EVALUATION OF REDUCED CHEMICAL KINETIC MECHANISMS USED FOR MODELLING MILD COMBUSTION FOR NATURAL GAS

by

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A numerical and parametric study was performed to evaluate the potential of reduced chemistry mechanisms to model natural gas chemistry including NO_x chemistry under mild combustion mode. Two reduced mechanisms, 5-step and 9-step, were tested against the GRI-Mech3.0 by comparing key species, such as NO_x, CO_2 and CO, and gas temperature predictions in idealized reactors codes under mild combustion conditions. It is thus concluded that the 9-step mechanism appears to be a promising reduced mechanism that can be used in multi-dimensional codes for modelling mild combustion of natural gas.

Key words: *mild combustion, reduced mechanisms, pollutant emission*

Introduction

Mild combustion has been acknowledged as one of the most interesting combustion technologies to meet both the targets of high energy efficiency and low pollutant emissions [1]. In order to optimize present mild combustion performances and in a view of its several applications, coming to an understanding of the physics on which this combustion regimes is based is essential, since a consistent explanation of the whole combustion process is still missing. So far, experiments [2] and numerical [3] studies have begun to show a strong coupling between turbulence and kinetics.

Issues such as ignition, flame stabilization, combustion efficiency, and pollutant formation are extremely important in the design of the combustion systems based on the mild combustion conditions. Accurate simulation of these phenomena requires that significant chemical kinetic detail be retained in computer model. Within CFD simulations, the number of species tracked impacts the memory usage and CPU time. As a result it is important to use reduced chemical kinetic mechanisms that can represent important aspects of the behavior of these detailed mechanisms using few enough scalars that they can be implemented into CFD simulations. The reduced mechanisms required for CFD simulation of combustion processes depends of the nature of the phenomenon and the type of information desired from the simulation.

Full mechanisms are usually validated using experimental measurements. These full mechanisms are then used to evaluate reduced mechanisms. Thus, reduced mechanisms are validated by comparing key species and temperature predictions to predictions of validated full mechanisms.

Table1. Reactions and species included in 5-step and 9-step reduced mechanisms

Mechanism	Species included	Reactions
5-step	H_2 O_2 OH H_2O CH_4 CO CO_2 NO N_2	$3H_2 + O_2 + CO_2 \quad 3H_2O + CO$ $H_2 + 2OH$ $H_2 + CO \quad C$ $H_2 + CO_2 \quad C$ $3H_2 + CO_2 + 2NO \quad 3H_2O + CO + N_2$
9-step	H_2 H O O_2 OH H_2O CH_3 CH_4 CO CO_2	$H_2 + O$ $4H + O_2$ $H + O$ $H_2 + 2O + CH_3 \quad 4H + OH + CO$ $CH_4 + O \quad CH_3 + OH$ $H + OH + CO \quad C$ $H + OH$ $5H + 2NO \quad 2H_2 + O + OH + N_2$ $O + N_2O \quad O_2 + N_2$

The GRI-Mech 3.0 mechanism [4] developed by the Gas Research Institute is one of the best mechanisms, currently available that accurately describes CH_4/NO_x chemistry for natural gas combustion under mild combustion conditions [5].

Two reduced mechanisms, 5-step and 9-step (tab. 1), have been developed from the GRI-Mech 2.11 [6] using the computer-assisted reduction mechanism (CARM) code [7] were then tested against the GRI-Mech 3.0 under three flame simulation codes: Perfectly Stirred Reactor [8], Steady Laminar 1-D Premixed Flame [9], and Plug-Flow Reactor [10]. These new global mechanisms were studied for their potential to model natural gas chemistry (including NO_x chemistry) and were optimized to model the mild combustion mode.

Perfectly-stirred-reactor

The reduced mechanisms were tested using perfectly-stirred-reactor (PSR) code under the initial conditions given in tab. 2. The effect of the equivalence ration on the chosen key species and the temperature is described by varying only the inlet O_2 mole fraction, such as indicated in tab. 2. It should be noted that, the amount of oxyden contained in the inlet CO_2, H_2O, and NO moles fraction, was not taken into the calculation of the eqivalence ratio. In the present computations, the exhaust gas recirculation was implicitly taken into account by including CO_2, H_2O, and NO in the reacting mixture. Thus, these conditions are representative of mild combustion.

Table 2. Initial conditions for PSR code calculations

T_{in} [K]	P [bar]	τ [ms]	$CH_{4,in}$ [vol.%]	$O_{2,in}$ [vol.%]	$CO_{2,in}$ [vol.%]	H_2O_{in} [vol.%]	$N_{2,in}$ [vol.%]	NO_{in} [ppm]
1300	1.0	100	1.5	$3.0/\phi$	10.0	20.0	65.5	100

Figure 1 shows predictions of temperature in a PSR as a function of equivalence ratio. It is seen that both reduced mechanisms show excellent agreement with the full GRI3.0 mechanism.

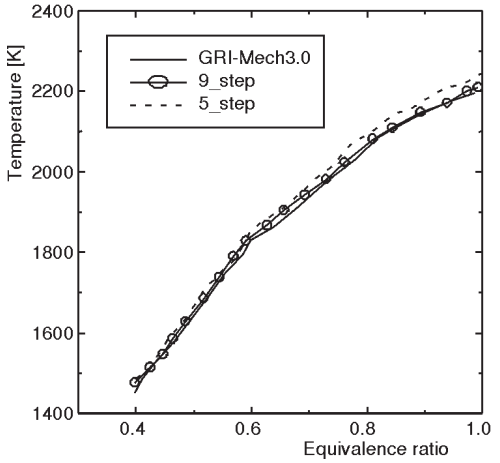

Figure 1. Predicted temperature *vs.* equivalence ratio for PSR with the reduced mechanisms and GRI-Mech3.0

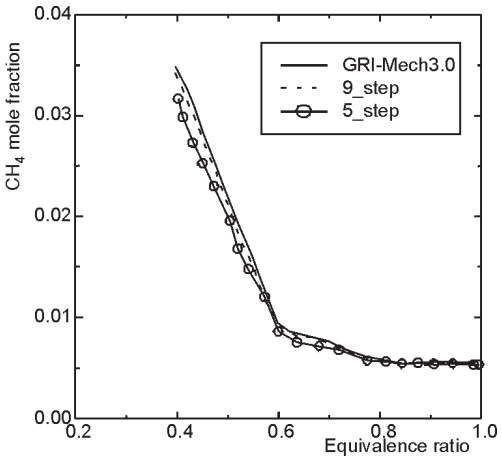

Figure 2. Predicted CH_4 mole fraction *vs.* equivalence ratio for PSR with the reduced mechanisms and GRI-Mech3.0

Figure 2 shows prediction of CH_4 concentrations in a PSR as a function of equivalence ratio. It is again seen that the two developed global mechanisms give very good prediction with the detailed mechanism for mole fraction of CH_4 at fuel-lean mixture.

Figure 3 represent the mole fraction profile of CO in a PSR as function of equivalence ratio. This figure show that at atmospheric pressure, the detailed GRI3.0 mechanism and both reduced mechanism are in good agreement.

Figure 4 show the predicted NO concentrations in a PSR as a function of equivalence ratio. It is seen that although the prediction of the two reduced mechanisms are extremely good at low equivalence ratio. The 5-step global mechanism is less accurate for atmospheric pressure at high equivalence ratio. At these and all other condition, as seen in fig. 4, the 9-step global mechanism is the most accurate reduced mechanisms.

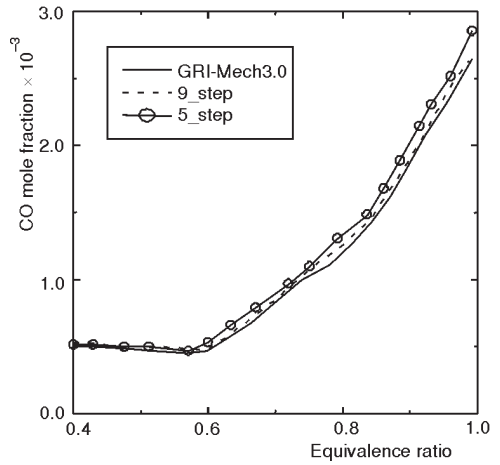

Figure 3. Predicted CO mole fraction *vs.* equivalence ratio for PSR with the reduced mechanisms and GRI-Mech3.0

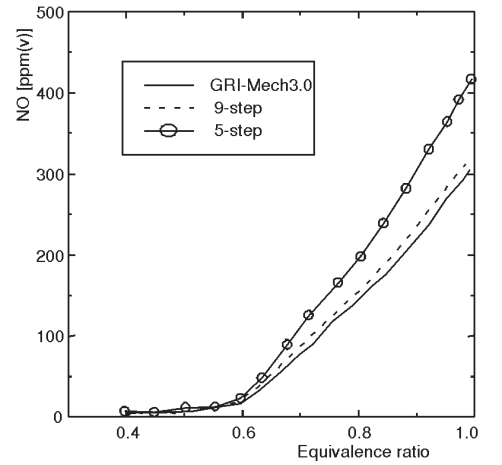

Figure 4. Predicted NO mole fraction *vs.* equivalence ratio for PSR with the reduced mechanisms and GRI-Mech3.0

Steady laminar 1-D premixed flame

Using Premixe code, the reduced mechanisms have been tested under steady laminar 1-D premixed flame at tow values of equivalence ratio: $\phi = 0.6$ and $\phi = 1.0$ at ambient pressure and inlet temperature of mixture at $T_{inlet} = 850$ K. The initial conditions for the numerical simulation are given in tab. 3. As indicated in the previous section, the amount of oxygen contained in $CO_{2,in}$, H_2O_{in}, and NO_{in} was not taken into account in the determination of the equivalence ratio ϕ.

Table 3. Initial conditions for Premixe code

	$CH_{4,in}$ [vol.%]	$O_{2,in}$ [vol.%]	$CO_{2,in}$ [vol.%]	H_2O_{in} [vol.%]	$N_{2,in}$ [vol.%]	NO_{in} [ppmv]	T_{in} [K]	P [bar]	τ [ms]
$\phi = 0.6$	1.5	5	10	20	60.5	100	850	1.0	100
$\phi = 1.0$	1.5	3.0	10.0	20.0	65.5	100			

Figures 5a and 5b show predictions of CH_4 concentration along the length of the premixed flow reactor for $\phi = 0.6$ and ϕ=1.0. As seen in figures, the combustion rates predicted by both reduced mechanisms are similar to the full Gri3.0 mechanism at all equivalence ratios.

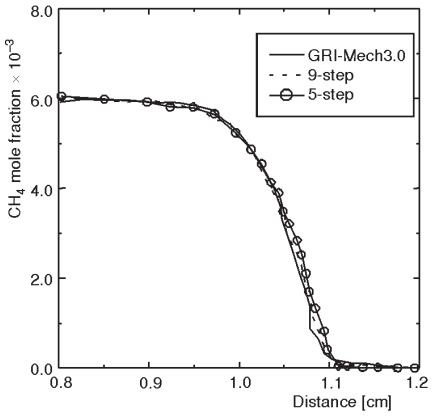

Figure 5a. Predicted CH_4 mole fraction *vs.* distance for steady laminar 1-D premixed flame at ϕ = 0.6 with the reduced mechanisms and GRI-Mech3.0

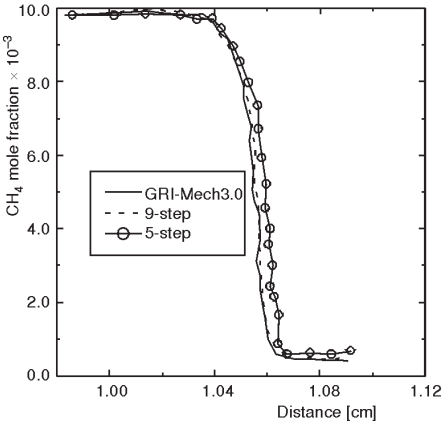

Figure 5b. Predicted CH_4 mole fraction *vs.* distance for steady laminar 1-D premixed flame at ϕ = 1.0 with the reduced mechanisms and GRI-Mech3.0

Figure 6a and 6b show the predicted CO and CO_2 concentrations as a function of distance in the premixed reactor for atmospheric pressure and at equivalence ratios of 0.6 and 1.0. As seen in figures, the predicted peaks of CO and CO_2 using the 9-step and 5-step global mechanisms are similar to the detailed mechanism Gri3.0 for both equivalence ratios ($\phi = 0.6$ and $\phi = 1.0$).

Figures 7a and 7b show predicted NO concentrations as a function of distance along the premixed flow reactor for equivalence ratio of ϕ 0.6 and ϕ 1.0. The NO formation rate is largely dependent on the conditions within the reactor. Figure 7a shows that, at 1 bar and $\phi = 0.6$, the peak NO concentration is ~3 ppm, which is predicted reasonably well by both the 9-step and

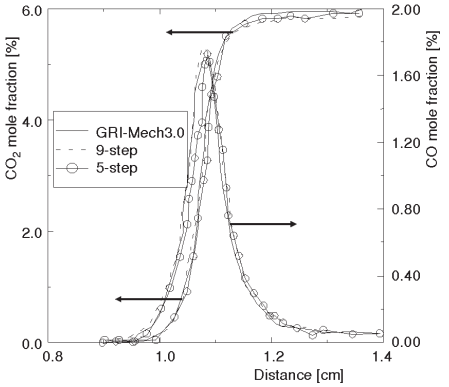

Figure 6a. Predicted CO_2 and CO moles fractions *vs.* distance for steady laminar 1-D premixed flame at ϕ = 0.6 with the reduced mechanisms and GRI-Mech3.0

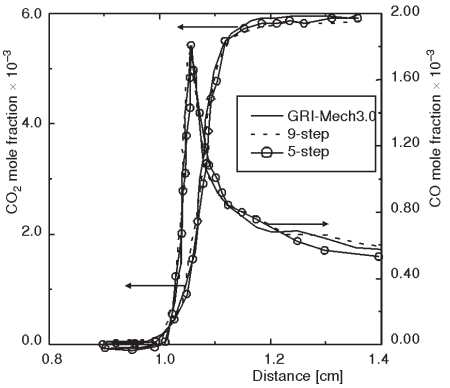

Figure 6b. Predicted CO_2 and CO moles fractions *vs.* distance for steady laminar 1-D premixed flame at ϕ = 1.0 with the reduced mechanisms and GRI-Mech3.0

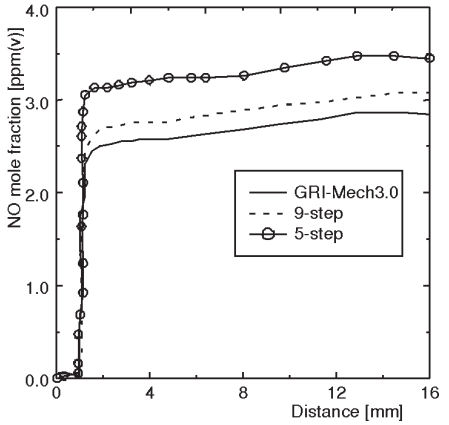

Figure 7a. Predicted NO mole fraction *vs.* distance for steady laminar 1-D premixed flame at ϕ = 0.6 with the reduced mechanisms and GRI-Mech3.0

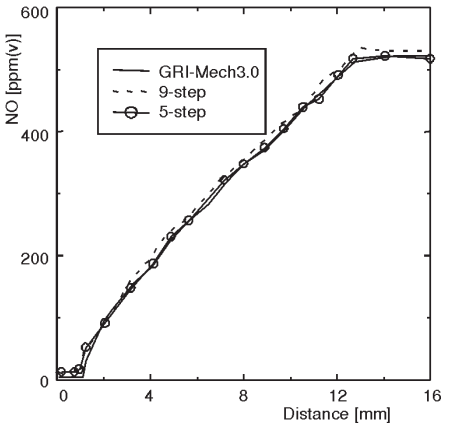

Figure 7b. Predicted NO mole fraction *vs.* distance for steady laminar 1-D premixed flame at ϕ = 1.0 with the reduced mechanisms and GRI-Mech3.0

5-step global mechanism. The increase in equivalence ratio from ϕ = 0.6 (fig. 7a) to ϕ = 1.0 (fig. 7b) increases NO. Increasing the flame equivalence ratio raises the gas temperatures, which directly increases the thermal-NO and hence increases the total NO_x formed.

Plug flow reactor

Cavaliere *et al*. [11] showed that MILD combustion can also take place under plug-flow reactor (PFR) conditions, they named this combustion mode "homogeneous flow flowing ignition". Therefore, we also used the plug-flow reactor model to evaluate the performance of reduced mechanisms with detailed mechanism. The initial conditions for the numerical simulation using the plug-flow reactor model are given in tab. 4, the initial temperature ranging from 1000 K to 1800 K.

Table 4. Initial conditions for PFR code calculations

T_{in} [K]	P [bar]	T [ms]	$CH_{4,in}$ [vol.%]	$O_{2,in}$ [vol.%]	H_2O_{in} [vol.%]	NO_{in} [ppm]
1000 to 1800	1	100	1.5	3	20	100

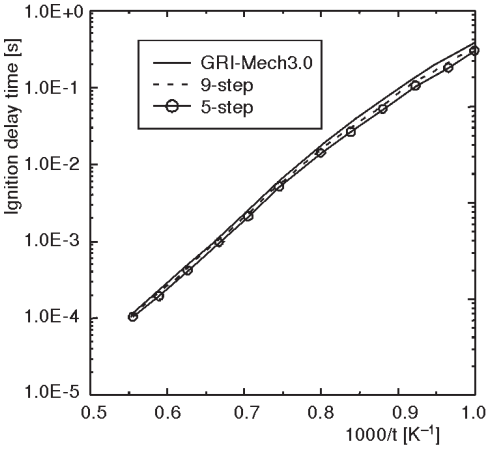

Figure 8. Predicted auto-ignition delay times for PFR with the reduced mechanisms and GRI-Mech3.0

Figure 8 summaries the predicted delay times suing the 9-step reduced chemistry and detailed Gri-Mech 3.0 mechanism. As seen in the figure, the agreement between the reduced and detailed mechanisms is quite satisfactory.

Conclusions

A major focus of this study was to evaluate the performance of reduced chemistry mechanisms of natural gas combustion and NO_x formation that describe mild combustion of natural gas. This included identifying a useful comprehensive mechanism and then comparing the reduced mechanisms to the full mechanism in idealized codes at practical experimental conditions. The potential reduced mechanisms tested were expected to predict gas temperature and concentrations of key species such as NO_x and CO.

Two reduced mechanisms, 5-step and 9-step have been developed from the Gri-Mech 2.11, which incorporates NO_x chemistry for combustion of natural gas. The newly-developed 5-step and 9-step global mechanisms were evaluated by comparing key species, such as NO_x, CO_2 and CO, and gas temperature predictions in these mechanisms to the full GRI-Mech3.0, in idealized code under mild combustion conditions.

Based on the PSR, Premixe, and PFR code calculations performed in this study, it is thus concluded that the 9-step global mechanism appears to be a promising reduced mechanism that can be used in multi-dimensional codes for modelling mild combustion of natural gas.

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