

## REDUCED MECHANISM FOR COMBUSTION OF HYDROGEN AND METHANE WITH NITROGEN CHEMISTRY

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**Abstract.** A reduced chemical kinetic reaction mechanism that could be used in CFD software was developed to describe the formation of nitrogen oxides and their subsequent destruction in hydrogen and/or hydrocarbon flames with or without seeding of nitrogen compounds. The research work presented here will describe the numerical work done with the application "Chemkin" in order to verify the quality of the reduced mechanism. The mechanism was validated through comparisons between computational data from a variety of different sources. In addition, numerical experiments were carried out to examine features of methane combustion in which the detailed mechanisms can be used to compare their response. The proposed reduced mechanism provides reasonable agreement with the studied detailed mechanisms, mainly in the species produced from the hydrocarbon oxidation process. Regarding the produced nitrogen species, the proposed reduced mechanism showed the same tendencies as the detailed mechanisms but there is a need for a better agreement regarding the quantities.

**Keywords:** Combustion, reduced mechanism, hydrocarbons, NO<sub>x</sub>, Chemkin

### 1. NOMENCLATURE

$k$	Rate constant	<b>Acronyms</b>	
$A$	Pre-exponential factor	FAR	Fuel-Air ratio
$T$	Temperature	CFD	Computational Fluid Dynamics
$n$	Temperature exponent	POA	Reduced reaction mechanism proposed in this work
$E_a$	Activation energy	ROM	Reduced reaction mechanism (Romero, 1998)
$R$	Universal gas constant	AA	Detailed reaction mechanism (Zabetta and Hupa, 2006)
<b>Greek symbols</b>		GRI	Detailed reaction mechanism (Smith et al., 1999)
$\varphi$	Equivalence ratio defined as $FAR_r/FAR_{st}$	KON	Detailed reaction mechanism (Konnov, 2000)
<b>Subscripts</b>		LLNL	Detailed reaction mechanism (Hori et al., 1998)
r	Real conditions	Leeds	Detailed reaction mechanism (Baulch, 2004)
st	Stoichiometric conditions	San Diego	Detailed reaction mechanism (Center for Energy Research, Combustion Division, 2005)
A	Fuel with 100% CH <sub>4</sub>		
B	Fuel with 50% CH <sub>4</sub> and 50% H <sub>2</sub>		
norm	Normalized trend		

### 2. INTRODUCTION

The *Fluent* software package, the computational fluid dynamics application that the authors intend to work with in a full 3D reactive flow, is limited to the use of 100 chemical species and 500 chemical reactions. There are several detailed kinetic mechanisms that use more than that chemical species or reactions.

Therefore, some of the available detailed chemical kinetic mechanisms were studied, Tab. 1. Other detailed mechanisms exist, however those mechanisms do not address the methane oxidation with nitrogen chemistry. As indicated in the table below the main differences amongst mechanisms are the reactions and the Arrhenius parameters considered. Although all mechanisms address the combustion process not all give a good response in certain conditions, e.g. the working temperature (1700 °C in premixed gas combustion or 850 °C in a biomass fired fluidized bed combustor).

The initial approach to the detailed mechanisms did allow eliminating 3 of the 6 detailed kinetic mechanisms (KON, LLNL and LUM). These mechanisms revealed several problems in their use, as incorrect syntax (problem found in all mechanisms), incompatibility between the *Chemkin* version for what the mechanisms were developed (II or III) and the *Chemkin* version used (IV) and, most of all, because divergence was found in several test cases indicating that those mechanisms could be intended for different purposes. *Chemkin* software enables the simulation of complex chemical reactions and it was used to simulate a 1D reactive flow. This way is fair to assume that some of the tested detailed kinetic mechanisms may not have been tested in combustion systems like the one used in this work, mainly regarding the combustion temperature achieved in the flame. Besides the combustion system, differences may exist in

the concentrations of the main reactants. Any of these situations may lead to divergences in the numeric results. However, the remaining mechanisms were found to be adequate to be used as reference for the analysis of the performance of reduced mechanisms.

Table 1. Detailed chemical kinetic mechanisms used in this study.

Mechanism	Symbol	Ch. Species	Ch. Reactions	Reference
AA Scheme	AA	60	371	(Zabetta and Hupa, 2008)
GRI-Mech	GRI	53	325	(Smith et al., 1999)
Konnov	KON	117	1198	(Konnov, 2000)
LLNL	LLNL	126	633	(Hori et al., 1998)
Leeds	LUM	43	164	(Baulch, 2004)
San Diego	SDM	62	288	(Center for Energy Research, Combustion Division, 2005)

The detailed mechanisms, presented in Tab.1 and not excluded on the first approach, were compared to a chemical kinetic reduced mechanism (ROM), and to the reduced mechanism proposed in this study and hereby denominated POA.

### 3. THE REDUCED MECHANISM

The POA reduced kinetic mechanism, presented in Tab.2, with 34 chemical species and 46 chemical reactions introduced in the present work, was compared with the remaining kinetic mechanisms: three more detailed mechanisms (AA, GRI and SDM) and one reduced kinetic mechanism (ROM) in the one-dimensional chemical kinetic package. The studied results included parameters like, flue gas composition distribution, temperature and velocity profiles along burner axial distance and residence time. The results were found to be in good agreement with those obtained with the detailed mechanisms.

### 4. THE PROBLEM

In order to study the formation and destruction mechanisms of nitrogen compounds, the methane oxidation had to be achieved in a nitrogen free environment. Therefore, the nitrogen of air was replaced by argon so that the only nitrogen introduced in the combustion system was the seeding of ammonia or nitric oxide.

Based on referenced kinetic mechanisms, tests were made in order to evaluate the response of the ROM mechanism. ROM is a reduced kinetic mechanism based in the 47 chemical species and 212 chemical reactions detailed mechanism of Drake and Blint (1991). Romero (1998) made a sensitivity analysis study to the detailed kinetic mechanism and reduced it to a proposed mechanism with 31 chemical species and 42 reversible chemical reactions.

Due to some limit conditions regarding the *Chemkin* package, it was not possible to produce a similar study for the detailed kinetic mechanisms, so the same reduced kinetic mechanism was used in this work. As Romero (1998) uses a detailed kinetic mechanism developed in 1991, which in turn uses a mechanism with parameters from Glarborg *et al.* (1998), a revision to the indicated parameters was made.

In general, the chemical reactions proposed in the ROM mechanism were maintained, although four new reactions were added (R43 to R46 from Tab. 2) identified with the ammonia chemistry that the original mechanism did not accounted for. The four new added reactions are based on the Sullivan *et al.* (2002) work which indicates that the main ammonia destruction mechanism reactions are the R43 and R44 and occur, respectively, in 65 % and 28 % of the cases. As a result it was found that NH<sub>2</sub> is destructed by way of R45 and R46 with 60 % and 25 % probability respectively. This way, the reactions R43 to R46 allow accounting for the ammonia seeding destruction (or reversely, producing it in small quantities) and produce some NO.

### 5. THE CASE

Tests were made with 2 different fuel compositions (Comb<sub>A</sub> with 100 % CH<sub>4</sub> and Comb<sub>B</sub> with 50 % CH<sub>4</sub> and 50 % H<sub>2</sub>) and 6 equivalence rations, ranging from 0.7 to 1.2, and maintaining the fuel content constant at 1.5 L.min<sup>-1</sup> (at standard temperature and pressure). The complete definition of test conditions can be found in Tab. 3.

The parameters used to compare the proposed mechanisms were the flue gases temperature and velocity and several molar fractions, such as CH<sub>4</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, OH, NO, HCN and NH<sub>3</sub>. Although in the case of nitrogenous species the molar fractions had to be normalized, all parameters were analyzed considering both axial distance to the burner and residence time.

Table 2. Reduced kinetic mechanism (POA).

Reactions	$k = A.T^n.exp(-Ea/RT)^*$			Reference
	<i>A</i>	<i>n</i>	<i>Ea</i>	
R1 CH <sub>4</sub> + OH ⇌ CH <sub>3</sub> + H <sub>2</sub> O	1.00E+08	1.60	3120	[2]
R2 CH <sub>3</sub> + O ⇌ CH <sub>2</sub> O + H	8.43E+13	0.00	0	[1], [6], [10], [12], [13]
R3 CH <sub>2</sub> O + OH ⇌ HCO + H <sub>2</sub> O	3.43E+09	1.18	-447	[2], [5], [6], [7], [14]
R4 HCO + M ⇌ CO + H + M	1.86E+17	-1.00	17000	[1], [2], [6], [10], [15]
R5 CO + OH ⇌ CO <sub>2</sub> + H	4.40E+06	1.50	-740	[6], [16]
R6 CH <sub>3</sub> + CH <sub>3</sub> + M ⇌ C <sub>2</sub> H <sub>6</sub> + M	2.10E+16	-0.97	620	[10]
H <sub>2</sub> /2.0/ CO/2.0/ CO <sub>2</sub> /3.0/ H <sub>2</sub> O/5.0/				
R7 C <sub>2</sub> H <sub>6</sub> + H ⇌ C <sub>2</sub> H <sub>5</sub> + H <sub>2</sub>	5.40E+02	3.50	5210	[6], [7], [9], [10], [12], [14], [18], [19]
R8 C <sub>2</sub> H <sub>4</sub> + H + M ⇌ C <sub>2</sub> H <sub>5</sub> + M	2.21E+13	0.00	2066	[6], [7], [14], [18]
H <sub>2</sub> /2.0/ CO/2.0/ CO <sub>2</sub> /3.0/ H <sub>2</sub> O/5.0/				
R9 C <sub>2</sub> H <sub>4</sub> + OH ⇌ C <sub>2</sub> H <sub>3</sub> + H <sub>2</sub> O	5.53E+05	2.31	2962	[6], [20]
R10 C <sub>2</sub> H <sub>3</sub> + M ⇌ C <sub>2</sub> H <sub>2</sub> + H + M	1.51E+14	0.10	32700	[6], [21]
R11 C <sub>2</sub> H <sub>2</sub> + O ⇌ CH <sub>2</sub> + CO	1.60E+14	0.00	9900	[6], [22]
R12 CH <sub>2</sub> + OH ⇌ CH + H <sub>2</sub> O	1.13E+07	2.00	3000	[1], [2], [6], [10], [12], [14], [18]
R13 CH + O <sub>2</sub> ⇌ HCO + O	3.30E+13	0.00	0	[6], [7], [10], [14], [18], [23], [24]
R14 CH + H ⇌ C + H <sub>2</sub>	1.50E+14	0.00	0	[1], [7], [10], [14], [18], [24]
R15 C + OH ⇌ CO + H	5.00E+13	0.00	0	[1], [2], [7], [10], [14], [18], [24]
R16 H + O <sub>2</sub> ⇌ O + OH	3.52E+16	-0.70	17060	[1], [16]
R17 H <sub>2</sub> + O ⇌ H + OH	5.06E+04	2.67	6290	[1], [6], [10], [16], [25]
R18 H <sub>2</sub> + OH ⇌ H <sub>2</sub> O + H	2.10E+08	1.52	3450	[1], [2], [6], [10], [25], [26]
R19 H + OH + M ⇌ H <sub>2</sub> O + M	2.21E+22	-2.00	0	[2], [24]
H <sub>2</sub> O/20.0/				
R20 HO <sub>2</sub> + OH ⇌ H <sub>2</sub> O + O <sub>2</sub>	2.89E+13	0.00	-500	[1], [6], [16], [17]
R21 H + O <sub>2</sub> + M ⇌ HO <sub>2</sub> + M	3.50E+16	-0.41	-1120	[27]
H <sub>2</sub> /3.3/ CO/2.0/ CO <sub>2</sub> /5.0/ H <sub>2</sub> O/21.0/ O <sub>2</sub> /0.0/ N <sub>2</sub> /0.0/				
R22 CH + N <sub>2</sub> ⇌ HCN + N	4.40E+12	0.00	21900	[1], [6], [28]
R23 HCN + O ⇌ NCO + H	1.38E+04	2.64	4980	[1], [7], [18]
R24 HCN + OH ⇌ CN + H <sub>2</sub> O	1.45E+13	0.00	10929	[7], [10], [14]
R25 CN + OH ⇌ NCO + H	4.00E+13	0.00	0	[2], [29]
R26 NCO + OH ⇌ NO + CO + H	1.00E+13	0.00	0	[7], [18]
R27 NCO + H ⇌ NH + CO	5.00E+13	0.00	0	[1], [6], [7], [18]
R28 NH + OH ⇌ N + H <sub>2</sub> O	5.00E+11	0.50	2000	[1], [7], [6], [10], [18], [30]
R29 NH + OH ⇌ HNO + H	2.00E+13	0.00	0	[1], [2], [7], [10], [18]
R30 HNO + OH ⇌ NO + H <sub>2</sub> O	1.30E+07	1.88	-955	[2], [31]
R31 HNO + M ⇌ H + NO + M	1.50E+16	0.00	48680	[1], [6], [7], [18]
H <sub>2</sub> /2.0/ N <sub>2</sub> /2.0/ O <sub>2</sub> /2.0/ H <sub>2</sub> O/6.0/				
R32 N + NO ⇌ N <sub>2</sub> + O	3.30E+12	0.30	0	[1], [7], [10], [18]
R33 N + O <sub>2</sub> ⇌ NO + O	6.40E+09	1.00	6275	[1], [6], [7], [10], [18]
R34 N + OH ⇌ NO + H	3.80E+13	0.00	0	[1], [6], [7], [10], [18]
R35 NCO + NO ⇌ N <sub>2</sub> O + CO	6.20E+17	-1.73	762	[1], [10]
R36 N <sub>2</sub> O + M ⇌ N <sub>2</sub> + O + M	4.00E+14	0.00	56100	[1], [10], [32]
H <sub>2</sub> /2.0/ CO/2.0/ CO <sub>2</sub> /3.0/ H <sub>2</sub> O/5.0/				
R37 NO + HO <sub>2</sub> ⇌ NO <sub>2</sub> + OH	2.10E+12	0.00	-480	[1], [2], [6], [7], [18], [33], [34]
R38 NO <sub>2</sub> + M ⇌ NO + O + M	1.10E+16	0.00	66000	[7]
R39 NO <sub>2</sub> + H ⇌ NO + OH	1.32E+14	0.00	360	[1], [2], [35]
R40 N <sub>2</sub> O + H ⇌ N <sub>2</sub> + OH	3.87E+14	0.00	18880	[2]
R41 CH + NO ⇌ HCN + O	1.10E+14	0.00	0	[1], [6], [7], [18], [36]
R42 C + NO ⇌ CN + O	1.90E+13	0.00	0	[1], [2], [37]
R43 NH <sub>3</sub> + H ⇌ NH <sub>2</sub> + H <sub>2</sub>	6.38E+05	2.39	10171	[1], [6], [10], [38]
R44 NH <sub>3</sub> + OH ⇌ NH <sub>2</sub> + H <sub>2</sub> O	2.04E+06	2.04	566	[6], [18]
R45 NH <sub>2</sub> + H ⇌ NH + H <sub>2</sub>	4.00E+13	0.00	3650	[1], [2], [6], [10]
R46 NH <sub>2</sub> + OH ⇌ NH + H <sub>2</sub> O	4.00E+06	2.00	1000	[1], [6], [10], [18]

\* Units are *A* [cm<sup>3</sup>.mol<sup>-1</sup>.s<sup>-1</sup>], *T* [K], *Ea* [cal.mol<sup>-1</sup>], *R* [cal.K<sup>-1</sup>.mol<sup>-1</sup>].

## 5. RESULTS

Regarding the combustible mixture used, significant differences between both types of fuel were not found, although Comb<sub>B</sub>, due to an increased velocity of reaction, had shown tendencies to smooth some of the variations found with Comb<sub>A</sub>.

Table 3. Test conditions.

Run name	Mixture composition (L.min <sup>-1</sup> )				Equivalence ratio
	CH <sub>4</sub>	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	
CH 01	1.5	-	4.286	16.220	0.7
CH 06	1.5	-	3.750	14.193	0.8
CH 11	1.5	-	3.333	12.616	0.9
CH 16	1.5	-	3.000	11.355	1.0
CH 21	1.5	-	2.727	10.322	1.1
CH 26	1.5	-	2.500	9.462	1.2
CH 03	0.75	0.75	2.679	10.138	0.7
CH 08	0.75	0.75	2.344	8.870	0.8
CH 13	0.75	0.75	2.083	7.885	0.9
CH 18	0.75	0.75	1.875	7.096	1.0
CH 23	0.75	0.75	1.705	6.451	1.1
CH 28	0.75	0.75	1.563	5.914	1.2

The results showed that Comb<sub>B</sub> is a faster fuel mixture than Comb<sub>A</sub> and all mechanisms increased their velocity along with the equivalence ratio. Temperature profiles showed that ROM yields certain difficulties mainly along the evolution curve and POA yields excellent results when the results analyses are made regarding the axial distance (Fig. 1). If the results are compared by residence time, POA yields less agreement with the remaining mechanisms.

Regarding the equivalence ratio, POA yields, most of the times, profiles in better agreement with the detailed mechanisms and is possible to verify that POA is a more versatile mechanism than ROM, except for the equivalence ratio of  $\varphi = 0.7$ . POA proved to achieve better agreements with the detailed mechanisms when temperature (Fig. 1), flame front (Fig. 2) and gases velocity (Fig. 3) are the analyzed parameters. Although Fig. 2 presents two distinctive groups, the difference is smaller when considering the axial distance of the burner due to the gases composition.

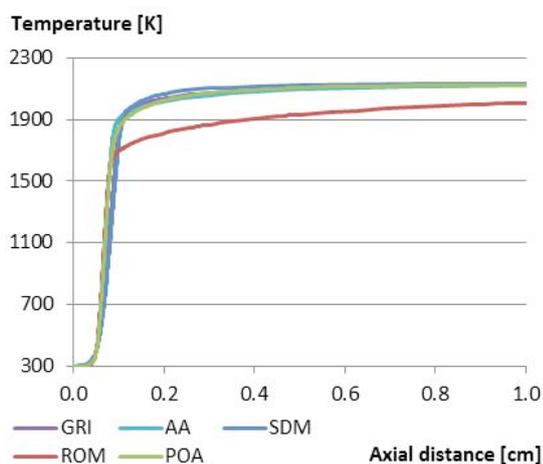


Figure 1. Temperature vs axial distance ( $\varphi = 1.2$  and Comb<sub>A</sub>).

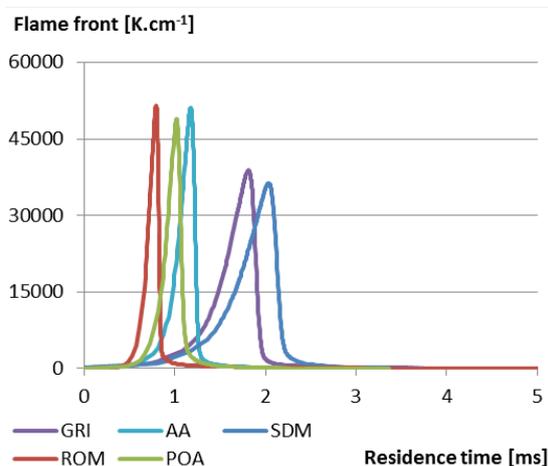


Figure 2. Flame front vs residence time ( $\varphi = 1.2$  and Comb<sub>A</sub>).

Regarding the methane oxidation, all mechanisms yield identical profiles, mainly in the reactants and products molar fractions although some deviations can be found in intermediary species as carbon monoxide (Fig. 4), hydrogen (Fig. 5) and hydroxyl radical (Fig. 6) where ROM detaches itself from the remaining mechanisms. In Fig. 3 and Fig. 4 is possible to verify that POA evolves inside the interval defined by the mean of the detailed mechanism added/subtracted of their standard deviation whilst ROM does not. In Fig. 4 is noticeable that ROM yields a maximum concentration value 42.6% above the mean value (standard deviation equals 9.48%) and somewhat before the remaining mechanisms.

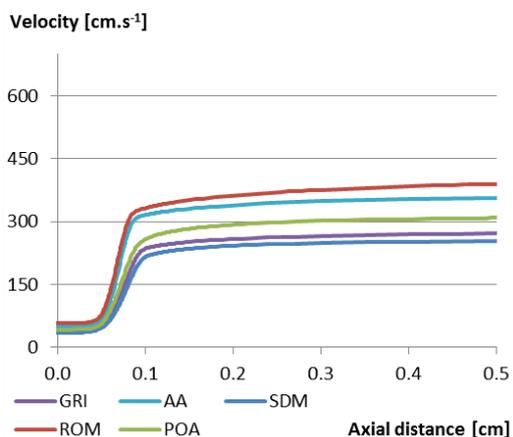


Figure 3. gas velocity vs axial distance ( $\varphi = 1.0$  and Comb<sub>A</sub>).

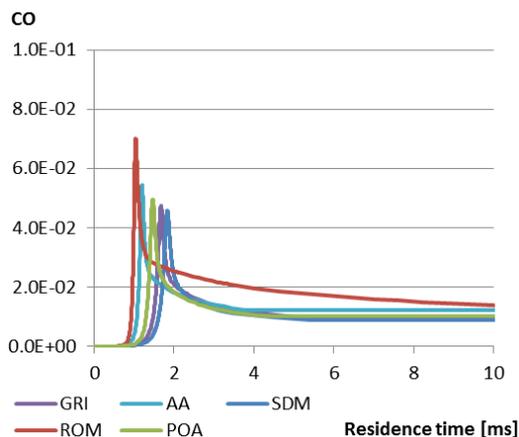


Figure 4. CO vs residence time ( $\varphi = 1.0$  and Comb<sub>A</sub>).

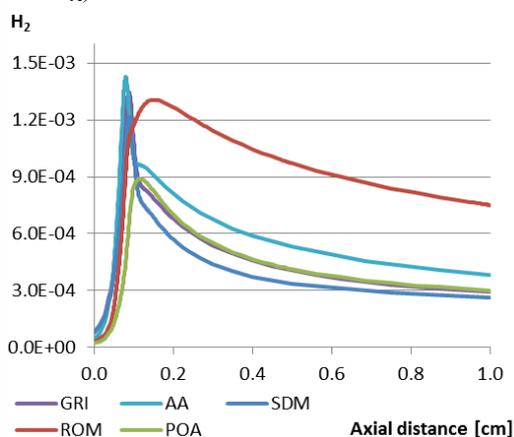


Figure 5. H<sub>2</sub> vs axial distance ( $\varphi = 1.0$  and Comb<sub>A</sub>).

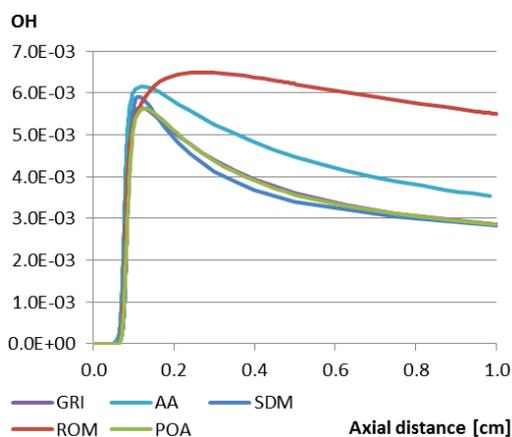


Figure 6. OH vs axial distance ( $\varphi = 1.0$  and Comb<sub>B</sub>).

Regarding the nitrogen species, two different situations occur. ROM does not include reactions to support the formation or destruction of NH<sub>3</sub> (Fig. 7) and POA does not perform well, mainly for equivalence ratios above 0.9. The differences for the detailed mechanisms are of several orders of magnitude. This way, absolute results were normalized considering the maximum value in the series as 100% and creating a relative trend.

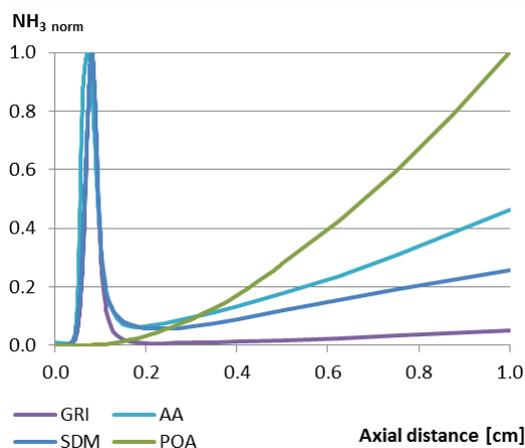


Figure 7. NH<sub>3</sub> (normalized) vs axial distance ( $\varphi = 1.2$  and Comb<sub>B</sub>).

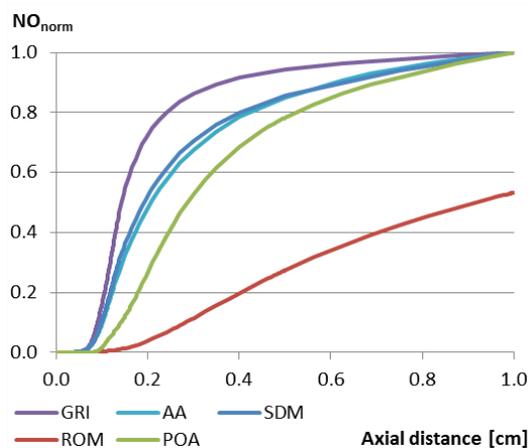


Figure 8. NO (normalized) vs axial distance ( $\varphi = 0.7$  and Comb<sub>A</sub>).

Considering the NO and HCN species, both ROM and POA yield a poor agreement with the detailed mechanisms, mainly with the stoichiometric fuel/air ratio and in fuel rich flames (Figs. 8, 9 and 10). Both species profiles showed

similar tendencies after profile normalization was made. Both reduced mechanisms showed problems with equivalence ratios greater than 1.0 (Fig. 10), although POA proved to have better agreement with the detailed mechanisms concerning the  $\text{NO}_{\text{norm}}$  trend.

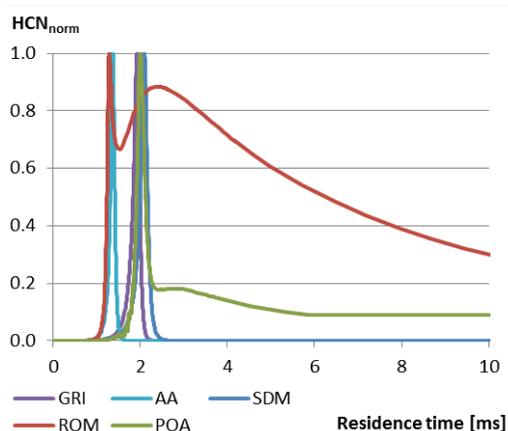


Figure 9: HCN (normalized) vs axial distance ( $\varphi = 0.9$  and  $\text{Comb}_A$ ).

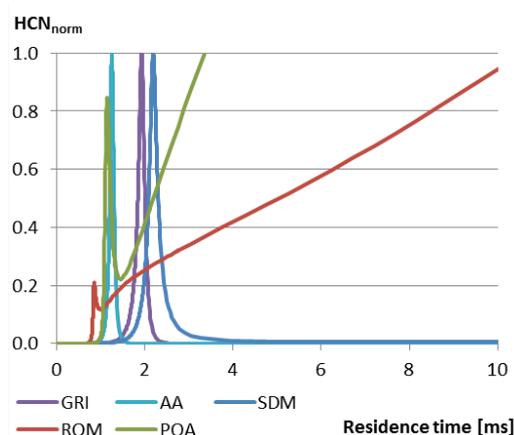


Figure 10: HCN (normalized) vs residence time ( $\varphi = 1.2$  and  $\text{Comb}_A$ ).

The  $\text{NO}$  profile in POA presented good agreement with the detailed mechanisms but ROM did not (Fig. 7). The profiles near de fuel mixtures inlets are important but much more difficult to find in good agreement. The aim of this work was more focused in the flue gases composition after stabilization and in this particular issue, POA yields a very good agreement.

Another aim for this study was to obtain a reduced computational effort besides a good agreement in the above parameters. In this way, there were made calculations to acquire some knowledge on the computational effort for the studied mechanisms. Tab. 4 presents computational effort results and shows a reduction in time of 12.9% to obtain a numerical solution.

Table 4. Computational effort.

Symbol	Species	Reactions	Solved case time [s]
GRI	53	325	307.42
AA	60	371	457.58
SDM	62	286	462.58
ROM	42	32	51.08
POA	46	34	44.50

POA yields good agreement with the detailed mechanisms in most of the studied profiles and has a reduced computational effort. This is of most importance because of the difficulties in using detailed kinetic mechanisms in a full 3D reactive flow working in a computational fluid dynamic application package.

## 7. CONCLUSIONS

Simplified representations of the chemistry of  $\text{NO}_x$  formation in laminar premixed flames are useful because of the savings in computational time associated to them. A set of elementary reactions were retrieved from a detailed mechanism and used to define a reduced mechanism for a freely propagating, adiabatic, laminar premixed methane/air flame. The proposed reduced mechanism includes the chemical kinetics for methane oxidation and  $\text{NO}_x$  formation with ammonia. This reduced mechanism was improved by parameters from different researchers.

The detailed reaction mechanism was reduced to a minimum set of 34 species (23 corresponding to the hydrocarbon system and 11 corresponding to  $\text{NO}_x$ ) and 46 reactions (21 for methane and 25 for  $\text{NO}_x$ ). The optimized scheme was evaluated by comparing the model predictions with the results of computer runs done with the detailed mechanism for a range of equivalence ratios from 0.7 to 1.2. The performance of the reduced mechanism was evaluated in terms of temperature, flame front and adiabatic flame velocity, maximum mole fraction of several species and radicals and nitrogen species.

The proposed mechanism provided good predictions of the adiabatic flame for the temperature, flame front and gases velocity, as well as for the methane oxidation species. The results for the nitrogenous species were not in good agreement although presented identical tendencies to the detailed mechanisms.

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