

The Role of Heat Recirculation and Flame Stabilization in the Formation of NO_x in a Thermo-Photovoltaic Micro-Combustor Step Wall

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ABSTRACT: The health and durability of micro thermophotovoltaic systems are contingent upon the level of gaseous emissions of micro combustors regarding their small size, thickness, and compactness. In small combustion devices, the flame stabilization is achieved via conjugated heat transfer from the stabilized flame to the fresh reactant via the step of the micro-combustors. The step could also create a recirculation of products, and a stagnation zone for the fluid, as a result leading to the accumulation of pollutants. In turbulent H₂ flame, the main attention is given to the NO_x as no other noxious emission, especially carbon emission (CO, CO₂, PAH, and VOC), form during the combustion of hydrogen. The existence of NO_x in the presence of water, as in the combustion of hydrogen is prevalent, could lead to corrosion in combustor interior walls and other detrimental impacts for the ecosystem. In the presented work, micro-combustion of H₂ flame in a cylinder with a step is simulated and the formation of nitrogen oxides is analyzed. The influence of different combustor specifications (equivalence ratio, solid materials) NO_x species are discussed and evaluated. Results revealed nitrogen oxides form and accumulate in the vertical step of the microchannel and that the microchannel walls are more prone to the high concentrations of nitrogen oxides. The application of cavity promotes the two-dimensionality of flow, resulting in effective heat transfer from the hot gas to the cavity walls. This not only leads to flame anchoring to the cavity walls but also results in significant NO_x.

Keywords: Hydrogen, micro-combustor, NO_x, micro combustion.

1. Introduction

The advent of micromachines is a major upheaval for the industrial world as they could benefit us in a more efficient way than conventional ways. However, they are not completely devoid of problems and challenges. One of the most significant challenges in micro-scale applications is to power the micromachines as they are small, sensitive and prone to the small variations in operating conditions [1]. Micropower generators are among the most efficient power generators as they could create power in small volume with higher energy density, thereby solving many problems associated with conventional combustion systems [2]. As one of the typical micro power generators, micro-

thermophotovoltaic could produce electricity through the high-energy photon released from the high-temperature radiation wall impinges on the thermophotovoltaic cells [3]. Here, the micro-combustor plays a key role in the production of heat and transfer it to the walls, as a result, impingement to the thermophotovoltaic cells. The flame stability and the external wall temperature distribution, which has a direct impact on the output power density and the energy conversion efficiency is determined by the design of thermophotovoltaic-micro combustor [4].

The application of hydrogen as a potential fuel has been brought into the attention of many designers it is free from carbon, thereby emanating a flue gas free from CO₂, CO, PAH and VOC [5, 6]. In small power generators, the hydrogen fuel is remarkably adventitious as it can be practically produced from the electrolysis [7] or methane reforming [8]. It could successfully solve the problems of the short residence time of micro combustors because it is a highly fast-burning fuel leading to the completion of combustion in a short amount of time. Other micro combustor drawbacks for hydrogen fuel is including high heat loss due to the large surface to volume ratio in micropower generators that could be solved in the process of design and manufacturing of micro power generators. Much of the attention in the literature has been given to the design and optimization of the micro combustors. The shape-whether it should be planar or cylindrical [9]- consideration of backward-facing step [10], bluff body [11-13], recirculation of exhaust gas[14], porous material [15], catalytic walls [16], for the purpose of higher radiation efficiency [17], flame stability [18], and enhancement of heat transfer between the burned gas and inner walls has been given fuel consideration for the application of hydrogen. The hydrogen has shown great potential to power micro thermophotovoltaic power generators.

The production-consumption chain cycle of hydrogen comprises of four main steps: a) production b) storage, c) application and d) repowering, which all may subject the explosion hazards of highly purified hydrogen [19]. It is necessary to process hydrogen with extreme caution and to find safe procedures for every step from generation to consumption. The hydrogen generation is viable through the hydrolysis reaction of hydrides (e.g., NaBH₄ [20], LiAlH₄ [21], MgH₂). This method for hydrogen

generation has been recently given significant attention because of its safety and its amenability to mild reaction conditions [22]. The process of hydrogen fuel via Mg-based materials is the new topic for hydrogen-energy process chain [23-26]. These methods are highly viable for producing pure hydrogen in small quantities.

The hydrogen as a fuel, however, could create the explosion hazards and high temperature during the oxidation which leads to significant NO_x emission [27]. The adiabatic flame temperature of hydrogen and oxygen mixture is nearly 3200 K which may lead to the formation of significant thermal nitrogen oxide [28, 29]. The occurrence of the hydrogen combustion in photovoltaic micro combustor could lead to sharp gradients of the temperature and appearance of the flame front, as a result elevating the level of nitrogen oxides significantly [30-32]. The small-scale combustors are more prone to the damage from the pollutants and impurities. In this study, the formation of nitrogen oxides with the onset of the combustion in a previously designed photovoltaic micro combustor in the National University of Singapore by Yang et al. [10] has been studied. The flame anchoring place in this combustor is the cavity wall [33]. This results in the high activity of the flame near the step walls and also the significant formation of NO_x emission. This paper is to represent the main mechanism of NO_x formation in a 2 mm microcylindrical combustor. For this purpose, the combustion of hydrogen in a micro combustor is simulated, verified, and validated using experiments. The Reynold-Average-Navier-Stokes was employed to model the turbulence. The Eddy Dissipation Concept (EDC) with direct integration scheme for elementary reactions were solved for the species considering its accuracy over conventional methods for handling the chemistry during the turbulent combustion. The obtained CFD model was used to analyze NO_x contours in the micro combustor. The in-depth analysis of the model will then be used to identify the NO_x formation mechanism and phenomenon that result in the evolution of nitrogen oxide in premixed hydrogen turbulent flame.

2. Simulation of the micro-combustor

2.1 Geometry

The simulations are performed in a micro combustor which is presented in Fig 1. It is an 18 mm long cylinder with a 2 mm long step. The inner diameters of the cylindrical micro combustor at the inlet d_1 and at the outlet d_2 are 2.0 mm and 3.0 mm, respectively. The outer diameter at both inlet and outlet surfaces is 4.0 mm. The premixed mixture of hydrogen/air is injected from the inlet surface and the exhaust gas emanates from the outlet surface. The stainless steel material was used to proceed with the modeling as the basic material at different operating points: $r = 8030 \frac{kg}{m^3}$,

$$C_p = 502.48 \frac{J}{kg.K}, k = 16.27 \frac{W}{m.K} .$$

Fig 1 The schematic of the micro-combustor

3. Model formulation

The modeling of the combustor was performed using ANSYS 19.2 Software to analyze the nitrogen chemistry of the flame in the micro-combustor. The conservation equations of mass, momentum, and energy are achieved using a steady-state solver with these assumptions that 1) no Dufour effects, 2) no work by pressure and viscous forces, 3) no surface reactions and 4) no gas radiation are present in the micro-combustor.

The mass balance is:

$$\tilde{N} \cdot (r \mathbf{u}) = 0 \quad (1)$$

where r and \mathbf{u} denote the gas density and velocity vector, respectively.

The momentum balance is:

$$r (\mathbf{u} \cdot \tilde{N} \mathbf{u}) = - \tilde{N} p + \tilde{N} \frac{\partial}{\partial x} \left(m \frac{\partial \mathbf{u}}{\partial x} \right) + (\tilde{N} \mathbf{u})^T - \frac{2}{3} \tilde{N} \cdot \mathbf{u} \mathbf{I} \quad (2)$$

where p , m and \mathbf{I} indicate the absolute pressure, molecular viscosity, and unit tensor, respectively.

The energy balance is:

$$\tilde{N} \cdot \nabla (r E_f + p) = \tilde{N} \cdot \nabla (k_{eff} \nabla T) - \sum_j \tilde{N} \cdot \nabla (h_j J_j) + \sum_j \tilde{N} \cdot \nabla (h_j J_j) + (\tilde{N} u)^T - \frac{2}{3} \tilde{N} \cdot \nabla (u \nabla u) + S_f^h \quad (3)$$

where T represent the temperature, E_f is total fluid energy, k_{eff} denotes the effective conductivity, J_j and h_j show the diffusion flux and enthalpy of species j , and S_f^h denote fluid enthalpy source term.

At the micro-combustor wall, the energy balance should be established:

$$\tilde{N} \cdot (k_w \cdot \nabla T) = 0 \quad (4)$$

where k_w is the thermal conductivity of the wall.

To model the combustion, the conservation of species is required:

$$\tilde{N} \cdot \nabla (r u Y_j) = - \tilde{N} \cdot \nabla J_j + R_j \quad (5)$$

In this equation, Y_j and R_j denote the mass fraction and the net production rate of the species in chemical reactions.

To solve the governing equations, a 3D computational domain was built by Ansys 19.2 software. The equations were solved using Fluent 19.2. The k- ϵ was employed to model the turbulence and find the velocity vector across the domain. The eddy dissipation concept (EDC) was utilized to handle combustion chemistry. The chemical reactions are obtained from Li [34] hydrogen combustion mechanism. The elementary chemical reactions for the hydrogen flame are all enlisted in table 1.

Table 1 N₂/H₂/O₂ combustion mechanism, $k = A T^n \exp(-E / RT)$.

NO	Reaction	A (cm, mol, s)	n	E (kcal mol ⁻¹)
(R1)	$H + O_2 \rightarrow O + OH$	3.55×10^{15}	-0.41	16.6
(R2)	$O + H_2 \rightarrow OH + H$	5.08×10^{04}	2.67	6.29
(R3)	$H_2 + OH \rightarrow H_2O + H$	2.16×10^{08}	1.51	3.43
(R4)	$O + H_2O \rightarrow OH + OH$	2.97×10^{06}	2.02	13.4
(R5)	$H_2 + M \rightarrow H + H + M$	4.58×10^{19}	-1.40	104.38
(R6)	$O + O + M \rightarrow O_2 + M^a$	6.16×10^{15}	-0.500	0.00
(R7)	$O + H + M \rightarrow OH + M^a$	4.71×10^{18}	-1.00	0.00
(R8)	$H + OH + M \rightarrow H_2O + M^a$	3.80×10^{22}	-2.00	0.00

(R9)	$H + O_2 + M \rightleftharpoons HO_2 + M^b$	k_0	6.37×10^{20}	-1.72	0.52
		k_∞	1.48×10^{12}	0.60	0.00
(R10)	$HO_2 + H \rightleftharpoons H_2 + O_2$		1.66×10^{13}	0.00	0.82
(R11)	$HO_2 + H \rightleftharpoons OH + OH$		7.08×10^{13}	0.00	0.30
(R12)	$HO_2 + O \rightleftharpoons OH + O_2$		3.25×10^{13}	0.00	0.00
(R13)	$HO_2 + OH \rightleftharpoons H_2O + O_2$		2.89×10^{13}	0.00	-0.50
(R14)	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2^c$		4.20×10^{14}	0.00	11.98
	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$		1.30×10^{11}	0.00	-1.63
(R15)	$H_2O_2 + M \rightleftharpoons 2OH + M^d$	k_0	1.20×10^{17}	0.00	45.5
		k_∞	2.95×10^{14}	0.00	48.4
(R16)	$H_2O_2 + H \rightleftharpoons H_2O + OH$		2.41×10^{13}	0.00	3.97
(R17)	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$		4.82×10^{13}	0.00	7.95
(R18)	$H_2O_2 + O \rightleftharpoons OH + HO_2$		9.55×10^{06}	2.00	3.97
(R19)	$H_2O_2 + OH \rightleftharpoons HO_2 + H_2O^c$		1.00×10^{12}	0.00	0.00
	$H_2O_2 + OH \rightleftharpoons HO_2 + H_2O$		5.80×10^{14}	0.00	9.56
(R20)	$N + NO \rightleftharpoons N_2 + O$		3.50×10^{13}	0.00	0.33
(R21)	$N + O_2 \rightleftharpoons NO + O$		2.65×10^{12}	0.00	6.40
(R22)	$N + OH \rightleftharpoons NO + H$		7.333×10^{13}	0.00	1.12
(R23)	$NO + NO \rightleftharpoons N_2 + O_2$		3.00×10^{11}	0.00	65.0
(R24)	$N_2O + O \rightleftharpoons N_2 + O_2$		1.40×10^{12}	0.00	10.810
(R25)	$N_2O + O \rightleftharpoons NO + NO$		2.90×10^{13}	0.00	23.15
(R26)	$N_2O + H \rightleftharpoons N_2 + OH$		4.40×10^{14}	0.00	18.88
(R27)	$N_2O + OH \rightleftharpoons N_2 + HO_2$		2.00×10^{12}	0.00	21.06
(R28)	$N_2O + M \rightleftharpoons N_2 + O + M$		1.30×10^{11}	0.00	59.62
(R29)	$NO + HO_2 \rightleftharpoons NO_2 + OH$		2.11×10^{12}	0.00	-0.48
(R30)	$NO + O + M \rightleftharpoons NO_2 + M$		1.06×10^{20}	-1.41	0.00
(R31)	$NO_2 + O \rightleftharpoons NO + O_2$		3.90×10^{12}	0.00	-0.24
(R32)	$NO_2 + H \rightleftharpoons NO + OH$		1.32×10^{14}	0.00	0.360

^a Efficiency factor for $\varepsilon_{H_2O} = 12$ and $\varepsilon_{H_2} = 12$.

^b Troe parameter is $F_c=0.8$. Efficiency factor for $\varepsilon_{H_2O} = 12$. Efficiency factor for $\varepsilon_{H_2O} = 11$, $\varepsilon_{H_2} = 2$ and $\varepsilon_{O_2} = 0.78$.

^c (R14) and (R19) are expressed as the sum of the two rate expressions.

^d Troe parameter is $F_c=0.5$. Efficiency factor for $\varepsilon_{H_2O} = 12$ and $\varepsilon_{H_2} = 2.5$.

For nitrogen chemistry, 13 additional reactions were added to the Li combustion mechanism including NO formation from the thermal mechanism and N₂O pathways, and reactions

corresponding to the formation and destruction of NO₂. Fig 2 gives the reaction path-line among nitrogen oxides.

Fig 2 The path-line of reaction among nitrogen oxides

The properties of the fuels and combustion mixture including all the species are needed for the simulations. They could affect the combustion [35-40] and NO_x emission [41, 42]. The density and specific heat are considered by incompressible-ideal-gas and mixing laws [43, 44] (specific heat of each component is obtained from a piecewise polynomial fitting of temperature), respectively. The viscosity and thermal conductivity are determined from the mass fraction-weighted mean of all species [4, 45].

The combustion is simulated at various inlet specifications. For the inlet, the mass flow rate is defined with specification defined by our operating points. In the next section, the operating points defined for this analysis will be given. The hydraulic diameter and turbulent intensity at the inlet for all operating points are 2 mm and 5%, respectively. The pressure outlet type is used at the outlet. The hydraulic diameter and turbulent intensity at the inlet are considered 2 mm and 5%, respectively. At the micro-combustor walls, no-slip condition and zero diffusive flux are employed to handle the gas-solid interfaces. The walls at the left and right side of the combustor are assumed adiabatic. The convective and radiative mechanism of heat transfer with the ambient is considered at the outer wall. The equation for the heat loss can be therefore from:

$$Q_{loss} = h_0 \sum A_i (T_{w,i} - T_o) + \epsilon \sigma \sum A_i (T_{w,i}^4 - T_o^4) \quad (6)$$

In this equation, A_i indicates the surface area of grid cells, $T_{w,i}$ denotes the temperature at the grid cells of the walls, σ represents the Stephan-Boltzmann constant, $5.67 \times 10^{-8} \text{ W / (m}^2\text{K}^4)$, h_0 is the heat transfer coefficient, $10 \text{ W / (m}^2\text{K)}$ for natural convection heat transfer and $32 \text{ W / (m}^2\text{K)}$ for turbulent convection heat transfer, and ϵ indicates the wall emissivity, 0.85.

The differential equations are discretized using second-order upwind. A steady solver with the coupled algorithm is employed to solved discretized equations. In the finite volume part of the model,

a steady segregated solver is used with the implicit formulation. A second-order upwind scheme is applied for space derivatives of advection terms in the transport equations and, PRESTO (PREssure Staggering Option) and PISO (Pressure Implicit with Split Operator) algorithms are employed for pressure and pressure-velocity coupling, respectively. The residuals for continuity, momentum, and transport of species are set 10^{-3} as a benchmark for convergence. For the energy equation, the residual criterion is set 10^{-6} . An area-averaged temperature at the micro-combustor outlet is defined to assure the completion of the simulation. The simulations are considered complete at each operating point when the area-averaged-total-temperature at the outlet was constant and the residuals of the differential equation met the required conditions.

Fig 3 The computational domain including structured grids

Before the final post-processing of the results, several fines to coarse meshes are tested starting with 524,546 to 5,890,285 cells. The mesh was uniform and structured to obtain a better convergence in differential equations. The computational domain is depicted in Fig 3. Our preliminary analysis has shown that by increasing the number of grids more than 3.2 million, the variation in results is less than 5%. Consequently, the 3.2 million grids are considered optimum in obtaining the required accuracy and saving computational costs for this study.

4. Operating conditions

The formation of NO_x during turbulent combustion is contingent upon several operational and design specifications. The temperature, quantity of hydrogen and air, the turbulence intensity, and other impurities in the fuel stream, (i.e., water, inert gases) could influence the level of nitrogen oxides. Taking this into account, several operating points are defined in this micro-combustor to verify the NO_x in micro-combustion. Table 1 gives the specification of operating conditions. The influence of hydrogen jet temperature, velocity, oxygen content, nitrogen content, water addition when it replaces both hydrogen and oxygen, and equivalence ratio has been thoroughly investigated and discussed in the following sections.

Table 2 Operating conditions for hydrogen combustion in thermophotovoltaic micro combustor

No.	Jet					
	u (m/s)	T (K)	x_{H_2}	x_{O_2}	x_{N_2}	x_{H_2O}
1 ^a	5	300	0.2942	0.1483	0.5575	0
2		350				
3		400				
4		500				
5	7.5					
6	10					
7	15					
8			0.3942		0.4575	
9			0.4942		0.3575	
10			0.3442	0.0983		
11			0.3442		0.5075	
12				0.0983		0.05
13					0.5075	0.05
14					0.4575	0.1
15					0.3575	0.2
16			0.1736	0.1736	0.6529	
17			0.2013	0.1677	0.6310	
18			0.2272	0.1623	0.61051	
19			0.3866	0.1288	0.4847	

All compositions are mole fractions.

^a Base case.

Empty place means that the operating point is the same as the base case.

5. Validation

Before the analysis and interpretation of the results, the model of the photovoltaic combustor is validated using experimental data. The experimental data were extracted from the literature [46]. The results giving the comparison between model and experiments are obtained similar to other

researchers. The discrepancy between the model and experiments is large near the inlet decreasing remarkably downstream of hydrogen jet in the micro-combustor. The difference between the modeling and experimental data may be attributed to the error of experiments and largely because of the mathematical models including RANS formulation, the choice of combustion mechanism, and etc. Since the difference along the micro-combustor length disappears, the maximum relative error will not transcend 10%. Far from the inlet, the relative error is around 4%. Since, the NO_x forms at a high temperature which in this case is in downstream of hydrogen jet, the model is reliable to verify the influence of different operating points on the nitrogen oxides for this combustor.

6. Results and discussion

6.1 Effect of the flow field

In this part, the role of flame stabilization and heat recirculation in the step of the channel is analyzed in the accumulation and formation of nitrogen oxides in the microchannel step. The level of nitrogen oxides reported here is normalized in dry flue gas with 5% oxygen content mgr/m^3 . Analysis of flame stabilization by H and OH mass fractions (as a marker of the flame reactive zone) has shown that the flame is stabilized by heat recirculation from the stabilized flame to the fresh reactant in the duct of the microchannel. Analysis of nitrogen oxides over all defined operating points has shown the majority of NO_x is observed in the vicinity of the microchannel step wall. For the quartz combustor, the contour plots of NO_x emission are given in Fig 4 at equivalence ratios=0.5, 0.6 and 0.7. At these operating points, the flame is anchored to the vertical wall of the microchannel step.

Fig 4. The contour plot of NO_x at different equivalence ratios=0.5, 0.6 and 0.7 (combustor material=quartz)

Fig. 5 shows the colored contour of H mass fraction overlaid with the velocity line at different equivalence ratios for the quartz channel. The H radicals could be a marker of the flame front and reactive zone in a hydrogen flame. Evidently, a part of the fluid moves backward against the normal direction of fresh reactant in the microchannel step, as a result leading to the establishment of a recirculation zone. The established recirculation zone leads to the stabilization of flame in the

microchannel step, providing a radical pool for chemical reactions and sustainable combustion. The recirculation zone and counter flow of combustion species could also prolong the residence time of reactive flow, being a good environment for slow evolving species such as nitrogen oxides.

Fig 5. The contour plot of H mass fraction overlaid with velocity line at different equivalence ratios=0.5, 0.6 and 0.7 (combustor material=quartz)

The temperature near the walls of the step is rather high, the pressure is low and the residence time of materials is high, as result conditions for dissociation of nitrogen exist. Fig 6 demonstrates the contour plots of temperature overlaid with streamlines. This graph demonstrates that the recirculation zone establishes with a hot combustion species at high temperatures (@1500 K). The appearance of recirculating materials limits the flame root from being pushing forwards as well as significant NO_x.

Fig 6. The contour plot of temperature overlaid with streamlines at different equivalence ratios=0.5, 0.6 and 0.7 (combustor material=quartz)

6.2 Effect of heat recirculation

The combustor material determines the combustion characteristics by affecting the heat recirculation [47-49]. Four solids including stainless steel, quartz (SiO₂), Inconel 625 and Silicon Carbide (SiC) were chosen as the solid wall material to investigate the effect of heat recirculation on NO_x. The physical characteristics of the materials are given in table 3.

Table 3 Properties of solid materials

Property	Stainless steel	Quartz	Inconel 625	Silicon Carbide
Density (gr/cm ³)	8.03	2.65	8.47	4.36
Specific heat (J/kg K)	502	730	647	650
Thermal conductivity (W/m. K)	16.27	1.5	29.6	20.7
Emissivity	0.85	0.92	0.71	0.90

Fig 7 gives the heat transfer path-lines in the combustor. The direction of heat transfer is shown through the channel walls. The released heat from the combustion is partly transferred to the

microchannel step vertical wall (Q_2) and partly to the interior horizontal wall by moving towards the outlet. The heat recirculated in the vicinity of the microchannel step is passing through the step walls (Q_2) and is partly (Q_1) transferred to the incoming hydrogen/air mixture. The heat transferred to the step walls (Q_2) is transferred by conduction through the solid walls, providing the required heat (Q_1) for the ignition of the premixed H_2/N_2 mixture. It may also shift the threshold of the formation of nitrogen oxides to the vicinity of microchannel interior walls.

Fig 7 The heat transfer network path line in the microchannel combustor (the bold arrows indicate the direction of heat flux).

The maximum gas temperature (combustion) depends on the combustor material. It is 1617 K for quartz (1.5 W/m. K), 1628 K for Inconel 625 (29.6 W/m. K), 1625 K for silicon carbide (16.27 W/m. K), and 1627 K (20.7 W/m. K) for stainless steel. The gas temperature is higher in combustor material with high thermal conductivity (Inconel 625 (29.6 W/m. K)). This ignition and as a result formation of nitrogen oxides are improved in the combustor manufactured from high conductive solids. The temperature along with the duct interior and step vertical wall is depicted in Fig 8 for equivalence ratio 0.5 in incoming H_2/O_2 mixture. The temperature on all solid materials is higher at step vertical walls than the combustor entrance leading to heat transfer from step to interior walls.

Fig 8 The wall temperature of the combustor along the interior duct and step vertical wall.

In this combustor, the heat is transferred from the hot reactive mixture to the step walls. The heat flux is higher in a channel with higher thermal conductivity. This preheats the incoming fresh reactant better ($T_{\text{interior, ave}}$ [K] in table 4) and could potentially lead to more NO_x . Table 4 gives the quantities of the heat flux (names are given in fig 7) and volumetric gas temperature in the entrance of the combustor ($T_{\text{interior, ave}}$) and overall ($T_{\text{channel, ave}}$).

Table 4 Heat transfer specifications in microchannel for different materials

Material	Q_1 [kW/m ²]	Q_2 [kW/m ²]	Q_3 [W/m ²]	$T_{\text{interior, ave}}$ [K]	$T_{\text{channel, ave}}$ [K]
Inconel 625	140	50.9	1.93	408	1200
Silicon Carbide	129	43.4	1.95	399	1183
Stainless steel	127	42.7	1.85	398	1187

When the ignition begins the microchannel, some elementary reactions are more active in the formation of nitrogen oxides. The preliminary results have shown the dominant rate of the following reactions in NO formation:



The destruction of N_2O is also analyzed in NO formation to show the dominant NO formation mechanism in this microchannel:



and the destruction of NO takes place mainly from:



The formation of nitrogen dioxide is also from the R29 and R30 reactions is dominant



R31 is for most of the NO_2 destruction



The Arrhenius rate of reactions in the formation of nitrogen oxides in the vicinity of the interior walls at the interior of the combustor is illustrated in Fig 9. These graphs show that the formation of NO_x happens in the microchannel interior walls ($y=2.975$ mm). All the above-mentioned reactions contribute to the formation of nitrogen oxides in the channel. In both the formation and destruction of NO, the walls thermal conductivity was a key component in determining the rate of reactions. However, NO_2 more facilely forms and destructs near the walls with low thermal conductivities

(quartz and steel). From these trends, the heat recirculation from the step to the interior walls could be said to play a pivotal role in the formation of nitrogen oxides.

Fig 9 Arrhenius rate of reactions R20-R21-R22-R32-R25-R25-R29-R30-R31 in the vicinity of the upstream inner wall ($y = 2.975$ mm) for different solid materials at equivalence ratio=0.5.

The influence of heat recirculation on combustion characteristics and possibly NO_x is illustrated in Fig 10. It gives the temperature difference (DT) between the step wall and combustion mixture located at $z=2.025$ mm and heat flux from the vertical cavity ($z=2$ mm) wall to the interior channel wall for different solid materials. The trend of these heat transfer variables is not uniform. Near the bottom of the cavity ($y=1.5$ mm), the quartz material combustor possesses the highest values of heat flux which corresponds to its higher DT . The overall heat transfer from the combustion mixture near the cavity to the cavity wall (integral over the entire step wall) Q_2 is bigger for solid materials with higher thermal conductivity. The Q_2 is 50.9, 43.4, 42.7 and 16.5 kW/m^2 for Inconel 645, silicon carbide, stainless steel, and quartz, respectively. A part of this which is transferred to the interior walls of the duct (Q_3) for Inconel 625, silicon carbide, stainless steel, and quartz is 1.93, 1.95, 1.85, and 0.968 W/m^2 , respectively. From these numbers, the more conductive solid with the highest thermal conductivity (Inconel 625) obtains and transfers the highest rate of heat to the interior walls at the duct of the microchannel. This effect could not only lead to flame stabilization and possible flame anchoring in the channel step but also results in significant NO_x emission in the vicinity of the step wall.

Fig 10 Heat flux from the hot gas ($x = 3$ mm) to the step vertical wall and the temperature difference between the vertical cavity wall and hot gas at $z=2.025$ mm for different solid materials at equivalence ratio 0.5.

Fig 11 shows that NO_x in the vicinity of step walls is controlled mainly by temperature and heat transfer. It gives the NO_x mass fractions (Y_{NO_x} [-]) and temperature along a vertical line parallel with the step of the combustor ($z=2.025$ mm). Besides the transfer of heat that is biggest near the solid material with the highest thermal conductivity, the temperature rises near the cavity walls of these

solid materials. This results in the formation of significant NO_x emission near the cavity walls. The effect of recirculated materials and a low-velocity zone could not be also neglected in NO_x near the cavity walls as this pollutant is a direct function of combustion mixture residence time. The maximum values of NO_x mass fraction and temperature shift toward the edge of the cavity near interior walls as indicated by dashed horizontal walls. From this, not only the NO_x and temperature but also the burning velocity of hydrogen premixed flame is concluded to increase in solid materials with high thermal conductivity.

Fig 11 NO_x mass fraction and temperature profiles in the proximity of microchannel vertical step wall (z= 2.025 mm) for materials at equivalence ratio=0.5.

6.3 Effect of preferential transport

The presence of different species with different mass diffusivities could result in a preferential transport of nitrogen oxides in the recirculation zone. To analyze the preferential transport of NO_x, a local nitrogen fraction (i_{local}) based on the balance of nitrogen/oxygen atoms for eleven major species (N₂, O₂, N, O, NO, NO₂, N₂O, OH, H₂O, HO₂ and H₂O₂) involved in the flame and participate directly and indirectly in the formation of nitrogen oxides is defined:

$$i_{local} = \frac{X_{N_2} + X_{N_2O} + 0.5(X_N + X_{NO} + X_{NO_2})}{X_{O_2} + X_{NO_2} + X_{HO_2} + X_{H_2O_2} + 0.5(X_O + X_{OH} + X_{H_2O} + X_{NO} + X_{N_2O})}$$

X denotes the species mole fractions.

The local nitrogen fraction varies in the channel because of two main reasons. First, the temperature in the channel is different during the occurrence of the combustion. As a result, the mass diffusivities of species vary significantly. This along with the occurrence of chain reactions change the mole fraction of combustion species in the channel. Second, the existence of the cavity enhances the two-dimensionality of fluid flow, thereby changing the nitrogen fraction along with the turbulent reacting flow in the channel. Fig 12 demonstrates the profiles of local nitrogen fraction (i_{local}), NO_x mass fraction temperature at the axis of quartz combustor for different equivalence ratios of the incoming mixture. The place at the axis of the chamber associated with the significant temperature rise is the

flame base and flame stabilization kernel. Near the flame front, local nitrogen fraction decreases slightly meaning that the nitrogen-oxygen balance disappears. At this location, NO_x mass fraction increases significantly. Similar trends were also observed for the equivalence ratio defined for combustion reactive species (Carbon and hydrogen) [50, 51].

Fig 12 Profiles of gas temperature, local nitrogen fraction, and NO_x mass fraction along the channel centerline of the quartz combustor for different incoming gas equivalence ratios

The colored contour plots of relative nitrogen fraction ($i_{\text{local}} - i_{\text{initial}}$) which is a deviation from the nitrogen fraction of mixture overlaid with velocity level lines for different equivalence ratios are demonstrated in Fig 13. From this figure, $i_{\text{local}} - i_{\text{initial}}$ mainly decreases near the cavity walls in the recirculation zones for three investigated equivalence ratios. In this location, the fluid is nearly stagnant because of the fluid flow domain is two dimensional near the cavity walls. As a result, The NO_x mass fraction rocketed near the cavity wall. Fig 14 demonstrates the colored contour plots of relative nitrogen fraction overlaid with the NO_x mass fractions near the cavity walls. It is evident from this figure that near the flame base, the local nitrogen fraction is much lower, and the potential for the formation of NO_x emission exists. This is also beneficial for chemical reactions and the stabilization of the flames from the cavity walls.

Fig. 13. The contour plots of $i_{\text{local}} - i_{\text{initial}}$ overlaid velocity level lines (black line) for different equivalence ratios in the quartz combustor.

Fig. 14. Colored contours of $i_{\text{local}} - i_{\text{initial}}$ with overlaid mass fraction level lines of NO_x mass fraction near the flame-anchoring location of the quartz combustor.

To have a good summary, the relative nitrogen fraction, flow velocity, temperature, NO_x concentration and NO_x mass fraction at different axial locations are demonstrated along the cavity wall in the transversal direction in channel and cavity ($2.5 \text{ mm} \leq y \leq 4 \text{ mm}$) at different axial distances ($z=2.5, 3, 3.5$ and 4 mm) in Fig 15. Before the flame base near the cavity wall, the balance between the nitrogen and oxygen disappears and relative nitrogen fraction decreases sharply in a low-velocity zone reaching the minimum value at the bottom of the cavity ($y=1.5 \text{ mm}$). As a result, total

temperature and both NO_x rocketed at the bottom of the cavity near the chamber wall. The two-dimensionality of flow, fluid stagnation, and heat transfer along with stabilization of flame can enhance the formation of NO_x and disappearance of nitrogen-oxygen balance. Meanwhile, the sharp velocity gradient near the cavity wall could also promote the preferential transport effects of nitrogen oxides.

Fig. 15. The relative nitrogen fraction, flow velocity, temperature, NO_x concentration and NO_x mass at $\phi = 0.5$ along the cavity wall different axial distances ($z=2.5, 3, 3.5$ and 4 mm).

Generally, the control and reduction of flame temperature, reduction of excess air, and burning low nitrogen fuels can minimize NO_x. For this combustor, the fuel is hydrogen and high temperature is also needed to power the cell. In this small-scale power generators, the options are limited for control the nitrogen oxide as the size of the combustor is small. The preferential NO_x mass transport shows that NO_x forms near the cavity wall as there is a radical pool, the residence time of the fluid flow is high enough for the evolution of even the slow chemistry reactions such as thermal NO_x. The viable option worthy of the further consideration includes the combustor reshaping so as the fluid residence time in the proximity of cavity walls is within the threshold of ignition and smaller than the timescale of thermal NO formation.

7. Conclusions

The photovoltaic cells are promising small energy gensets to extract the hydrogen potential energy for the production of electricity because they are efficient without producing the carbon emissions. In this study, the micro combustion of hydrogen premixed flame is simulated and analyzed in terms of NO_x and elementary reactions contributing to the level of NO, NO₂ and N₂O. The NO_x at different operating points and solid combustors are interpreted using the analysis of nineteen different combustion operating points. The maximum level of NO_x emission at every operating point is observed in the proximity of the microchannel walls where the fluid is stagnant with a high residence time in the channel and heat recirculation is effectively recirculated from the gas mixture to the cavity walls. The heat recirculation from the step wall to the interior walls has a key effect in NO_x as it

could lead to the initiation of combustion chain reactions and more intense reaction rates near the flame anchoring place. The fluid flow near the cavity wall is nearly two dimensional which varies the balance between the nitrogen and oxygen. This results in NO_x preferential transport effect near the cavity walls. The NO_x preferential transport effect is analyzed by defining the nitrogen mass fraction based on local nitrogen/oxygen atom between eleven major species (N₂, O₂, N, O, NO, NO₂, N₂O, OH, H₂O, HO₂, and H₂O₂). The nitrogen mass fraction near cavity walls decreases which confirms that the balance between nitrogen and oxygen disappears. This is likely due to the presence of a radical pool of combustion species from by recirculation of hot gas. This not only leads to the flame anchoring from the cavity walls but also leads to significant NO_x formation. To sum, the mechanism of flame anchoring by the cavity wall in the microchannel leads to early initiation of combustion reactions as well as NO_x in the interior upstream walls. These reactions are promoted further downstream by facing the reticulated radicals in the hot gas which present near the cavity walls. The role of low velocity could not be neglected there as the formation of NO_x is usually sluggish. Thus, the recirculation zone, low-velocity zone near the cavity wall, effective heat transfer via upstream walls, and lower local nitrogen fraction near the flame base are the main mechanism of NO_x formation in the investigated micro combustor. This research makes a direct leeway towards the improvement in terms of NO_x with minor considerations in the design of of the photovoltaic cell combustor, necessitating more research and intricate analysis of hydrogen flame in this combustor.

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