higher preheat \( T_{IN} = 650 \) K. The maximum wall temperature in Fig. 9b was \( T_{w,max} = 1738 \) K, i.e. only 241 K above the adiabatic equilibrium temperature \( T_{ad} = 1497 \) K. Characteristically, computations without the inclusion of gaseous chemistry, yielded a much higher \( T_{w,max} = 1878 \) K.

In summary, two important conclusions could be reached from Figs. 6–9. The first one is that, contrary to the common premise that gas-phase combustion could pose a concern for the catalytic reactor thermal management, gas-phase chemistry was actually desirable in lean catalytic combustion of hydrogen. The second outcome was the enhanced suppression of the degree of superadiabaticity with increasing equivalence ratio and mixture preheat. This was highly desirable, since such operating conditions would have otherwise led to much higher superadiabaticities that would have in turn endangered the catalyst and reactor thermal stability. Finally, as seen in Figs. 6, 8 and 9, the attained temperatures (wall and mean gas temperatures as well) at the channel exit were modestly lower than the corresponding \( T_{ad} \) (by 25 K in Fig. 9b and by 6 K in Fig. 8b) due to radiation heat losses towards the colder entry.

The attained reactor temperatures for all examined CST cases have been summarized in Fig. 10. For the three investigated equivalence ratios, plots are provided for the computed maximum wall temperatures \( T_{w,max} \) (symbols) as a function of the inlet temperature, \( T_{IN} \), at the two investigated velocities \( U_{IN} = 10 \) and 20 m/s. For three selected \( T_{IN} \) at \( \varphi = 0.2 \) and 0.3 and for \( U_{IN} = 10 \) m/s, the attained wall temperatures in the presence of only catalytic chemistry are further shown (filled triangles). Also plotted in Fig. 10 are the corresponding adiabatic equilibrium temperatures, \( T_{ad} \), the theoretically maximum wall temperatures, \( T_{w,max-theory} \), from Eq. (19) and an upper limit for the tolerable wall temperature \( T_{w,limit} = 1500 \) K that warranted thermal stability of the FeCr-alloy structure. This limit temperature obviously depended on the specific wall material and catalyst formulation. For the leaner cases at \( \varphi = 0.1 \) it could be shown that gas-phase combustion was absent, apart for the highest preheat \( T_{IN} = 800 \) K, whereby the integrated (over-x) G rate reached 25% of the corresponding C rate. The attained maximum surface temperatures \( T_{w,max} \) for \( \varphi = 0.1 \) never exceeded the limiting temperature \( T_{w,limit} = 1500 \) K (Fig. 10a). With increasing \( \varphi \) and \( T_{IN} \), the differences between \( T_{w,max-theory} \) and \( T_{w,max} \) increased (see Fig. 10a, b, c) due to the corresponding enhancement in gaseous combustion. Moreover, the attained \( T_{w,max} \) at \( \varphi = 0.3 \) were always higher than \( T_{w,limit} \) (Fig. 10c), and this was of course the case for all \( \varphi > 0.3 \). At \( \varphi = 0.2 \) the \( T_{w,limit} \) was not exceeded only for \( T_{IN} < 500 \) K (Fig. 10b). Therefore, the standard CST mode in Fig. 1a with hydrogen fuel was primarily limited to the sufficiently lean stoichiometries \( \varphi \leq 0.2 \).

The results in Fig. 10 showed that the \( U_{IN} = 20 \) m/s cases always yielded higher \( T_{w,max} \) than the corresponding \( U_{IN} = 10 \) m/s cases. An increase of the inlet velocity augmented the transverse reactant fluxes towards the catalytic wall and this could have potentially increased the fuel leakage through the gaseous flame (and thus the catalytic hydrogen conversion) according to the foregoing discussion in the context of [54]. However, while a modest change of parameters directly affecting gaseous chemistry (\( \varphi, T_{IN} \))

Fig. 9 - Predictions at \( \varphi = 0.3, U_{IN} = 10 \) m/s, \( T_{IN} = 650 \) K for the CST (a, b) and the i-CST (c, d) modes; (a, c) 2-D maps of OH concentration (in ppm mass), (b, d) axial profiles of wall temperature \( (T_w) \), mean gas temperature \( (T_{m,gas}) \), catalytic (C) and gas-phase (G) hydrogen conversion. The horizontal lines marked \( T_{ad} \) provide the adiabatic equilibrium temperature of the incoming mixture. For clarity, in (b, d) the first 15 mm are shown in an expanded scale.
produced appreciable modifications in the gas-phase/catalytic hydrogen chemistry coupling, the aerodynamic parameter $U_{IN}$ required a substantial change to affect this coupling. It could be shown that the enhancement of $T_{w,max}$ in Fig. 10 with the increase of $U_{IN}$ mostly reflected the reduced importance of heat losses compared to the increased heat generation and also the increased homogeneous ignition distance $x_{ig}$ that in turn allowed for detrimental pure catalytic conversion without shielding from gaseous combustion.

The CST mode yielded nearly complete hydrogen conversion at the channel outlet (>99.9% for $U_{IN} = 10$ m/s and >99.0% for $U_{IN} = 20$ m/s except for the $\phi = 0.2$, $T_{IN} = 300$ K case with 95.1% conversion) due to the high molecular diffusivity of hydrogen. A fractional hydrogen conversion (so as to accommodate a post-catalyst flame zone in Fig. 1a) would thus require shorter channel lengths. Even then, superadiabatic surface temperatures cannot be mitigated since the peak wall temperature is always close to the channel entry.

3.3. Inverse catalytically stabilized combustion (i-CST)

i-CST as well as CST results are shown in Figs. 6, 8 and 9, so as to facilitate comparison of the two fuel-lean modes. For low inlet temperatures and/or for high inlet velocities, gaseous combustion in i-CST was stabilized close to the end of the inert section ($x = 15$ mm) as shown in Fig. 6c, d. This always resulted in superadiabatic wall temperatures irrespective of the relative magnitudes of the $C$ and $G$ hydrogen conversion rates. As seen in Fig. 6d, the maximum wall temperature was $T_{w,max} = 1648$ K, i.e. 415 K above the adiabatic equilibrium temperature $T_{ad} = 1233$ K; this happened despite the strong $G$ conversion (homogeneous ignition was achieved at $x_{ig} = 13.5$ mm) that nearly diminished the $C$ conversion. The attained superadiabaticity was thus not catalytically-induced (as in the CST case of Fig. 6b) but was a result of the upstream heat conduction inside the solid wall (also known as heat recirculation in the solid). While down to the homogeneous ignition position $x_{ig} = 13.5$ mm no hydrogen was depleted (owing to the catalytically inert section), the gas-temperature was significantly higher than $T_{IN} = 350$ K. At $x_{ig} = 13.5$ mm the temperature at the gas–wall interface was $T_{w} = 1010$ K while the mean gas temperature was $T_{m,gas} = 430$ K. The ignition-
relevant preheat temperature for the gas was in turn closer to $T_w = 1010$ K rather than $T_{m,gas} = 430$ K since homogeneous ignition was always achieved at the wall proximity, as evidenced by the flame shape in Fig. 6c. Under the operating conditions of Fig. 6, the advantage of i-CST over CST in terms of wall superadiabaticity reduction was hence marginal.

For cases where the catalytically-induced superadiabaticity was smaller (e.g. lower $\varphi$ and hence lower $\Delta T$), in Eq. (19)) and also where the $G$ conversion of hydrogen was much weaker than the $C$ conversion, the i-CST mode could even result in higher superadiabatic temperatures that the CST mode, as illustrated in Fig. 8. The effect of heat recirculation in i-CST was stronger than the catalytically-induced effect in CST, leading to a higher wall temperature for the former ($T_{w,max} = 1444$ K, Fig. 8d) compared to the latter ($T_{w,max} = 1431$ K, Fig. 8b). The main advantage of i-CST could be seen for cases with sufficiently high inlet temperatures $T_{IN}$ (Fig. 9d). In such cases, the flame practically anchored at $x \sim 0$ (see Fig. 9c, d), thus diminishing heat recirculation effects in the solid and at the same time consuming all hydrogen homogeneously and thus suppressing the catalytically-induced superadiabaticity. Fig. 9d indicated a slightly underadiabatic maximum wall temperature $T_{w,max} = 1492$ K for the i-CST case (due to radiation heat losses), which was in turn substantially lower than the superadiabatic $T_{w,max} = 1738$ K shown in Fig. 9b for the corresponding CST case.

Computed temperatures have been summarized in Fig. 11 for all examined i-CST cases. For a given equivalence ratio, there existed a value of $T_{IN}$ above which the maximum wall temperature approached the adiabatic equilibrium temperature $T_{ad}$ since in these cases flames anchored close to $x \sim 0$. This clearly demonstrated that for practical preheats of large power generation systems ($600$ K $< T_{IN} < 800$ K), the i-CST mode was limited by the $T_{ad}$ value and did not yield superadiabatic surface temperatures. The dependence of the wall temperature on the inlet velocity was stronger in the i-CST mode when compared to CST (see Figs. 10 and 11), the reason being that the magnitude of $U_{IN}$ determined how close the flame anchored to $x \sim 0$ and hence the degree of suppression of the heat-recirculation-induced superadiabaticity.

When compared to the CST results in Fig. 10, the i-CST mode had a wider safe operational envelope ($T_w < T_{w,limit}$), which for $U_{IN} = 10$ m/s encompassed the entire examined $T_{IN}$ range at $\varphi = 0.2$ and considerable part of the $T_{IN}$ range at $\varphi = 0.3$. Certainly the design of more complex upstream gaseous combustion zones (such as porous burners with increased residence times) could further improve the higher $U_{IN}$ characteristics in Fig. 11 by reducing heat recirculation in the solid matrix. Similarly to the CST mode of the foregoing section, the i-CST mode led to nearly complete hydrogen conversion at the channel exit (>99.9% for $U_{IN} = 10$ m/s, and >99.0% for $U_{IN} = 20$ m/s except for the $\varphi = 0.1$, $T_{IN} = 300$ K case with 98.5% conversion).

Finally, the effect of different reaction mechanisms is discussed. In an earlier study [22] we evaluated the impact of different catalytic and gaseous reaction mechanisms on the hetero-/homogeneous combustion of H$_2$/air over platinum. For the case in Figs. 8a and 12 provides comparisons of the wall temperature and the H$_2$ catalytic conversion rate axial profiles, which were obtained using three different catalytic reaction mechanisms, the mechanism of Deutschmann [42] used throughout this work, and the mechanisms from Park et al. [43] and Fridell et al. [44]; the gas-phase scheme was the same [47] in all simulations of Fig. 8a. The fist two catalytic schemes [42,43] gave almost the same result, while the last one [44] resulted in wall temperatures at most 15 K lower. The overall good agreement between the three surface mechanisms was largely attributed to the nearly mass-transport-limited H$_2$ catalytic conversion, which in turn yielded nearly the same H$_2$ catalytic conversion rates in Fig. 12.

3.4. Fuel rich catalytic combustion

Stable combustion (pure heterogeneous or combined hetero-/homogeneous) could be achieved for all conditions of Mode B in Table 3 (i.e. even with the largest examined stoichiometry in the catalytic channel, $\varphi_{CAT} = 5.0$). While in the fuel-lean CST and i-CST modes nearly complete hydrogen conversion was attained, for the fuel-rich mode there was always unconverted hydrogen (for $\varphi_{CAT} > 1.0$) at the channel outlet, which increased with increasing $\varphi_{CAT}$ and required a post-catalyst flame to complete fuel conversion.

Predictions for a total equivalence ratio $\varphi_{TOT} = 0.2$ and $T_{IN} = 300$ K are illustrated in Fig. 13 for two fuel-rich stoichiometries in the catalytic channel, $\varphi_{CAT} = 1.0$ and 5.0. The inlet velocities in the catalytic channel and the bypass air (provided in the caption of Fig. 13) resulted in the same mass flux as the CST and i-CST modes at $\varphi = 0.2$, $T_{IN} = 300$ K and $U_{IN} = 10$ m/s. The $\varphi_{CAT} = 1.0$ case was an extreme limit for the fuel-rich combustion mode and was only included for comparison purposes. Fig. 13(a2, b) gives the catalyst wall temperature, $T_w$, the mean gas temperature in the catalytic channel, $T_{m,gas}$, the mean temperature in the bypass air, $T_{m,bypass}$, the adiabatic equilibrium temperature based on the total stoichiometry $\varphi_{TOT} = 0.2$, $T_{ad}$, and the catalytic (C) and gas-phase (G) hydrogen conversions. Homogeneous ignition was achieved only for the $\varphi_{CAT} = 1.0$ case, as shown from the 2-D OH distribution in Fig. 13(a1) and the G conversion in Fig. 13(a2), while for $\varphi_{CAT} \geq 2.0$ only catalytic conversion was present. For
the catalytic channel by the bypass air and also due to the catalytic process itself that led to underadiabatic surface temperatures for the $L_eO_2 > 1$ deficient fuel, as discussed in Section 3.1 and the accompanying Fig. 3. Despite these factors that resulted in reduced wall temperatures, flames were established, at least for high $T_{IN}$, computations illustrated that for $\varphi_{TOT} > 0.3$ and $T_{IN} \geq 700$ K homogeneous combustion was always present for all examined $\varphi_{CAT}$. It is noted that our recent fundamental kinetic studies [48] have shown that, contrary to pure gaseous combustion whereby the reactivity of lean hydrogen/air mixtures was higher than the corresponding reactivity of rich mixtures, in catalytic combustion homogeneous ignition could be achieved easier for rich hydrogen mixtures. This was an outcome of the low molecular diffusivity of oxygen that led to reduced catalytic depletion of the deficient $O_2$ reactant over the gaseous induction zone; on the other hand, in lean catalytic combustion the large hydrogen molecular diffusivity led to a fast catalytic depletion of the deficient $H_2$, thus depriving it from the gaseous reaction pathway. Finally, in Figs. 13(a2) and 14(b) it was evident that the catalytic conversion rate $C$ became slightly negative (indicating catalytic production of hydrogen) at the flame location. Reaction flux analysis indicated that this was a result of the large concentration of $H$ radicals produced homogeneously inside the flame, which in turn adsorbed on the catalyst (reaction $S_4$ in Table 1) and then shifted the balance of hydrogen adsorption/desorption reactions ($S_3$ and $S_{12}$, respectively) towards desorption.

Fig. 13 – Predictions at $\varphi_{TOT} = 0.2$, $T_{IN} = 300$ K for the fuel-rich mode (Fig. 2b); (a1, a2) $\varphi_{CAT} = 1.0$, $U_{IN,CAT} = 4.35$ m/s, and $U_{IN,bypass} = 6.13$ m/s; (b) $\varphi_{CAT} = 5.0$, $U_{IN,CAT} = 2.19$ m/s and $U_{IN,bypass} = 8.47$ m/s. In (a1) 2-D maps of OH concentration (in ppm mass) are provided. In (a2, b) axial profiles of wall temperature ($T_w$), mean gas temperature ($T_{m,gas}$), temperature at the channel center ($T_{center}$) and gas-phase ($G$) hydrogen conversion are plotted. In (a2) $T_{center}$ is the temperature along the channel center ($y = 0$). The horizontal lines marked $T_{ad}$ provide the adiabatic equilibrium temperature of the total mixture.

Fig. 14 – Predictions at $\varphi_{TOT} = 0.5$, $T_{IN} = 500$ K for the fuel-rich mode (Fig. 2b), $\varphi_{CAT} = 3.0$, $U_{IN,CAT} = 5.28$ m/s, $U_{IN,bypass} = 5.84$ m/s. In (a) 2-D maps of OH concentration (in ppm mass) are provided. In (b) axial profiles of wall temperature ($T_w$), mean gas temperature ($T_{m,gas}$), temperature at the channel center ($T_{center}$), bypass air mean temperature ($T_{m,bypass}$), catalytic ($C$) and gas-phase ($G$) hydrogen conversion are plotted. $T_{m,bypass}$ provides the mean bypass air temperature computed with a 2-D model. The horizontal lines marked $T_{ad}$ provide the adiabatic equilibrium temperature of the total mixture.
In rich catalytic combustion closed flames were formed (see Fig. 14), in contrast to the fuel-lean CST mode whereby the low Lewis number of the deficient hydrogen reactant led to open flames with two separate branches (Figs. 6 and 8). Moreover, whenever a flame was established in the reactor, the peak temperatures were located in the gas-phase, and specifically at the plane of symmetry (y=0, see T_center profiles in Fig. 13(a2) and Fig. 14(b)) rather than at the channel walls, thus greatly facilitating the reactor thermal management. The reactor wall temperatures for all examined cases in Mode B were summarized in Fig. 15 for \( U_{IN} = 10 \) m/s; results for a total \( U_{IN} = 20 \) m/s are also provided in Fig. 15 at \( \phi_{CAT} = 3.0 \). Comparing Fig. 15 to Figs. 10 and 11, it was evident that the fuel-rich mode had a much wider range of applicability (\( T_{w,\text{limit}} < T_{w,\text{max}} \)). Specifically, the fuel-rich mode could accommodate gas-turbine relevant operating conditions (total equivalence ratios \( \phi_{TOT} = 0.5 \) and \( \phi_{TOT} = 0.4 \) for hydrogen fuel, this mode was suitable for gas turbines (\( \phi_{TOT} \) up to 0.5 and \( T_{IN} \) up to 800 K) and justified its application despite the more complex design requirements. It is finally noted that although operation at \( \phi_{CAT} = 5 \) was feasible (experiments in a subscale gas-turbine reactor with hydrogen fuel have even shown safe and stable combustion up to \( \phi_{CAT} = 6 [55] \)), it was desirable to limit \( \phi_{CAT} \) in the fuel rich mode below about 4. The reason was

3.5. Mode comparison

Operating regimes for the three investigated modes are summarized in Fig. 16, which was constructed using results from Figs. 10, 11 and 15. The lines in Fig. 16 demarcated the operating envelopes in the total equivalence ratio versus inlet temperature parametric space: areas below the corresponding lines signified safe reactor operation (\( T_{w,\text{max}} = 1500 \) K). For \( U_{IN} = 10 \) m/s (Fig. 16a) CST exhibited the narrower operating envelope; nonetheless, it offered the simplest reactor design solution for applications with \( \phi_{TOT} < 0.2 \). The operating envelope in i-CST was broader than that of CST; moreover, the highest acceptable \( \phi_{TOT} \) in i-CST exceeded 0.3 in the intermediate temperature range 450 K < \( T_{IN} < 650 \) K.

For the fuel-rich mode, results are shown in Fig. 16a for two catalytic equivalence ratios \( \phi_{CAT} = 2 \) and 3. For \( \phi_{CAT} = 3 \), operation with \( \phi_{TOT} > 0.4 \) for \( T_{IN} < 750 \) K became possible. In addition, all of the \( \phi_{TOT} \) - \( T_{IN} \) parametric space in Fig. 16 was accessible for \( \phi_{CAT} = 4 \) and 5. Thus, for hydrogen fuel, this mode was suitable for gas turbines (\( \phi_{TOT} \) up to 0.5 and \( T_{IN} \) up to 800 K) and justified its application despite the more complex design requirements. It is finally noted that although operation at \( \phi_{CAT} = 5 \) was feasible (experiments in a subscale gas-turbine reactor with hydrogen fuel have even shown safe and stable combustion up to \( \phi_{CAT} = 6 [55] \)), it was desirable to limit \( \phi_{CAT} \) in the fuel rich mode below about 4. The reason was

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**Fig. 15** – Computed maximum wall temperatures at \( U_{IN} = 10 \) m/s (open symbols) versus inlet temperature (\( T_{ad} \)) for the fuel-rich mode at four different total equivalence ratios: a) \( \phi_{TOT} = 0.2 \), b) \( \phi_{TOT} = 0.3 \), c) \( \phi_{TOT} = 0.4 \) and d) \( \phi_{TOT} = 0.5 \). The equivalence ratios in the catalytic channel are \( \phi_{CAT} = 1.0 \) (open circles), \( \phi_{CAT} = 2.0 \) (lower open triangles), \( \phi_{CAT} = 3.0 \) (open squares), \( \phi_{CAT} = 4.0 \) (open diamonds), and \( \phi_{CAT} = 5.0 \) (upper open triangles). The filled squares provide the maximum wall temperatures for \( \phi_{CAT} = 3.0 \) and \( U_{IN} = 20 \) m/s. The adiabatic equilibrium temperatures (\( T_{ad} \)) based on \( \phi_{TOT} \) and a limiting wall temperature for reactor thermal stability \( T_{w,\text{limit}} = 1500 \) K are also plotted.

**Fig. 16** – Operating regimes for the three combustion modes in Fig. 2, in terms of total equivalence ratio (\( \phi_{TOT} \)) and mixture preheat (\( T_{IN} \)). The areas below the lines define safe operating envelopes for each mode: a) \( U_{IN} = 10 \) m/s and b) \( U_{IN} = 20 \) m/s.
that the resulting NOx emissions at the end of the post-catalyst gaseous combustion zone (Fig. 2b) dropped appreciably with rising hydrogen conversion inside the catalyst [55].

Finally, the \( u_{IN} = 20 \text{ m/s} \) results (Fig. 16b) have qualitatively the same trends as those at \( u_{IN} = 10 \text{ m/s} \). For \( u_{IN} = 20 \text{ m/s} \), however, the i-CST mode exhibited narrower envelope compared to that for \( u_{IN} = 10 \text{ m/s} \), the reason being the sensitivity of the homogeneous ignition distance on \( u_{IN} \) as discussed in Section 3.3.

4. Conclusions

The catalytic combustion of fuel-lean hydrogen/air mixtures (overall equivalence ratios, \( \varphi_{TOT} \), ranging from 0.1 to 0.5) was investigated numerically in Pt-coated plane channels for three different combustion modes: the conventional catalytically stabilized thermal combustion (CST), the inverse catalytically stabilized thermal combustion (i-CST), and the fuel-rich catalytic/gaseous-lean combustion. In the lean CST mode, the less-than-unity Lewis number of hydrogen led to superadiabatic surface temperatures that endangered the reactor integrity and the catalyst thermal stability. Open flames could be established in CST for \( \varphi_{TOT} \geq 0.2 \), which extended along the catalytic walls and moderated the surface temperature superadiabaticity by shielding the catalyst from the hydrogen fuel. Even though the gaseous-combustion-induced suppression of the above-mentioned superadiabaticity was proportionally stronger at higher \( \varphi_{TOT} \) and mixture preheats \( (T_{D0}) \), reactor and catalyst thermal stability considerations limited the CST mode to \( \varphi_{TOT} \leq 0.2 \).

The maximum attained wall temperatures in the i-CST mode strongly depended on the location of homogeneous ignition. Long ignition distances facilitated further preheating of the incoming mixture via heat recirculation inside the solid walls and led to superadiabatic surface temperatures, even in cases where homogeneous combustion dominated over catalytic combustion. The i-CST mode had advantages over CST in terms of reactor thermal management particularly at higher \( T_{IN} \) and extended the range of applicable \( \varphi_{TOT} \) up to 0.3.

In the fuel-rich catalytic combustion mode, the combination of bypass cooling air and the high Lewis number of the deficient oxygen reactant led to surface temperatures below the adiabatic value and allowed safe operation for \( \varphi_{TOT} \) up to 0.5 and \( T_{IN} \) up to 800 K, at least for sufficiently high fuel-rich catalytic stoichiometries in the catalytic channel \( (\varphi_{CAT} > 3) \). Homogeneous ignition could be achieved in the catalytic channel at low \( \varphi_{CAT} \) and high \( T_{IN} \) resulting in the formation of closed flames, which however did not pose thermal management concerns. The operational range of the fuel-rich mode made it suitable for gas-turbines fueled with either hydrogen or syngases.

Acknowledgments

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>( b )</td>
<td>channel half-height, m</td>
</tr>
<tr>
<td>( c_{p,k} )</td>
<td>specific heat at constant pressure of ( k )-th gaseous species, J/(kg K)</td>
</tr>
<tr>
<td>( D_{tm} )</td>
<td>mixture-average species diffusion coefficient, ( m^2/\text{s} )</td>
</tr>
<tr>
<td>( D_{k}^r )</td>
<td>species thermal diffusion coefficient, ( m^2/\text{s} )</td>
</tr>
<tr>
<td>( h, h_k^o )</td>
<td>total enthalpy, chemical enthalpy of ( k )-th gaseous species, J/kg</td>
</tr>
<tr>
<td>( K_g )</td>
<td>total number of gaseous species</td>
</tr>
<tr>
<td>( L )</td>
<td>catalytic channel length, m</td>
</tr>
<tr>
<td>( L_i )</td>
<td>catalytically inert channel length, m</td>
</tr>
<tr>
<td>( Le )</td>
<td>Lewis number (thermal over mass diffusivity)</td>
</tr>
<tr>
<td>( m )</td>
<td>mass flow rate per unit channel width, kg/(s m)</td>
</tr>
<tr>
<td>( M_s )</td>
<td>total number of surface species</td>
</tr>
<tr>
<td>( p )</td>
<td>pressure, Pa</td>
</tr>
<tr>
<td>( R )</td>
<td>universal gas constant, J/(mol K)</td>
</tr>
<tr>
<td>( \sigma_k )</td>
<td>catalytic production rate of ( k )-th species, mol/(m(^2) s)</td>
</tr>
<tr>
<td>( T, T_0 )</td>
<td>temperature and reference temperature, K</td>
</tr>
<tr>
<td>( u, u_{IN} )</td>
<td>streamwise velocity and inlet streamwise velocity, m/s</td>
</tr>
<tr>
<td>( \nu )</td>
<td>transverse ((-y)) velocity component, m/s</td>
</tr>
<tr>
<td>( V_k )</td>
<td>species diffusion velocity vector, m/s</td>
</tr>
<tr>
<td>( W_k, W )</td>
<td>species molecular weight and average molecular weight, kg/mol</td>
</tr>
<tr>
<td>( Y_k )</td>
<td>mass fraction of ( k )-th gaseous species ( x, y ) streamwise and transverse coordinates</td>
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Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>( \Gamma )</td>
<td>surface site density, mol/m(^2)</td>
</tr>
<tr>
<td>( \lambda_g, \lambda_s )</td>
<td>thermal conductivity of gas and solid, J/(s m K)</td>
</tr>
<tr>
<td>( \mu )</td>
<td>dynamic viscosity, kg/(m s)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>density, kg/m(^3)</td>
</tr>
<tr>
<td>( \sigma_m )</td>
<td>surface species site occupancy</td>
</tr>
<tr>
<td>( \varphi )</td>
<td>hydrogen-to-oxygen equivalence ratio</td>
</tr>
<tr>
<td>( \omega_k )</td>
<td>homogeneous molar production rate of ( k )-th species, mol/(m(^3) s)</td>
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Subscripts

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<tr>
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<tbody>
<tr>
<td>( \text{IN} )</td>
<td>inlet</td>
</tr>
<tr>
<td>( \text{ig} )</td>
<td>homogeneous ignition</td>
</tr>
<tr>
<td>( g )</td>
<td>gas</td>
</tr>
<tr>
<td>( s )</td>
<td>surface</td>
</tr>
<tr>
<td>( k, m )</td>
<td>indices for gas-phase and surface species</td>
</tr>
<tr>
<td>( W )</td>
<td>wall</td>
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</tbody>
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References


