NO$_X$ FORMATION IN H2-CH4 BLENDED FLAME UNDER MILD CONDITION

A. Mardani* and S. Tabejamaat*
Amir_Mardani@aut.ac.ir
* Department of Aerospace Engineering, Amirkabir University of Technology, Tehran, Iran
Po.Box: 15875-4413

Abstract

In this paper, NO production mechanisms for CH4-H2 combustion under MILD (moderate or intense low-oxygen dilution) condition are studied using CDF and also zero-dimensional WSR analysis. A H2/CH4 jet into a heated and diluted co-flow is modelled in CFD analysis. The RANS equations with modified $k-\varepsilon$ equations are solved in an axisymmetric 2D computational domain. The GRI2.11 full mechanism is considered to represent the chemical reactions. The effects of oxidizer oxygen concentration, fuel hydrogen content, and fuel jet Reynolds number are studied on NO formation reactions. Results show that the measurements are predicted with an acceptable accuracy. The NNH and N2O routes are the most important pathways in NO formation under MILD conditions. An increase in oxidizer O2 level or decrease in fuel hydrogen content address to decrease in importance of the mentioned NO formation routes.

Introduction

The elimination of greenhouse gas, unburned hydrocarbons (UHC), CO and NOx emissions are more focused these days. This mission can be suppressed by using the hydrogen as pure fuel or additive to other fuels. Hydrogen is a clean fuel without any CO, CO2, SOx and UHC emission. Rørtveit et al. [1] showed that hydrogen flame under counter flow configuration produced lower NO in comparison with methane flames at the same flame temperature. On the other hand, Skottene et al. [2] illustrated that the hydrogen-air flame could produce higher NOx as a results of higher flame temperature due to higher hydrogen reactivity. However, hydrogen replacement for hydrocarbons fuels is not simple and there are some problems such as storage, safety and cost which arise from characteristics of hydrogen. The storage and safety technological challenges of Hydrogen usage are due to its high reactivity and molecular diffusivity which they address to potential of explosion hazards. Moreover, hydrogen can be produced from different ways but it does not exist as natural resource.

MILD combustion is another possibility for improving the environmental friendly standards of combustion systems regarding to pollutants. MILD is acronym of “Moderate or Intense Low-oxygen Dilution” combustion, [3]. It is combustion of fuel-oxidizer mixture under high diluted and preheated conditions, in such a way that the mixture initial temperature is higher than its auto-ignition temperature and the temperature increase is lower than preheated temperature. MILD combustion is known as a new technology and broadly similar to High Temperature Air Combustion (HiTAC) [4,5,6], High Temperature Combustion Technology (HiCOT) [3,7] and Flameless Combustion [8]. Different numerical and experimental reports have shown the interesting characteristics of this new combustion regime. They are lower emission production and fuel consumption [9,10,11], larger reaction zone [12,13], more uniform and lower fluctuations in temperature field [8,14], kinetics-controlled low Damköhler number combustion [15] and lower noise [8] with respect to the “traditional” combustion process.

Using hydrogen-hydrocarbon blended fuels and hydrogen added fuel mixtures in MILD regime could be an interesting approach to have more efficient and cleaner combustion. This idea has been studied in some experimental and numerical researches. In 2002, Dally et al. [16] reported the measurements on temperature, OH, H_2O, O_2, and NO distribution in a H_2/CH_4 jet flame under MILD conditions. Christo et al. [17], in 2005, predicted the Dally's measurements numerically except for NOx. Medwell et al. [18] studied the flame structure of H_2/CH_4 jet in Dally's burner experimentally. Furthermore, importance of molecular diffusion in MILD regime and also Effect of hydrogen on hydrogen-methane turbulent non-premixed flame under MILD condition is studied by the authors in 2010, respectively [19,20].

NOx formation in ordinary combustion of hydrocarbons and hydrogen or their mixture are studied in several reports. Effects of diluents on NOx formation in Hydrogen counter flow flame is studied by Rørtveit et al. [1] in 2002. They illustrate significant formation of NO from N_2O and NNH mechanism at lower temperature. In 2007, Skottene et al. [2] tested four different mechanisms for eight laminar and further two turbulent jet flames. They investigated the importance of NO formation through NNH radicals in the hydrogen-air flames.

Yang et al. [21] reported, in 2005, that NO emission formation by N_2O route is very important during the HiTAC condition for fuel of LPG. They used the N_2O route with thermal-NO, prompt-NO and NO-reburning models for prediction of NO emission. Nicole et al. [22], in 2006, studied the occurrence of NO-reburning in MILD combustion for methane. They investigated that NO formation by thermal and N_2O pathways grow in importance after auto ignition while NO-reburning may occur for fuel rich mixture. NOx formation under MILD condition for fuel mixture of CH_4/H_2 is studied by Yu et al. [23] in 2010. They employed a zero dimensional method using the PSRN model to investigate the NOx and CO emissions at different H_2 containing fuel mixture. NO emission from a lab-scale burner fed with CH_4/H_2 mixture was investigated numerically and experimentally by Galletti et al. [24], in 2009. They report the dominant role of NNH and N_2O pathways for NO formation under MILD condition. Although hydrogen and hydrogen-hydrocarbon fuels have been studied in many reports under ordinary combustion conditions, it is less mentioned under MILD combustion regime specially regarding to NOx formation mechanisms. This paper is part of an effort to improve the knowledge of MILD combustion characteristics. Indeed the main objective of this work is the better understanding of NOx formation mechanisms in CH_4/H_2 flame under MILD condition and also investigation of effect of fuel hydrogen content on NOx formation. In this way CFD modeling of well setup jet flame of Dally et al., [16] are done. Furthermore a zero dimensional analysis of a well stirred reactor (WSR) is performed. Effects of oxidizer oxygen concentrations, fuel jet Reynolds number, and also fuel mixture hydrogen content on NO formation are studied.

Numerical Method

The CFD method which is used in this paper is identical with those of the previous studies of the authors [19,20] and hence will be abbreviated here. The JHC burner of Dally et al.[16] is a co-flow burner in which the fuel jet issues into the co-flow preheated and diluted air. The JHC burner is mounted in a wind tunnel in which air flows with a velocity of 3.2 m/s in parallel with jet axis. The wind tunnel air consists of 23% O_2 and 77% N_2 (mass basis). The fuel jet Reynolds number is around 10000 and the velocity of hot co-flow air is also 3.2 m/s. temperature of fuel jet, hot co-flow, and wind tunnel air are 305, 1300, and 305 k, respectively.

The JHC burner is modeled using the 2D-axisyymetric computational domain, Fig. 1, with 39000 cells. Navier-stokes equations and modified $k-\varepsilon$ equations are solved by Patankar Simpler algorithm. The equations are discritized by third order quick method. Differential diffusion method using the molecular kinetic theory is considered. However the radiation is neglected. Turbulence chemistry interaction is modeled by EDC model [25]. This model applied the Arrhenius finite rate model to each control volume using the flow field turbulence characteristics. This model has been recommended by some other researches [26,27,28]. Chemical reactions are considered according GRI 2.11 full mechanisms.

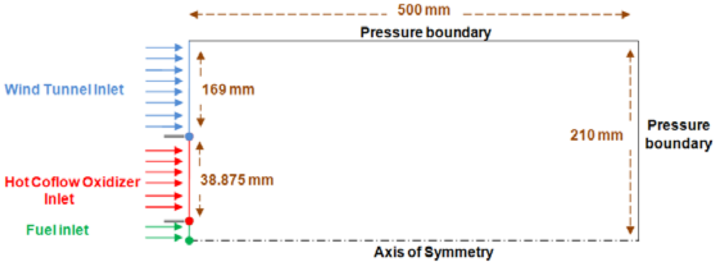


Figure 1. Computational domain of JHC burner [16]

The well stirred reactor (WSR) analysis is performed by solving the species conservations equations under constant reactor temperature over a residence time using an in-house Fortran code which includes some subroutines of the Chemkin open source code, [29]. The WSR analysis is at T = 1345K and P = 1 atm for a 0.1-s residence time. Moreover the sensitivity analysis of NO formation to reactions parameters is done. The sensitivity is defined as;

$$\frac{\partial LnY_{No}}{\partial Lnkr_i} = \frac{kr_i}{Y_{No}} \frac{\partial Y_{No}}{\partial kr_i} \tag{1}$$

Where kr_i is reaction constant of reaction number i and Y_{No} is the mass fraction of NO species.

Results and Discussion

In this study NOx formation pathways for H2/CH4 jet flame under MILD condition is illustrated by defining Ten Numerical test cases which as shown in Table 1. They are considered for CFD or zero-dimensional WSR analysis. At the first, the accuracy of CFD modeling is validated by comparing the numerical prediction and Dally's measurements for 9 % O2 at 30mm above the nozzle (Fig. 2).

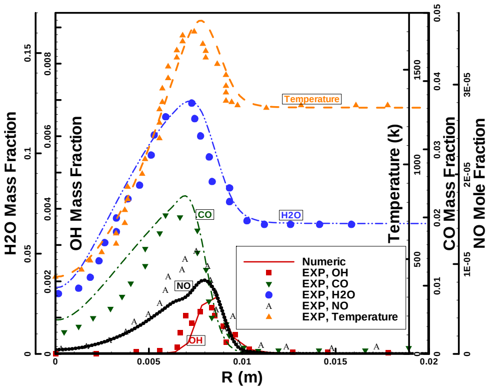
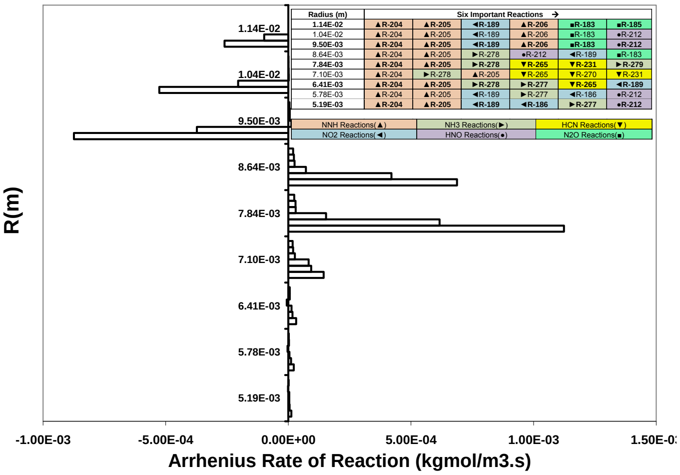


Figure 2. Radial numerical Predictions versus measurements for 9% O2 at Z=30 mm, (Case 1 in Table 1).



Radius (m)	Six Important Reactions →					
1.14E-02	**▲R-204**	**▲R-205**	**◀R-189**	**▲R-206**	**■R-183**	**■R-185**
1.04E-02	▲R-204	▲R-205	◀R-189	▲R-206	■R-183	●R-212
9.50E-03	**▲R-204**	**▲R-205**	**◀R-189**	**▲R-206**	**■R-183**	**●R-212**
8.64E-03	▲R-204	▲R-205	▶R-278	●R-212	◀R-189	■R-183
7.84E-03	**▲R-204**	**▲R-205**	**▶R-278**	**▼R-265**	**▼R-231**	**▶R-279**
7.10E-03	▲R-204	▶R-278	▲R-205	▼R-265	▼R-270	▼R-231
6.41E-03	**▲R-204**	**▲R-205**	**▶R-278**	**▶R-277**	**▼R-265**	**◀R-189**
5.78E-03	▲R-204	▲R-205	◀R-189	▶R-277	◀R-186	●R-212
5.19E-03	**▲R-204**	**▲R-205**	**◀R-189**	**◀R-186**	**▶R-277**	**●R-212**

NNH Reactions(▲)	NH3 Reactions(▶)	HCN Reactions(▼)
NO2 Reactions(◀)	HNO Reactions(●)	N2O Reactions(■)

Figure 3. First sixth important N containing reactions which are selected by sorting N containing reactions according to the absolute rate of reactions at each radial distance for Z=30 mm and 9% O2 configuration, (Case 1 in Table 1).

It can be understood that there are a reasonable accuracy of numerical prediction regarding to temperature, OH, CO, and H2O species. Furthermore, the Nitric oxide prediction could be considered acceptable, although it is under predicted and there is some deviation in Maximum concentration of NO.

Table 1. Numerical test cases(in mass bases)

No.	Fuel composition	Hot oxidizer Composition	CFD	WSR	Fuel Re	Chemical Mechanism
1	20%H2+80%CH4	9%O2+6.5%H2O+5.5%CO2+79%N2	*		10000	GRI2.11
2	20%H2+80%CH4	3%O2+6.5%H2O+5.5%CO2+85%N2	*		10000	GRI2.11
3	10%H2+90%CH4	9%O2+6.5%H2O+5.5%CO2+79%N2	*		10000	GRI2.11
4	5%H2+95%CH4	9%O2+6.5%H2O+5.5%CO2+79%N2	*		10000	GRI2.11
5	20%H2+80%CH4	3%O2+6.5%H2O+5.5%CO2+85%N2		*		GRI2.11
6	100%CH4	23%O2+77%N2		*		GRI2.11
7	20%H2+80%CH4	9%O2+91%N2		*		GRI2.11
8	10%H2+90%CH4	9%O2+91%N2		*		GRI2.11
9	5%H2+95%CH4	9%O2+91%N2		*		GRI2.11
10	20%H2+80%CH4	9%O2+6.5%H2O+5.5%CO2+79%N2	*		5000	GRI2.11

In order to understand the NO mechanism formation under MILD conditions, at the first, the most dominant reaction of N containing species are mentioned. They are sorted according to the magnitude of absolute rates at each radial position for Z=30mm in Fig.3. In this figure, each reaction is colored according to one included identified species (i.e. N2O, NO2, HNO, HCN, NH3, and NNH). The numbers of reactions are according to GRI 2.11 reactions. For instance, the reaction R204 is the reaction number 204 in GRI 2.11 reaction table. These reactions are shown in Table 2.

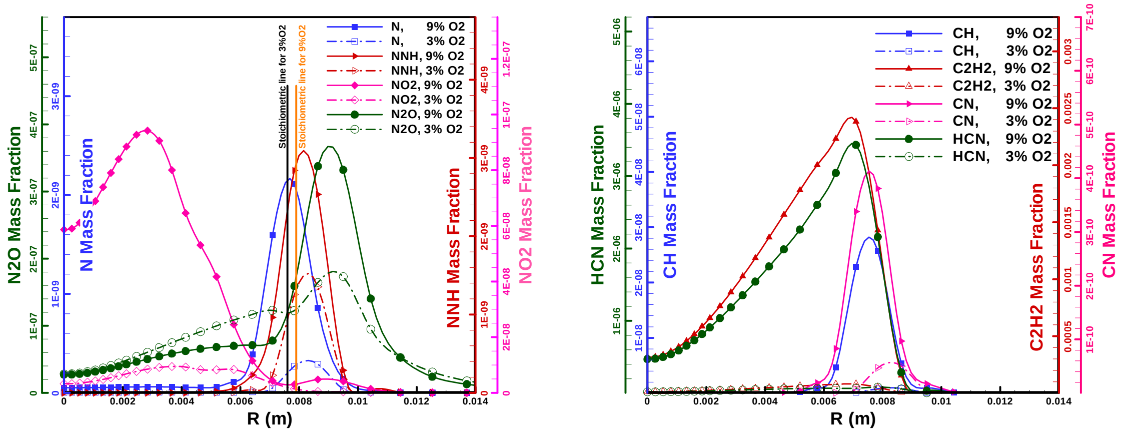
Table 2. N containing reactions of GRI2.11 mechanism

Reaction No.	Reaction	Reaction No.	Reaction	Reaction No.	Reaction
178	N+NO<=>N2+O	**212**	H+NO+M<=>HNO+M	**246**	CH+NO<=>HCN+O
179	N+O2<=>NO+O	**213**	HNO+O<=>NO+OH	**247**	CH+NO<=>H+NCO
180	N+OH<=>NO+H	**214**	HNO+H<=>H2+NO	**248**	CH+NO<=>N+HCO
181	N2O+O<=>N2+O2	**215**	HNO+OH<=>NO+H2O	**249**	CH2+NO<=>H+HNCO
182	N2O+O<=>2NO	**216**	HNO+O2<=>HO2+NO	**250**	CH2+NO<=>OH+HCN
183	N2O+H<=>N2+OH	**217**	CN+O<=>CO+N	**251**	CH2+NO<=>H+HCNO
184	N2O+OH<=>N2+HO2	**218**	CN+OH<=>NCO+H	**252**	CH2(S)+NO<=>H+HNCO
185	N2O(+M)<=>N2+O(+M)	**219**	CN+H2O<=>HCN+OH	**253**	CH2(S)+NO<=>OH+HCN
186	HO2+NO<=>NO2+OH	**220**	CN+O2<=>NCO+O	**254**	CH2(S)+NO<=>H+HCNO
187	NO+O+M<=>NO2+M	**221**	CN+H2<=>HCN+H	**255**	CH3+NO<=>HCN+H2O
188	NO2+O<=>NO+O2	**222**	NCO+O<=>NO+CO	**256**	CH3+NO<=>H2CN+OH
189	NO2+H<=>NO+OH	**223**	NCO+H<=>NH+CO	**257**	HCNN+O<=>CO+H+N2
190	NH+O<=>NO+H	**224**	NCO+OH<=>NO+H+CO	**258**	HCNN+O<=>HCN+NO
191	NH+H<=>N+H2	**225**	NCO+N<=>N2+CO	**259**	HCNN+O2<=>O+HCO+N2
192	NH+OH<=>HNO+H	**226**	NCO+O2<=>NO+CO2	**260**	HCNN+OH<=>H+HCO+N2
193	NH+OH<=>N+H2O	**227**	NCO+M<=>N+CO+M	**261**	HCNN+H<=>CH2+N2
194	NH+O2<=>HNO+O	**228**	NCO+NO<=>N2O+CO	**262**	HNCO+O<=>NH+CO2
195	NH+O2<=>NO+OH	**229**	NCO+NO<=>N2+CO2	**263**	HNCO+O<=>HNO+CO
196	NH+N<=>N2+H	**230**	HCN+M<=>H+CN+M	**264**	HNCO+O<=>NCO+OH
197	NH+H2O<=>HNO+H2	**231**	HCN+O<=>NCO+H	**265**	HNCO+H<=>NH2+CO
198	NH+NO<=>N2+OH	**232**	HCN+O<=>NH+CO	**266**	HNCO+H<=>H2+NCO
199	NH+NO<=>N2O+H	**233**	HCN+O<=>CN+OH	**267**	HNCO+OH<=>NCO+H2O
200	NH2+O<=>OH+NH	**234**	HCN+OH<=>HOCN+H	**268**	HNCO+OH<=>NH2+CO2
201	NH2+O<=>H+HNO	**235**	HCN+OH<=>HNCO+H	**269**	HNCO+M<=>NH+CO+M
202	NH2+H<=>NH+H2	**236**	HCN+OH<=>NH2+CO	**270**	HCNO+H<=>H+HNCO
203	NH2+OH<=>NH+H2O	**237**	H+HCN+M<=>H2CN+M	**271**	HCNO+H<=>OH+HCN
204	NNH<=>N2+H	**238**	H2CN+N<=>N2+CH2	**272**	HCNO+H<=>NH2+CO
205	NNH+M<=>N2+H+M	**239**	C+N2<=>CN+N	**273**	HOCN+H<=>H+HNCO
206	NNH+O2<=>HO2+N2	**240**	CH+N2<=>HCN+N	**274**	HCCO+NO<=>HCNO+CO
207	NNH+O<=>OH+N2	**241**	CH+N2(+M)<=>HCNN(+M)	**275**	CH3+N<=>H2CN+H
208	NNH+O<=>NH+NO	**242**	CH2+N2<=>HCN+NH	**276**	CH3+N<=>HCN+H2
209	NNH+H<=>H2+N2	**243**	CH2(S)+N2<=>NH+HCN	**277**	NH3+H<=>NH2+H2
210	NNH+OH<=>H2O+N2	**244**	C+NO<=>CN+O	**278**	NH3+OH<=>NH2+H2O
211	NNH+CH3<=>CH4+N2	**245**	C+NO<=>CO+N	**279**	NH3+O<=>NH2+OH

It can be understood from Fig. 3 that the NNH included reactions of R204 and R205 have the largest rates. For discussing the second and third important reactions, it could be helpful if the region is divided to three sub-regions such as, $R \le 0.0071(m)$ which is fuel rich region and located inside the jet, region of $0.0071(m) < R < 0.00884(m)$ which is reaction zone and located inside the shear layer, and at last, the region of $0.00884(m) \le R$ which is the airside and fuel lean region. The figure shows that in the fuel side region and inside the jet, the reactions of NO2 and NH3 are in second and third importance level, respectively. In the shear layer region, the reactions of NH3 and HCN are important reactions after NNH reactions. The HCN reactions are a part of the Prompt NO formation pathways family. In the airside region, the reactions of NH3 and N2O are the second and third important reactions, respectively. These results give an overall view on significant role of NNH pathway in NO formation of H2/CH4 combustion under MILD condition. For more detail, the effect of main features of combination of MILD combustion regime and hydrogen flame such as oxygen, fuel Reynolds number, and hydrogen concentration on NO formation are studied in which as follows. Moreover, NO formation pathways, result in CFD analysis and Zero dimensional WSR calculations, are compared with each other and more discussed. Such a comparison, while is accompanied by the study of Reynolds number effects, may reveal the effect of fluid dynamic on NO formation.

Effect of Oxygen Concentration

Low oxygen concentration in the reaction zone is one of the main characteristics of MILD combustion regime. Therefore, in this part, the effect of oxygen concentration on the NO formation is studied. The radial distributions of main species which are important in NOx formation are depicted for two oxygen levels of 3 and 9 percent in Fig.4.a and b.



(a) (b)

Figure 4. Radial distribution of species at Z=30 mm for two oxygen concentrations of 3 and 9 % O2, (Cases 1 & 2 in Table 1).

They show that the concentrations of N, NNH, NO2, N2O, CH, C2H2, CN, and HCN decrease resulting from reduction of oxygen concentration. That means the NOx formation is suppressed at lower oxygen levels. Decrease in CH, CN, and HCN mass fractions indicate that the prompt mechanism is limited at lower O2 concentrations. Comparison of reduction of the mentioned species by decrease in O2 concentration shows that the change of NNH and N2O mass fractions are relatively lower than the others. It may refer to importance of NNH and N2O pathways in NO formation under MILD condition. This idea is studied in more detail using the WSR analysis. In this way, the important reactions which directly produce NO, are selected by the sensitivity analysis. Moreover, the NO formation by each of the reactions is calculated and non-dimensionalized by net total NO production. Correlation of the mentioned calculation and sensitivity analysis for each selected reaction are depicted in Fig.5 for two oxygen concentrations of 3 and 23 percent (in mass basis). These calculations are referred to the cases 5 and 6 in Table 1.

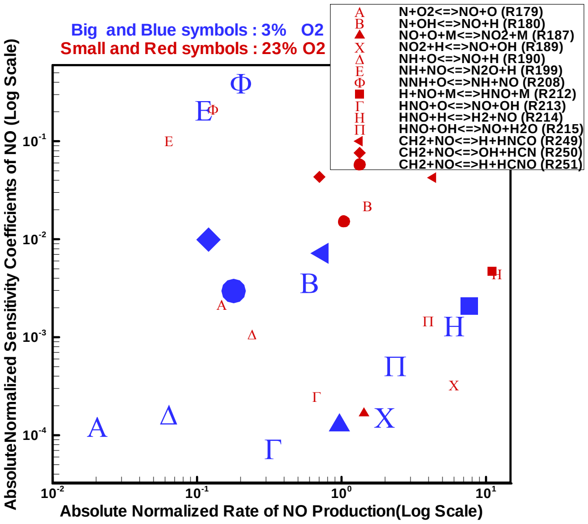


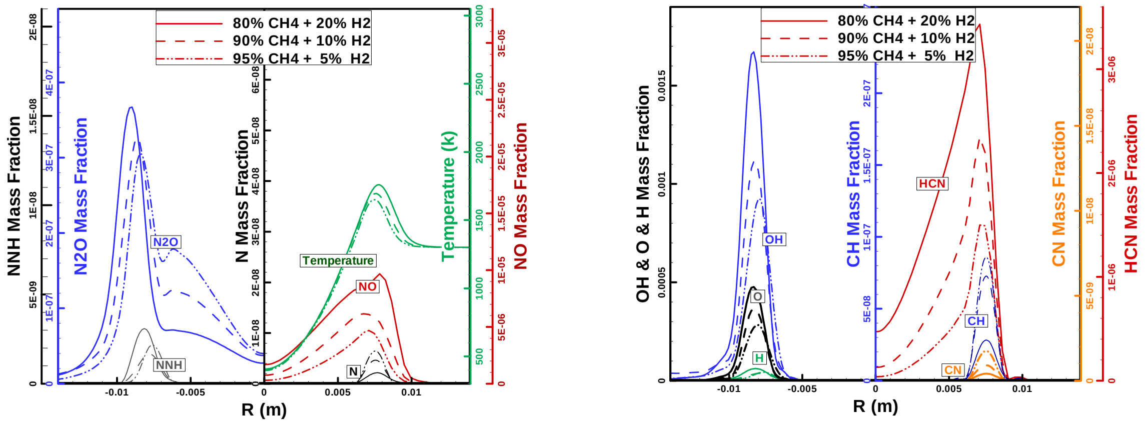
Figure 5. Correlation between NO sensitivity to each reaction, which include NO, versus the absolute NO rate of formation or consumption, which is non-dimensionalized by total NO formation, resulting from WSR analysis for two oxygen concentration of 3 and 9 %, (Cases 5 and 6 in Table 1). The reactions with negative sensitivity and rate of reaction (reactions which consumes NO) are indicated by solid symbols. The WSR analysis is at T = 1345K and P = 1 atm for a 0.1-s residence time. Reaction numbers refer to Table 2.

In Fig. 5, the big and red colored symbols represent the case of 23% O2 and the small and blue colored symbols are for 3% O2. Moreover, the solid symbols indicate that the sensitivity and rate of production are negative. In the figure, the reaction numbers are for GRI 2.11 mechanism according to Table 2. This figure shows some important points which are as follows. First of all, regarding sensitivity analysis, the NNH reaction (R208) has the highest sensitivity and after that NO formation shows the high sensitivity to the N2O reaction (R199) although their portions in NO production are not considerable at higher O2 concentrations, i.e. 23 % O2. Secondly, by decrease in O2 concentration, the importance of all of the reactions decrease regarding the sensitivity analysis and their role in NO production except NNH and N2O reactions (i.e. R208 & R199), which their importance increase at lower O2 concentrations. Moreover, NO formation by thermal mechanism (i.e. R179 & R180) suppress strongly at lower O2 concentrations. It can be concluded from the above discussion that the NNH and N2O pathways are very importance and also influential on NO formation under MILD combustion of H2/CH4 blended fuels.

Effect of Hydrogen Concentration

In addition to which is mentioned in introduction about the importance of hydrogen in this work, the numerical experiments of the authors, [19], has showed that the hydrogen was added to the methane to improve the ignition and burn off in the present setup. Therefore, in this section the effect of fuel hydrogen content on NO formation in MILD combustion is studied by decrease in the hydrogen content of fuel mixture from 20% (by mass) to 5% for condition of Oxygen concentration of 9%. In this way three fuel mixture of 20%H2+80%CH4, 10%H2+90%CH4, and 5%H2+95%CH4 are considered in Cases 1, 3, and

4 in Table 1, respectively. The radial distribution of temperature and species of N, NO, NNH, N2O, HCN, CH, CN, OH, O, and H are depicted for Z=30 mm in Fig.6.a & b.



(a) (b)

Figure 6. Radial distribution of species for three different fuel hydrogen contents at Z=30mm and for 9% O2, (Cases 1, 3, and 4 in Table 1).

It can be seen that the maximum of temperature decreases for lower hydrogen concentrations. It is predictable as a result of higher reactivity of hydrogen in comparison with methane. Moreover the figure shows a decrease in the concentrations of NO, N2O, and NNH by reduction of fuel hydrogen content, although the concentration of N has increased. That means the NO formation routes are suppressed at lower Hydrogen levels. Fig. 6.b shows that the mass fractions of CH and HCN minor species decrease at lower hydrogen levels in fuel. That indicates that the prompt route weakens by reduction of hydrogen. Furthermore decrease in concentrations of O, OH, and H radicals, by decrease in fuel hydrogen content, are responsible for suppression of main routes of NOx formation, like NNH and N2O pathways, under MILD condition. On the other hand an increase in concentrations of CN can be seen at lower fuel hydrogen percent which is probably result of higher N concentration. For more detail WSR analysis are done for three fuel mixture and the correlation of sensitivity and NO formation via each reaction are depicted in Fig. 7 (cases 7, 8, and 9 in Table 1).

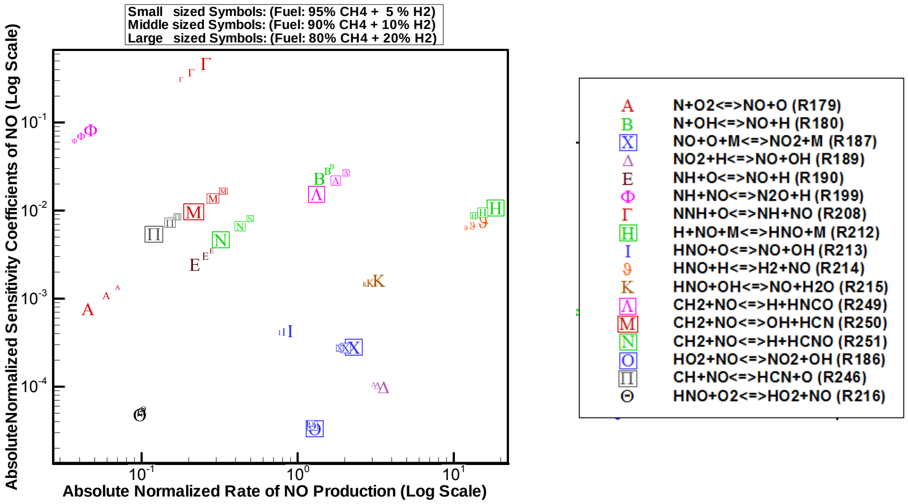


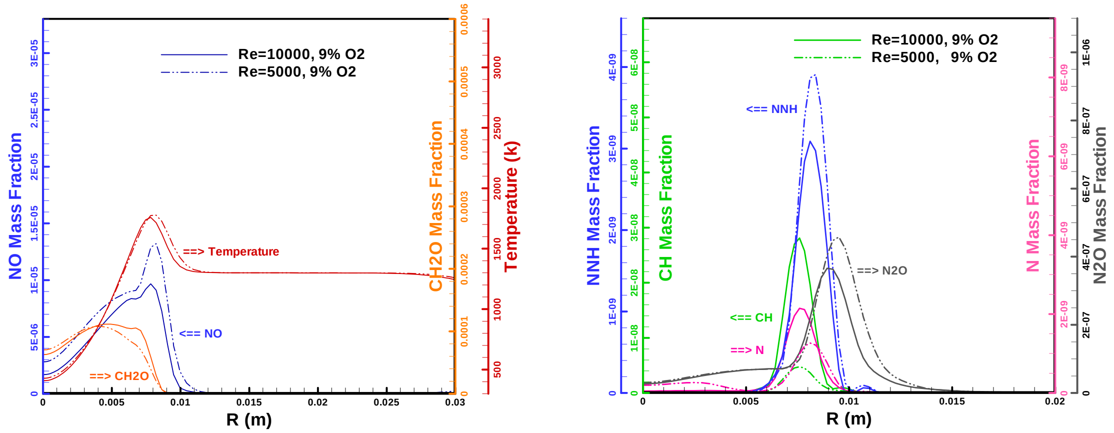
Figure 7. Correlation between NO sensitivity to each reaction, which include NO, versus the absolute NO rate of formation or consumption, which is non-dimensionalized by total

NO formation, resulting from WSR analysis for three fuel hydrogen content of 5, 10, and 20 %, (Cases 7, 8, and 9 in Table 1). The reactions with negative sensitivity and rate of reaction (reactions which consumes NO) are indicated by solid symbols. The WSR analysis is at T = 1345K and P = 1 atm for a 0.1-s residence time. Reaction numbers refer to Table 2.

This figure is extracted same as which is done for Fig. 5. In Fig.7 the reactions are identified by symbols in which big symbols are for fuel mixture containing 20% H2 and medium size symbols are for 10% H2 and small symbols are for 5% H2. Furthermore the reactions which have negative sensitivity and rate of productions are indicated by symbols inside the squares. Figure shows that the highest sensitivity of NO formation is to the NNH (R208) and N2O (R199) reactions which these sensitivities decrease by reduction of fuel hydrogen percent. Furthermore the importance of HNO reactions (i.e. R212-5) decrease for fuel mixture with lower hydrogen although the reactions of HCN(i.e. R249-51), which are important in prompt route, growth in important. As a whole although most of the NO formation is via the HNO→NO pathway by reactions R212 and R213, the NNH and N2O routes have key roles in NOx formation for CH4/H2 mixture under MILD regime.

Effect of Flow Dynamic on NOx Generation

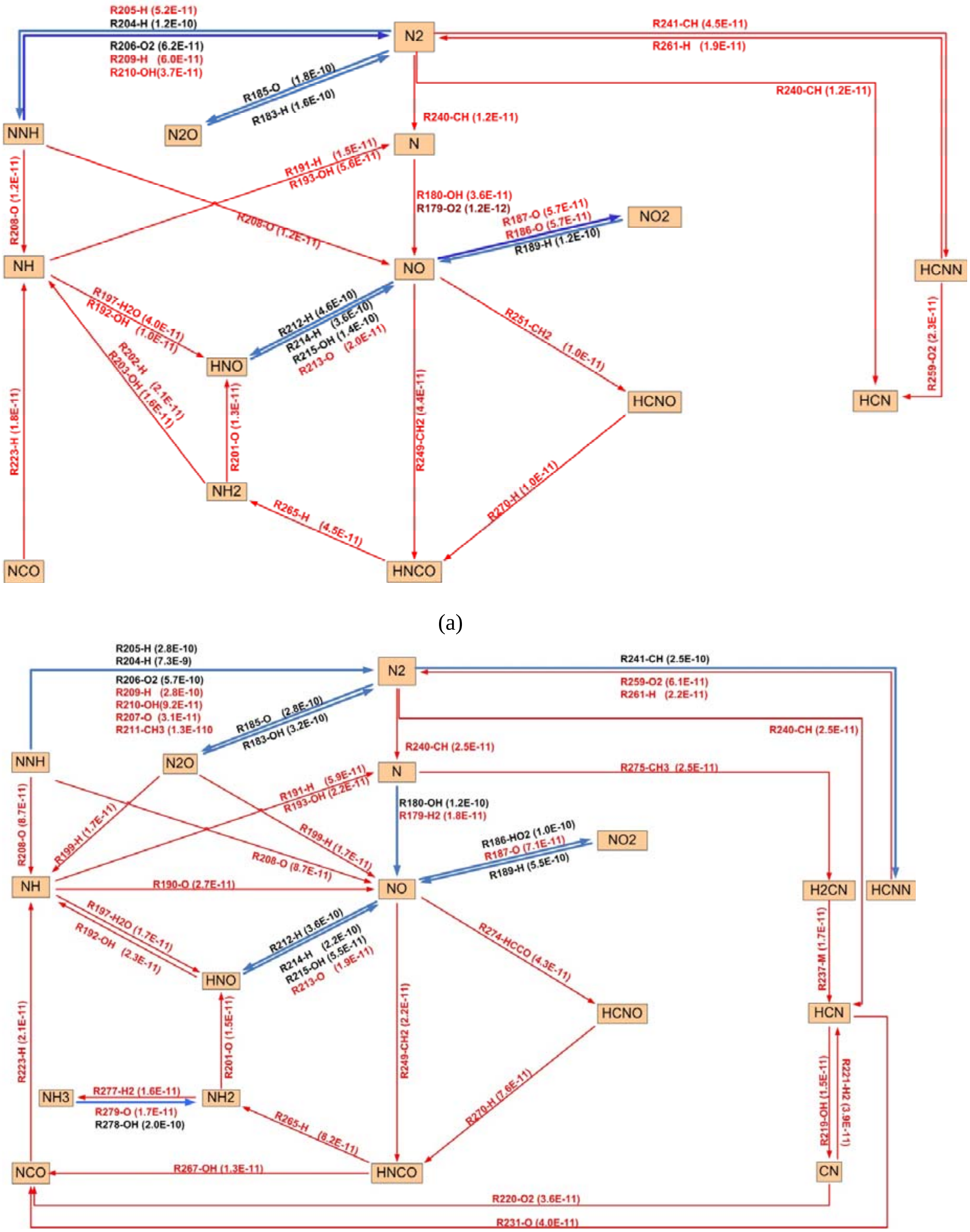
In this part, the effect of flow dynamic on NOx generation is studied by changing the jet Reynolds number from 10000 to 5000. Results of two Reynolds number are compared with each other in Figs 8.a and b. Fig 8.a shows an increment in maximum of radial temperature profile at lower Reynolds number. Furthermore the NO mass fraction is increased by reduction of fuel jet Reynolds number. The other numerical results of the authors [19] and also the experimental results of Medwell et al. [18] show that there is a marginal increase in temperature by decrease of jet Reynolds number although the concentration of intermediate species like CH2O has decreased. Maybe it is because of higher heat transfer from reaction zone and also incomplete combustion due to increase of flow velocity. Although an increase in temperature and also flow residence time at lower Reynolds number could be an acceptable reason of higher NOx formation for the present experimental setup, for more detail the radial distribution of NNH, N2O, CH which is important in prompt NOx formation, and N, which has a key role in thermal NOx formation, are depicted in Fig 8.b. The reduction in N and CH mass fractions at lower Reynolds number could be referred to suppression of Thermal and prompt routes, respectively, at Reynolds number of 5000 in compassion with 10000. These species are important in thermal and prompt routes of NOx formation. In the other hand, an increase in concentrations of NNH and N2O show the increasing importance of NNH and N2O routes in NOx formation by decreasing of Reynolds number. In the other word, under MILD condition, the importance of the unusual NOx formation routes like NNH and N2O mechanisms increase as a result of temperature behavior and also probably larger residence time at lower Reynolds number.



(a) (b)

Figure 8. Radial profiles of a) temperature, NO, and CH2O b) NNH, N2O, N, and CH for two Reynolds numbers of 5000 and 10000 at Z=30 mm and 9% O2 (Cases 1 and 10 in Table 1)

In order to better understanding of NOx formation, the pathway of N2 oxidation to NO and NO2 are illustrated by WSR analysis and CFD calculations for fuel mixture of 20%H2 +80%CH4 and 3% O2 in Figs. 9.a and b. Each arrow indicates a conversion of species at its tail to the species at the head. The mentioned conversion is addresses by elementary reactions which are indicated along the length of the arrow by number of reactions in GRI 2.11 mechanism and the additional reactant species in the mentioned reaction, while the rate of destruction of reactant is quantified by the parenthetical numerical value. Furthermore the width and color of arrows gives a visual indication of the relative importance of each pathway. The elementary reactions with rates larger than 1.0e-12 (gmole/cm3-s) are considered for pathway extractions and the other reactions are filtered. For CFD, the rates of reactions are averaged by cell surface in region of MILD combustion. The region of MILD combustion is identified by two conditions. First the distances below 100 mm from the nozzle are considered. According to Ref. [16], the mixing with fresh air of tunnel air affects the flame above 100 mm from the nozzle and the MILD combustion regime occurs at the region below this height. At each distance from the nozzle the maximum OH concentration is identified and the radius with OH mass fraction larger than 1% of maximum are considered as MILD combustion region. The comparison of Figs 9.a and b shows some points which are as follows. First if it is considered that in spite of Fig. 9.a the flow dynamics effects are included in Fig 9.b, it can be seen that flow dynamic increases rate of reactions generally and in specific strengths the NNH, N2O, and Prompt routes for NO formation. Second, both figures illustrate the much more importance of NNH route in comparison with N2O and prompt routes.



(a)

(b)

Figure 9. N2 oxidation pathways for 3 % O2 extracted from a)WSR analysis b)CFD analysis, (Cases 2 and 5 in Table 1).

Conclusion

In this work the NO formations mechanism is studied for combustion of hydrogen-methane blended fuel under MILD conditions. In this way, two systematic analyses are performed. The reacting flow modeling is done for a H2/CH4 jet into a hot and diluted co-flow air using CFD tools. The RANS equations with the EDC model are solved to predict the flame characteristics. Furthermore a well stirred reactor (WSR) analysis is considered to study the reactions pathways. The GRI2.11 full mechanism is used to represents the chemical reactions. The comparison between numerical predictions and measurements shows the acceptable accuracy of CFD results.

Results show significant role of NNH pathway in NO formation for H2/CH4 combustion under MILD condition. The reduction in hot co-flow oxygen concentration leads to decrease concentrations of N, NNH, NO2, N2O, CH, C2H2, CN, and HCN although the change of NNH and N2O mass fractions are relatively lower than the others. Moreover the zero dimensional WSR analysis refers to growth in importance of NNH and N2O routes by decrease of oxidizer O2 level.

Calculations for different fuel hydrogen content illustrate that the NO formation routes are suppressed at lower Hydrogen levels. Furthermore the highest sensitivity of NO formation is to the NNH (R208) and N2O (R199) reactions which these sensitivities decrease by reduction of fuel hydrogen percent.

Changing of fuel inlet Reynolds number and also Comparison between N2 oxidation pathways resulting from CFD and WSR analysis shows that the NNH and N2O routes for NO formation could be important under MILD combustion at different flow dynamic conditions.

References

---

[1] Rørtveit, G. J., Hustad, J. E., Li, S., Williams, F. A., “Effects Of Diluents On Nox Formation In Hydrogen Counter flow Flames”, *Combust. Flame., 130:48–61 (2002)*

[2] Skottene, M., Rian, K. E., “A study of NOx formation in hydrogen flames”, *Int. J. Hydrogen Energy, 32: 3572 – 3585 (2007).*

[3] Cavaliere, A., Joannon, M. D., ”MILD Combustion*”, Prog. Energy Combust. Sci., 30: 329-366(2004).*

[4] Niioka, T., “Fundamentals and Applications of High-Temperature Air Combustion”, *5th ASME/ JSME Jt. Therm. Conf. (AJTE) 99- 6301(1999), pp.1-6.*

[5] Gupta, A. K., Li, Z., “Effect of Fuel Property on the Structure of Highly Preheated Air Flames”, *Proc. Int. Jt. Power Gener. Conf., ASME EC- vol. 5(1997),p p. 247–258.*

[6] Gupta, A. K., “Flame characteristics and challenges with high temperature air combustion”, *Proc. of Int. Jt. Power Gener. Conf. (IJPGC), Miami, Florida, 2000.*

[7] Niioka, T., “Impact of Knowledge Gained from the HiCOT Project on Development of Combustors”, *Fifth Asia-Pacific Conf. Combust., Adelaide(2005), pp.1-4*

[8] Wünning, J. G., “Flameless Combustion in Thermal Process Technology*”, 2th Int. Seminar High Temperature Air Combust., Sweden, 2000.*

[9] Fuse, R., Kobayashi, H., Ju, Y., Maruta, K., Niioka, T., “NOx Emission from High-Temperature Air/ Methane Counterflow Diffusion Flame”, *Int. J. Therm. Sci., 41: 693-698(2002).*

[10] Hasegawa, T., Tanaka, R., Niioka, T., “High Temperature Air Combustion Contributing to Energy Saving and Pollutant Reduction in Industrial Furnace”, *Proc. Int. Jt. Power Gener. Conf., ASME, Book No.G 01072(1997),p p. 259-266.*

[11] Guo, H., Ju, Y-G., Maruta, K., Niioka, T., Junichi, S., “Numerical Study of NOx Emission in High Temperature Air Combustion”, *JSME Int. J., B41(2): 331-337(1998).*

[12] Ito, Y., Gupta, A. K., Yoshikawa, K., Shimo, N., “Combustion characteristics of low calorific value gas with high temperature and low-oxygen concentration air”, *Proc. 5th High Temperature Air Combust. Gasif. Conf., Yokohama, Japan, 2002.*

[13] Mortberg, M., Blasiak, W., Gupta, A. K., “Experimental investigation of flow phenomena of a single fuel jet in cross-flow during highly preheated air combustion conditions”, *J. Eng. Gas Turbines Power, 129: 556(2007).*

[14] Katsuki, M., Hasegawa, T., “The Science and Technology of Combustion in Highly Preheated Air”, *27th Symp. Combust./Combust. Inst. (1998),pp. 3135-3146.*

[15] Plessing, T., Peters, N., Wunning, J. G., “Laser Optical Investigation of Highly Preheated Combustion with Strong Exhaust Gas Recirculation”, *27th Symposium Combust./Combust. Inst. (1998), pp. 3197-3204.*

[16] Dally, B. B., karpetis, A. N., Barlow, R. S., “Structure of Turbulent Non-Premixed Jet Flames in a Diluted Hot Coflow”, *proc. Combust. Inst., 29:1147-1154(2002).*

[17] Christo, F. C., Dally, B. B., “Modeling Turbulent Reacting Jets Issuing into a Hot and Diluted Coflow”, *Combust. Flame, 142:117-129(2005).*

[18] Medwell, P. R., Kalt P. A. M., Dally, B. B., “Simultaneous imaging of OH, formaldehyde, and temperature of turbulent non-premixed jet flames in a heated and diluted coflow”, *Combust. Flame, 148:48–61(2007).*

[19] Mardani, A., Tabejamaat, S., Ghamari, M., “Numerical Study of Influence of Molecular Diffusion in the MILD Combustion Regime”, *Combust. Theory and Modelling, 14:747–774(2010).*

[20] Mardani, A., Tabejamaat, S., “Effect of hydrogen on hydrogene-methane turbulent non-premixed flame under MILD condition”, *Int. J. Hydrogen Energy, 35:11324-11331 (2010).*

[21] Yang, W., Blasiak, W., “Mathematical modelling of NO emissions from high-temperature air combustion with nitrous oxide mechanism”, *Fuel Processing Technology, 86:943– 957 (2005).*

[22] Nicolle, A., Dagaut, P., “Occurrence of NO-reburning in MILD combustion evidenced via chemical kinetic modeling”, *Fuel, 85:2469–2478 (2006).*

[23] Yu, Y., Gaofeng, W., Qizhao, L., Chengbiao, M., Xianjun, X., “Flameless combustion for hydrogen containing fuels”, *Int. J. Hydrogen Energy, 35:2694 – 2697 (2010).*

[24] Gallettia, C., Parentea, A., Derudib, M., Rotab, R., Tognottia, L., “Numerical and experimental analysis of NO emissions from a lab-scale burner fed with hydrogen-enriched fuels and operating in MILD combustion”, *Int. J. Hydrogen Energy, 34:8339–8351(2009).*

[25] Gran, I. R., Magnussen, B. F., “A numerical study of a bluff-body stabilized diffusion flame. part 2. influence of combustion modeling and finite-rate chemistry”, *Combust. Sci. Technol., 119-1: 191-217 (1996).*

[26] Galletti, C., Parente, A., Tognotti, L., “Numerical and Experimental Investigation of a MILD Combustion Burner”, *Combust. Flame, 151:649-664 (2007).*

[27] Parente, A., Galletti, C., Tognotti, L., “Effect of the combustion model and kinetic mechanism on the MILD combustion in an industrial burner fed with hydrogen enriched fuels”, *Int. J. Hydrogen Energy, 33:7553 – 7564 (2008).*

[28] Frassoldati, A., Sharma, P., Cuoci, A., Faravelli, T., Ranzi, E., “Kinetic and fluid dynamics modeling of methane/hydrogen jet flames in diluted coflow”, Applied Therm. Eng., 30:376–383 *(2010).*

[29] Kee, R. J., Miller, J. A., Jefferson, T. H., “CHEMKIN: A General-Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package”, *Sandia National Laboratories Report SAND80-8003 (1980).*