COMPARISON OF DIFFERENT GLOBAL COMBUSTION MECHANISMS UNDER HOT AND DILUTED OXIDATION CONDITIONS

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COMPARISON OF DIFFERENT GLOBAL COMBUSTION MECHANISMS UNDER HOT AND DILUTED OXIDATION CONDITIONS

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Moderate and intensive low-oxygen dilution (MILD) combustion is a new combustion technology. It features as combustion under a hot and diluted oxidation condition. The objective of this article is to optimize global mechanisms for predicting the major species concentration of CH_4 combustion under MILD condition. For this purpose, six different global combustion mechanisms, including the four-step mechanism of Jones and Lindstedt (1988), the two-step mechanism of Westbrook and Dryer (1981), and several modified versions of them, were investigated. Reference calculations were also conducted with detailed chemical kinetic mechanism GRI-Mech 3.0. The interaction between turbulence and chemistry was modeled by eddy dissipation concept (EDC). All of these global mechanisms are validated first by a fictitious plug flow reactor and then by a non-premixed turbulent jet flame of a H_2/CH_4 fuel mixture (Dally et al., 2002). The results show that modified the Westbrook and Dryer mechanism (WD4), which includes both CO oxidation rate and H_2 oxidation rate modification, shows the best agreement with experiment.

Keywords: Global mechanism; MILD combustion; Turbulent jet flame

INTRODUCTION

The rising concentration of atmospheric greenhouse gases, which are widely accepted to lead to climate change, have intensified discussion about the combustion of fossil and alternative fuels. CO_2 emissions from combustion account for about 80% of anthropogenic greenhouse gases (IEA report, 2002), so their mitigation is vital. The improvement of combustion efficiency to reduce fossil fuel consumption and CO_2 emission is a key issue in combustion research.

Among others, moderate and intense low oxygen dilution (MILD) combustion shows its high thermal efficiency and energy saving potential. The technology originated from the concept of excess enthalpy combustion (Hardestry and Weinberg, 1974). It is also called "high temperature air combustion" in Japan (Tsuji et al., 2003), "flameless oxidation" in Germany (Wünning and Wünning, 1997), and "low NOx injection" in the USA (Orsino et al., 2001). Generally, MILD combustion

technology utilizes the concept of heat and exhaust recirculation to achieve stable
combustion under a hot oxidant diluted condition. It reduces the concentration of   35
reactants, thereby reducing the reaction rates to avoid the formation of peak zones
of high temperature (Kumar et al., 2002).

In contrast to conventional combustion, MILD combustion is a kind of volu-
metric combustion and takes place similarly to a perfectly stirred reactor (Plessing
et al., 1998). The process is based on high flue gas recirculation, which lead to a   40
low oxygen dilution condition, so it can be called a "mixing control process"
(Cavaliere and De Joannon, 2004). In order to improve MILD combustion tech-
nology, a deeper insight into the physical and chemical phenomena in the
combustion process is desired.

Computational fluid dynamics (CFD) is an important tool for exploring   45
MILD combustion. Detailed chemical reaction mechanisms, although accurate,
always demand a lot of computational efforts. Reduced or global mechanisms are
instead preferred for numerical simulation of the MILD combustion.

Up to now, many of studies have emerged on the global mechanism of normal
air combustion, for example, the well-known Jones–Lindstedt (JL) mechanism   50
(Jones and Lindstedt, 1988) and the Westbrook–Dryer (WD) mechanism
(Westbrook and Dryer, 1981). However, if considering the low oxygen and flat
temperature profile of MILD combustion, the applicability of these mechanisms is
questionable. For the purpose of optimizing global mechanisms under MILD con-
dition, many studies have been developed. Black and Smith (2005) discussed ways   55
to generate reduced mechanisms to adequately represent the chemical kinetics for
gas turbine combustor under MILD combustion condition. Moreover, the effects
of reduced and detailed combustion mechanisms are evaluated by numerical simula-
tion of an industrial burner fed with hydrogen enriched fuels in MILD combustion
regime, but the results are not validated by experimental data (Parente et al., 2008).   60
Recently, different global mechanisms have been adopted for predicting CO emis-
sion of MILD combustion, but the validations of these mechanisms are performed
under Sandia Flame D, which is not a typical MILD combustion operating manner
(Kim et al., 2008). Additionally, several global mechanisms are evaluated for pre-
dicting Oxy-fuel combustion and the results are compared with experimental data   65
(Andersen et al., 2009a, 2009b). The available literature on systematical analysis
of global mechanisms for MILD combustion is still sparse.

In the present study, several global reaction mechanisms are evaluated for a
well-documented flame, jet hot coflow flame (JHC) (Christo and Dally, 2004,
2005; Dally et al., 2002). That flame shows the main characteristics of MILD com-   70
bustion mode. These global reaction mechanisms are first evaluated in a simple reac-
tor network that performs like a well-stirred reactor. Then numerical simulation is
performed for the JHC flame with these global reaction mechanisms. The eddy dis-
sipation concept (EDC) (Gran and Magnussen, 1996a, 1996b), which performs like a
well-stirred reactor, is used to model the turbulence-chemistry interaction.   75

MODELING APPROACH

The EDC (Gran and Magnussen, 1996a, 1996b) is a popular chemistry inter-
action model for CFD analysis of combustion applications. In this model, the total

computational space is subdivided into a reaction space, called the reacting "fine structures" and "the surrounding fluid." All homogeneous reactions having more than one reactant are assumed to take place only in the fine structures that are locally treated as perfect-stirred reactors (PSR). Mass and energy are transferred between the fine structures and the surrounding fluid (Gran et al., 1994).

The commercial CFD code Fluent6.3 (2006) is used for the calculations. A modified k–ε turbulence model is adopted along with discrete ordinates (DO) radiation model. Second-order upwind discretization scheme is used for all transported scalars. The EDC model is applied to model the JHC combustion. In the present study, the following reaction mechanisms are investigated.

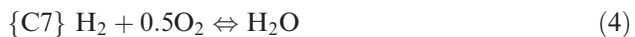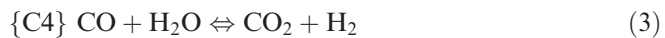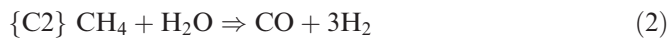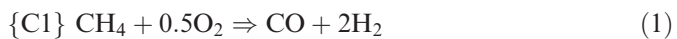## OXIDATION MECHANISMS FOR HYDROCARBON FUELS

Detailed Reaction Mechanism Model

In this work, a detailed reaction mechanism of GRI-Mech 3.0 (Smith et al., 2000) is used to predict CO, O_2, and CO_2 concentrations in the reactor network, and it is a reference calculation for optimization of different global mechanisms.

The Jones and Lindstedt Four-Step Mechanism (JL1)

A four-step global mechanism has been developed for premixed and non-premixed flames of hydrocarbons (Jones and Lindstedt, 1988). It involves the following steps. In this mechanism, {C4} is the usually called "water–gas shift reaction." It was suggested that the MILD combustion can be schematized as a two-stage process where the first occurs under fuel rich diluted condition and the second stage is highly diluted (De Joannon et al., 2000), so the {C1} is dominant at fuel-lean condition, whereas the {C2} is important at fuel-rich conditions. A H_2 oxidation model was developed by Marinov et al. (1996), and was evaluated in a MILD condition by Kim et al. (2008). Reactions are listed as the following:

$$\{C1\} \ CH_4 + 0.5O_2 \Rightarrow CO + 2H_2 \tag{1}$$

$$\{C2\} \ CH_4 + H_2O \Rightarrow CO + 3H_2 \tag{2}$$

$$\{C4\} \ CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{3}$$

$$\{C7\} \ H_2 + 0.5O_2 \Leftrightarrow H_2O \tag{4}$$

The reverse rate parameters of {C4} and {C7} are calculated by using the equilibrium constant. These constants can be calculated by the standard-state Gibbs free energy. The tabulated equilibrium constants can be presented by a polynomial fit (Kuo, 1986):
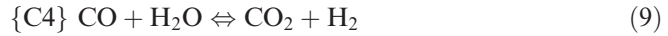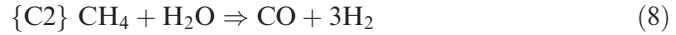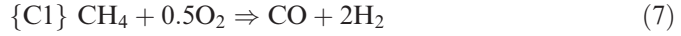
$$\begin{aligned} \log K_{\{C4\}} = &-1.2056(\lg T)^5 + 18.244(\lg T)^4 - 131.58(\lg T)^3 \\ &+ 482.16(\lg T)^2 - 899.39(\lg T) + 683.05 \end{aligned} \tag{5}$$

$$\log[K_{\{C4\}}/(RT)^{(1/2)}] = -5.9608(\lg T)^5 + 105.04(\lg T)^4 - 749.52(\lg T)^3$$
$$+ 2716.0(\lg T)^2 - 5019.5(\lg T) + 3801.3 \qquad (6)$$

where R is the universal gas constant $[m^3 \cdot atm/(K \cdot kmol)]$ and T is the temperature [K]. In the present work, the derivation of the backward rates is done by evaluating the forward rates divided by the equilibrium constant at a series of temperatures (from 1000 K to 2000 K with 50 K increments) and then fitting an Arrhenius expression to the results.
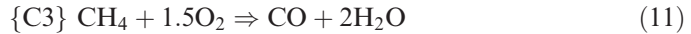
The Modified JL Mechanism ("JL2")

Because of lower oxygen partial pressure under MILD combustion condition, the oxidation rate of fuel may become slower, so the H_2 oxidation scheme proposed by Marinov et al. (1996) is used to modify {C7}. The new mechanism is listed as the following:

$$\{C1\} \ CH_4 + 0.5O_2 \Rightarrow CO + 2H_2 \qquad (7)$$

$$\{C2\} \ CH_4 + H_2O \Rightarrow CO + 3H_2 \qquad (8)$$

$$\{C4\} \ CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (9)$$

$$\{C8\} \ H_2 + 0.5O_2 \Leftrightarrow H_2O \qquad (10)$$

The reverse rate parameters of {C8} are calculated from the equilibrium constant, which is expressed by Equation (6), namely $K_{\{C8\}} = K_{\{C7\}}$.

The Westbrook and Dryer Two-Step Mechanism (WD1)

Westbrook and Dryer (1981) developed a two-step reaction mechanism, where the oxidation of CO to CO_2 is reversible. The rate constants for {C3} and {C5} originated from their studies for CH_4 and CO oxidation reactions under fuel lean conditions in a turbulent flow reactor, and now they are widely used for hydrocarbon combustion modeling. The reverse reaction step for CO_2 decomposition is used in order to reproduce proper heat of reaction and pressure dependence of the [CO]/[CO_2] equilibrium.

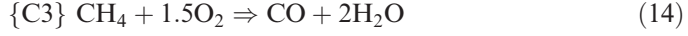$$\{C3\} \ CH_4 + 1.5O_2 \Rightarrow CO + 2H_2O \qquad (11)$$

$$\{C5\} \ CO + 0.5O_2 \Leftrightarrow CO_2 \qquad (12)$$

The H_2 oxidation rate is calculated by an additional {C7}.

$$\{C7\} \ H_2 + 0.5O_2 \Leftrightarrow H_2O \qquad (13)$$

The Modified Mechanism of Westbrook and Dryer (WD2)

In this mechanism, the oxidation rates of CH_4 and CO are the same as WD1, which are calculated by {C3} and {C5}, respectively. The modified H_2 oxidation model in {C8} is adopted:

$$\{C3\} \quad CH_4 + 1.5O_2 \Rightarrow CO + 2H_2O \tag{14}$$

$$\{C5\} \quad CO + 0.5O_2 \Leftrightarrow CO_2 \tag{15}$$

$$\{C8\} \quad H_2 + 0.5O_2 \Leftrightarrow H_2O \tag{16}$$

The Modified Mechanism of Westbrook and Dryer (WD3)

As we know, the oxidation of CO strongly depends on the pressure equilibrium of $[CO]/[CO_2]$. The initial volume fraction of CO_2 strongly influences the process of CO oxidation. Moreover, H_2O can also greatly affect the CO oxidation, but in WD1, all of these are not considered in the rate equation expression. Recently, Andersen et al. (2009b) modified the original WD mechanism and gave a different reaction expression and rate parameters.
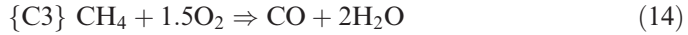
$$\{C3\} \quad CH_4 + 1.5O_2 \Rightarrow CO + 2H_2O \tag{14}$$

$$\{C6\} \quad CO + 0.5O_2 \Leftrightarrow CO_2 \tag{15}$$

$$\{C7\} \quad H_2 + 0.5O_2 \Leftrightarrow H_2O \tag{16}$$

Table 1 Different global combustion mechanisms with kinetic rate data

No.	A	β	E_a/R	Reaction orders	Ref.
{C1}	4.40×10^{11}	0	15095	$[CH_4]^{0.5}[O_2]^{1.25}$	Jones and Lidstedt, 1988
{C2}	3.00×10^{8}	0	15095	$[CH_4][O_2]$	Jones and Lidstedt, 1988
{C3}	5.03×10^{11}	0	24056	$[CH_4]^{0.7}[O_2]^{0.8}$	Westbrook and Dryer, 1981
{C4$_f$}	2.75×10^{9}	0	10065	$[CO][H_2O]$	Jones and Lidstedt, 1988
{C4$_r$}	6.71×10^{10}	0	13688	$[CO_2][H_2]$	Calculated in present work
{C5$_f$}	2.24×10^{12}	0	20484	$[CO][O_2]^{0.25}[H_2O]^{0.5}$	Westbrook and Dryer, 1981
{C5$_r$}	5.00×10^{8}	0	20484	$[CO_2]$	Westbrook and Dryer, 1981
{C6$_f$}	2.24×10^{6}	0	5032	$[CO][O_2]^{0.25}[H_2O]^{0.5}$	Andersen et al., 2009
{C6$_r$}	1.10×10^{13}	-0.97	39452	$[CO][O_2]^{-0.25}[H_2O]^{0.5}$	Andersen et al., 2009
{C7$_f$}	5.69×10^{11}	0	17609	$[[H_2][O_2]^{0.5}$	Marinov et al., 1996
{C7$_r$}	2.51×10^{14}	0	47859	$[H_2O]$	Calculated in present work
{C8$_f$}	7.91×10^{10}	0	17609	$[[H_2][O_2]^{0.5}$	Marinov et al., 1996
{C8$_r$}	3.48×10^{13}	0	47907	$[H_2O]$	Calculated in present work

Units in kmol, m3, K, s, KJ.

The Modified Mechanism of Westbrook and Dryer (WD4)

In this mechanism, the CH_4 and CO oxidation rates are the same as WD3, which are calculated by {C3} and {C6}. The H2 oxidation rate is calculated by {C8}.

$$\{C3\} \ CH_4 + 1.5O_2 \Rightarrow CO + 2H_2O \tag{14}$$

$$\{C6\} \ CO + 0.5O_2 \Leftrightarrow CO_2 \tag{15}$$

$$\{C8\} \ H_2 + 0.5O_2 \Leftrightarrow H_2O \tag{16}$$
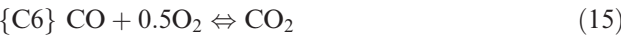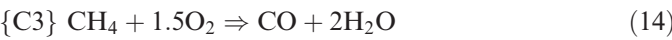
All reaction parameters of these global mechanisms are listed in Table 1.

TEST CASES

Plug Flow Reactor

170

A gas-mixer and a plug flow reactor (PFR) are employed, and the CHEMKIN 4.0 package (Kee et al., 2004) is used to handle the non-integer reaction orders, which are often applied in global mechanisms. The simple reactor network is shown as Figure 1. There, a gas-mixer model and an isothermal fixed temperature PFR model are both used to simulate the process of MILD combustion. The initial con- 175 dition is the same as the HM2 case, which is displayed in Table 2. All global mechanisms are evaluated under different temperatures and different air access ratios.
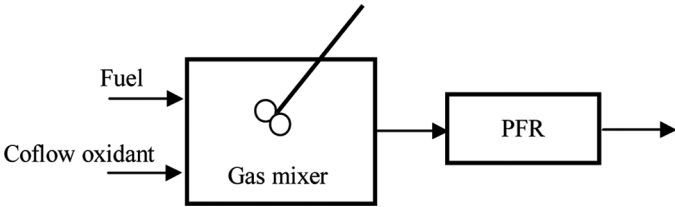

Figure 1 Sketch map of reactor network for mixer-PFR combination used in chemical reactor modeling.

Table 2 Parameters of JHC combustion system

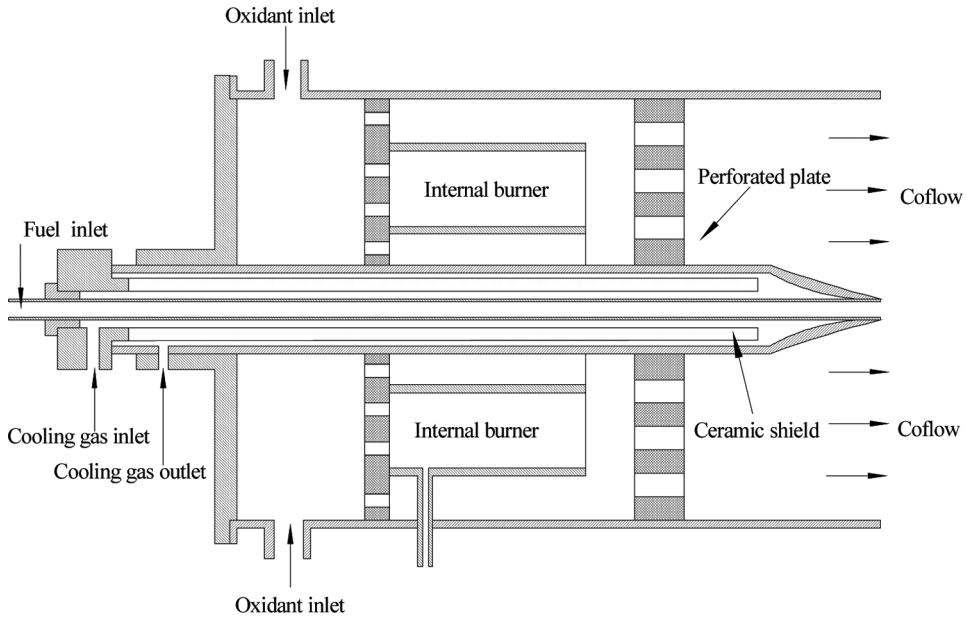|	Fuel inlet			Coflow			Air flow	
Velocity (m/s)	60			3.2			3.2	
Temp (K)	305			1300			300	
Species (mass basis)	$CH_4(\%)$	$H_2(\%)$	$O_2(\%)$	$H_2O(\%)$	$CO_2(\%)$	$N_2(\%)$	$O_2(\%)$	$N_2(\%)$
HM1	80	20	3	6.5	5.5	85	23.3	76.7
HM2	80	20	6	6.5	5.5	82	23.3	76.7
HM3	80	20	9	6.5	5.5	79	23.3	76.7

Figure 2 Cross-section plane of jet in hot coflow burner.

JHC Combustion System

The numerical configuration adopted in this study is based on the experimental jet burner in hot coflow (JHC) (Christo and Dally, 2004; Dally et al., 2002; Kim et al., 2005) which was designed to evaluate the MILD combustion regime. The experimental burner, shown in Figure 2, consists of an insulated and cooled central fuel jet (i.d. $= 4.25$ mm) and an annulus (i.d. $= 82$ mm) with a secondary burner mounted upstream of the exit plane. The secondary burner provides hot combustion products that are mixed with air and nitrogen via two side inlets at the bottom of the annulus to control the O_2 levels in the mixture. The cold mixture of air and nitrogen also assists in cooling the secondary burner. The geometry and boundary conditions are shown in Figure 3. Table 2 displays the experimental conditions used in this study.
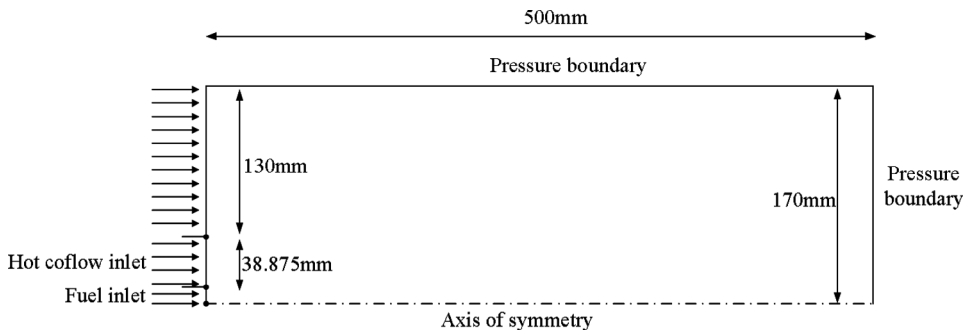
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Figure 3 Numerical model geometry and boundary conditions.

Due to the symmetry of the burner, a geometrically simplified 2D axisymmetric computational model was constructed. The computational domain starts at the exit plane of the burner and extends 500 mm downstream in the axial direction and 170 mm in the radial direction.

RESULTS AND DISCUSSION

Performance of Different Global Mechanisms for PFR Reactor Modeling

Both the JL and the WD global mechanisms (JL1 and WD1) have been used extensively in CFD models for conventional combustion without preheating. In the MILD combustion scheme, it shows a high flat temperature profile and low oxygen dilution condition. Both of these lead to a reaction zone weakening (Medwell et al., 2010). So, before these mechanisms are applied for MILD combustion prediction, they are evaluated under high temperature and low oxygen condition by comparing with the reference calculation with GRI3.0 mechanism.

Figure 4 compares CH_4, H_2, CO, and O_2 concentrations in an isothermal fixed temperature plug-flow reactor at different temperatures of $\lambda = 1.0$ under HM2 condition. As expected, the results show differences in predicting ignition time between these global mechanisms and the detailed mechanism. Only the detailed model can describe the slow build-up of radical pool that can lead to ignition in a plug-flow reactor. The global mechanisms cannot resolve an ignition delay. However, it is still difficult to assess how inaccuracies in the description of ignition affect a CFD calculation. In the EDC approach, PSR/PFR reactor residence times may be in the range of 10^{-4}–10^{-3} s (Andersen et al., 2009b), i.e., influence of differences of time scale on numerical prediction will be considerable. From the figure, it can be seen that most mechanisms predict the time scale for complete conversion of CO to CO_2 to be above the order of 10^{-3} s, which shows that the chemical reaction process of MILD combustion is slower compared to conventional combustion.

Both the WD1 and the JL1 global mechanisms have been used extensively in CFD models for conventional combustion. There, they are first evaluated. The results are shown in Figures 4 and 5. It can be observed that the oxidation rate of CH_4 predicted by the JL1 mechanism is fast compared to the detailed mechanism calculation. However, it is relatively slow predicted by the WD1 mechanism, but agrees with the detailed mechanism calculation well. Meanwhile, the oxidation rate of H_2 for both mechanisms is faster than that of the detailed mechanism calculation. Both for fuel-lean and fuel-rich conditions, the major species concentrations predicted by the JL1 global mechanism have a good agreement with the detailed mechanism calculation for a long time. Considering that there would be a slower oxidation rate for H_2 under MILD combustion conditions due to lower O_2 concentration, these two mechanisms are modified to the JL2 and WD2 mechanisms, respectively. It can be seen that the oxidation rate of O_2 and H_2 predicted by both of the JL2 and WD2 mechanisms is slower than predicted by both of the JL1 and WD1 mechanisms, respectively, and it is more accurate. However, the WD1 and the WD2 mechanisms cannot predict the CO concentration accurately at exit, because atomic hydrogen converts CO_2 to CO, resulting in a change in both the
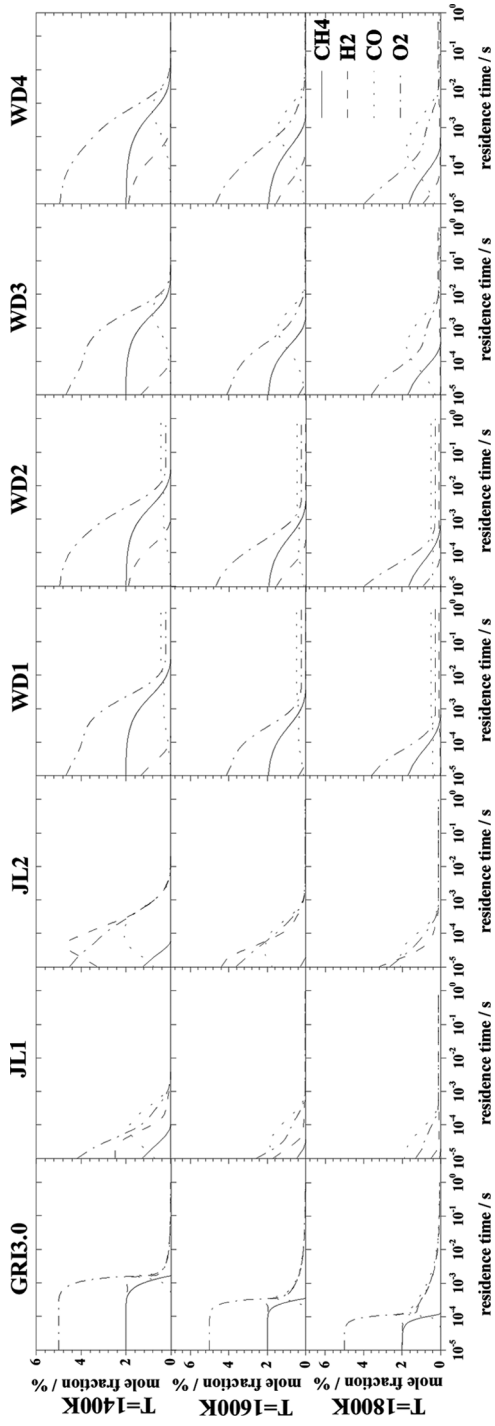
Figure 4 Major species concentrations in reactor network calculations. Comparison between different global reaction mechanisms at $\lambda = 1.0$ and T = 1400 K (top), T = 1600 K (middle), and T = 1800 K (bottom) under HM2 conditions in Table 2.
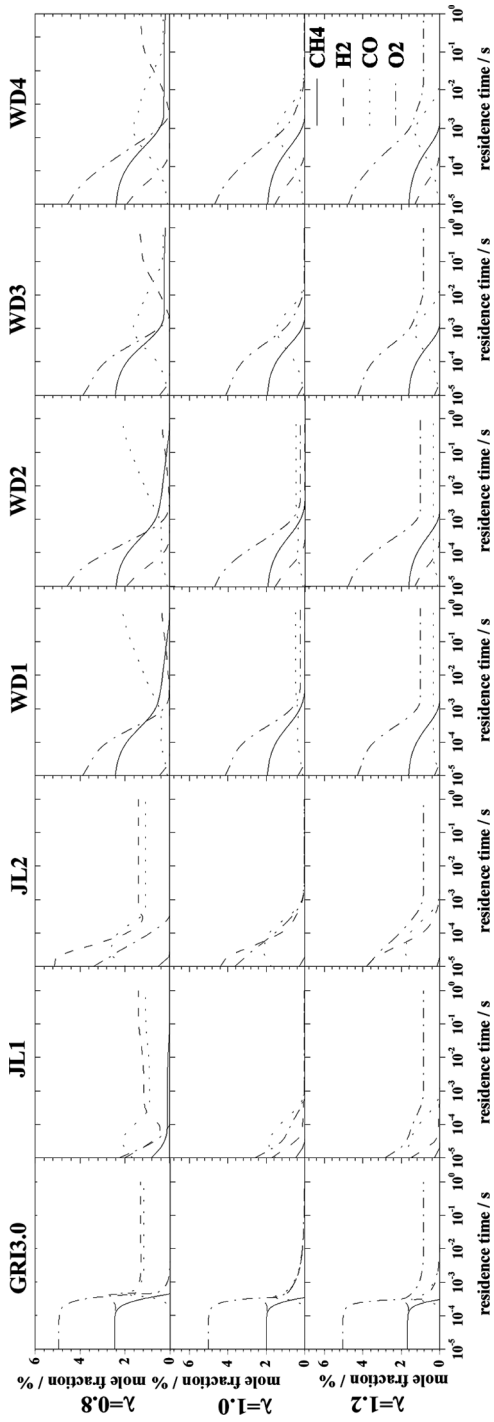
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Figure 5 Major species concentrations in reactor network calculations: Comparison between different global reaction mechanisms at T = 1600 K and λ = 0.8 (top), λ = 1.0 (middle), and λ = 1.2 (bottom) under HM2 conditions in Table 2.

10

CO_2/CO ratio and the composition of the O/H radical pool. All differences are seen at different temperatures and different air excess ratios (Figures 4 and 5). So the WD1 and the WD2 mechanisms should be improved suitable for MILD combustion due to the poor CO prediction. An equilibrium approach for the $CO-CO_2$ reaction is applied and this change will be expected to make the prediction of $CO-CO_2$ equilibrium correctly. The modification of CO oxidation rate involves temperature of 1200–2000 K and stoichiometries in the range 0.8–1.5 for the WD3 and the WD4 mechanisms. It is observed that predictions of CO level for the WD3 and the WD4 mechanisms are similar except for a little deviation for peak CO concentration. This change causes the WD3 and the WD4 mechanisms to predict the trend correctly. The improvement is most pronounced for the WD3 and the WD4 mechanisms, and both of them predict the trend and the approach to equilibrium concentration quite well.

From the above discussion, it can be deduced that the JL1, JL2, WD3, and WD4 mechanisms can predict major species concentrations well at different temperature and different air excess ratios. H2 oxidation reaction in the JL2 and the WD4 mechanisms may be more suitable for application of MILD combustion prediction. Oxidation of CH_4 and CO predicted by the WD3 and the WD4 mechanisms agrees with the detailed mechanism well. All these global mechanisms will be further evaluated and validated by a turbulent jet hot coflow flame.

CFD Modeling with Different Global Mechanisms

The turbulent mixing scales applied in the individual CFD cells are in the order of 0.1–100 ms (Kjadman et al., 2000). As expected, global mechanisms do not match the detailed mechanism on smaller timescales and have a limited accuracy in describing changes occurring on a small scale or on an individual cell basis in a CFD computation. However, in terms of larger time scales, the global mechanisms are capable of predicting satisfactorily the heat release and major species concentrations (Andersen et al., 2009). This means that the turbulence modeling should provide accurate turbulence level predictions as input for the EDC turbulence chemistry interaction model. So before global mechanisms with EDC model are evaluated, different turbulent models such as the K–ε model, the Reynolds stress model, etc. are evaluated and improved to predict the turbulent mixing more accurately. A modified K–ε model with the value of $C_{\varepsilon 1}$ constant in the dissipation rate equation, which is modified from 1.44 to 1.6, is adopted. It illustrates mixture fraction profiles along the axis of jet and also radial profiles of mixture fraction up to an axial distance of Z = 30, 60, and 120 mm in Figure 6 and the mean mixture fraction that was computed by Bilger's formula (Bilger et al., 1990). The numerical results agree well with experimental data, and it shows that the modified K–ε model can more accurately predict the turbulent mixing.

Before global mechanisms are evaluated, it should be point out that the molecular diffusion on major species prediction is important under coflow combustion especially for low oxygen configuration (Mardani et al., 2010). Moreover, EDC is prematurely predicting a flame liftoff, which is important for the prediction of ignition and major species distribution under MILD conditions (Christo and Dally, 2005). So the deviations between the CFD predictions and experimental results can only partly be attributed to inadequacy of global mechanisms.
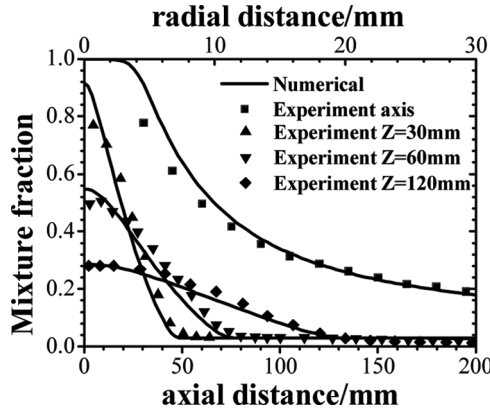
Figure 6 Comparison mixture fraction profiles with experimental data for HM1 in Table 2 along the axis and the radii at Z = 30 mm, Z = 60 mm, and Z = 120 mm (Z is measured from the jet exit plane).

    In Figure 7, for HM1, HM2, and HM3 cases, the comparison between the predicted and measured temperature profile is shown in detail at different axial positions. The calculated peak temperature agrees with measurement data well for all cases, and it indicates that the DO model can successfully describe the radiation characteristic in MILD combustion processes. Difference of prediction by different global mechanisms can be observed especially in the higher mixture-fraction side ($\xi > 0.08$), which is surrounded by the hot coflow stream. In the HM1 case, differences between the predictions by global mechanisms without H_2 oxidation (JL1, WD1, and WD3) and experimental data are greater compared to predictions by global mechanisms with H_2 reaction modification (JL2, WD2, WD4). It indicates that in the low oxygen conditions of MILD combustion, the oxidation rate of H_2 is slower than that in conventional combustion, compared to {C7} and {C8}, represents a slower oxidation rate, and it is significant for MILD combustion. In higher oxygen cases (HM2 and HM3), differences of predictions by global mechanisms are not so obvious. Global mechanisms with {C8} reaction can still describe the process of heat release well. All of these show that the modification of the H_2 oxidation reaction is helpful for improvement of MILD combustion prediction.

    The CO profiles predicted by different global mechanisms are illustrated in Figure 8 and compared with experimental data. Differences for predictions between these global reaction mechanisms can be observed, especially near burner zones (large mixture fraction zone), because of different consumption or production rates of major species. The peak CO concentration and the whole distribution predictions change obviously for different mechanisms. For all cases, the CO concentration profiles calculated by the JL mechanism (JL1 and JL2) are overpredicted, while they are underpredicted for the WD mechanism (WD1, WD2, WD3, WD4) compared to experimental data. From the previous PFR calculations, we can deduce that the consumption rate of CH_4 predicted by the JL1 and the JL2 mechanisms is fast, but that it is slow for the WD1, WD2, WD3, and WD4 mechanisms. For all global mechanisms, the prediction of oxidation rate of CO is slow, as shown in Figure 4. From the expressions of CH_4 reactions displayed in Table 1, we can see that the production
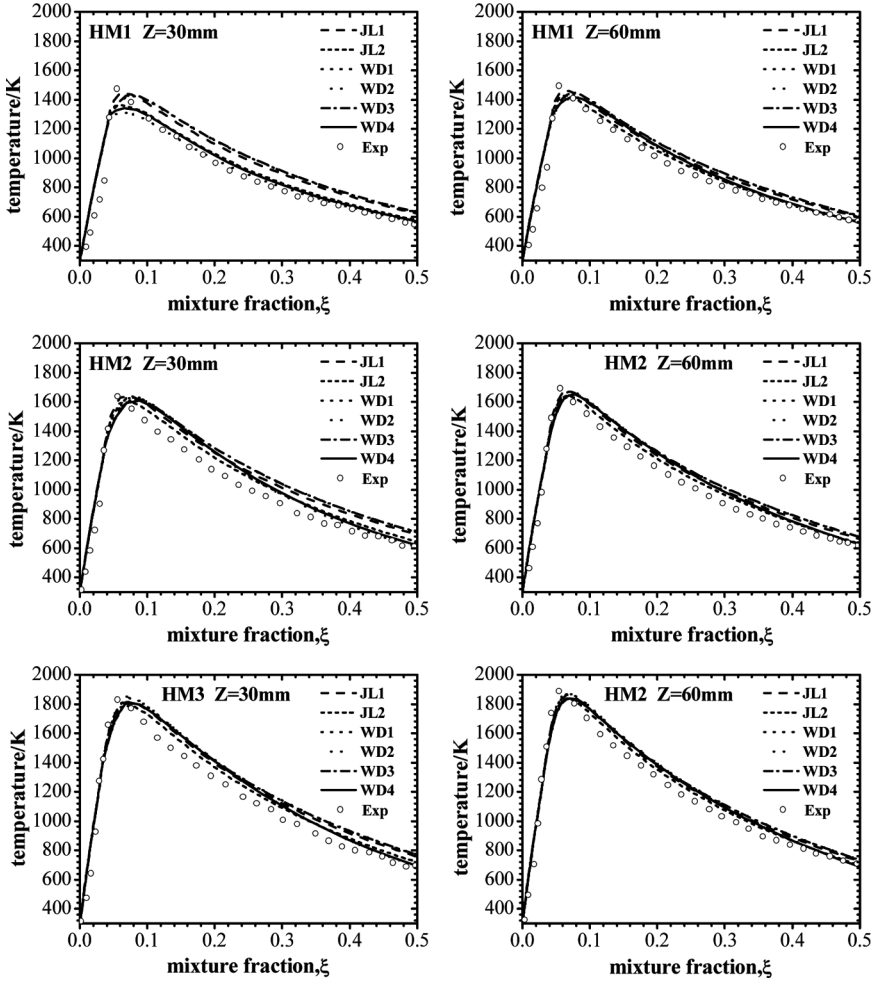
Figure 7 Comparison among experimental and numerical temperature profiles at various axial locations for the HM1, HM2, and HM3 conditions reported in Table 2 (Z is measured from the jet exit plane).

rate of CO is dominated by both O_2 and H_2O in JL1 and JL2. So the CH_4 oxidation rate is fast, even under low oxygen case (HM1), because of high H_2O concentration in the initial condition. The oxidation rate of CO is partially controlled by the production of H_2O concentration. Because of low concentration of O_2, in JL1 and JL2 mechanisms, the consumption rate of CO is slow. But in the WD mechanisms (WD1, WD2, WD3, WD4), the production and consumption of CO is totally dominated by O_2 concentration. The consumption of CH_4 in the PFR calculations is very slow for the WD mechanisms because of lack of O_2. This means that the production of CO is slow, but the consumption of CO is fast, as we can see from the results of the PFR calculations. In the HM1 case, the CO concentration is greatly underpredicted, while in higher oxygen cases (HM2 and HM3), it is greatly improved. Compared with the WD1 and WD2 mechanisms, at high mixture fraction, predicted results of the WD3
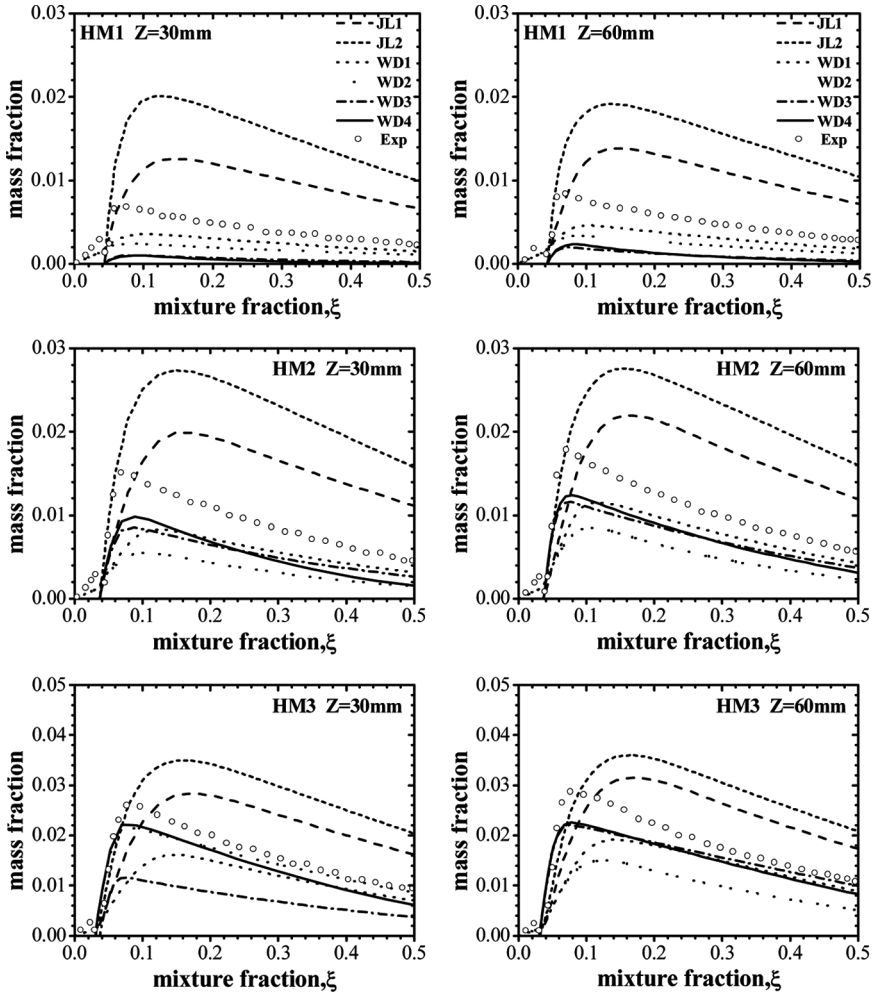
Figure 8 Comparison among experimental and numerical CO mass fraction profiles at various axial locations for the HM1, HM2, and HM3 conditions reported in Table 2 (Z is measured from the jet exit plane).

and the WD4 mechanisms do not improve so much at low oxygen cases, but greatly improve in higher oxygen cases. However, at low mixture fraction, the predicted results of the WD3 and the WD4 mechanisms agree with experimental data more accurately compared to results predicted by the WD1 and the WD2 mechanisms. It means that the WD3 and WD4 mechanisms can predict the CO distribution profile more reasonably compared with the WD1 and WD2 mechanisms under MILD combustion conditions.

Meanwhile, a comparison of the predicted and measured concentration profiles of H_2O is illustrated in detail in Figure 9. It can be seen that for all cases, H_2O concentration predicted by the JL2, WD2, and WD4 mechanism agrees better with experiment than that of the JL1, WD1, and WD3 mechanism, respectively, especially at higher mixture fractions. As we know, the oxidation rate of H_2 predicted by the
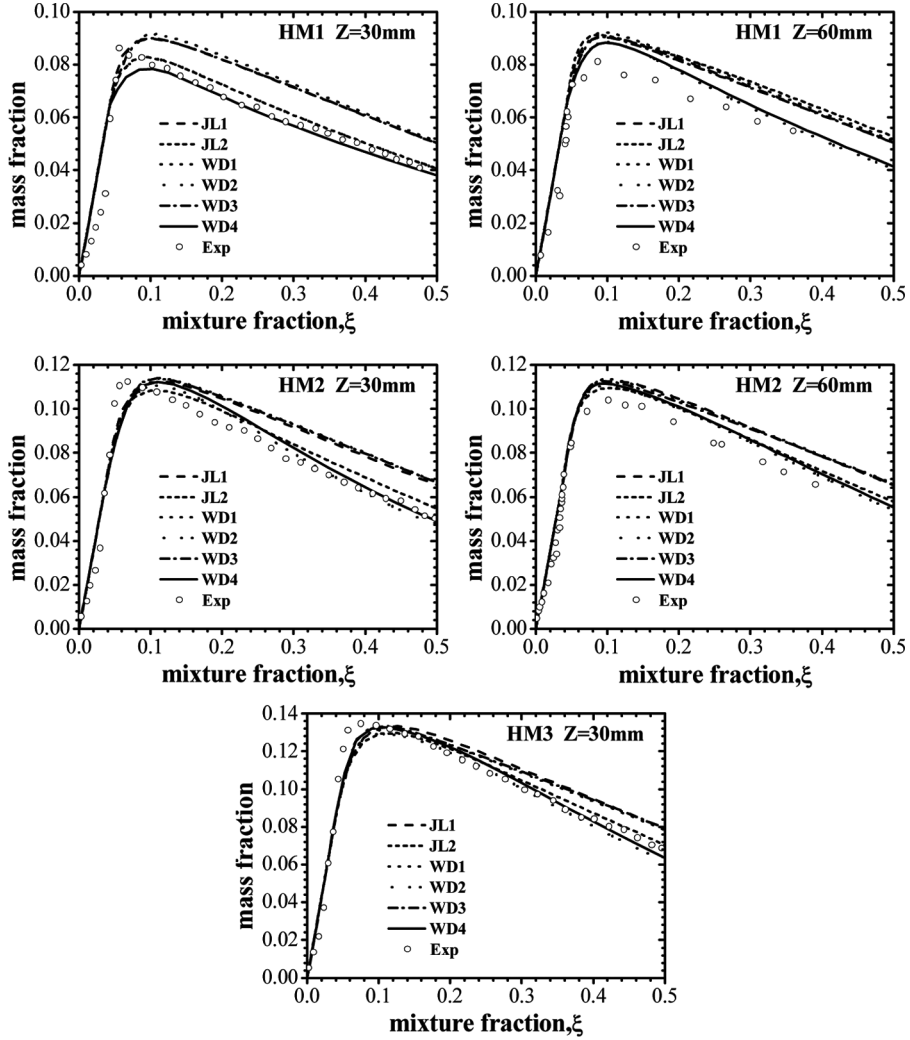
Figure 9 Comparison among experimental and numerical H_2O mass fraction profiles at various axial locations for the HM1, HM2, and HM3 conditions reported in Table 2 (Z is measured from the jet exit plane).

JL2, WD2, and WD4 mechanisms is slower than that predicted by the JL1, WD1, and WD3 mechanisms, respectively. In the MILD combustion regime, the reaction zone weakening effect leads to simultaneous reduction in reaction rate (Medwell et al., 2010), and hydrogen reactivity is usually overestimated by global reaction mechanisms (Galletti et al., 2009), which are usually used to predict conventional combustion. This indicates that the H_2 oxidation rate modification is significant for improvement of H_2O concentration prediction. For all cases, the results predicted by the WD4 mechanism show the best agreement with the experiment.

The effect of modification of H_2 oxidation on O_2 concentration prediction is displayed in Figure 10. Partly due to the effect of molecular differential diffusion
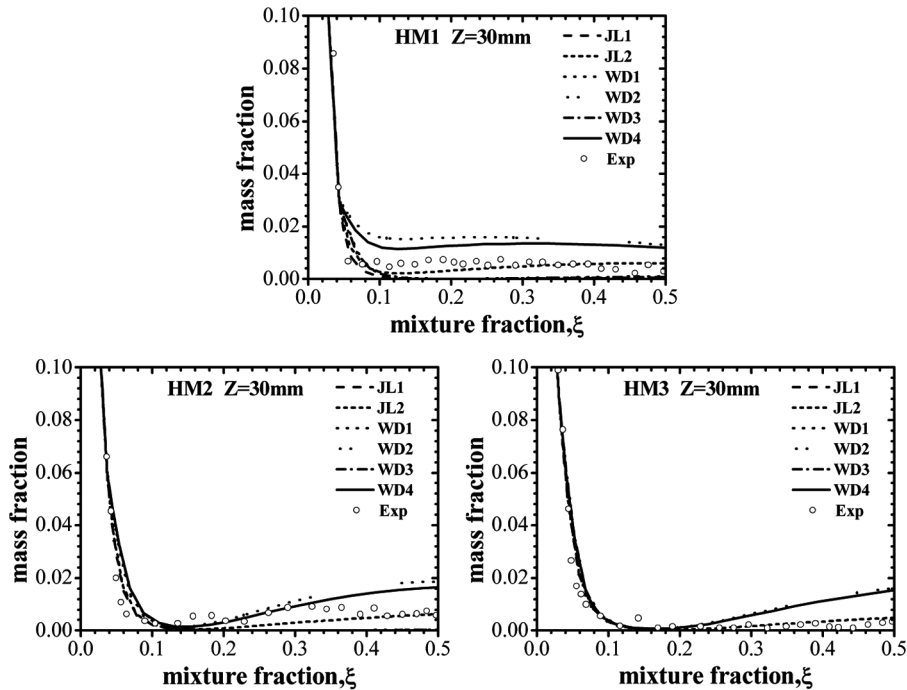
Figure 10 Comparison among experimental and numerical O_2 mass fraction profiles at various axial locations for the HM1, HM2, and HM3 conditions reported in Table 2 (Z is measured from the jet exit plane).

(Christo and Dally, 2005; Medwell et al., 2010), slight leakage of O_2 at high mixture fraction is observed. But at low mixture fraction, all global mechanisms can reasonably describe the process of the O_2 consumption. For all cases, it can be seen that O_2 levels predicted by the JL1, WD1, and WD3 mechanisms are underpredicted, but for the WD2 and the WD4 mechanisms, they are slightly overpredicted. The prediction of O_2 levels by the JL2 mechanism agrees with the experimental data. However, in the HM2 case, the WD4 mechanism reasonably describes the process of O_2 consumption. All of these indicate that the modification of H_2 oxidation to some extent improves the prediction of O_2 concentration.

From a general comparison of these mechanisms, it should be noted that the WD4 mechanism, which includes both CO oxidation rate and H_2 oxidation rate modification, shows the best agreement with experiment.

CONCLUSIONS

Six global reaction mechanisms, which originate from the mechanism by Jones and Lindstedt (JL) and by Westbrook and Dryer (WD), are tested and refined for MILD combustion conditions, based on comparison with model predictions with a detailed chemical kinetic mechanism.

Major species are predicted in an isothermal plug-flow reactor under MILD combustion conditions by all of these global mechanisms. The global reaction

mechanisms with H_2 oxidation rate modification (JL2, WD2, and WD4) offer a slight improvement in predicting H_2 trends. The improvement is most pronounced for the WD mechanism, where the modified schemes (WD3 and WD4) yield better prediction of the peak and exit concentrations of CO.

All global mechanisms are validated by a CFD analysis of a turbulent jet hot coflow flame. This shows that CH_4 is overpredicted by the JL1 and the JL2 mechanisms, while the WD3 and the WD4 mechanisms offer a better result. Results of H_2 and O_2 predicted by mechanisms with H_2 oxidation rate modification are improved more accurately. From a general comparison of these mechanisms, the WD4 mechanism shows best agreement with the experiment.

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