

1 **Nitric Oxide Pollutant Formation in High Hydrogen Content (HHC)**
2 **Syngas Flames**

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Abstract

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41 Three-dimensional direct numerical simulations (DNS) of high hydrogen content (HHC)
42 syngas nonpremixed jet flames with a Reynolds number of $Re=6000$ have been carried out to
43 study the nitric oxide (NO) pollutant formation. The detailed chemistry employed is the GRI
44 3.0 updated with the influence of the NCN radical chemistry using flamelet generated
45 manifolds (FGM). Preferential diffusion effects have been considered via FGM tabulation
46 and the reaction progress variable transport equation.

47 The DNS based quantitative results indicate a strong correlation between the flame
48 temperature and NO concentration for the pure hydrogen flame, in which NO formation is
49 mainly characterised by the Zeldovich mechanism. The results also indicate a rapid decrease
50 of maximum NO values in H_2/CO syngas mixtures due to lower temperatures associated with
51 the CO-dilution into H_2 . Results on NO formation routes in H_2/CO syngas flames show that
52 while the Zeldovich mechanism dominates the NO formation at low strain rates, the high NO
53 formation rate at high strain rates is entirely caused by the NNH mechanism. We also found
54 that the Fenimore mechanism has a least contribution on NO formation in H_2/CO syngas
55 flames due to absence of CH radicals in the oxidation of CO. It is found that, due to
56 preferential diffusion, NO concentration exhibits higher values near the flame base depending
57 on the hydrogen content in H_2/CO syngas fuel mixture.

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61 **Key Words:** Syngas, Direct Numerical Simulation, Preferential Diffusion, Zeldovich
62 Mechanism, NNH Mechanism

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65 **1. Introduction**

66 In moving towards cleaner combustion technologies, high hydrogen content (HHC)
67 alternative fuel blends are undoubtedly significant, because they are environmentally friendly
68 and can be used as an alternative feedstock for energy resources in clean energy conversion
69 [1-2]. There is a significant current interest in combustion of HHC syngas fuels with a
70 broader reactant class such as hydrogen diluted with carbon monoxide. As with any fuel, the
71 combustion of HHC syngas fuel can produce gaseous pollutant such as nitric oxides (NO_x),
72 carbon monoxide (CO), sulphur dioxide (SO_2), volatile organic compounds (VOCs) etc.
73 which cause a substantial negative impact on the environment. While the HHC syngas fuel
74 burning has abilities to lower CO_2 emissions, the NO formation is critical as a pollutant,
75 which is sensitive to local flame temperature, O atom concentrations and residence times at
76 the NO forming conditions [3-4]. Progress with respect to further reduction of NO levels in
77 syngas as a major pollutant requires better understanding the burning issues of clean fuels and
78 their correlation with the pertinent chemical kinetics. Currently there is a significant interest
79 in better understanding the NO formation in HHC syngas flames and particularly the different
80 NO mechanisms with respect to HHC syngas fuel variability.

81 Many theoretical, experimental and computational efforts have been devoted to identifying
82 mechanisms of the NO formation in turbulent jet flames. There is a wealth of experimental
83 investigations available for NO formation in turbulent hydrogen, methane and
84 methane/hydrogen blended nonpremixed jet flames, which includes effects of residence time
85 on NO levels [5], NO formation and its relationship to flame temperature [6], radiation
86 effects on NO concentration [7], and NO formation during the flame vortex interactions [8].
87 Experimental investigations on NO detection in turbulent premixed flames [9-11] as well as

88 effects of hydrogen addition on NO formation in fuel-rich and fuel-lean ethane, propane and
89 CH₄/O₂/N₂ flames [12, 13] were also reported in the literature.

90 In the meantime, several computational studies of NO concentration of turbulent jet flames
91 were also carried out. For example, stochastic modelling of NO concentration in premixed
92 methane combustion [14], prediction of NO concentration in hydrogen nonpremixed jet flame
93 [15], tabulation of NO chemistry for large eddy simulation of turbulent nonpremixed
94 combustion [16], prediction of NO concentration with radiation in nonpremixed flames [17]
95 and prediction of NO concentration in lean premixed flames [18] were also reported. In
96 addition, several other research questions relevant to NO formations have been addressed by
97 numerical modelling on turbulent flames, which include recent investigations of influence of
98 airstream dilution and jet velocity on NO emission characteristics of CH₄ bluff-body flames
99 [19], the formation/destruction mechanisms of NO in CH₄/H₂ jet flames in a hot co-flow [20]
100 and the effects of hydrogen addition on NO characteristics in MILD (Moderate or Intense
101 Low-oxygen Dilution) combustion of CH₄/H₂ fuel blends [21].

102 However, only a few investigations focused on NO formations of hydrogen-rich to hydrogen-
103 lean H₂/CO syngas flames for laboratory scale fundamental flames as well as practical engine
104 like conditions. For example, experimental and numerical investigations on nitric oxide
105 formation in laboratory scale H₂/CO jet flames have been reported in the recent literature.
106 These include experimental investigations such as NO emission characteristics and scaling of
107 H₂/CO syngas flames [22], assess NO production from different formation routes from
108 syngas and biogas fuel blends [23] as well as numerical studies such as effects of syngas
109 composition and diluents on emission characteristics of syngas nonpremixed flames [24],
110 effects of the fuel-side nitrogen dilution on the structure and NO_x formation characteristics of
111 syngas nonpremixed flames [25], and effects of syngas composition, pressure and dilution

112 gases on the NO_x emission of H_2/CO syngas nonpremixed flames [26]. Limited advances
113 have been also made in understanding the global NO formation characteristics of H_2/CO
114 syngas flames in practical engine like conditions, for example in industrial gas turbine
115 combustor [27] and in spark-ignition direct-injection internal combustion engine [28].
116 However, detailed understanding on NO formation in turbulent flames with variable fuel
117 compositions is still lacking, particularly with respect to hydrogen-rich to hydrogen-lean
118 H_2/CO syngas fuel blending.

119

120 Over the last several years, computationally intensive direct numerical simulation (DNS)
121 technique which provides detailed information on turbulent reacting flows has been
122 successfully applied to simulate a broad range of combustion problems [29-33]. Many review
123 articles also reported advances in DNS of turbulent combustion, for example [34, 35].
124 However, despite many DNS investigations of turbulent combustion problems have been
125 carried out including hydrogen combustion, no three-dimensional DNS with detailed
126 chemistry is reported for NO formation of HHC syngas fuel burning in turbulent flames. The
127 aim of the present work is to study the NO formation in pure hydrogen and HHC H_2/CO
128 syngas turbulent nonpremixed jet flames using DNS and flamelet generated manifold (FGM)
129 tabulated chemistry [36], and to explore the possibility of better understanding the behaviour
130 of basic mechanisms of NO formations for high hydrogen content nonpremixed syngas
131 burning. This new work on investigation of NO formation in HHC syngas fuel mixture with
132 the influence of preferential diffusion is a continuation of our previous DNS investigations
133 focused on burning characteristics of H_2/CO , $\text{H}_2/\text{CO}/\text{CO}_2$, $\text{H}_2/\text{CO}/\text{CO}_2/\text{N}_2$ syngas combustion
134 [37], effects of preferential diffusion on hydrogen-rich to hydrogen-lean H_2/CO syngas
135 combustion [38], influence of chemical reactions on major, minor and radical species
136 concentrations of hydrogen-rich to hydrogen-lean H_2/CO syngas burning [39], analysis of the

137 Wobbe index, flame index, flame normal, flame surface and a micromixing process of
138 hydrogen-rich to hydrogen-lean H_2/CO syngas flames [40], and turbulence-chemistry
139 interaction and the local flame extinction of CO_2 -diluted oxy-syngas combustion [41].

140

141 Given the nature of HHC turbulent nonpremixed syngas combustion, it is important to ask
142 two key questions: (i) how does NO form with respect to hydrogen content in the HHC
143 syngas fuel mixture in turbulent nonpremixed flames, (ii) how does preferential diffusion
144 influence NO distribution in the HHC syngas fuel mixture in turbulent nonpremixed flames.

145 To answer these two questions, we performed a new set of unsteady compressible three-
146 dimensional DNS calculations including a transport equation for the NO mass fraction. The
147 remainder of the paper is organised as follows: the governing equations, chemistry and
148 numerical details are presented in section 2 followed by results and discussion in section 3.
149 Finally, conclusions and recommendations for further work are presented in section 4.

150

151 **2. DNS Equations, Chemistry and Numerical Implementation**

152 The set of governing equations solved in present DNS for turbulent nonpremixed jet flames is
153 the time-dependent compressible flow Navier-Stokes equations, the energy equations,
154 transport equations of mixture fraction, reaction progress variable and mass fraction of nitric
155 oxide and the state equation. The governing equations for mass, momentum, energy, mixture
156 fraction, reaction progress variable and the state equations in their non-dimensional form can
157 be found in [38]. It is important to note that we added an additional model term for the
158 diffusion term in the transport equation of reaction progress variable in order to include the
159 non-unity Lewis number effects (preferential diffusion). With an additional model term, the
160 non-dimensional transport equation of reaction progress variable, Y can be written as:

161
$$\frac{\partial(\rho Y)}{\partial t} + \frac{\partial(\rho u_k Y)}{\partial x_k} - \frac{1}{\text{Re Pr}} \frac{\partial}{\partial x_k} \left(\frac{\lambda}{C_p} \frac{\partial Y}{\partial x_k} \right) - \frac{1}{\text{Re Sc}_Y} \underbrace{\frac{\partial}{\partial x_k} \left(\rho D_{Y\xi} \frac{\partial \xi}{\partial x_k} \right)}_{\text{additional model term}} - \omega_Y = 0, \quad (1)$$

162 Here the additional term which accounts for non-unity Lewis number explicitly (preferential
 163 diffusion) is given by $\frac{\partial}{\partial x_k} \left(\rho D_{Y\xi} \frac{\partial \xi}{\partial x_k} \right)$ [38].

164 The non-dimensional transport equation for NO mass fraction, Y_{NO} is given by:

165
$$\frac{\partial(\rho Y_{\text{NO}})}{\partial t} + \frac{\partial(\rho u_k Y_{\text{NO}})}{\partial x_k} - \frac{1}{\text{Re Pr}} \frac{\partial}{\partial x_k} \left(\frac{\lambda}{C_p} \frac{\partial Y_{\text{NO}}}{\partial x_k} \right) - \omega_{Y_{\text{NO}}} = 0. \quad (2)$$

166 Where t stands for time, u_j is the velocity components in the x_j direction, λ stands for heat
 167 conductivity, C_p for specific heat at constant pressure, ξ is the mixture fraction, ω_Y is the
 168 source term of the progress variable, $\omega_{Y_{\text{NO}}}$ is the source term of the NO transport equation, ρ
 169 is the density, $\rho D_{Y\xi}$ is the additional diffusion coefficient for non-unity Lewis number
 170 calculation respectively. In addition, Pr , Re and Sc_Y represent Prandtl number, Reynolds
 171 number and Schmidt number respectively.

172
 173 The detailed flame chemistry of HHC syngas flames is represented by databases of the FGM
 174 tabulated chemistry [36], accounting for both chemical and transport processes using the
 175 laminar flamelet concept [42]. In order to demonstrate the NO formation mechanism with
 176 respect to reaction between N_2 and CH radicals, we employed detailed chemistry tabulation
 177 with recently identified critical radical species NCN and corresponding chemical reactions in
 178 this investigation. The FGM tables were created with updated GRI-Mech 3.0 [43] with the
 179 NCN radical chemistry. The mechanism contains 54 species, in which 53 species are from

180 GRI 3.0 and the NCN radical, and 329 reactions, in which 325 reactions are from GRI 3.0
 181 and 4 reactions involving the NCN radical reactions. The resolution of the manifolds is 301
 182 points in the mixture fraction direction and 101 points in the progress variable direction. For
 183 H_2 -Air combustion, the mass fraction of H_2O was selected as the progress variable, while
 184 for H_2/CO -Air combustion, sum of the mass fractions of H_2O , CO and CO_2 was selected as
 185 the progress variable.

186

187 Turbulent nonpremixed round jet flame is adopted as a model problem. The Cartesian cubic
 188 configuration of turbulent nonpremixed jet flame including domain size and boundary
 189 conditions is shown in Fig. 1. The configuration consists of 10 jet nozzle diameters (10D) in
 190 axial direction and 7 jet nozzle diameters (7D) in radial direction. There are
 191 $640 \times 640 \times 640$ computational grid points in the $L_x \times L_y \times L_z$ cubic computational domain
 192 resulting 262 million grid points. The full compressible governing equations noted above are
 193 solved using the parallel DNS flame solver, DSTAR [37-41, 44]. The equations are
 194 discretised in space on a three-dimensional Cartesian grid with high-order finite difference
 195 numerical schemes. Derivatives are computed using centered explicit schemes of order six
 196 except at boundaries where the order is progressively reduced to four [45]. Temporal
 197 integration is realized with a Runge-Kutta algorithm of order three [46]. A Courant-
 198 Friedrichs-Levy (CFL) condition for the convective terms is treated to ensure the stability of
 199 the explicit integration and determine a suitable time step. All simulations were performed at
 200 a Reynolds number of 6,000. Boundary conditions are treated with the help of non-reflecting
 201 inflow/outflow Navier-Stokes characteristics boundary condition (NSBC) [47]. The inflow
 202 mean axial velocity is specified using a hyperbolic tangent profile with profile

203 $\bar{w} = W_{fuel}/2 \{ 1 - \tanh[(0.5/4\delta)(r/0.5 - 0.5/r)] \}$ with $r = \sqrt{(x-0.5L_x)^2 + (y-0.5L_y)^2}$. Here r is the radial

204 direction of the round jet, originating from the centre of the inlet
205 domain ($0 \leq x \leq L_x, 0 \leq y \leq L_y$). The initial momentum thickness δ was chosen to be 10% of
206 the jet radius. The inflow turbulent fluctuations were artificially generated in a sinusoidal
207 form and added to all three velocity components. The boundary conditions for scalars such as
208 mixture fraction and reaction progress at outlet boundary were specified with zero-gradient.
209 Table 1 summarised the fuel compositions of the three numerically simulated HHC flames H,
210 HCO1 and HCO2, their stoichiometric mixture fractions, adiabatic flame temperatures, and
211 physical and numerical parameters for turbulent round jet configuration.

212

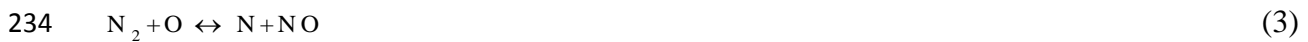
213 **3. Results and Discussion**

214 In the following, the NO formation mechanisms and results are presented and discussed
215 under three sections with two principal aims. The first section discusses basic mechanisms of
216 NO formation. The second section compares the NO formation of pure hydrogen flame H
217 between the unity Lewis number case and the non-unity Lewis number case. This section also
218 discusses comparison between the DNS data and the experimental measurements in order to
219 demonstrate the accuracy of DNS based NO prediction with the influence of preferential
220 diffusion. The third and final section discusses the NO distributions of pure hydrogen flame
221 H, H₂/CO syngas flames HCO1 and HCO2 with the influence of preferential diffusion by
222 highlighting corresponding basic NO mechanisms and dominant chemical reactions. The
223 results are discussed in several forms which include instantaneous contour plots, one-point
224 data analysis and probability density function distributions. Subsequently, important chemical
225 reactions and mechanisms for NO formation are highlighted, where HHC fuels are unique in
226 terms of pollutant formation during combustion.

227

228 3.1 Basic mechanisms of NO formation

229 Generally, there are two well-known routes for NO formation in combustion environments,
230 namely the thermal-NO [48] and prompt-NO [49] mechanisms. Moreover, there exist two
231 additional routes for NO formations, known as the N₂O route [50] and the NNH route [51].
232 The thermal NO mechanism involves breaking up N₂ triple-bond by O atoms at high
233 temperature, which includes two principal reactions proposed by Zeldovich [48]:



236 and the reaction of N atom with OH radical:



238 The Eqs. (3), (4) and (5) involve radical species O, N, H and OH that are initially formed
239 through decomposition or abstraction reactions. Due to the inherent stability of the N₂
240 molecule, considerable energy is required to oxidise N₂, and thus thermal NO is only formed
241 in appreciable quantities at temperatures approximately above 1700K.

242 The Fenimore's prompt-NO mechanism [49] involves reaction between N₂ and CH radicals
243 which was originally described through HCN such that:



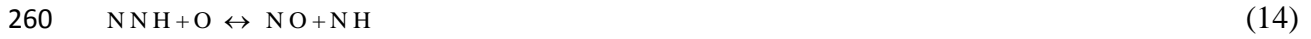
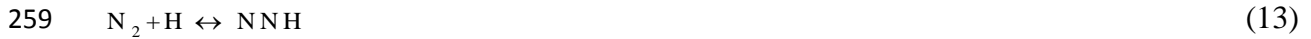
245 However, recent studies have shown that the NCN radical is the major pathway to prompt
246 NO for the reaction CH+N₂ [52]. In the present work, we consider the NCN radical pathway
247 to study prompt-NO, which includes two major reactions [53]:



250 The N₂O route [50] is originated by the N₂O interaction with radicals H or O and yield NO
251 and can be described by the following elementary reactions:



256 The NNH route [51] takes place due to the reaction of H radicals with N_2 and it is likely that
257 the NNH route can have an important role in the hydrogen combustion primarily at short
258 residence times [54] and includes reactions:



261 and the reaction of NNH and O has the following channels: $NH + NO$, $N_2O + H$ and $N_2 + OH$
262 [51].

263 **3.2 Preferential diffusion effects on NO formation in hydrogen flame H**

264 In order to identify the influence of preferential diffusion on NO formation and distribution,
265 we compare instantaneous three-dimensional NO structures, and scattered data of NO mass
266 fraction in the mixture fraction space between the unity Lewis number and the non-unity
267 Lewis number cases as shown in Fig.2. Three-dimensional structure of mass fraction of NO
268 displays local increase of NO values with strong vortical structures in shear layer region and
269 outer region layer in the non-unity Lewis number case compared to the unity Lewis number
270 case. It is seen from the unity-Lewis number three-dimensional structure that the high NO
271 zone is insensitive to steady straining in the absence of non-unity Lewis number. This
272 confirms that the strain rate effects remain closely tied to non-unity Lewis number and
273 preferential diffusion effects and therefore NO formation for hydrogen flame H. Fig. 2
274 (bottom) shows scattered NO values of the full domain and the near nozzle region between
275 the unity Lewis number and the non-unity Lewis number. The scattered data of the non-unity

276 Lewis number case show much higher NO values compared to the unity Lewis number case
277 for each mixture fraction range of NO values around the stoichiometric mixture fraction
278 region, and on the fuel-lean side.

279

280 In order to evaluate the success of DNS predictions of quantitative NO values, we now
281 discuss the comparison of mass fraction of NO values with the closest possible experimental
282 data of turbulent nonpremixed hydrogen jet flame carried out by Barlow and Carter [6]. Fig.
283 3 shows comparisons for scattered data of NO values between DNS values (a1, b1, c1) and
284 the experimental data (a2, b2, c2) at three different downstream axial locations $z=4, 8$ and 10 .

285 It is important to note that DNS of nonpremixed hydrogen jet flame was performed at a
286 Reynolds number of 6000, while experimental investigation was carried out at a much higher
287 Reynolds number of 10000. With two different Reynolds numbers, one can expect
288 differences in the jet shear layer on the developing flames. For example, the shear layer
289 dynamics affect the internal chemical structure including NO formation. Despite the
290 difference of Reynolds number and its influence on flow field and flame structure, the
291 comparison between DNS data and the experimental measurements show reasonably good
292 agreement at all three axial locations. Particularly, we observe the occurrence of peak NO
293 values on fuel lean side close to stoichiometric mixture fraction of 0.028 for DNS data (Fig. 3
294 (a1, b1, c1)). This has been also observed by the experimental measurements (Fig. 3 (a2, b2,
295 c2)). In summary, the comparison between DNS results and the experimental measurements
296 indicates that our DNS results with the inclusion of preferential diffusion reasonably predict
297 the NO formation and its distribution in turbulent nonpremixed hydrogen flame.

298

299

300 **3.3 NO formation in hydrogen flame H and H₂/CO syngas flames HCO1 and HCO2**
301 **with the influence of preferential diffusion**

302 Instantaneous cross-sectional mid-plane contour plots of flame temperature and mass fraction
303 of NO at non-dimensional time instant $t=30$ are shown in Fig.4. To obtain an idea of the
304 temperature distribution and NO formation more locally, and to facilitate the subsequent one-
305 point data analysis, the flames are divided into three different zones, defined as the upstream
306 zone A ($0 < z < 2$), intermediate zone B ($2 < z < 8$) and downstream zone C ($8 < z < 10$). The flame
307 structures between the three cases show large differences with respect to CO-dilution, which
308 is a regulated pollutant and a component of unburned syngas, resulting from inefficient
309 mixing that yields equivalence ratio outside the ignition range and an incomplete combustion
310 of hydrocarbon species in the syngas. The flame temperatures of the three flames show a
311 decreasing maximum value but an increasing vortical level from flames H to HCO1 and
312 HCO2, because of the decreasing hydrogen content and the increasing CO content in H₂/CO
313 syngas fuel mixture. Moreover, temperature distributions in Fig.4 show intense burning and
314 strong flame width for the pure hydrogen flame H, but moderate burning and relatively weak
315 flame width for the CO-diluted HCO1 and HCO2 syngas flames depending on the CO
316 content in syngas fuel mixture. It is important to note that the similar flame appearances were
317 recently observed by Hwang et al. [22] in their experimental investigation for turbulent
318 nonpremixed pure H₂, H₂-rich H₂/CO syngas, and H₂ and CO equally blended H₂/CO syngas
319 jet flames at Reynolds number of 9000.

320 Furthermore, as seen in Fig. 4 the distribution of NO mass fraction exhibits some formation
321 near the flame base in zone A for the pure hydrogen flame H. The contour plots indicate a
322 strong correlation between the flame temperature and the mass fractions of NO, particularly
323 for the pure hydrogen flame H. Moreover, as we move downstream in Fig. 4, pockets of high

324 NO values are apparent for H₂/CO syngas flames HCO1 and HCO2 at intermediate zone B
325 and downstream zone C. The rise of NO concentration of H₂/CO syngas flames at these
326 pockets may also correspond to regions with high scalar dissipation rate. In addition, large
327 fluid parcels can be observed in the vortical regions of the upstream jet of all cases, as
328 indicated by the distributions of temperature and NO mass fractions, indicating the existence
329 of non-reacting zones associated with the flow structures in the reacting flow field.

330 For the pure hydrogen flame, NO is mainly formed through the Zeldovich mechanism (Eqs.
331 (3), (4) and 5)) as the Fenimore mechanism cannot occur at all due to the absence of CH
332 radicals. Furthermore, the formation of NO appears to be rapid for the pure hydrogen flame
333 H, thus indicating possible reaction between H radicals and N₂ via the NNH mechanism (Eqs.
334 (13) and (14)).

335 However, NO formation mechanism in H₂/CO blended syngas flames is questionable and
336 needs further analysis. To investigate the NO formation mechanisms in hydrogen-rich H₂/CO
337 syngas flame HCO1, laminar counterflow flames are computed by using an updated GRI 3.0
338 mechanism with 54 species and 329 reactions [43]. In the following, the results of two
339 calculations having different strain rates are compared. The strain rates are selected such that
340 one flame is close to chemical equilibrium ($a = 1 \text{ s}^{-1}$) and the other is close to extinction
341 ($a = 1 \times 10^4 \text{ s}^{-1}$). Fig.5 (a) and (b) shows the temperature and net NO formation rate as
342 functions of mixture fraction. A high strain induces high gradients and therefore high
343 conductive heat losses, which lead to a relatively low flame temperature. It is observed that
344 the higher temperature of the low strained flame does not lead to a higher NO formation rate.
345 While the Zeldovich mechanism is expected to produce more NO for the low-strained flame,
346 the net formation rate is actually higher for the high-strained flame with the lower
347 temperature. To further investigate this behaviour in hydrogen-rich H₂/CO syngas flame, the

348 contributions of various NO formation mechanisms are analysed. In Fig.6 (a) and (b) the
349 reaction rates of different NO formation routes are plotted for the two cases. It is found that
350 low strained H₂/CO syngas flame with the highest flame temperature, the Zeldovich
351 mechanism accounts for almost the total NO production. Other NO formation mechanisms
352 have a negligible contribution. However, in the high strained syngas flame, the Zeldovich
353 formation rate is virtually zero, because of the low temperature. Fig. 6(a) and (b) also show
354 that the Fenimore mechanism is negligible in low and high strain rates cases, because CH
355 radicals are not formed in the oxidation of CO. Interestingly, we found that the high NO
356 formation rate in the high strained syngas flame is almost exclusively caused by the NNH
357 route. The high concentration of H radicals results in a high formation rate of NNH (Eq. 13).
358 The NNH radicals then can react with O radicals to form NO and NH (Eq. 14). The NH
359 radicals subsequently react with various partners to form NO directly or via N and HNO.

360 In summary, for hydrogen-rich H₂/CO syngas flames the NO formation rate is highest at low
361 flame temperatures, i.e. at high strain (or scalar dissipation) rates. At high temperatures (i.e.
362 at low strain), the Zeldovich mechanism is the main NO formation route, but at low
363 temperatures the NNH route dominates. The Fenimore mechanism has a negligible
364 contribution in low and high strained rates, because the concentration of CH radicals is
365 practically zero. Moreover, the present findings of NO distribution in hydrogen-rich and
366 hydrogen-lean H₂/CO syngas flames are also consistent with recent NO study carried out by
367 Shih and Hsu [26] for their one-dimensional laminar opposed-jet syngas nonpremixed flames,
368 in which they found that hydrogen-rich H₂/CO syngas flames produce NO emission from
369 Zeldovich and NNH routes.

370 Figs. 7-9 show the instantaneous scatter plots of flame temperature, mass fraction of NO and
371 source term of the transport equation of NO versus mixture fraction in zones A, B and C. The

372 scattered data of pure H₂ flame H does not exhibit local flame extinction for all three zones. It
373 is observed that the range of mixture fraction for pure H₂ flame H is much narrower than CO-
374 diluted flames HCO1 and HCO2. As a result of the preferential diffusion effects, the peak
375 temperature occurs on the lean side of the stoichiometric mixture fraction, which are the
376 strongest for the flame H. The wide range of mixture fraction distribution at a fixed
377 temperature can be attributed to the preferential diffusion which enhances the chemical
378 reactions at the molecular level and leads to chemical reactions at leaner conditions with high
379 flame temperatures. However, this behaviour is starting to deviate more towards local
380 extinction with CO addition to H₂. The scattered data of flame temperature of both the flames
381 HCO1 and HCO2 show that a wide range of temperature is found in a range of relatively high
382 mixture fraction compared to the pure H₂ flame H.

383 The scatter data of mass fraction of NO between the three flames show noticeable differences
384 in zones A, B and C. The pure hydrogen flame H shows considerably higher flame
385 temperatures for all three zones therefore highest NO values compared to the CO-diluted
386 H₂/CO flames. For example, the scatter data of temperature in Figs. 7-9 show the peak values
387 of 2637K for pure hydrogen flame H, 2480K for H₂-rich H₂/CO syngas flame HCO1 and
388 2434K for equally blended H₂/CO syngas flame HCO2. The NO concentration of flame H
389 shows the peak values of 150 (ppm) in zone A, 130 (ppm) in zone B and over 150 (ppm) in
390 zone C. This confirms the formation of high NO concentration near the flame base for the
391 hydrogen flame due to high diffusivity, mainly via the Zeldovich mechanism with possible
392 influence from the NNH mechanism. The scatter plots also reveal decrease of the maximum
393 NO value due to lower temperature of the post-flame gas with respect to CO-dilution, thereby
394 reducing the contribution of the Zeldovich mechanism. The NNH mechanism takes place in a
395 thin area of the flame with large concentration of H radical and therefore can be the dominant

396 route of NO formation in H₂/CO syngas combustion. For example, the NO concentration of
397 syngas flame HCO1 shows peak values of 90 (ppm) in zone A, 120 (ppm) in zone B and 110
398 (ppm) in zone C. A similar trend is also observed for the syngas flame HCO2. Furthermore,
399 more populated NO concentration forms for the entire mixture fraction range at the upstream
400 zone A for all three flames irrespective of the fuel mixture. However, this behaviour
401 disappears in zone B, where NO concentrations start to compress towards fuel lean side.
402 Similar trends with further compact NO concentrations are observed in zone C.

403 In addition to the differences found for the NO concentration, differences are also exhibited
404 for the source term of the NO transport equation for all three flames. To identify the
405 distribution between the NO concentration and the source term of the NO transport equation,
406 scatter plots of the source term of the NO transport equation are also plotted in zones A, B
407 and C respectively. For pure hydrogen flame H, densely populated NO source term particles
408 are found in the fuel lean region with a Gaussian shape distribution. However, as seen in
409 syngas flames HCO1 and HCO2, the Gaussian shape is slightly deviated with CO-dilution. It
410 is also noticed that the negative values of NO source term occur for CO-diluted flames
411 HCO1, HCO2, while it shows zero as a minimum value for the undiluted flame H. There is
412 also a considerable difference in the maximum values of the NO source term between the
413 three cases depending on the amount of CO-dilution in the fuel.

414 To explicitly identify the behaviour of NO formation and its relation with temperature,
415 conditional mean value of mass fraction of NO as a function of temperature and probability
416 density functions (pdf) of temperature and NO mass fraction are plotted. Fig. 10 shows the
417 conditional mean values of mass fraction of NO as a function of temperature for pure
418 hydrogen flame H and H₂/CO syngas flames HCO1 and HCO2. The conditional mean values
419 of NO show considerably high peak for hydrogen flame H compared to syngas flames HCO1

420 and HCO₂ at high temperature regions with main contribution from the Zeldovich route. It is
421 also observed in Fig. 8 that CO addition (HCO₁ and HCO₂) tends to reduce the strength of
422 high NO peak value considerably. This effect is presumably due to considerable energy
423 required to oxidise highly stable N₂ molecule as the CO-dilution lower the flame temperature
424 and therefore energy level.

425 Figs. 11 and 12 show pdf of temperature and NO mass fraction for flames H, HCO₁ and
426 HCO₂. The pdf distribution of pure hydrogen flame H remains fully Gaussian with
427 significantly high NO values at high temperature. However, pdfs of H₂/CO syngas flames
428 HCO₁ and HCO₂ display a relatively less-Gaussian behaviour compared to pure hydrogen
429 flame H. From Figs. 11 and 12 one can conclude that pdf of NO mass fraction has a large
430 variance for pure hydrogen flame H in which data points are spread out around the mean and
431 from each other, but relatively a small variance for CO-diluted flames HCO₁ and HCO₂ in
432 which data points tend to be close to the mean values and hence to each other.

433 It is known that the NO chemistry is sensitive to reactions governing the fuel oxidation and
434 the present results indicate possible avenues for future studies of important interactions
435 between emissions. In particular, further investigation on NO-CO interactions and their
436 correlation with main CO oxidation reaction $\text{O} + \text{H} + \text{CO} \leftrightarrow \text{H} + \text{CO}_2$ flame temperature and
437 effective flame zone residence time of syngas combustion would be of great interest. In the
438 future, NO-CO interactions via the NCN radicals will be investigated in detail, which will
439 help us to further understand how critical pollutants interact with each other in hydrogen-rich
440 and hydrogen-lean syngas combustion.

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443 **4. Conclusions**

444 Nitric oxide formation in hydrogen and hydrogen-rich H₂/CO syngas turbulent nonpremixed
445 jet flames have been investigated using direct numerical simulation and tabulated FGM
446 chemistry. Simulations were performed at a Reynolds number of 6000. The influence of
447 preferential diffusion on nitric oxide formation is checked by comparing DNS results
448 between the unity Lewis number and the non-unity Lewis number cases. Statistics of
449 instantaneous flame temperature, mass fraction of NO, source term of transport equation of
450 NO, conditional mass fraction of NO, and probability density functions of NO from direct
451 numerical simulations were compared for pure hydrogen flame H and two hydrogen-rich
452 H₂/CO syngas flames.

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454 The main conclusions are as follows:

- 455 a. In pure hydrogen flame and hydrogen-rich syngas flames studied here, the peak
456 temperature occurs on the lean side of the stoichiometric mixture fraction as a result
457 of the preferential diffusion effects associated with the hydrogen content in the fuel
458 mixture, which are the strongest for pure hydrogen flame.
- 459 b. Comparing statistics of NO distribution between the unity Lewis number and the non-
460 unity Lewis number showed that preferential diffusion plays a significant role in
461 capturing accurate and higher NO levels depending on the hydrogen content in the
462 fuel mixture.
- 463 c. The analysis indicates a strong correlation between the flame temperature and the
464 mass fractions of NO, particularly for the flame H, in which NO is mainly formed
465 through the Zeldovich mechanism and partially via the NNH mechanism.
- 466 d. The results also indicate a decrease of NO concentration values due to the lower
467 temperature of the post-flame gas with respect to CO-dilution in the H₂/CO syngas

468 mixture, thereby reducing the contribution of the Zeldovich mechanism. To fill the
469 gap, the NNH mechanism takes place in a thin area of the flame with the presence of
470 high concentration of H radical results in a high formation rate of NNH. The
471 Fenimore mechanism is not found due to absence of CH radical in the H₂/CO syngas
472 mixture.

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634 **Tables:**

635 **Table 1.** Simulated test cases, flame properties, physical and numerical parameters.

Simulated Flames, Properties and Parameters	Flame H	Flame HCO1	Flame HCO2
Fuel Properties	100% H ₂ by volume	70% H ₂ by volume 30% CO by volume	50% H ₂ by volume 50% CO by volume
Stoichiometric mixture fraction	0.028	0.124	0.179
Adiabatic flame temperature	2637K	2480K	2434K
Jet Diameter (D)	5mm	5mm	5mm
Domain size (L _x × L _y × L _z)	35 m m × 35 m m × 50 m m	35 m m × 35 m m × 50 m m	35 m m × 35 m m × 50 m m
Number of grid points (N _x × N _y × N _z)	640 × 640 × 640	640 × 640 × 640	640 × 640 × 640
Mean inlet jet velocity (U _j)	20.94 m s ⁻¹	20.94 m s ⁻¹	20.94 m s ⁻¹
Inlet Jet temperature	300K	300K	300K
Jet Reynolds number ¹ (Re = U _j × D / ν)	6000	6000	6000
Velocity fluctuation ² (u'/U _j)	0.23	0.21	0.2
Integral length scale ^{2,3} (l ₃₃ /D)	0.36	0.37	0.39
Turbulence Reynolds number ^{2,3} (Re _t = u' l ₃₃ / ν)	230	224	218

636 ¹ Kinematic viscosity at the inflow conditions, $\nu = 1.574 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ is used to calculate the
637 Reynolds number.

638 ² The turbulence scales evolve from the artificial turbulence specified at the inflow. The
639 u' value is evaluated at the 1/2 stream location along the jet centreline.

640 ³ Integral length scale l_{33} is defined as the integral of the auto-correlation of the spanwise
641 component of velocity in the spanwise direction. The u' value is evaluated at the 1/2 stream
642 location along the jet centreline.

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681 **Figure Captions**

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683 **Fig.1.** Configuration of the turbulent non-premixed round jet flame. Fuel is injected from the
684 fuel inlet with a nozzle diameter D (here we show iso-contours of flame structure of
685 hydrogen flame H and dashed line indicates the flammable layer).

686 **Fig.2.** Comparison of iso-contours of NO mass fraction, scatter plots of NO mass fraction vs.
687 mixture fraction at full domain ($0 \leq z \leq 10$), and scatter plots of NO mass fraction vs.
688 mixture fraction at near nozzle region ($z \leq 2$) between unity Lewis number (a1, b1, c1) and
689 non-unity Lewis number (a2, b2, c2) of hydrogen flame H at a non-dimensional time instant
690 $t=30$.

691 **Fig.3.** Comparison of scatter plots of NO mass fraction vs. mixture fraction of hydrogen
692 flame H between DNS data (a1, b1, c1) at Reynolds number of 6000, and the experimental
693 data (a2, b2, c2) at Reynolds number of 10000, at different non-dimensional axial locations
694 $z=4$ (a), 8 (b) and 10 (c).

695 **Fig.4.** Snapshots of flame temperature and NO mass fraction for flames H, HCO1 and HCO2
696 at non-dimensional time $t=30$.

697 **Fig.5.** Temperature (a) and net NO formation rate (b) as functions of mixture fraction for a
698 low strain rate $a = 1 \text{ s}^{-1}$ and high strain rate $a = 10^4 \text{ s}^{-1}$ for syngas flame HCO1.

699 **Fig.6.** Reaction rates of different NO formation mechanisms as functions of mixture fraction
700 (a) for a low strain rate $a = 1 \text{ s}^{-1}$ and (b) for a high strain rate $a = 10^4 \text{ s}^{-1}$ for syngas flame
701 HCO1.

702 **Fig.7.** Scatter plots for flame temperature, NO mass fraction and source term of the transport
703 equation of NO mass fraction vs. mixture fraction in near-inflow zone A ($0 < z < 2$) for flames
704 H, HCO1 and HCO2 at non-dimensional time $t=30$.

705 **Fig.8.** Scatter plots for flame temperature, NO mass fraction and source term of the transport
706 equation of NO mass fraction vs. mixture fraction in intermediate zone B ($2 < z < 8$) for flames
707 H, HCO1 and HCO2 at non-dimensional time $t=30$.

708 **Fig.9.** Scatter plots for flame temperature, NO mass fraction and source term of the transport
709 equation of NO mass fraction vs. mixture fraction in near-outflow zone C ($8 < z < 10$) for
710 flames H, HCO1 and HCO2 at non-dimensional time $t=30$.

711 **Fig.10.** Conditional mean values of mass fractions of NO as a function of temperature for
712 flames H, HCO1 and HCO2 at non-dimensional time $t=30$.

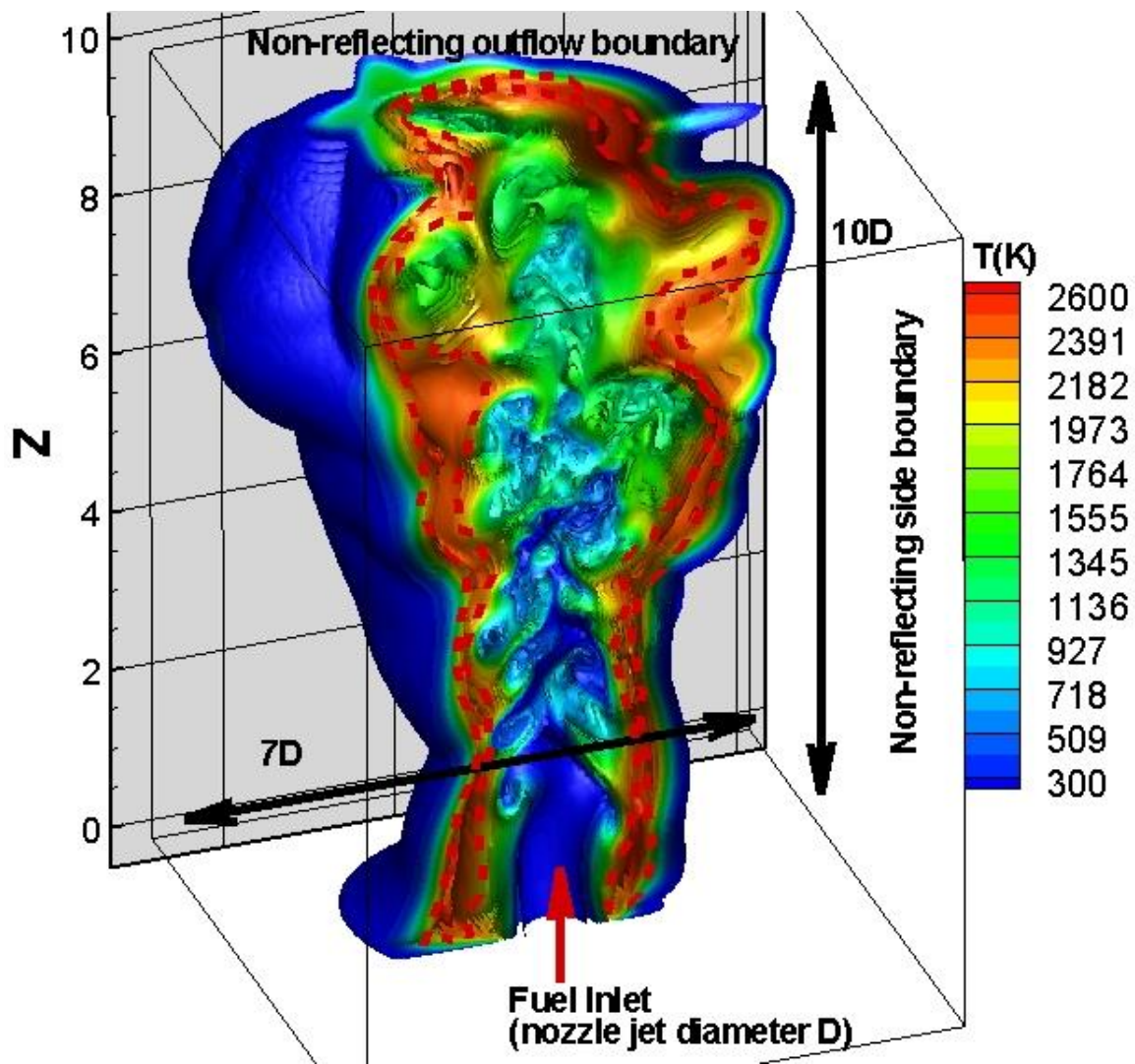
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714 **Fig.11.** Probability density function (pdf) of temperature for flames H, HCO1 and HCO2 at
715 non-dimensional time $t=30$.

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717 **Fig.12.** Probability density function (pdf) of mass fractions of NO for flames H, HCO1 and
718 HCO2 at non-dimensional time $t=30$.

719 **Figures:**



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722 **Fig.1.** Configuration of the turbulent non-premixed round jet flame. Fuel is injected from the
723 fuel inlet with a nozzle diameter D (here we show iso-contours of flame structure of
724 hydrogen flame H and dashed line indicates the flammable layer).

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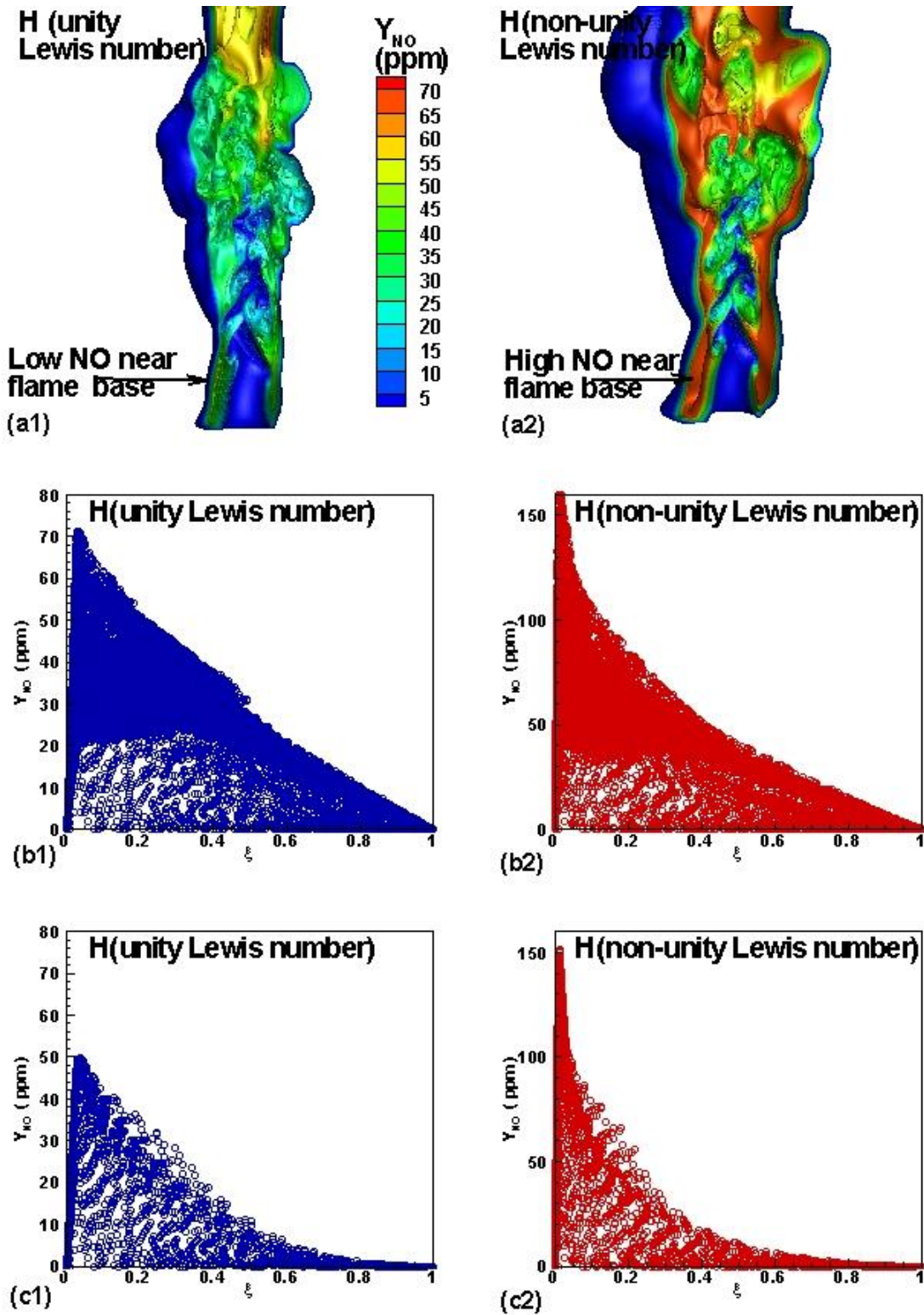
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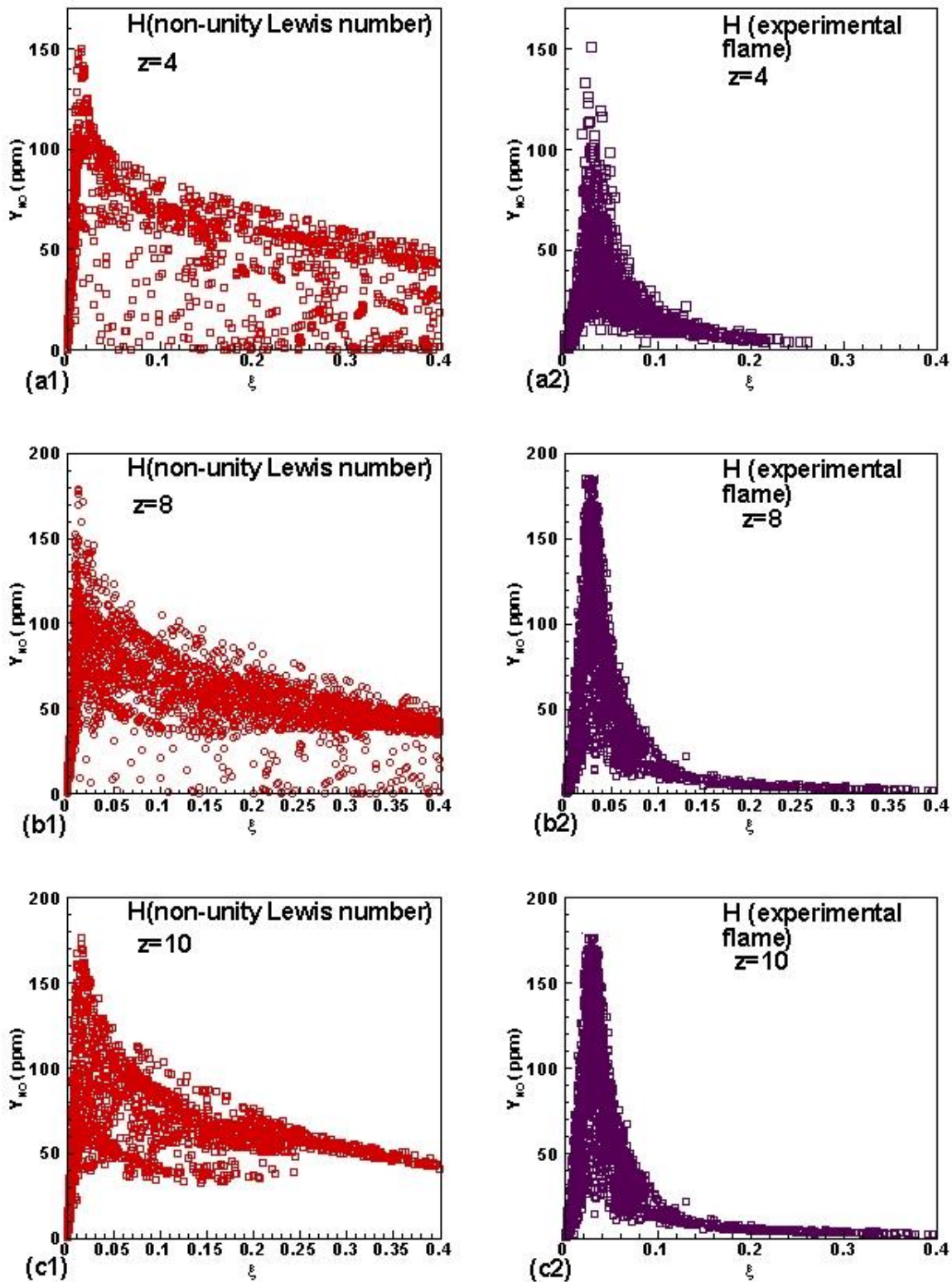
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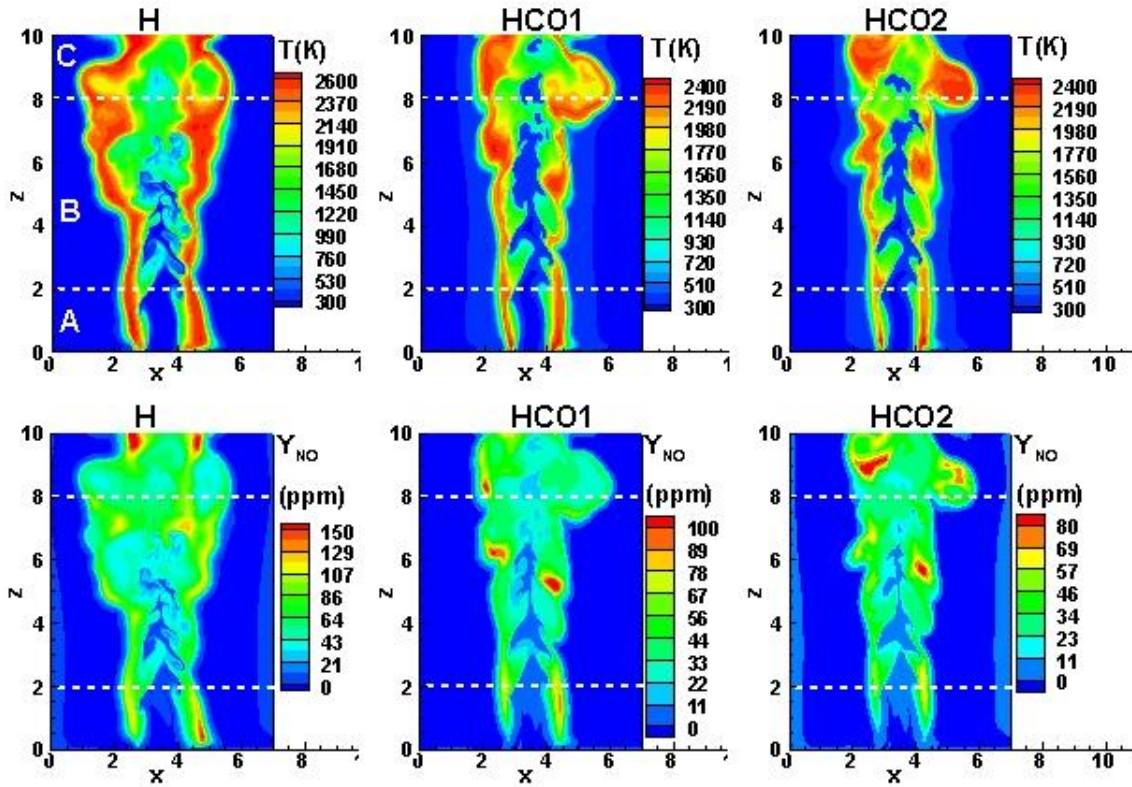
732 **Fig.2.** Comparison of iso-contours of NO mass fraction, scatter plots of NO mass fraction vs.
 733 mixture fraction at full domain ($0 \leq \xi \leq 1$), and scatter plots of NO mass fraction vs.
 734 mixture fraction at near nozzle region ($z \leq 2$) between unity Lewis number (a1, b1, c1) and
 735 non-unity Lewis number (a2, b2, c2) of hydrogen flame H at a non-dimensional time instant
 736 $t=30$.



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738 **Fig.3.** Comparison of scatter plots of NO mass fraction vs. mixture fraction of hydrogen
 739 flame H between DNS data (a1, b1, c1) at Reynolds number of 6000, and the experimental
 740 data (a2, b2, c2) at Reynolds number of 10000, at different non-dimensional axial locations
 741 $z=4$ (a), 8 (b) and 10 (c).

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744 **Fig.4.** Snapshots of flame temperature and NO mass fraction for flames H, HCO1 and HCO2
 745 at non-dimensional time $t=30$.

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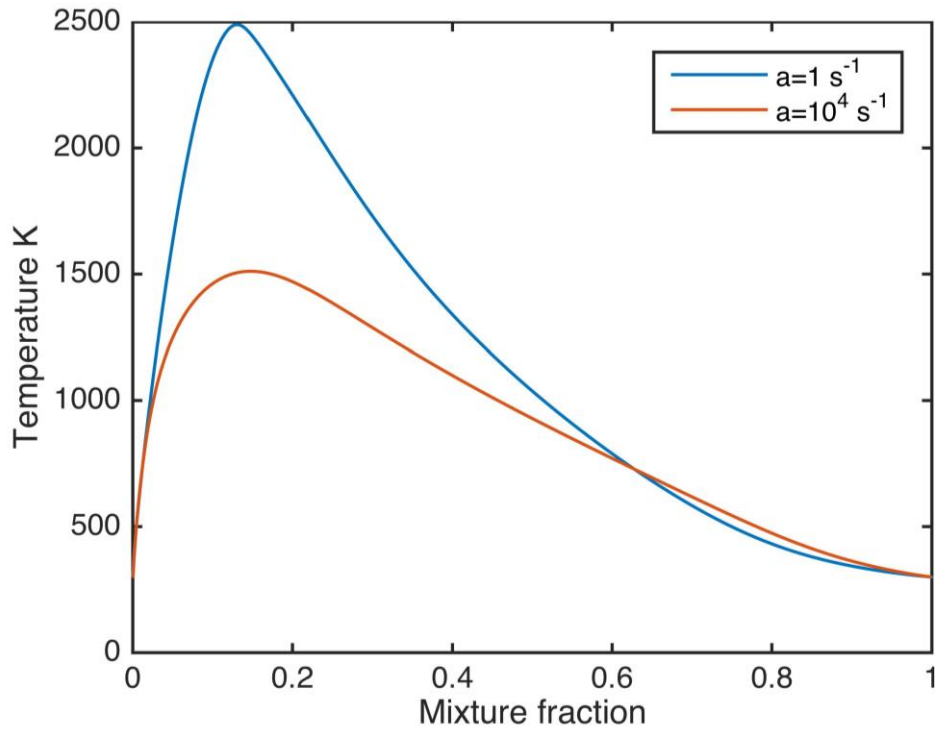
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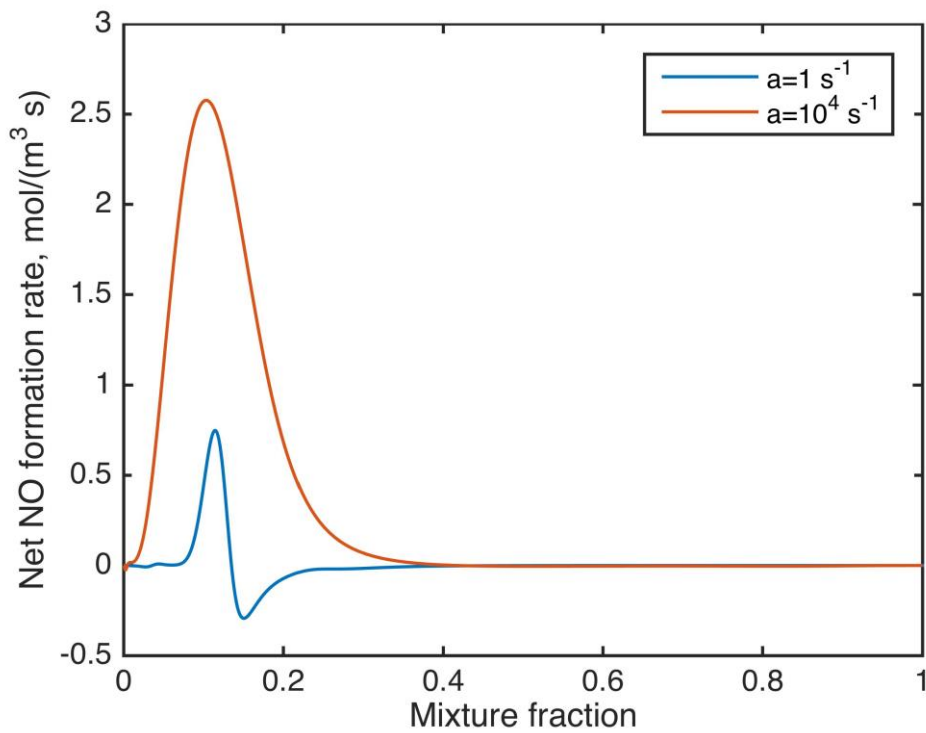
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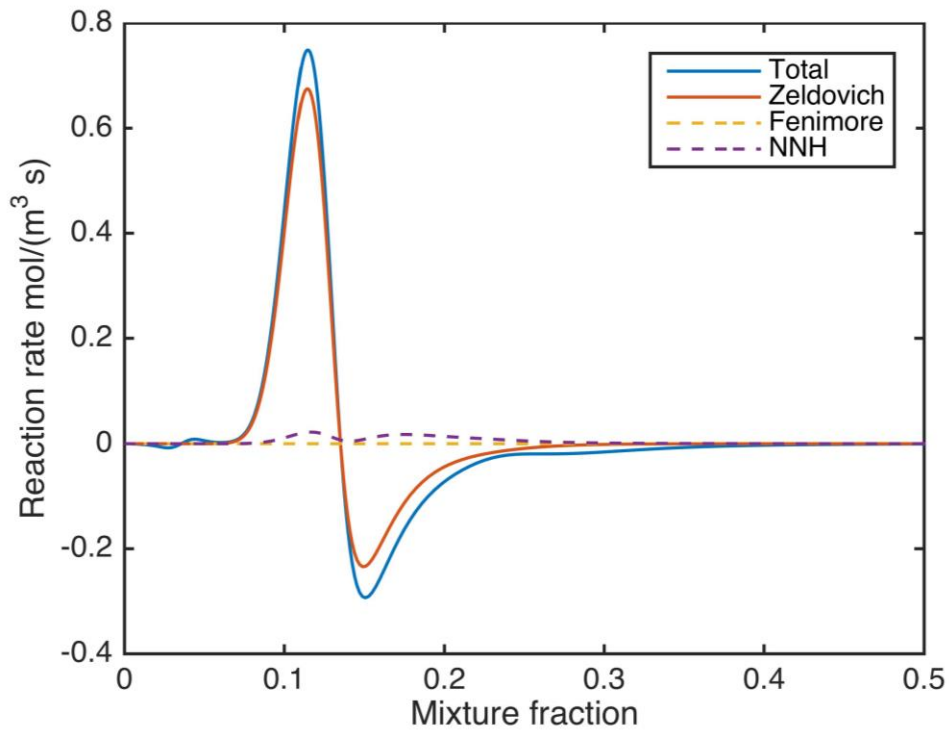
(a)



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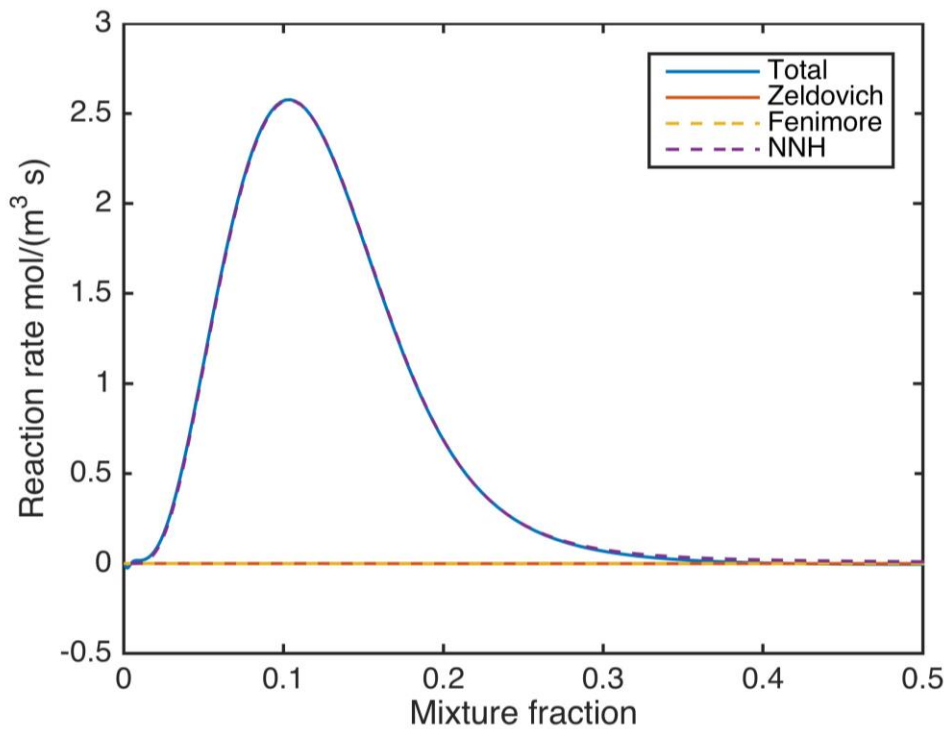
(b)

763 **Fig.5.** Temperature (a) and net NO formation rate (b) as functions of mixture fraction for a
764 low strain rate $a = 1 \text{ s}^{-1}$ and high strain rate $a = 10^4 \text{ s}^{-1}$ for syngas flame HCO1.



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(a)

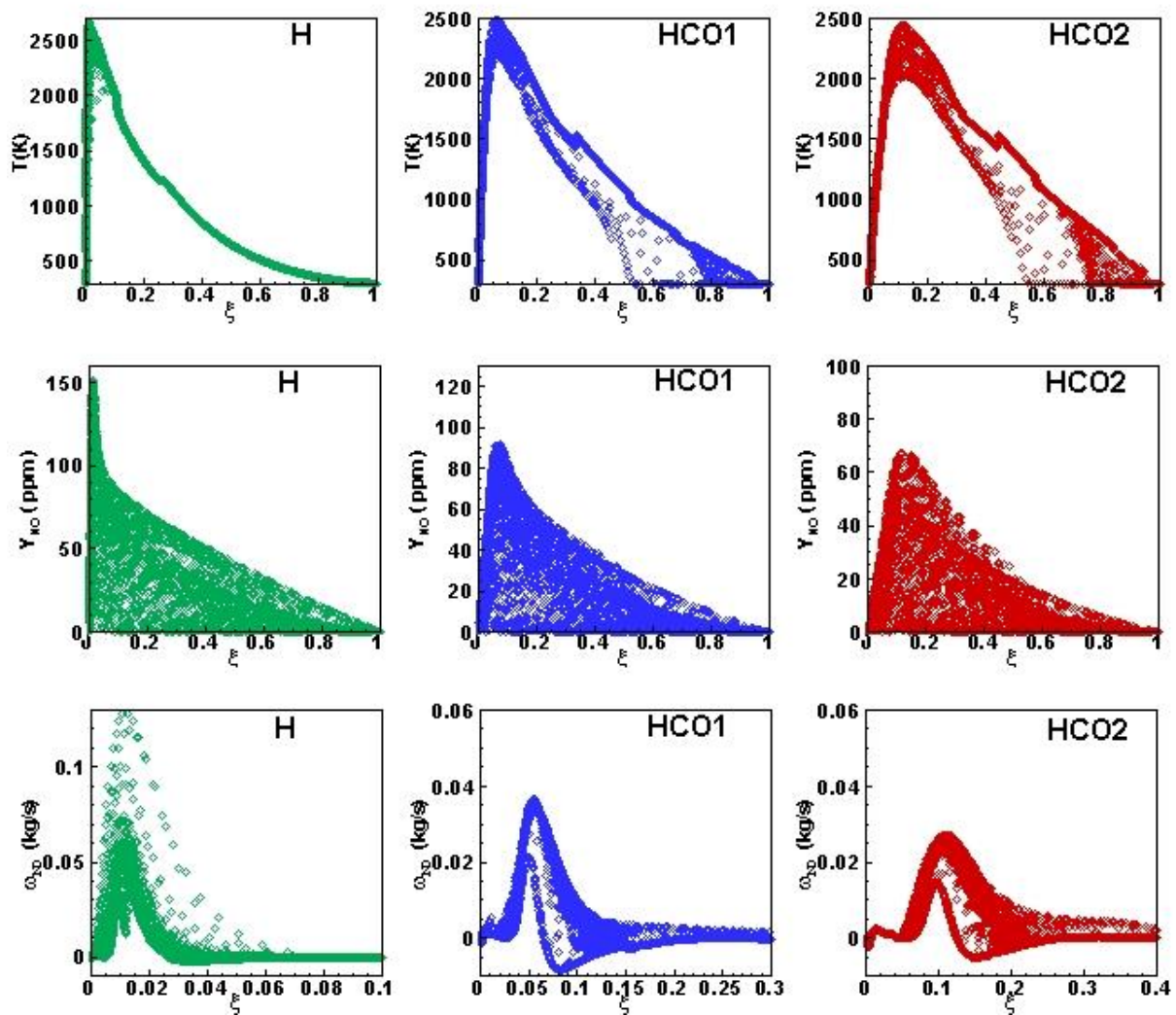


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(b)

770 **Fig.6.** Reaction rates of different NO formation mechanisms as functions of mixture fraction
771 (a) for a low strain rate $a = 1 \text{ s}^{-1}$ and (b) for a high strain rate $a = 10^4 \text{ s}^{-1}$ for syngas flame
772 HCO1.

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776 **Fig.7.** Scatter plots for flame temperature, NO mass fraction and source term of the transport
 777 equation of NO mass fraction vs. mixture fraction in near-inflow zone A ($0 < z < 2$) for flames
 778 H, HCO1 and HCO2 at non-dimensional time $t=30$.

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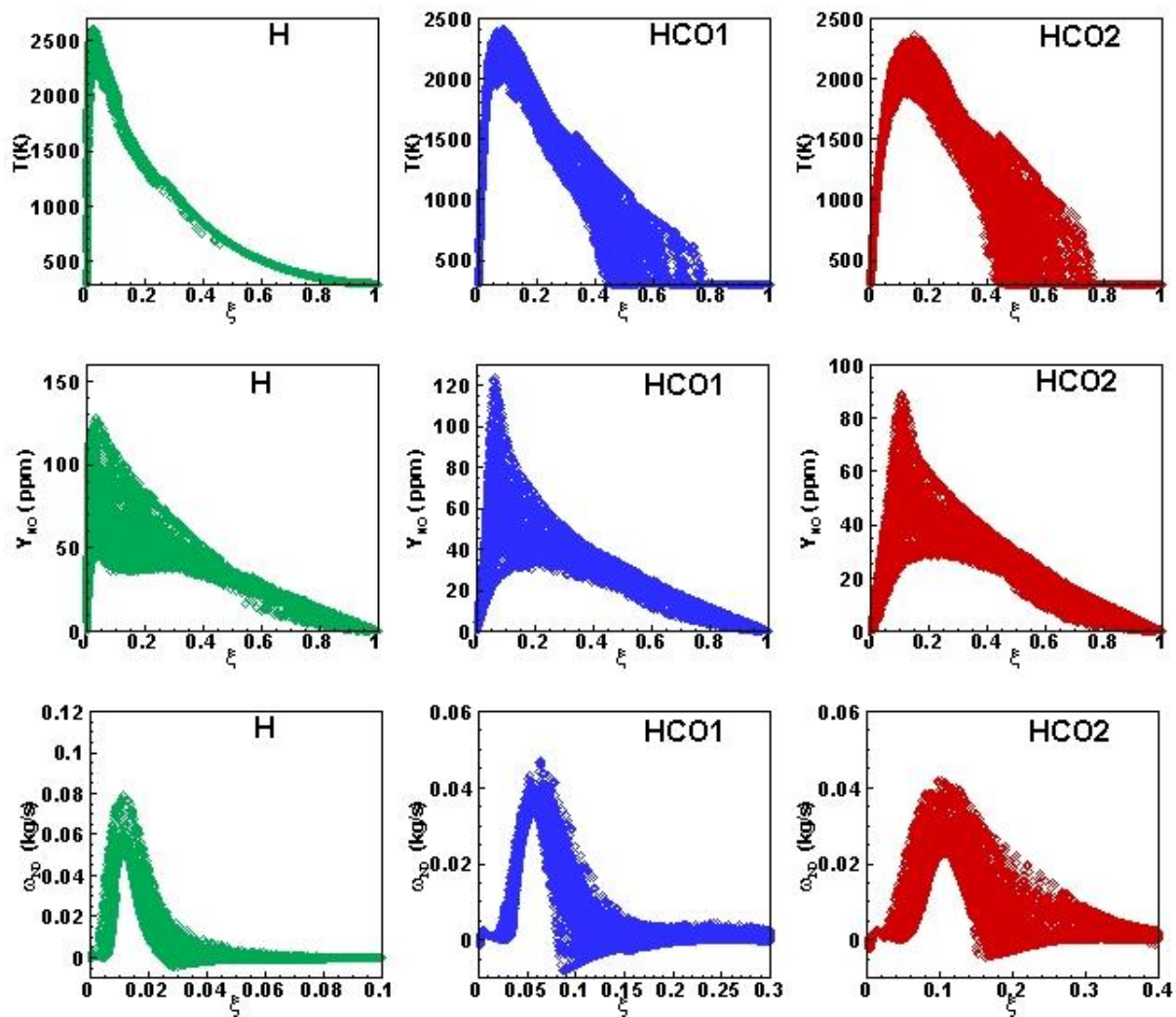
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788 **Fig.8.** Scatter plots for flame temperature, NO mass fraction and source term of the transport
 789 equation of NO mass fraction vs. mixture fraction in intermediate zone B ($2 < z < 8$) for flames
 790 H, HCO1 and HCO2 at non-dimensional time $t=30$.

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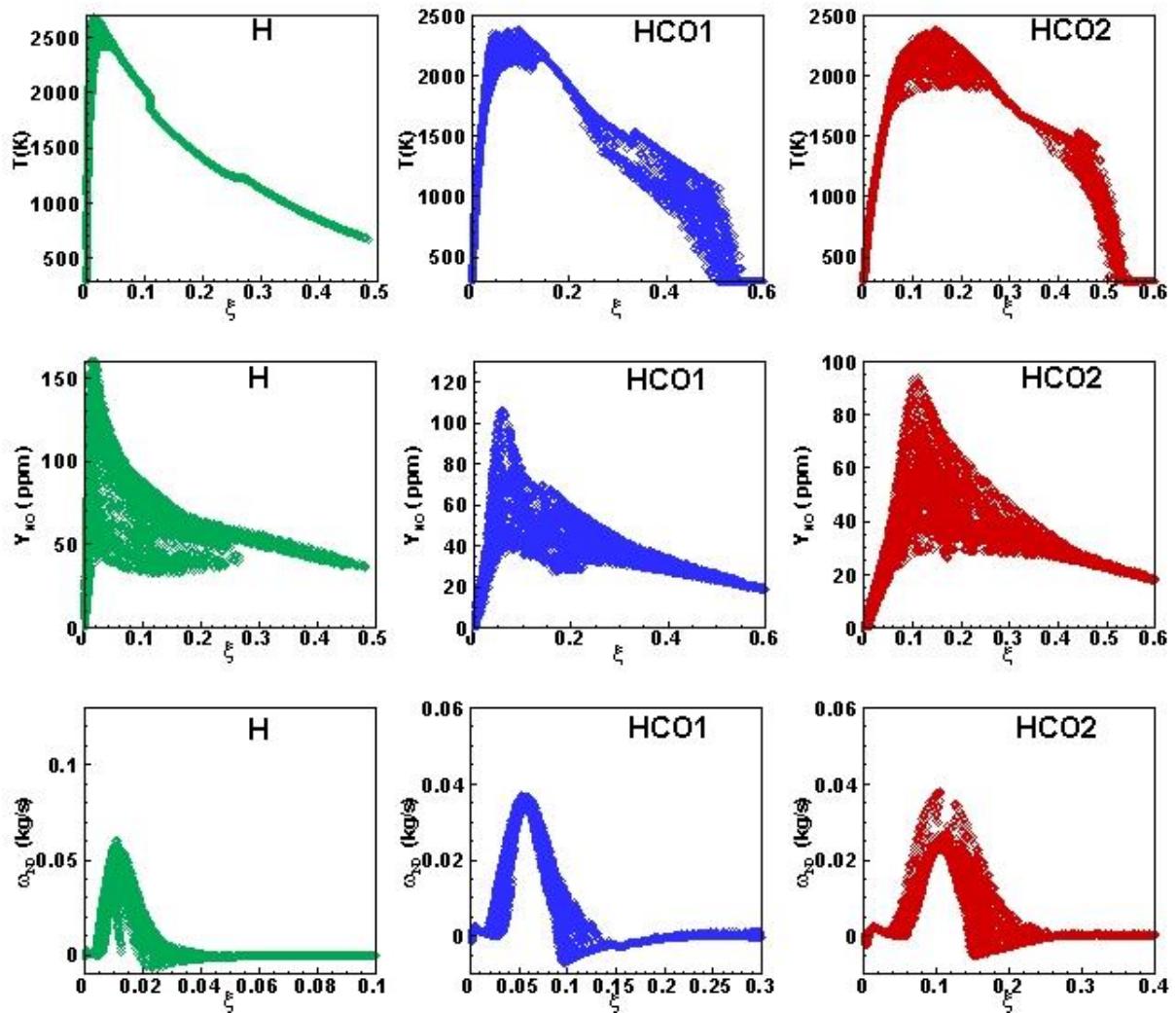
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800 **Fig.9.** Scatter plots for flame temperature, NO mass fraction and source term of the transport
 801 equation of NO mass fraction vs. mixture fraction in near-outflow zone C ($8 < z < 10$) for
 802 flames H, HCO1 and HCO2 at non-dimensional time $t=30$.

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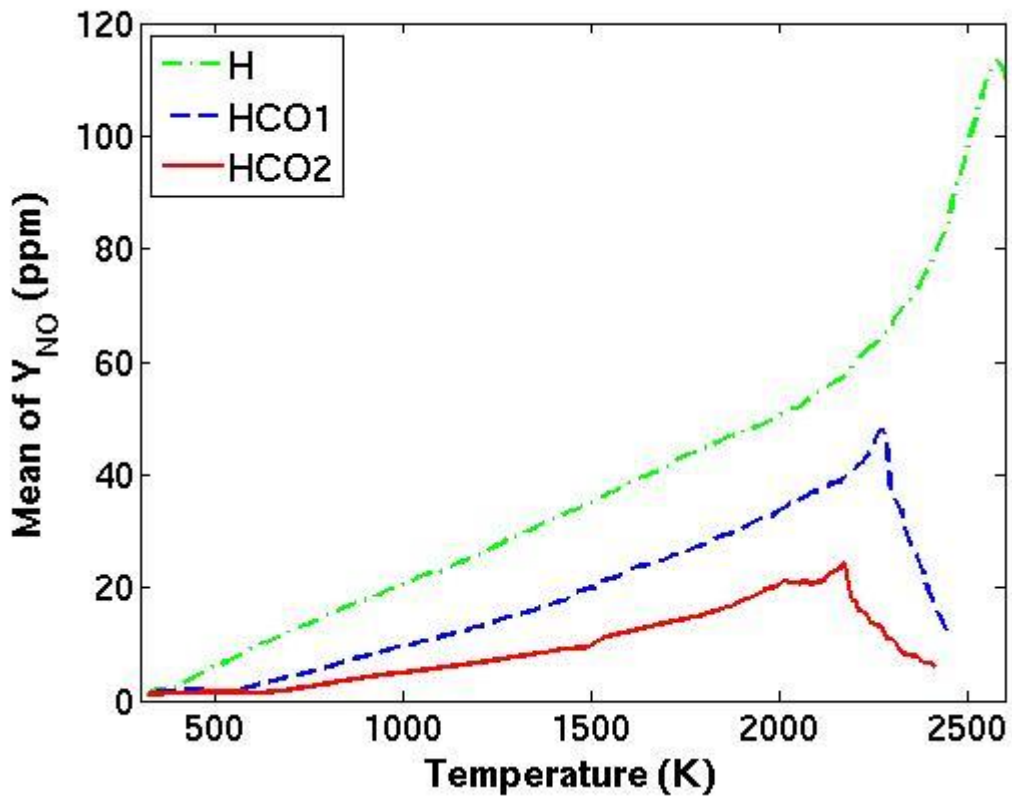
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812 **Fig.10.** Conditional mean values of mass fractions of NO as a function of temperature for
813 flames H, HCO1 and HCO2 at non-dimensional time $t=30$.
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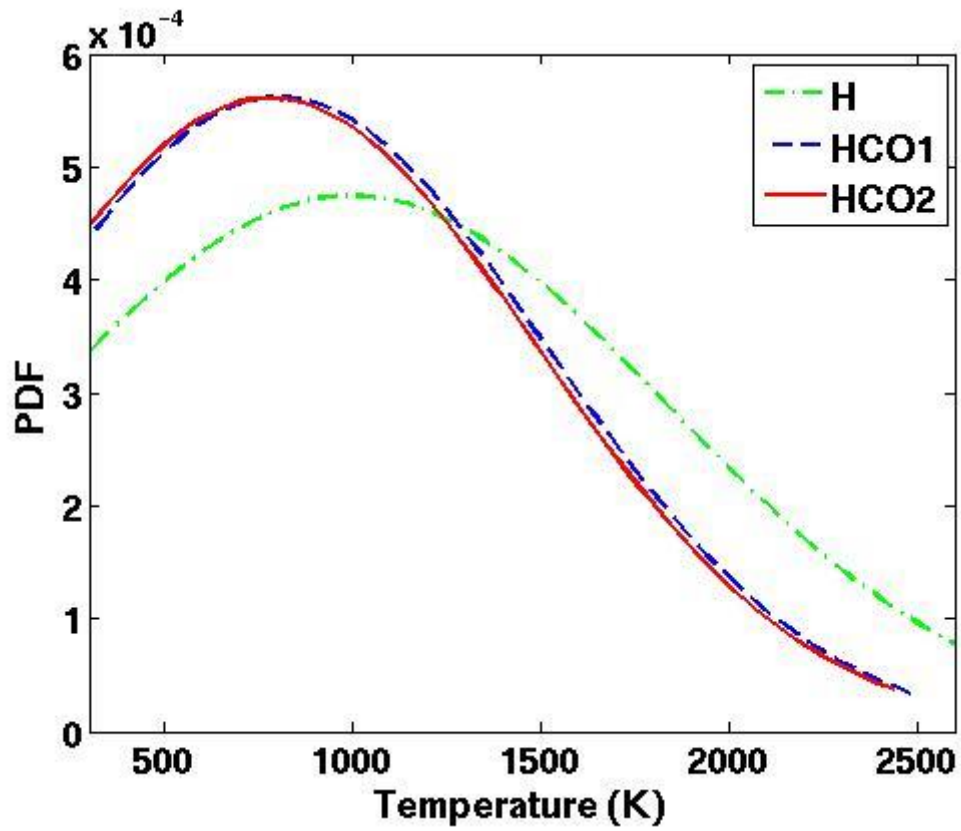
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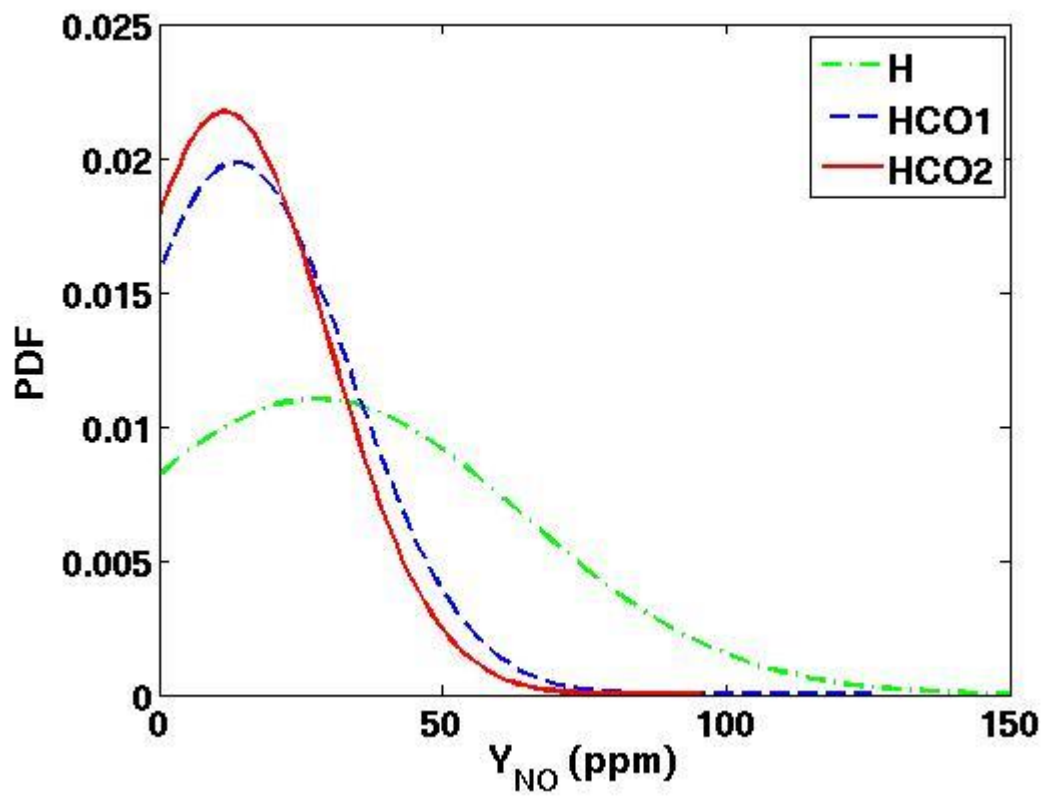
826

827 **Fig.11.** Probability density function (pdf) of temperature for flames H, HCO1 and HCO2 at
828 non-dimensional time $t=30$.

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Fig.12. Probability density function (pdf) of mass fractions of NO for flames H, HCO1 and HCO2 at non-dimensional time $t=30$.