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Author(s)	Kim, Yu Jeong; Oh, Chang Bo; Fujita, Osamu
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Research Article

Prediction Performance of Chemical Mechanisms for Numerical Simulation of Methane Jet MILD Combustion

Yu Jeong Kim,¹ Chang Bo Oh,¹ and Osamu Fujita²

¹ Department of Safety Engineering, Pukyong National University, San 100, Yongdang-dong, Nam-gu, Busan 608-739, Republic of Korea

² Division of Mechanical and Space Engineering, Hokkaido University, N13 W8 Kita-ku, Sapporo, Hokkaido 060-8628, Japan

Correspondence should be addressed to Chang Bo Oh; cboh@pknu.ac.kr

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The prediction performance of five chemical mechanisms (3-STEP, WD4, SKELETAL, DRM-19, and GRI-2.11) was investigated to confirm their suitability for use in numerical simulations of methane combustion in moderate or intense low-oxygen dilution (MILD). A wall-confined jet geometry was introduced to simulate MILD combustion. The oxygen level in the coflowing air was adjusted by mixing the air with combustion products. Each chemical mechanism was analyzed with respect to the flame structure and main product, including CO and NO; the emission indices for CO were also discussed. The temperature distributions and heat-release rates predicted by the chemical mechanisms were similar when the flames were stably attached to the fuel jet exit. The temperature distributions and heat-release rates were dependent on the flame liftoff characteristics, as were the CO and NO emissions. The NO concentration predicted by GRI-2.11 was lower than those predicted using other chemical mechanisms, although DRM-19 predicted a relatively similar value. The emission indices for NO (EINO) and CO (EICO) predicted by each chemical mechanism decreased with increasing dilution rate. The predicted EICO had a negative value even at a small dilution rate, which implies that some of the CO supplied to the air stream is consumed during MILD combustion.

1. Introduction

Common high-temperature facilities adopt a combustion process to transform the chemical energy of fossil fuels into thermal energy. A major portion of the energy used worldwide is still derived from the combustion of various fossil fuels. However, this combustion causes many environmental problems, including pollutant emission and greenhouse effect, and also inevitably depletes the limited energy resources. Recent problems with respect to the environment and energy supply and demand require innovative combustion technologies in order to reduce the pollutant emission and greenhouse effect by enhancing the thermal efficiency of high-temperature facilities.

Moderate or intense low-oxygen dilution (MILD) combustion [1], also known as flameless oxidation (FLOX) [2] or high-temperature air combustion (HiTAC) [3–5], is a promising combustion technology that results in high thermal efficiency and reduced emission of pollutants, such as NO_x, CO, and soot, by using heat-regenerated, high-temperature,

low-oxygen air from the product gases. Recently, numerous studies have focused on high-temperature air combustion and the development of a MILD combustor.

Dally et al. [6, 7] evaluated turbulent and combustion models for the numerical simulation of MILD combustion in a jet burner with hot coflow (JHC) by comparing the simulation results with those of experiments. In the studies, the standard k - ϵ turbulent model with a modified $C_{1\epsilon}$ constant in the dissipation transport equation was suggested as a suitable model for the simulation of MILD combustion. As a combustion model, the eddy dissipation concept (EDC) model adopts global or detailed chemical mechanisms and is known to best predict the flow and mixing fields during MILD combustion. The prediction performance of global and detailed chemical mechanisms for the simulation of CH₄/H₂ MILD combustion was investigated. Wang et al. [8] examined the suitability of six global mechanisms for predicting the major species concentrations during CH₄/H₂ combustion under MILD conditions. A modified Westbrook-Dryer global mechanism (WD4), which includes modified

CO and H_2 oxidation rates, showed the best agreement with experiment results. Parente et al. [9] investigated the effects of combustion models and chemical mechanisms on the MILD mode of CH_4/H_2 combustion in the longitudinal combustor section. In their study, two different combustion models, that is, the eddy dissipation/finite rate (ED/FR) and EDC models, and three chemical mechanisms, that is, a global mechanism, a developed reduced mechanism including 22 species (DRM-19), and GRI-v3.0, were tested. The EDC model with DRM-19 provided the best prediction of the results obtained by GRI-v3.0 for the flame structure and global NO emission.

Numerous simulation studies have also focused on investigating the prediction performance with respect to NO formation under MILD conditions [10–13]. The JHC proposed by Dally et al. [10] was used in these studies. Measurements of temperature and O_2 , H_2O , OH , and NO distributions during CH_4/H_2 combustion in a JHC under MILD conditions were conducted using the single-point Raman-Rayleigh laser-induced fluorescence (LIF) technique [10]. The temperature and species distribution results were compared with the laminar flamelet calculations in the mixture fraction space, and different chemical pathways, especially for the formation of OH and NO , were found. Mardani and Tabejamaat [11] investigated the NO production mechanisms of CH_4/H_2 MILD combustion in a JHC. In the study, the numerical results obtained by computational fluid dynamics (CFD) and the zero-dimensional well-stirred reactor (WSR) approaches were compared with previous measurements obtained by Dally et al. [10]. The GRI-v2.11 full mechanism was considered to represent the chemical reactions, and the numerical results were found to predict the measurements with an acceptable accuracy. The NNH and N_2O routes were also reported to be the most important pathways for NO formation under MILD conditions. Khoshhal et al. [12] predicted the NO_x emission from a HiTAC furnace and showed that the numerical simulation results were in good agreement with the experimental results when the N_2O -intermediate model was used. Kim et al. [13] performed numerical simulations of the flame structures and NO formation in the MILD combustion mode of a JHC using the conditional moment closure (CMC) model. In this study, the numerical simulations that adopted the GRI-v2.11 full mechanism predicted the experimental measurements reasonably well.

In addition, numerous studies have focused on the fundamental MILD combustion characteristics using simple geometries [14] and various fuels [15, 16].

To design an optimized MILD combustion burner, we require further information regarding the factors that affect combustor performance, such as the flow, mixing, and reaction characteristics inside the combustor. Numerical approaches provide a less time- and cost-intensive method of investigating flow and reaction characteristics inside a MILD combustor than that achieved during the experiments. Hence, CFD simulation is very useful for investigating MILD combustion. However, reliable flow and combustion models are required for effectively utilizing CFD simulation in order to acquire the key factors for designing a MILD combustor. With respect to the combustion model, the prediction performance of the chemical mechanisms should be validated for

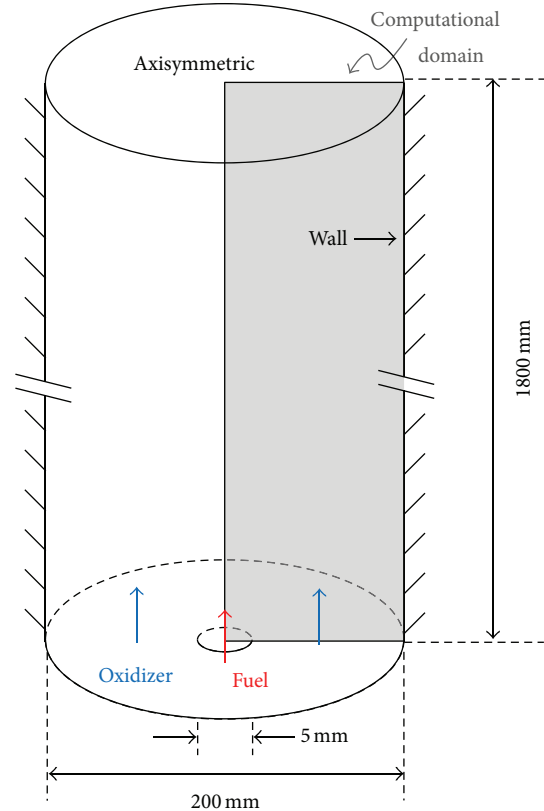


FIGURE 1: Axisymmetrically wall-confined jet geometry for MILD combustion.

the combustion mode considered. Although some chemical mechanisms have been validated for MILD combustion of certain fuels [8, 9], more specific information on the chemical mechanisms of various fuels and the dilution conditions is still required.

The objective of this study is to investigate the prediction performance of five chemical mechanisms to confirm their suitability for the numerical simulation of MILD combustion. A wall-confined jet geometry was introduced to simulate MILD combustion. Methane, which is the main species of liquid natural gas (LNG), was used as the fuel, and the O_2 level in the coflow air was adjusted by mixing air with the combustion products. The chemical mechanisms were compared with respect to the flame structure and main species, including NO, and the prediction performance of each chemical mechanism for the NO and CO emission characteristics is discussed.

2. Numerical Methods

2.1. Geometry and Boundary Conditions. Numerical simulations were performed for a wall-confined coflow methane jet flame with the commercial code FLUENT 13.0 [17]. Figure 1 shows the geometry and simulation domain for a wall-confined axisymmetric coflow jet combustor with a diameter of 200 mm and a height of 1.8 m. A structured nonuniform two-dimensional (2D) grid system was generated for the

TABLE 1: Velocity (m/s) of air stream with the variation of dilution rate and air-stream temperature.

T_{air}	Dilution rate (Ω)			
	0.0	0.3	0.5	0.7
1100 K	0.375	0.530	0.740	1.221

TABLE 2: Composition of the main species in the air stream with variation of dilution rate.

Species	Dilution rate (Ω)			
	0.0	0.3	0.5	0.7
O ₂	0.210	0.147	0.105	0.063
N ₂	0.790	0.766	0.750	0.734
CO	0.000	0.003	0.005	0.007
CO ₂	0.000	0.027	0.045	0.063
H ₂ O	0.000	0.057	0.095	0.133

simulation of the coflow jet combustor. The total number of grids used in the simulations was determined as 50,400 by comparing the flame structure and species concentration distribution with those obtained by the 127,000- and 200,000-grid systems. The grid system was designed to give a finer grid in the flame region and near the fuel nozzle inlet. The inner diameter of the fuel nozzle was 5 mm and the thickness of the fuel nozzle was neglected for simplicity. Coflowing air was supplied to the outside of the fuel nozzle.

The amounts of fuel and air were controlled by adopting the global equivalence ratio (Φ), which is the ratio of the stoichiometric air-to-fuel mass ratio to the actual air-to-fuel mass ratio. The equivalence ratio is defined as

$$\Phi = \frac{(A/F)_{\text{st}}}{(A/F)_{\text{act}}}, \quad (1)$$

$$\left(\frac{A}{F}\right) = \frac{(\dot{m}_{\text{air}} \times Y_{\text{O}_2})}{(\dot{m}_{\text{fuel}} \times Y_{\text{CH}_4})},$$

where A and F indicate the mass of air and fuel, respectively, $\dot{m}$ represents the mass flow rate, Y represents the mass fraction, and the subscripts st and act indicate the stoichiometric and actual conditions, respectively.

Pure methane was used as the fuel and the fuel velocity was fixed at 12 m/s, which corresponds to a Reynolds number of ~ 3400 . The value of Φ was fixed at 0.7 in this study. The inflow velocities of the air stream for each given condition are listed in Table 1. The temperature of the fuel was fixed at 300 K, while the temperature of the air stream was fixed at 1100 K for high-temperature MILD combustion. In this study, the confined wall temperature was held at 900 K, as determined by considering the results of previous experimental studies on various MILD combustors [18, 19].

In this study, only four species, that is, CO₂, CO, H₂O, and N₂, were considered as the main products in the combustion gas. Their concentrations were determined via simulation with a UPSR code [20]. In the UPSR simulation, the combustion product compositions of a perfectly mixed methane/air mixture were calculated at a Φ value of 1.0. Table 2 shows the

concentrations of the main species (mole fractions) in the air stream with varying dilution rates (Ω). The dilution rate is defined as

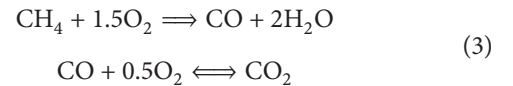
$$\Omega = \frac{\text{volume of product gas}}{\text{volume of total gases in air steam}}. \quad (2)$$

An outflow boundary condition, where the diffusion fluxes for all flow variables in the exit direction are zero, was applied at the outlet boundary, and a no-slip condition for the velocity was applied at the wall. For the species equations, a zero-diffusive flux boundary condition was imposed at all boundaries.

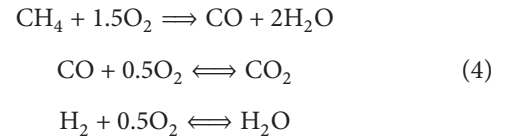
2.2. Turbulence Model and Chemical Mechanisms. The flow was calculated using a modified standard k - ϵ turbulence model, where the dissipation equation constant ($C_{1\epsilon}$) is set at 1.6 instead of 1.44, as suggested by Dally et al. [6]. It has been reported that this model showed an excellent prediction performance of MILD jet combustion results [7]. For the radiation heat transfer, the discrete ordinates (DO) radiation model and weighted sum of gray gases model (WSGGM) were incorporated into the simulations. To calculate the MILD combustion reaction, the EDC model [21–23] with multistep chemical mechanisms was used.

In this study, the prediction performances of five chemical mechanisms were investigated by comparing the flame and pollutant emission characteristics predicted by each chemical mechanism. The five models of chemical mechanisms considered in the simulations are as follows.

- (1) A 3-step global chemical mechanism (3-STEP) [24], where the reactions for CH₄ and CO oxidation are



- (2) A modified global chemical mechanism (WD4) [11, 24, 25], in which the H₂ oxidation reaction was added to 3-STEP; the oxidation rate of CH₄ is the same as for 3-STEP, while the CO oxidation is as follows:



- (3) A skeletal chemical mechanism (SKELETAL) [26], which consists of 16 species and 41 elementary reactions.
- (4) A shortened full chemical mechanism of GRI-v1.2 (DRM-19) [27], which consists of 21 species and 84 elementary reactions.
- (5) A GRI-v2.11 full chemical mechanism (GRI-2.11) [28], which consists of 49 species and 279 elementary reactions.

For the full reaction parameters of these chemical mechanisms, please refer to the corresponding references.

2.3. NO Calculations. To assess NO emission during MILD combustion, three routes to the formation of the thermal, prompt, and N_2O -intermediate NO were considered for each simulation, except for those with GRI-2.11, which already includes elementary reactions for NO formation. For the other mechanisms, that is, 3-STEP, WD4, SKELETAL, and DRM-19, NO formation via the three routes was calculated for the simulations, as follows:

(1) *Thermal NO Route.* The formation of thermal NO was determined from the following three extended Zeldovich mechanisms, and the rate coefficients for (5)–(7) were taken from Baulch et al. [29]:



Based on a quasi-steady assumption for the concentration of N radicals, the net rate of NO formation via reactions (5)–(7) could be described by

$$\frac{d[NO]}{dt} = 2k_{f,5}[O][N_2] \times \frac{(1 - ((k_{r,5}k_{r,6}[NO]^2) / (k_{f,5}[N_2]k_{f,6}[O_2])))}{(1 + ((k_{r,5}[NO]) / (k_{f,6}[O_2] + k_{f,7}[OH])))}, \quad (8)$$

where $[X]$ indicates the concentration of species X and $k_{f,j}$ and $k_{r,j}$ are the rate constants for the forward and reverse reactions, respectively. The subscript j represents the equation number (i.e., (5)–(7)).

In (8), $[O]$ and $[OH]$ are required. In this study, the effect of $[OH]$ was neglected and $[O]$ can be obtained using the partial equilibrium approach. Considering third-body reactions during the O_2 dissociation-recombination process, the partial equilibrium $[O]$ was calculated using the following expression [30]:

$$[O] = 36.64T^{1/2}[O_2]^{1/2}e^{-27123/T} [\text{mol/m}^3]. \quad (9)$$

(2) *Prompt NO Route.* Prompt NO, which is also called Fenimore NO [31], can form in a significant quantity in some combustion environments, such as under low-temperature, fuel-rich conditions, and with short residence times. In this study, the prompt NO was calculated using De Soete's model [32] for gas-phase fuels, and the rate of overall prompt NO formation is expressed as

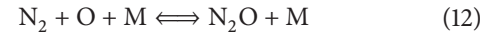
$$\frac{d[NO]}{dt} = fk'_{pr}[O_2]^a[N_2][FUEL]e^{-E'_a/RT}, \quad (10)$$

where f is the correction factor and is given by $f = 4.75 + 0.0819n - 23.2\Phi + 32\Phi^2 - 12.2\Phi^3$, n is the number of carbon atoms per molecule for the hydrocarbon fuel, and Φ is the

equivalence ratio. Also, $k'_{pr} = 6.4 \times 10^6(RT/p)^{a+1}$ and $E'_a = 303474.125$ [J/gmol]; these equations were developed at the Department of Fuel and Energy at the University of Leeds, England. The superscript a represents the oxygen reaction order, which is related to the oxygen mole fraction in the flame. For the conditions used in this study $a = 0$; for other conditions, the following equation can be used:

$$a = \begin{cases} 1.0, & X_{O_2} \leq 4.0 \times 10^{-3}, \\ -3.95 - 0.9 \ln(X_{O_2}), & 4.1 \times 10^{-3} \leq X_{O_2} \leq 1.11 \times 10^{-2}, \\ -0.35 - 0.1 \ln(X_{O_2}), & 1.11 \times 10^{-2} < X_{O_2} < 0.03, \\ 0, & X_{O_2} \geq 0.03. \end{cases} \quad (11)$$

(3) *N_2O -Intermediate NO Route.* The formation route of N_2O -intermediate NO may also be important in MILD combustion. A previous study suggested that the N_2O -intermediate route may contribute ~90% of NO formed during MILD combustion. In this study, only the following two reversible elementary reactions are taken into account [33]:



The rate of NO formation via the N_2O -intermediate route can be expressed by

$$\frac{d[NO]}{dt} = 2(k_{f,13}[N_2O][O] - k_{r,13}[NO]^2), \quad (14)$$

where $[O]$ is obtained from (9) and $[N_2O]$ is calculated from the quasi-steady-state assumption for N_2O ($d[N_2O]/dt = 0$). The resulting $[N_2O]$ can be expressed by

$$[N_2O] = \frac{k_{f,12}[N_2][O][M] + k_{r,13}[NO]^2}{k_{r,12}[M] + k_{f,13}[O]}. \quad (15)$$

2.4. Emission Indices for NO and CO. The emission index [34] was introduced to quantify NO and CO emission. The emission index of pollutants represents the ratio of the mass of species i produced during the combustion process to the mass of consumed fuel. The emission index for species i (EI_i) is defined as

$$EI_i = \frac{\text{mass of produced } i\text{th species}}{\text{mass of destroyed fuel input}} = \frac{(\dot{m}_{\text{tot}} \times Y_i)_{\text{outlet}} - (\dot{m}_{\text{air}} \times Y_i)_{\text{inlet}}}{(\dot{m}_{\text{CH}_4})_{\text{inlet}} - (\dot{m}_{\text{tot}} \times Y_{\text{CH}_4})_{\text{outlet}}}, \quad (16)$$

where $\dot{m}_{\text{CH}_4}$ and $\dot{m}_{\text{air}}$ are the mass flow rates of the fuel and air streams, respectively; $\dot{m}_{\text{tot}}$ indicates the total inflowing mass flow rate, that is, the summation of $\dot{m}_{\text{CH}_4}$ and $\dot{m}_{\text{air}}$; Y_i is the mass fraction of species i (i.e., NO or CO); and

the subscripts *inlet* and *outlet*, indicate the inlet and outlet locations, respectively. The mass flow rate for species *i* at the outlet was calculated from the density, velocity, and exit area for each grid point.

3. Results and Discussion

Figure 2 shows the results of the simulations from four chemical mechanisms for the HM3 condition of H_2/CH_4 reacting in a MILD jet issuing into a hot and diluted coflow, as measured by Dally et al. [6]. The 3-STEP simulation for H_2/CH_4 reacting in a MILD jet was not meaningful because H_2 was not considered. The SKELETAL, DRM-19, and GRI-2.11 simulations provided good prediction of the measured temperatures and H_2O and O_2 concentrations. The WD4 simulation also agreed well with the measured temperature and main species, except for the peak temperature values and H_2O mass fraction. For the CO and OH species, the SKELETAL simulation results were higher than those of the other chemical mechanisms, while the prediction performances of the DRM-19, and GRI-2.11 were very similar. Additionally, the SKELETAL, DRM-19, and GRI-2.11 simulations reasonably predicted the measured NO mole fraction, but the WD4 simulation highly overestimated the measured NO. It was confirmed from Figure 2 that the prediction performances of the DRM-19 and GRI-2.11 simulations were very similar, and both were very suitable for simulating the reaction of H_2/CH_4 in a MILD jet. Recently, the prediction performances of DRM-19 and GRI-2.11 were also validated with respect to a small-scale combustor fired with CH_4 fuel [35], except for the NO concentration. Thus, the prediction performance of simple chemical mechanisms such as 3-STEP, WD4, and SKELETAL as compared to the simulation results obtained using DRM-19 and GRI-2.11 for a CH_4 -reacting MILD jet will be discussed.

Figure 3 shows the simulation results of the 2D temperature distributions obtained using the five different chemical mechanisms for $0.0 < \Omega < 0.7$. Please note that the maximum scales in each legend are different. For $\Omega \leq 0.3$, only the result of the GRI-2.11 simulation was plotted because the temperature distributions obtained from the other chemical mechanisms were nearly identical. Overall, the temperature distributions differed according to the dilution and chemical mechanisms. The high-temperature region increased with increasing dilution rate. Using DRM-19 and GRI-2.11, the flame liftoff was identified at $\Omega = 0.5$ and the liftoff distance was largely dependent on the chemical mechanisms. At $\Omega = 0.7$, the flame liftoff and blowout were also identified using WD4 and GRI-2.11, respectively. The temperature distributions predicted by 3-STEP and DRM-19 were similar to those predicted by WD4 and GRI-2.11, respectively. The sensitivity of the dilution rate to the flame liftoff distance predicted by each chemical mechanism decreased in the following order: GRI-2.11 > DRM-19 > 3-STEP $\approx$ WD4 > SKELETAL.

Figure 4 shows the temperature and heat-release rate profiles at selected axial locations for the given conditions. The overall temperature profile decreased with increasing dilution rate at the same location. For $\Omega \leq 0.3$, the temperature

profiles predicted by each chemical mechanism were similar to each other except for the inner region with respect to the peak temperature, especially those upstream. However, for $\Omega \geq 0.5$, the temperature profiles simulated using DRM-19 and GRI-2.11 were different from those obtained using other chemical mechanisms; this was attributed to the prediction performance of each chemical mechanism toward the liftoff and blowout characteristics of the flames. The heat-release rate was also dependent on the liftoff and blowout characteristics of the flames. The peak locations of the heat-release rates simulated via each chemical mechanism were in rough agreement when the flames were stabilized near the fuel jet exit. In particular, the magnitude and location of the heat-release rates simulated using 3-STEP and WD4 were nearly identical regardless of the dilution rate. Double peaks for the heat-release rate were identified near the edge of the liftoff flame; that is, the heat-release rates of DRM-19 at $x = 0.6$ m for $\Omega = 0.5$ and of 3-STEP and WD4 at $x = 0.2$ m for $\Omega = 0.7$ showed double peaks. The double-peak profile of the heat-release rate was closely related to the edge flame structure of the liftoff flame. The overall flame shape and liftoff characteristics directly affected the distributions of species concentrations and pollutant emissions; the relevance of those features has been discussed using the following Figures 5–10.

Figure 5 shows 2D distributions of the CO concentrations (mole fraction) obtained from the simulation using each chemical mechanism for $\Omega = 0.0$ and $\Omega = 0.5$. For $\Omega = 0.0$, the distributions of CO concentrations were largely dependent on the chemical mechanisms even when the flames were stably attached to the fuel jet exit. For $\Omega = 0.0$, the distribution shapes of the CO concentrations for all simulations were similar except for that using WD4, while the magnitudes of the CO concentrations differed somewhat. The magnitude of the maximum CO concentration predicted by each chemical mechanism for $\Omega = 0.0$ decreased in the order GRI-2.11 > DRM-19 > SKELETAL > 3-STEP > WD4. However, the distribution of CO concentration was also dependent on the flame liftoff characteristics. For $\Omega = 0.5$, the magnitudes and distribution shapes of the CO concentrations varied significantly with different chemical mechanisms. Using DRM-19, the distribution of CO concentrations was significantly affected by the flame liftoff characteristics, and the location of the downstream CO concentration tail was similar to those of 3-STEP and SKELETAL. It should be noted that the distribution and magnitude of CO concentrations simulated using WD4 showed larger differences than those simulated with the other chemical mechanisms for both $\Omega = 0.0$ and $\Omega = 0.5$.

Figure 6 shows 2D distributions of the NO concentrations simulated by each chemical mechanism for $\Omega = 0.0$ and $\Omega = 0.5$. For $\Omega = 0.0$, the distribution shapes of NO simulated by chemical mechanisms were similar except for the magnitudes. For each result at $\Omega = 0.0$, NO was mainly generated near the high-temperature flame surface upstream, and the NO concentration became uniform downstream. The magnitude of the maximum NO concentration predicted by each chemical mechanism for $\Omega = 0.0$ decreased in the order 3-STEP > WD4 > SKELETAL > DRM-19 > GRI-2.11. Similar

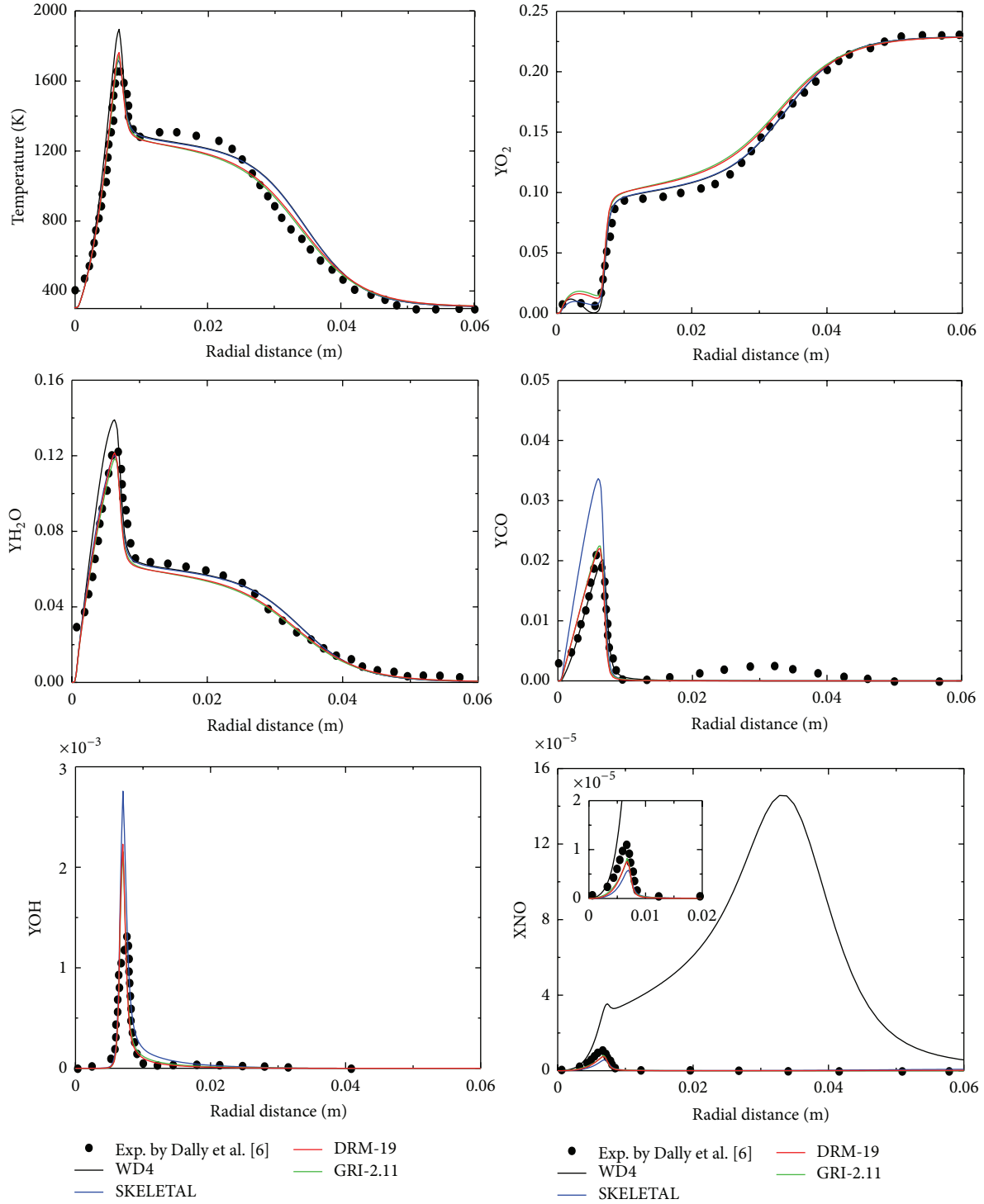


FIGURE 2: Comparison of the numerical results predicted by each chemical mechanism and measurement at 9% O_2 at $Z = 30$ mm in Dally's burner (JHC) [6].

to the CO distribution, the distribution of NO concentrations was also dependent on the flame liftoff characteristics; this feature was identified for $\Omega = 0.5$. Overall, the magnitude of the NO concentration for $\Omega = 0.5$ was much lower than that for $\Omega = 0.0$. For $\Omega = 0.5$, GRI-2.11 predicted that NO was primarily generated near the high-temperature wall.

However, the conditions were not appropriate for investigating the NO concentration because a very small portion of the NO distribution region was captured in the simulation domain. For $\Omega = 0.5$, the maximum NO concentration predicted by DRM-19 was higher than those predicted by the other chemical mechanisms, even though the maximum

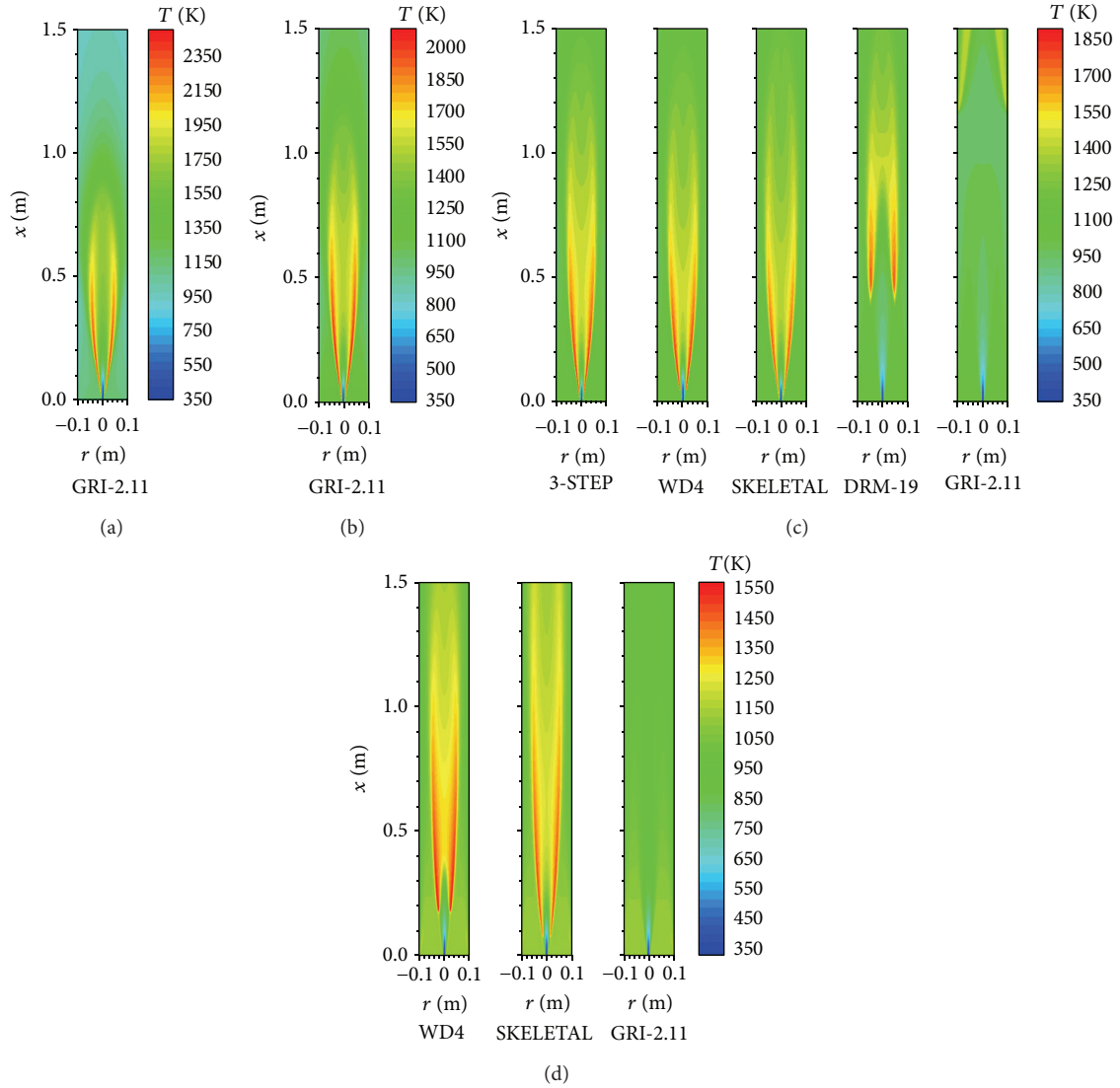


FIGURE 3: 2D temperature distributions with varying chemical mechanisms and varying dilution rates: (a) $\Omega = 0.0$; (b) $\Omega = 0.3$; (c) $\Omega = 0.5$; (d) $\Omega = 0.7$.

NO concentration predicted by DRM-19 was not as high as that for $\Omega = 0.0$. This implies that the roles of the reactions related with NO formation during the simulations can change according to the dilution rate; that is, they are affected by the combustion product gas. Even though the 2D plots clearly show the distributions of NO concentration, it is difficult to quantitatively compare the amount of NO emission predicted by each chemical mechanism. A more detailed comparison of the NO emission predicted by each chemical mechanism is discussed later using the NO concentration profile and EINO values.

Figure 7 shows a comparison of the CO concentration profiles predicted by each chemical mechanism at selected axial locations for $\Omega = 0.0$, $\Omega = 0.3$, and $\Omega = 0.5$. Since the flames predicted by DRM-19 and GRI-2.11 were extinguished at $\Omega = 0.7$, only the results for $\Omega = 0.0$ – 0.5 are plotted hereafter. The CO concentration decreases with

increasing dilution rate at the same axial location. Some differences in the magnitude of the CO concentrations were identified, especially upstream; at the far downstream location, the CO concentration profiles predicted by each chemical mechanism were similar except for that predicted by WD4. At $x = 0.2$ m, the peak CO concentration predicted by WD4 was located at the center-line, while those predicted by the other chemical mechanisms were located near $r = 0.025$ m for all dilution rates. Additionally, the magnitude of the CO concentration predicted by WD4 was much lower than those predicted by the other chemical mechanisms. The CO concentration profiles, except for that predicted by WD4, became similar with increasing dilution rate when the flame was stably attached to the fuel jet exit ($\Omega < 0.5$). In a previous study on CH_4/H_2 MILD combustion in a JHC burner, the modified k - ϵ model, EDC, and GRI-2.11 full chemical mechanisms, which are the same used in

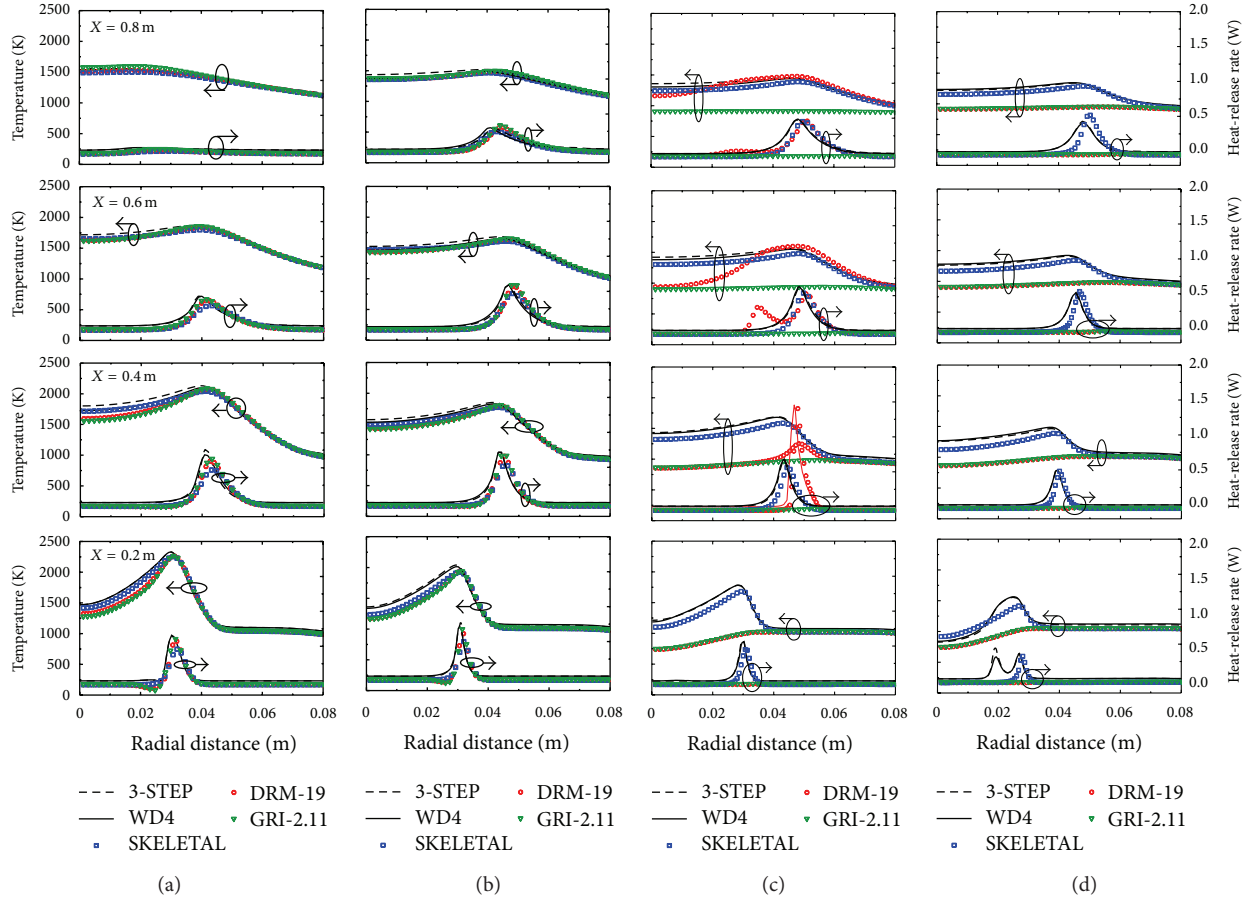


FIGURE 4: 1D cross-sectional temperature and heat of reaction distributions at different axial locations. Comparison between the five chemical mechanisms with varying dilution rates: (a) $\Omega = 0.0$; (b) $\Omega = 0.3$; (c) $\Omega = 0.5$; (d) $\Omega = 0.7$.

this study, predicted the CO concentration reasonably well even though the simulated CO concentration was slightly higher than the experimental result [11]. Considering the CO prediction performance of GRI-2.11, the CO prediction performance of DRM-19 was better than those of the other chemical mechanisms for stable combustion conditions. From Figure 5, it is evident that the predicted maximum CO concentration decreased in the order GRI-2.11 > DRM-19 > SKELETAL > 3-STEP > WD4 under stable combustion conditions. Comparing these results with the experimental ones showed that WD4 showed good simulation of the flame temperature and species concentrations for CH_4/H_2 MILD combustion [8]. However, the prediction performance of the global chemical mechanisms, especially WD4, for CO concentration was not as good as those of the chemical mechanisms that include the elementary CO reactions.

Figure 8 shows a comparison of the NO concentration profiles predicted by each chemical mechanism at selected axial locations for $\Omega = 0.0$, $\Omega = 0.3$, and $\Omega = 0.5$. Please note that the maximum value of the NO mole fraction scale differs for the given dilution rates. The predicted NO concentrations decreased with increasing dilution rate for all chemical mechanisms except GRI-2.11. Contrary to the CO distribution, the NO concentration predicted by GRI-2.11 was lower than those predicted by other chemical mechanisms

for the undiluted condition of $\Omega = 0.0$. For $\Omega = 0.0$, the NO concentration predicted by the chemical mechanisms decreased in the order 3-STEP > WD4 > SKELETAL > DRM-19 > GRI-2.11. Only GRI-2.11 calculated the NO concentration using the full NO elementary reactions. In a previous study on CH_4/H_2 MILD combustion in a JHC burner, the simulation using GRI-2.11 with full chemistry predicted the NO concentration reasonably well even though the simulated NO concentration was somewhat lower than the experimental result [11]. Considering the prediction performance of GRI-2.11 for NO, it seems that the DRM-19 and SKELETAL can also reasonably predict the NO concentration. In particular, it has been reported that DRM-19 showed a good result for NO emission in the exhaust gases [9]. At this stage, there was no difference between the prediction performances of DRM-19 and GRI-2.11 for NO concentration. Additional validation involving comparisons with the experimental NO concentrations is required for the NO predictions by DRM-19 and GRI-2.11. As mentioned earlier, the flame structure including the NO concentration for $\Omega \geq 0.5$ was affected by the flame stabilization characteristics. Although not shown here, the prediction performance of radicals, such as H, O, and OH, by DRM-19 was very similar to that of GRI-2.11, while SKELETAL relatively overpredicted the radical concentrations. Consequently, it is evident that DRM-19 was

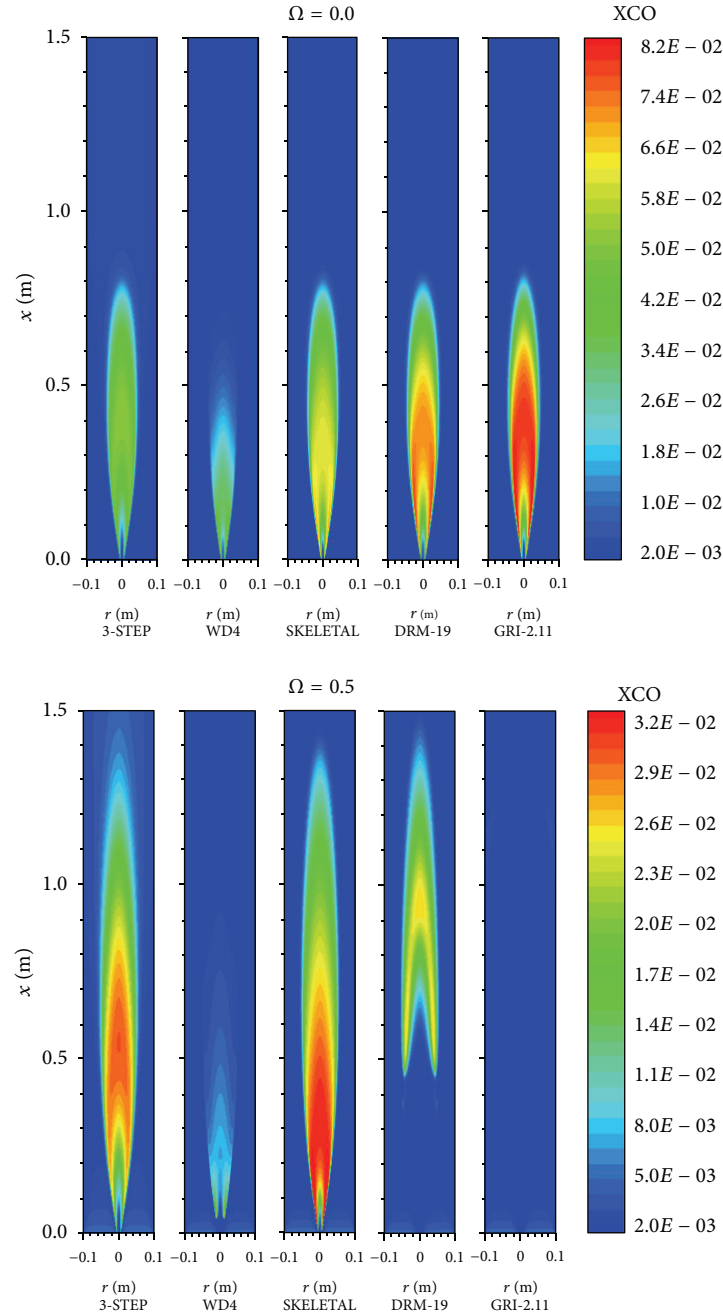


FIGURE 5: 2D distributions of the CO mole fractions at $\Omega = 0.0$ and $\Omega = 0.5$ predicted by the five different chemical mechanisms, that is, 3-STEP, WD4, SKELETAL, DRM-19, and GRI-2.11.

as proficient as GRI-2.11 at predicting the flame temperature and species concentrations, including CO and NO concentrations.

Figure 9 shows the net production rate of CO profiles predicted by each chemical mechanism at selected axial locations for $\Omega = 0.0$, $\Omega = 0.3$, and $\Omega = 0.5$. Please note that the minimum and maximum scales of the CO production rate in the vertical axes were adjusted differently according to the dilution rate. Similarly to the CO concentration shown in Figure 7, the CO production and consumption rates

simulated using WD4 were smaller than those obtained using the other chemical mechanisms. WD4 could not predict the CO consumption in the downstream region as well as the other chemical mechanisms. DRM-19 showed a similar prediction performance as GRI-2.11 for the CO production and consumption rates, except for in the downstream region, for $\Omega = 0.0$. For $\Omega = 0.5$, the CO production rate simulated with DRM-19 was different than those obtained using the other chemical mechanisms because the flame predicted by DRM-19 was lifted off. It should be noted that, at the outside

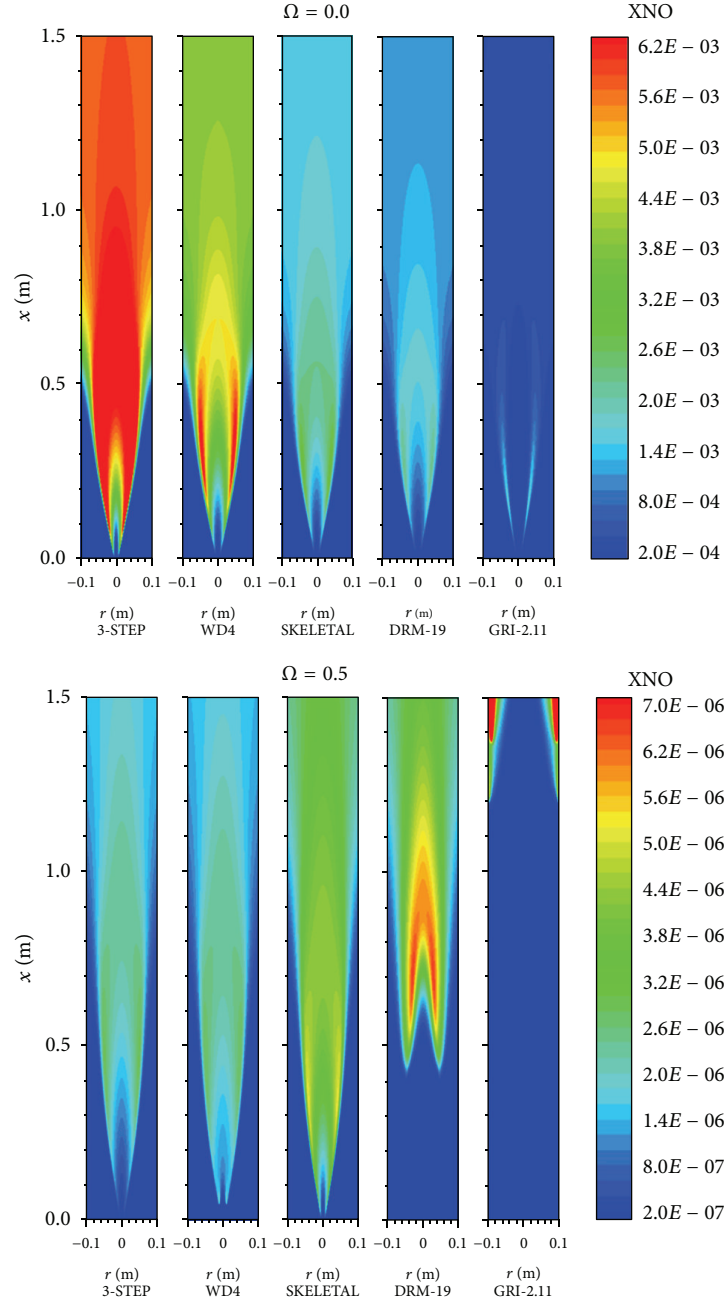


FIGURE 6: 2D distributions of the NO mole fractions at $\Omega = 0.0$ and $\Omega = 0.5$ predicted by the five different chemical mechanisms, that is, 3-STEP, WD4, SKELETAL, DRM-19, and GRI-2.11.

of the flame surface, the CO consumption rate was larger than the CO production rate inside the surface. The CO consumption rate was closely related with the destruction of CO supplied by the hot air stream and it reduced the CO emission in the exhaust gas. The CO emission characteristics are discussed in detail in Figure 11.

Figure 10 shows the net NO production rate profiles predicted by each chemical mechanism at selected axial locations for $\Omega = 0.0$, $\Omega = 0.3$, and $\Omega = 0.5$. At a fixed dilution rate, the magnitudes of the net NO production rates decreased from upstream to downstream except for under lift-off flame conditions. In contrast to the net CO production

rate shown in Figure 9, the net NO production rates predicted by each chemical mechanism showed very large differences in profile shapes and magnitudes. Although not shown here, significant differences in the net NO production rate profiles obtained from each chemical mechanism were also identified at other axial locations. In particular, the GRI-2.11 showed a large difference in the net NO production rate profile. The net NO production rate predicted by DRM-19 was also significantly different than that predicted by GRI-2.11, especially for the negative NO production rate. The NO concentration predicted by GRI-2.11 was lower near the center-line (i.e., inside the peak-temperature location) than those predicted

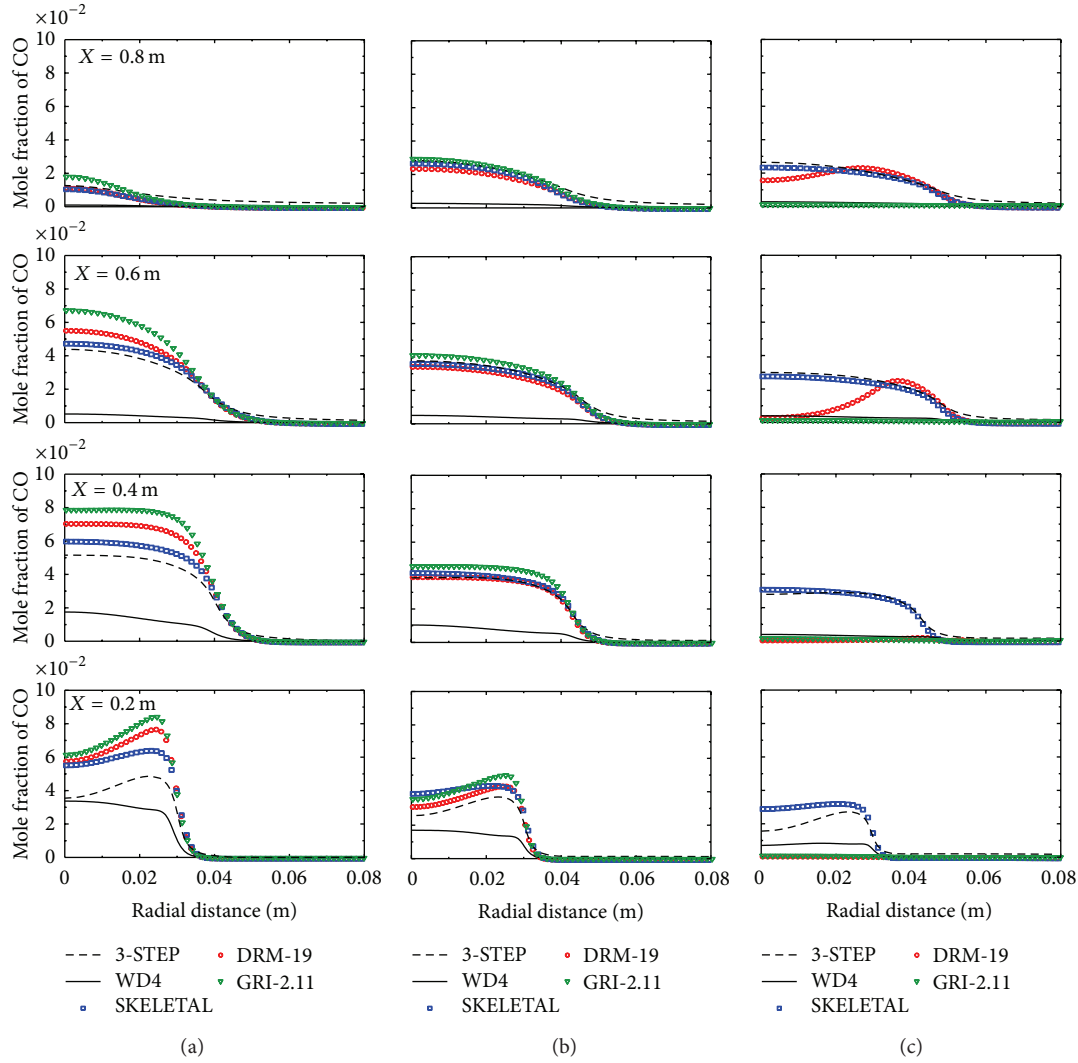


FIGURE 7: 1D cross-sectional distributions of the CO mole fractions at different axial locations. Comparison between the five chemical mechanisms with varying dilution rates: (a) $\Omega = 0.0$; (b) $\Omega = 0.3$; (c) $\Omega = 0.5$.

by the other chemical mechanisms due to the large negative NO production rate obtained using GRI-2.11. The negative NO production rate affected the NO concentration inside the peak-temperature location. As mentioned earlier, the full chemistry of GRI-2.11 predicted a slightly lower NO concentration inside the region of the peak temperature than was experimentally found. It is known from previous studies that the global NO emission in the exhaust gas was reasonably predicted, even by DRM-19. This implies that the NO chemistry requires further validation. Thus, more studies are required to examine the chemical mechanisms that are most suitable for simulating CH_4 MILD combustion, especially with respect to NO concentration; measurements of the global NO emission in the exhaust gas, as well as the local NO distribution, are first required for more precise validation of the NO chemistry.

Figure 11 shows the emission indices for NO and CO with varying dilution rates. As the dilution rate increased, both the EINO and EICO decreased significantly. For a small range of dilution

rates, the magnitude of EINO predicted by GRI-2.11 was lower than those predicted by the other chemical mechanisms. All the EINOs decreased rapidly with increasing dilution rate except for those predicted by GRI-2.11 within a small range of dilution rates. As the dilution rate increased, the EINO predicted by GRI-2.11 decreased gradually for $0.0 < \Omega \leq 0.3$ but then decreased rapidly, similar to those predicted by the other chemical mechanisms outside of this range. The EINO predicted by DRM-19 was larger than that predicted by GRI-2.11 for $\Omega < 0.2$ and became comparable to that predicted by GRI-2.11 with increasing dilution rate. For $\Omega > 0.4$, the flames simulated using DRM-19 and GRI-2.11 were lifted off or blown out and were not captured within the simulation domain. Thus, the discussion of EINO was meaningless under those conditions. Considering that DRM-19 provided reasonable predictions of the NO emission in the exhaust gas in a previous study [9], both DRM-19 and GRI-2.11 are suitable for simulating the NO generated from CH_4 MILD combustion. The EICO obtained from each chemical

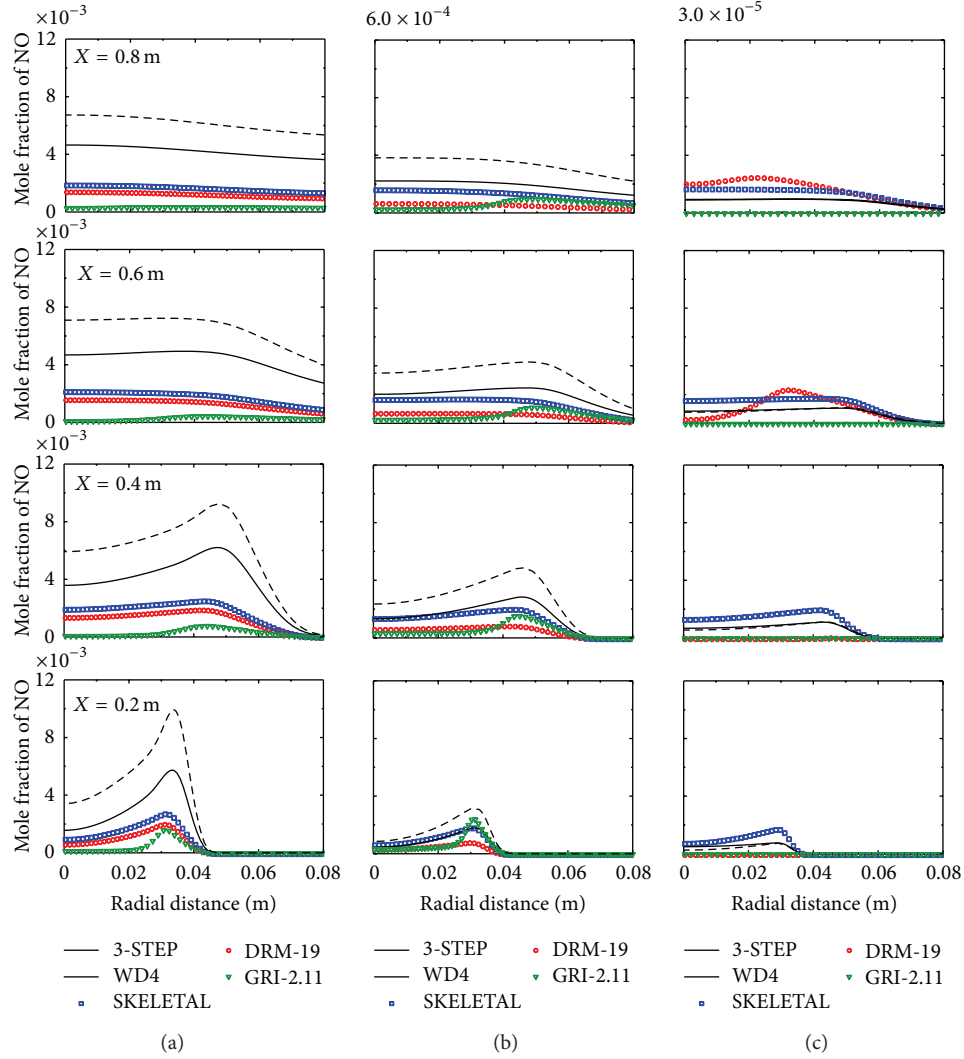


FIGURE 8: 1D cross-sectional distributions of the NO mole fractions at different axial locations. Comparison between the five chemical mechanisms with varying dilution rates: (a) $\Omega = 0.0$; (b) $\Omega = 0.3$; (c) $\Omega = 0.5$.

mechanism decreased with increasing dilution rate. For $\Omega \leq 0.5$, the EICO values were very similar except for those predicted by 3-STEP, which even predicted a slightly different local distribution of CO concentration, as shown in Figure 7. The reason that the EICO obtained by WD4 at $\Omega = 0.7$ was much lower than those obtained using the other chemical mechanisms was attributed to the flame liftoff characteristics. It should be noted that the EICO was negative even at a small dilution rate; this means that some part of the CO supplied to the air stream as a combustion product is consumed during MILD combustion. Moreover, this negative EICO implies that MILD combustion might be very effective for reducing CO emission. Thus, additional studies including numerical simulations and experiments are required to further validate the CO consumption mechanism in MILD combustion.

4. Conclusions

The prediction performances of five different chemical mechanisms for CH_4 turbulent MILD jet combustion were

investigated. Two global chemical mechanisms and three detailed chemical mechanisms that include the elementary reactions were tested, (1) 3-STEP, (2) WD4, (3) SKELETAL, (4) DRM-19, and (5) GRI-2.11 full mechanisms. The effects of the dilution rate on the prediction performance with respect to flame temperature, heat-release rate, and CO and NO were discussed. Several concluding remarks are evident.

- (1) The temperature and heat-release rate predicted by each chemical mechanism were similar when the flames were stably attached to the fuel jet exit (i.e., when $\Omega \leq 0.3$). As the dilution rate increased ($\Omega \geq 0.5$), the distributions of temperatures and heat-release rates became dependent on the flame liftoff characteristics; the CO and NO emissions were also affected by the liftoff characteristics. Thus, it was found that a reasonable prediction of the flame stabilization location was important for numerical simulation of MILD combustion at a high dilution rate.

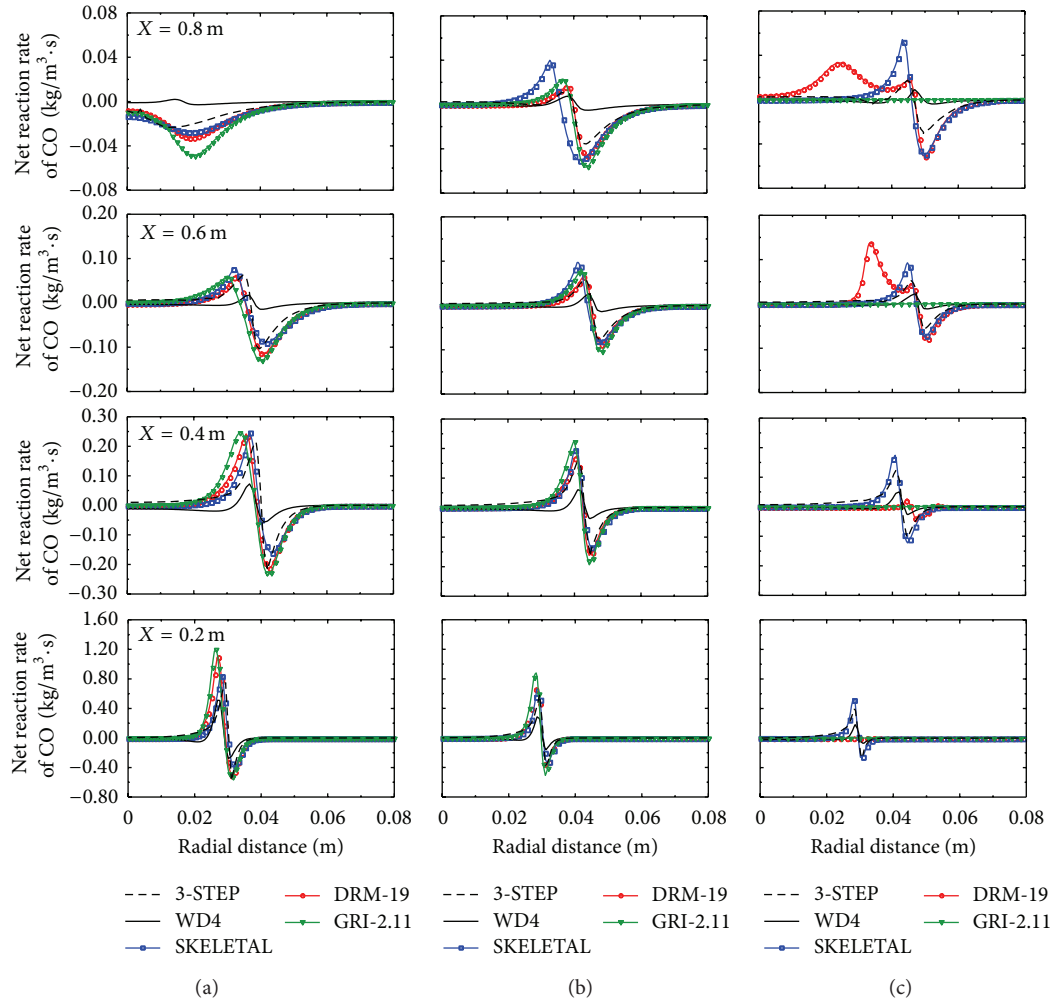


FIGURE 9: 1D cross-sectional distributions of the CO net reaction rates at different axial locations. Comparison between the five chemical mechanisms under varying dilution rates: (a) $\Omega = 0.0$; (b) $\Omega = 0.3$; (c) $\Omega = 0.5$.

- (2) The CO concentrations predicted by each chemical mechanism were more disparate upstream than downstream, especially for the undiluted condition of $\Omega = 0.0$. As the dilution rate increased, each chemical mechanism had a similar prediction performance with respect to the CO concentrations, except for WD4. WD4 predicted a lower CO concentration than those predicted by the other chemical mechanisms and could not predict the peak CO concentration location reasonably upstream. However, DRM-19 followed the CO concentration trends predicted by GRI-2.11 relatively well for all conditions where the flame was not lifted off.
- (3) The NO concentration predicted by GRI-2.11 was lower than those predicted by the other chemical mechanisms. DRM-19 predicted a similar NO concentration as GRI-2.11, although the NO concentration predicted by DRM-19 was somewhat higher than that predicted by GRI-2.11 under undiluted conditions. The net NO production rate of GRI-2.11 was much different than those predicted by the

other chemical mechanisms, especially inside the region of the peak temperature, and the net NO production rate of GRI-2.11 significantly affected the NO concentration distribution in this region.

- (4) The EINOs predicted by each chemical mechanism significantly decreased with increasing dilution rate. The EINO predicted by GRI-2.11 was smaller than those predicted by the other chemical mechanisms at low dilution rates. As the dilution rate increased, the EINO predicted by GRI-2.11 decreased rapidly when $\Omega > 0.3$. The EINO predicted by DRM-19 was larger than that predicted by GRI-2.11 for $\Omega < 0.2$ and became comparable to that predicted by GRI-2.11 with increasing dilution rate. Thus, DRM-19 and GRI-2.11 are suitable for simulating the NO generated from CH_4 MILD combustion.
- (5) The EICOs predicted by each chemical mechanism decreased with increasing dilution rate. For $\Omega \leq 0.5$, the EICOs were very similar except for that predicted by 3-STEP, although the local CO concentration profiles predicted by each chemical mechanism were

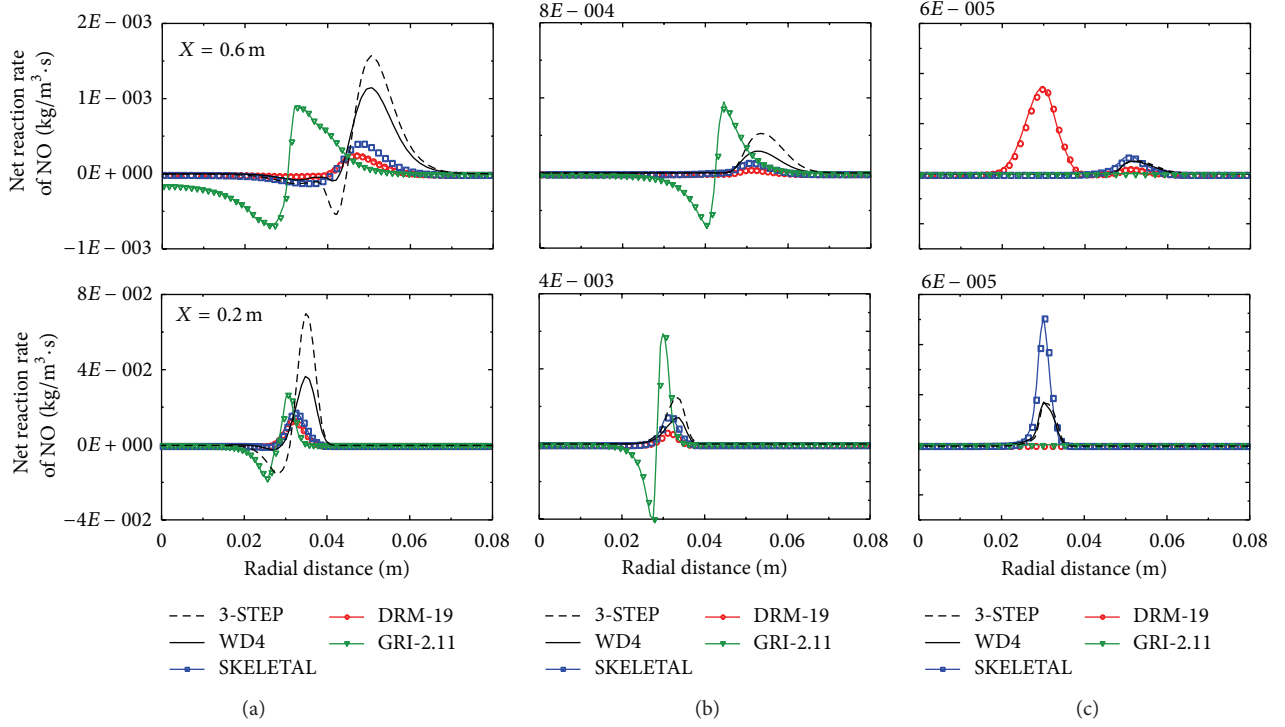


FIGURE 10: 1D cross-sectional distributions of the NO net reaction rates at selected axial locations: $x = 0.2$ m and $x = 0.6$ m. Comparison of the predictions of the five chemical mechanisms with varying dilution rates: (a) $\Omega = 0.0$; (b) $\Omega = 0.3$; (c) $\Omega = 0.5$.

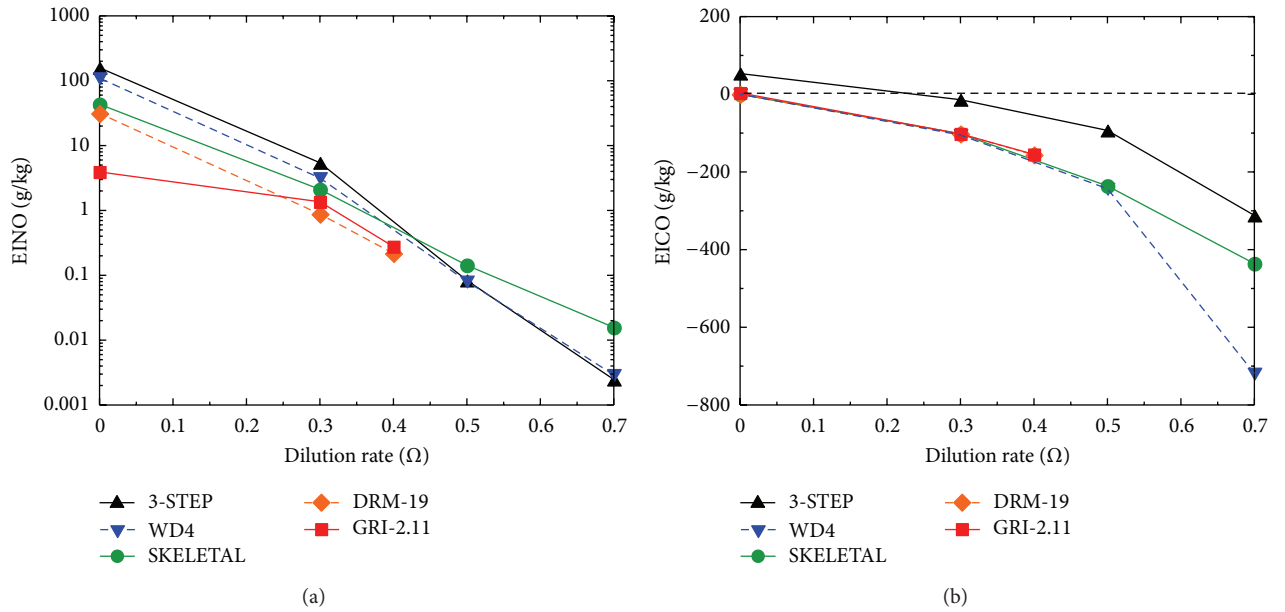


FIGURE 11: Emission indices for (a) NO (EINO) and (b) CO (EICO) predicted by the five chemical mechanisms with varying dilution rates.

slightly different. The EICO was negative even at a low dilution rate. The negative EINO value indicates that some part of the CO supplied to the air stream is consumed during MILD combustion and also implies that MILD combustion might be very effective for reducing CO emissions.

Nomenclature

- Φ : Global equivalence ratio (—)
- (A/F) : Air-to-fuel ratio (—)
- $\dot{m}$: Mass flow rate (kg/s)
- Y_i : Mass fraction of species i (—)

Ω :	Dilution rate (—)
$C_{1\varepsilon}$:	Dissipation equation constant of the k - ε model (—)
$[X]$:	X species concentration (mol/m ³)
$k_{f,j}$, $k_{r,j}$:	Rate constants of reaction j , the forward and reverse (m ³ /mol·s)
f :	Correction factor (—)
α :	Oxygen reaction order (—)
EI_i :	Emission index for species i (g/kg).

Acknowledgments

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