A Detailed Numerical Study of NOx Kinetics in Counterflow Methane Diffusion Flames: Effects of Fuel-Side versus Oxidizer-Side Dilution

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Dilution combustion has been widely utilized due to various merits, such as enhanced efficiency, fewer pollutants emissions, and even a promising future in alleviating global warming. Diluents can be introduced through the oxidizer or fuel side to achieve the desired combustion properties, and H2O and CO2 are the most common ones. A comprehensive comparison between the different dilution methods still lacks understanding and optimizes the dilution combustion technologies. This study numerically compared the effects of H2O and CO2 dilution in the oxidizer or fuel stream on counterflow methane diffusion flames, emphasizing NO formation kinetics. Results showed that the impact of different radiation heat transfer models on NO emissions diminishes with increasing the dilution ratio. The calculations of radiation heat transfer were treated in three ways: radiation-neglected, optically thin, and using a non-grey radiation model. When keeping the oxygen content and methane fraction constant, CO2 dilution in the air-side has the most profound influence on NO reduction, and CO2 dilution in the fuel-side has the least. H2O dilution showed a medium impact with a larger degree on air-side than that on fuel-side. To gain a deeper understanding of this effect order, the contributions of different NO formation routes were quantified, and analyses were made based on the diluents’ chemical and thermal effects. It was found that the oxidizer-side dilution and fuel-side dilution affect the NO formation pathway similarly. Still, the influence of H2O dilution on the NO formation pathway differs from that of CO2 dilution.

1. Introduction

Several advanced combustion technologies have been proposed to address the challenges of both fossil fuel depletion and environmental pollution. Additives are widely used to enhance combustion efficiency, control nitric oxide emissions, or achieve low-cost CO2 capture. For example, humidified air turbines (HATs) [1] with a mixture of air and water as the working fluid promise high electrical efficiencies and low NOx emissions. Fossil fuels combust with pure oxygen in a Graz Cycle Gas Turbine [2] by using CO2 to control the flame temperature, enabling the cost-effective separation of the CO2 in flue gas physical condensation. In combustion technologies based on exhaust gas recirculation (EGR) [3], part of the exhaust gas (mainly H2O and CO2) is introduced back to the combustion chamber, and NOx emissions could be substantially reduced. Internal Combustion Rankine Cycle (ICRC) power plants [4] run under an oxy-fuel combustion model with recycled water to achieve high efficiency and specific power output. Other systems using water to provide power can be found in [5, 6].
To gain the full potential benefits of dilution combustion, it is crucial to understand the effects of the following three primary factors: (1) the type of diluents, (2) the amount of dilution, and (3) the location (oxidizer or fuel stream) where the diluents are injected.

Among the various combustion technologies mentioned above, carbon dioxide and steam (water vapor) are the most common additives. As H₂O and CO₂ are two main combustion products, adding these two diluents to the combustion zone will not introduce new species but increase H₂O and CO₂ concentrations in the flue gas. As a result, CO₂ capture becomes much more manageable and economical. Besides, the high heat capacity of H₂O and CO₂ enables many favorable combustion properties, such as low flame temperature [7, 8] and low NOx emissions [9]. To grasp the dilution mechanism of H₂O and CO₂, many efforts have been made. For example, Park et al. [10] simulated the flame structure and NO emission behavior in CH₄ diffusion flames with different diluents (H₂O, CO₂, and N₂) added to the air stream. Their results showed that CO₂ addition reduces the flame temperature through both the thermal and chemical effects. In contrast, the addition of H₂O enhances the reaction through chemical effect and limits the decrease of temperature thermally. They also pointed out that the NO emission index decreases with increasing the volume percentage of diluents. The effectiveness of these diluents on NO emission reduction follows the order of CO₂ > H₂O > N₂. Xie et al. [11] found that the elementary reaction corresponding to the peak ROP (rate of production) of OH in CO/H₂/air mixture changes from OH + H₂ = H + HO₂ to HO₂ + H = OH + OH when CO₂ and H₂O are added, and CO₂ has a more potent chemical effect than H₂O. Xu et al. [8] investigated the effects of H₂O and CO₂ diluted oxidizer on the structure and shape of laminar co-flow syngas diffusion flames. They found that the thermal and radiative effects of CO₂ decrease the centerline temperature to a much larger degree than those of H₂O; thus, CO₂ reduces the centerline temperature more effectively than H₂O. Besides, they also found that as the dilution level increases, the maximum OH mole fraction in CO₂ diluted flames decreases monotonously, whereas in H₂O diluted flames, OH mole fraction first increases then decreases. Ning et al. [12] numerically studied the radiation effect on NO formation in H₂/CO/air counterflow diffusion flames, and results showed that, as the CO₂ content in the fuel stream increases, the radiation effect on NO emission increases first and then decreases for H₂-rich syngas. In contrast, for H₂-rich syngas, the radiation effect is monotonic. Ozturk [13] studied the effects of CO₂, N₂, and H₂O dilution on the adiabatic, turbulent, partially premixed combustion of synthesis gas and pointed out that increasing the dilution rates gradationally reduces the NO concentration and H₂O has the best effect on reduction of NO emissions, followed by CO₂ and N₂. Although these studies help fundamental understanding of the influence of diluents and dilution level on the combustion characteristics of hydrocarbon fuels, they were conducted for either fuel-side dilution or air-side dilution. They hence did not provide a direct comparison of the relative effectiveness between fuel-side dilution and oxidizer-side dilution.

Researchers have made a few attempts to explore the difference between air- and fuel-side dilutions for jet diffusion flames. For instance, Feese and Turns [14] experimentally studied the effects of N₂ dilution in the air- or fuel-side on NOx emissions in laminar CH₄ jet diffusion flames. They found that air dilution was more effective than fuel dilution in reducing NOx emissions. They also pointed out that the visible flame height increases somewhat as a diluent is added to the airstream but does not change noticeably for fuel-side dilution, even for the same diluent fraction. Unfortunately, Feese et al. did not analyze the NO formation routes or provide kinetic explanations for their results. In addition, an experimental study by Cho and Chung [15] showed that fuel-side dilution is more effective in reducing flame temperature and NO emissions than air-side dilution. It should be noted that, although Cho and Chung also studied jet diffusion flames, they reached a different conclusion from that in [14]. This contradiction is due to the different dilution parameters used in these two studies when comparing the fuel-side dilution and the air-side dilution. In Cho and Chung’s study [15], the dilution ratio was defined as the ratio of the exhaust gas flow rate to the total flow rate of the fuel (or air). Because the fuel stream’s exit area is much smaller than that of the oxidizer stream, the fuel stream velocity increases more than the oxidizer stream velocity increases. The much higher increase in fuel stream velocity enhances the mixing in dilution combustion. In the study of Feese and Turns, however, they introduced a new dilution parameter (Z), calculated as the mass of diluent to the stoichiometric mixture’s mass. In this way, under the same Z, the amount of diluent added to the air stream for air-side dilution is much more considerable than that added to the fuel stream for fuel-side dilution.

The effect of dilution on NO formation is one of the issues this study aimed to resolve since one of the advantages of dilution combustion is the low NO emissions, which is strongly dependent on the combustion conditions, reported in the previous papers, i.e., Refs. [16–18].

To obtain a fundamental understanding of the effect of dilution position (i.e., through air or fuel stream) on flame characteristics, attention has also been paid to one-dimensional diffusion flames, which excludes the burner’s complexity and flow field in multidimension flames. Using spherical diffusion flames, Chernovskiy et al. [19] experimentally investigated the impact of adding CO₂ on the oxidizer side versus the fuel side. Their results showed that CO₂ dilution affects the flame in these two dilution scenarios by different mechanisms. On the oxidizer side, radiation reabsorption played an essential role in strengthening the flames. In contrast, the enhanced CO₂ concentration increased radiative heat losses on the fuel-side without prompting radiation reabsorption. Park et al. [20] numerically investigated the effects of CO₂ addition to the fuel and the oxidizer streams on the structure of H₂/O₂ diffusion flame in counterflow configuration, and results showed that the temperature reduction caused by the chemical effects is more remarkable when CO₂ is added to the oxidizer stream than that to the fuel stream. Liu et al. [21] numerically studied the chemical effects of CO₂ addition to both the fuel side and the oxidizer side of a laminar counterflow ethylene
diffusion flame. The study of Liu et al. is highly relevant to the present study, and their results showed that the chemical effects of CO$_2$ are weaker when added to the fuel side than to the oxidizer side. NOx formation pathway analyses are essential to reveal how CO$_2$ addition affects NOx formation mechanisms; however, Liu et al. did not conduct this work but only focused on the chemical effects of CO$_2$.

Despite several studies that have been conducted to understand the difference between fuel- and air-side dilutions, there is still a lack of comprehensive comparison between H$_2$O dilution and CO$_2$ dilution in the fuel- and oxidizer side. Many questions remain unanswered regarding NO emissions, such as the radiation effect on NO emissions and the chemical effect of diluents on the NO formation mechanism. To this end, the objectives of this study were to investigate the influence of H$_2$O and CO$_2$ dilution in the air and fuel stream on methane/air counterflow diffusion flames with an emphasis on the detailed NO formation process, including not only the formation and destruction routes, but also the reaction pathway analysis. The importance of gas radiation in modeling the methane/air diffusion flames was first demonstrated for different diluting levels and in the air and fuel stream with H$_2$O or CO$_2$. The effects of H$_2$O and CO$_2$ dilutions in the fuel and air stream on flame temperature and NO concentration were next examined by adopting the DOM/SNBCK radiation model. The diluents’ chemical effects and thermal effects were isolated and analyzed. Finally, to reveal the impact of different diluents and dilution locations (air or fuel stream) on the NO formation mechanism, the contributions of different NO formation routes were calculated, and the NO formation pathways were revealed.

2. Mathematical Model and Numerical Methods

2.1. Simulation Methods. The OPPDIFF code [22] coupled with the thermal and transport subroutines in the CHEMKIN package [23] was adopted in this study to compute the counterflow diffusion flames. This code has been extensively validated and used to model one-dimensional laminar flames (nonpremixed or premixed) using detailed combustion chemistry and thermal and transport properties. The methane oxidation chemistry was modeled using the GRI-Mech 2.11 mechanism [24]. Many studies [25, 26] have demonstrated that GRI-Mech 2.11 produces a better prediction for NOx formation than the GRI-Mech 3.0 mechanism when modeling methane combustion. To illustrate the importance of radiation heat transfer, three different treatments of thermal radiation were considered, namely, no radiation heat loss, the optically thin approximation (OTA) [27], and the discrete-ordinates method (DOM) coupled with the statistical narrow-band correlated-K-based radiative property model (DOM/SNBCK) for solving the radiative transfer equation (RTE) [28]. The OTA only accounts for radiation loss due to emissions. It neglects radiation gain by absorption, while the DOM/SNBCK model considers both radiation emission and absorption, as well as the non-gray nature of gas radiative properties. Multi-component transport properties and thermal diffusion were considered to deal with the preferential diffusion of H$_2$ and H. The grid adaptation parameters of GRAD and CURV were both set to 0.05 to ensure that the computational meshes are sufficiently refined, and the simulation results are grid size independent. The global strain rate $a_g$ defined in equation (1) is fixed at 50 s$^{-1}$ for the flames modeled in this paper unless otherwise indicated. The fuel and oxidizer streams’ outlet velocities were chosen to satisfy the momentum balance [29] expressed in equation (2):

\[ a_g = \frac{2|V_O|}{L} \left( 1 + \frac{|V_F|}{|V_O|} \sqrt{\frac{\rho_O}{\rho_F}} \right), \]

\[ \rho_O V_O^2 = \rho_F V_F^2, \]

where $\rho$ and $V$ represent the density and velocity, respectively, and the subscripts “$F$” and “$O$” indicate the fuel and oxidizer streams. Symbol $L$ is the distance between the fuel and oxidizer nozzles, specified as 2 cm in this study.

2.2. Simulation Conditions. The flame conditions investigated in this study are summarized in Table 1. It is worth pointing out that when a certain amount of diluent (H$_2$O or CO$_2$) was added to the fuel or the oxidizer stream, the same amount of N$_2$ was removed; therefore, the CH$_4$ and O$_2$ mole fractions could keep unchanged at 50 vol% and 21 vol% in the fuel and oxidizer stream, respectively. The pressure was 1 atm, and the inlet temperature of both the oxidizer and fuel streams was ranged from 400 K to 800 K in this study.

2.3. NO Formation Mechanism. To identify the contributions of different NO formation routes, NO is considered to be formed by four pathways and destructed through NO-reburning. First, the thermal NO is formed through the N$_2$ triple bond break-up by the O atom, and O$_2$ and OH subsequently oxidize the N atom. This process has very high activation energy and is strongly affected by flame temperature. The main reactions related to NO formation in the GRI-Mech 2.11 mechanism are listed in Table 2. Reactions responsible for thermal NO include R178, R179, and R180. Second, the prompt NO can be prevalent in hydrocarbon radicals, and R240 is usually considered as the major initiation step for the formation of prompt NO. The reactions involved in prompt NO are rate-limiting, leading to the prompt NO formation less temperature-dependent. Third, the N$_2$O-intermediate NO is formed through the path of N$_2$→N$_2$O→NO, with N$_2$O being the intermediate species. Fourth, the NNH NO begins with N$_2$ reacting with H to form NNH (R204 and R205), which then yields NO through R208. Lastly, NO-reburning is an important destruction mechanism of NO by a group of reactions involving hydrocarbon radicals, CH$_4$. The calculation method of these NO formation routes has been widely employed in previous studies, e.g., Refs. [27, 30, 31].

The full GRI-Mech 2.11 mechanism contains 49 species and 279 elementary reactions, and the number of reaction steps decreases to 177 when excluding NO formation.
clarity, we abbreviate these two mechanisms as "the full GRI-Mech 2.11 mechanism" respectively. To quantify NO formation from the four formation routes plus one destruction route, each simulation was performed six times with different NO formation kinetics models, namely, "Full chemistry" (marked as SIM1), "no NO chemistry" with only the thermal, prompt, NNH, or N₂O-intermediate NO formation route, marked as SIM2 ∼ SIM5, respectively, and "Full chemistry" excluding NO-reburning route (SIM6). The elementary steps involved in calculating each NO formation route are identical to those in Ref. [30]. As a result, NO formations through the thermal, prompt, NNH, or N₂O-intermediate routes can be obtained by subtracting results of the corresponding SIM2 ∼ SIM5 with that of the SIM1. NO-reburning effect on NO was calculated by the difference in results of SIM6 and SIM1.

### 2.4. Chemical and Thermal Effects of H₂O/CO₂

To quantitatively investigate the chemical and thermal effects of H₂O or CO₂ dilution, calculations with real H₂O and CO₂ and their chemically inert counterpart were conducted as we did in the previous work [8]. Specifically, this chemical effect refers to the diluents’ impact through their participation in the chemical reaction network.

### Table 1: Conditions of diluted methane/air counterflow diffusion flames with and without H₂O or CO₂ replacement of N₂, 400 K, 1 atm.

| No. | Fuel stream composition (vol%) | Oxidizer stream composition (vol%) | Remark |
|-----|-------------------------------|-----------------------------------|--------|
|     | CH₄  | N₂   | H₂O  | CO₂ | O₂   | N₂   | H₂O  | CO₂ |        |
| Case 1 | 50   | 50   | 0    | 0   | 21   | 79   | 0    | 0   |        |
| Case 2 | 50   | 40   | 10   | 0   | 21   | 79   | 0    | 0   |        |
| Case 3 | 50   | 30   | 20   | 0   | 21   | 79   | 0    | 0   |        |
| Case 4 | 50   | 10   | 40   | 0c  | 21   | 79   | 0    | 0   |        |
| Case 5 | 50   | 40   | 0    | 10  | 21   | 79   | 0    | 0   |        |
| Case 6 | 50   | 30   | 0    | 20  | 21   | 79   | 0    | 0   |        |
| Case 7 | 50   | 10   | 0    | 40  | 21   | 79   | 0    | 0   |        |
| Case 8 | 50   | 50   | 0    | 0   | 21   | 59   | 10   | 0   |        |
| Case 9 | 50   | 40   | 0    | 10  | 21   | 59   | 10   | 0   |        |
| Case 10 | 50  | 30   | 0    | 20  | 21   | 59   | 10   | 0   |        |
| Case 11 | 50  | 10   | 0    | 40  | 21   | 59   | 10   | 0   |        |
| Case 12 | 50  | 50   | 0    | 0   | 21   | 39   | 40   | 0   |        |
| Case 13 | 50  | 40   | 0    | 10  | 21   | 39   | 40   | 0   |        |

### Table 2: Main reactions involved in NO formation (more information can be found in the GRI-Mech 2.11 mechanism [24]).

| Reaction no. | Reaction steps | Reaction no. | Reaction steps |
|--------------|----------------|--------------|----------------|
| R178         | N + NO ⇌ N₂ + O | R179         | N + O₂ ⇌ NO + O |
| R180         | N + OH = NO + H | R182         | N₂O + O ⇌ 2NO  |
| R183         | N₂O + H = N₂ + OH | R185         | N₂O(+M) ⇌ N₂ + O(+M) |
| R186         | HO₂ + NO = NO₂ + OH | R187         | NO + O + M = NO₂ + M |
| R189         | NO₂ + H = NO + OH | R190         | NH + O = NO + H |
| R191         | NH + H = N + H₂ | R192         | NH + OH = HNO + H |
| R193         | NH + OH = N + H₂O | R194         | NH + O₂ = HNO + O |
| R195         | NH + O₂ = NO + OH | R197         | NH + H₂ = HNO + H₂ |
| R199         | NH + NO = N₂O + H | R200         | NH₂ + O = H₂ + HNO |
| R201         | NH₂ + H = NH + H₂ | R202         | NH₂ + OH = NH + H₂O |
| R203         | N₂H + O₂ = N₂ + H₂ | R205         | N₂H + NO = NO₂ + H + M |
| R204         | N₂H = N₂ + H | R206         | N₂H + O₂ = H₂O + N₂ |
| R207         | N₂H + O = NH + NO | R208         | N₂H + O = H₂ + N₂ |
| R209         | N₂H + OH = H₂ + N₂ | R210         | N₂H + O₂ = NO + O |
| R212         | N₂H + O₂ = N₂ + H₂ | R213         | N₂H + O = NO + OH |
| R214         | N₂H + OH = NO + H₂O | R216         | N₂H + O₂ = NO₂ + O |
| R217         | CN + O = CO + N | R218         | CN + OH = CO + H |
| R219         | CN + H₂O = HCN + OH | R220         | CN + O₂ = N₂O + O |
| R221         | CN + H₂ = HCN + H | R222         | N₂O + H = NH + CO |
| R231         | HCN + O = NCO + H | R232         | HCN + OH = NHCO + H |
| R233         | HCN + OH = HOCN + H | R235         | HCN + OH = NHCO + H |
| R236         | HCN + OH = NH₂ + CO | R240         | CH₃ + N₂ = HCN + N |
| R246         | CH + NO = HCN + O | R249         | CH₃ + NO = H + HNCO |
| R250         | CH₃ + NO = HCN + HCN | R251         | CH₃ + NO = H + HCN |
| R255         | CH₃ + NO = HCN + H₂O | R265         | HNCO + H = NH₂ + CO |
| R270         | HCN = H + HNCO | R272         | HCN + H = NH₂ + CO |
| R273         | HOCN + H = H + HNCO | R274         | HCCO + NO = HNCO + CO |

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chemical reactions. The thermal effect means the influence caused by the difference of the diluents’ thermal properties from those of N₂. The two artificial species, FH₂O and FCO₂, have the same thermal, transport, and radiative properties as those of the real H₂O and CO₂, respectively, except that FH₂O and FCO₂ are chemically inert and do not participate in chemical reactions. To be specific, when evaluating CO₂ and H₂O’s chemical effects, two sets of simulations were conducted. One was using the real CO₂ and H₂O as the diluent, and the other was using FCO₂ and FH₂O. Therefore, differences between results based on FH₂O and FCO₂ and those using H₂O and CO₂ are attributed to H₂O and CO₂’s chemical effects. Similarly, to quantify H₂O and CO₂’s thermal effects, another pair of artificial species, TH₂O and TCO₂, having the same chemical, transport, and radiative properties as FH₂O and FCO₂ but share the same thermal properties with N₂ were introduced to the reaction mechanisms. As a result, differences in the numerical results using TH₂O (or TCO₂) additions and these using FH₂O (or FCO₂) additions are caused by H₂O and CO₂’s thermal effects.

3. Results and Discussion

3.1. Effect of Radiation Models. Since H₂O and CO₂ are the most critical radiative gases in hydrocarbon combustion, it is expected that H₂O and CO₂ enhance radiation heat transfer in the combustion zone. The results calculated using the three radiation models were first examined to investigate radiation treatment’s effect on modeling the different diluted flames. Figure 1 displays the predicted peak flame temperatures using the three radiation heat transfer treatments for CO₂ and H₂O dilution added to the fuel and air streams. Some common behaviors can be observed from this figure. For example, CO₂ dilution has a more decisive influence than H₂O dilution due to its higher specific heat capacity per volume [7, 8]. As expected, neglecting the thermal radiation results in overprediction of flame temperature, while OTA under predicts the peak flame temperature. Since the DOM/SNCK model considers both emission and absorption of radiation, it predicts the peak flame temperature lower than that of no radiation but higher than OTA. It is interesting to notice that the peak temperature predicted by DOM/SNCK is much closer to that of no radiation, suggesting that there is significant radiation reabsorption in flames to reduce the net radiation loss. These results also show that the air-side dilution (black lines) has a stronger influence on suppressing the flame temperature than the fuel-side dilution (red lines). Kinetics analysis shows this is attributed to that the heat release rate of reactions O + C₂H₂ = CO + CH₄ and H + O₂ + H₂O = HO₂ + H₂O is more suppressed when dilution occurs at the air-side than that at the fuel-side. In particular, an interesting phenomenon observed in Figure 1 is that the impact of H₂O and CO₂ dilution on the peak flame temperature is nearly linear for dilution ratio up to 40%, no matter dilution occurs in the fuel side or the air-side.

The effects of radiation models on the predicted peak NO mole fractions for CO₂ and H₂O dilution on the fuel and air stream are shown in Figure 2. The variation of peak NO mole fraction with dilution ratio is clearly nonlinear. Besides, the radiation model’s effect on the NO mole fraction is quite significant. Consistent with the radiation model’s effects on the peak flame temperature, when neglecting the radiation heat transfer, OTA predicts the lowest NO mole fraction. At a given flame condition, the NO mole fraction predicted by the DOM/SNCK model falls between no radiation and OTA but closer to no radiation. However, the radiation model’s effect on the predicted peak NO mole fraction weakens with increase in the dilution ratio, especially for the air-side dilution. As shown in Figure 2, when dilution occurs in the air-side (black lines), both H₂O dilution and CO₂ dilution reduce the peak NO mole fraction significantly; however, the reduction rate continuously weakens as the dilution ratio increases. The different influence of dilution on the peak NO mole fraction form the impact on the peak flame temperature, i.e., the nonlinear reduction of the peak NO mole fraction in Figure 2 and nearly linear reduction in the peak flame temperature in Figure 1, implies that the temperature-sensitive thermal NO route is not the primary pathway for NO formation under the conditions of this study. This point will be discussed later. Since the effect of fuel-side dilution on the NO mole fraction maximum is much weaker than that of air-side dilution, the nonlinear trend is not pronounced, especially for CO₂ dilution on the
fuel-side. For the fuel-side dilution, thermal NO is not the dominant route, as illustrated in Section 3.4.

3.2. Flame Temperature. From this section, the numerical results were calculated using the DOM/SNBCK radiation model since this radiation treatment provides the most accurate treatment of radiation heat transfer. In this part, the influence of H2O and CO2 dilution on flame temperature is discussed in detail. Figure 3 displays the temperature distributions for H2O and CO2 dilution up to 40% on the fuel and air-side as a function of the distance from the fuel nozzle. The differences in the peak flame temperature between Case 1 (no dilution) and the cases of 40% H2O and 40% CO2 dilution are also indicated. Although H2O and CO2 dilution on either the air or the fuel-side lowers the flame temperature consistently, differences between H2O dilution and CO2 dilution still exist. First, CO2 is more effective than H2O in reducing the flame temperature, regardless of if it being added to the air or the fuel side. This difference is mainly caused by the higher heat capacity of CO2. Second, H2O dilution always slightly shifts the peak flame temperature towards the air nozzle, but CO2 dilution can shift the peak temperature slightly towards either the fuel nozzle or the oxidizer nozzle when, respectively, added to the fuel or air stream. This difference is related to the relative molar weights of N2, H2O, and CO2. Nevertheless, the flame sheet almost remains at the same position since the momentum was balanced by equation (2) in all the cases.

To gain further insights into how H2O and CO2 dilution affect the flame temperature, Figure 4 shows the separate effects of 20% H2O and 20% CO2 dilution to the air and fuel side on the peak temperature. The chemical and thermal effects were analyzed in this paper since the transport and radiation effects are less important [8], though the radiation effect can become significant at low strain rates. It can be seen that the thermal effects of both H2O and CO2 dilution reduce the flame temperature. Although the chemical effect of CO2 lowers the flame temperature, the chemical effect of H2O increases it, albeit only slightly. This finding agrees with that reported in the previous studies [7, 8]. Besides, Figure 4 also shows that the dilution position (air-side or the fuel-side) does not change the individual effects of H2O and CO2 dilution on flame temperature qualitatively, namely, the chemical effects of CO2 and the thermal effects of H2O and CO2 always lower the flame temperature while the chemical effect of H2O slightly increases it. In addition, both the overall and individual effects of H2O and CO2 dilutions to the air-side are greater than those to the fuel-side. Kinetics analyses show that it is because that heat released by reactions O + C2H2 = CO + CH2 and H + O2 + H2O = HO2 + H2O is more suppressed when dilution occurs at the air-side than that at the fuel-side.

3.3. NO Mole Fraction. Figures 5(a) and 5(b) present the distributions of NO mole fraction as a function of the distance from the fuel nozzle for H2O and CO2 dilution, respectively. It is evident that both H2O and CO2 dilution reduces NO formation significantly and dilution to the air stream has a stronger influence on NO reduction than the fuel side, regardless of CO2 or H2O dilution. The effects of CO2 and H2O dilution on NO mole fraction correlate well with those on flame temperature. When the air-side is diluted (red lines), CO2 dilution suppresses NO formation more significantly than H2O dilution, again consistent with their effects on the peak flame temperature. While for the fuel-side dilution (blue lines), the effect of H2O dilution on suppressing NO formation is more significant than that of CO2 dilution, which deserves further investigations because the importance of these two kinds of diluents on decreasing NO formation is opposite to that on lowering the flame temperature (Figure 3).

To understand the phenomenon that the effect of fuel-side dilution by H2O on NO reduction is greater than that by CO2 dilution, CH radical distributions with or without 40% H2O and CO2 dilution in the air- and fuel-side are compared in Figure 6. H2O dilution on the fuel-side inhibits CH production more significantly than CO2, which explains the greater suppression impact of H2O dilution than CO2 dilution on NO formation in Figure 5. Although the temperature of fuel-side CO2 dilution is higher than that of fuel-side H2O dilution, the significantly reduced CH concentration of fuel-side H2O dilution slows down the initial reaction of prompt NO, i.e., CH + N2 = HCN + N (R240). Consequently, the total NO emission is inhibited
Figure 3: Distributions of flame temperature in CH$_4$/air counterflow diffusion flames with (a) H$_2$O dilution and (b) CO$_2$ dilution as a function of distance from the fuel nozzle: $a_v = 50$ s$^{-1}$, $L = 2$ cm, 400 K.
since the prompt NO is the dominant NO formation route. This point will be discussed in more detail in Section 3.4.

Most simulations in this study were conducted at \( T = 400 \) K and \( a_i = 50 \text{ s}^{-1} \). To show that the effects of dilution on NO reduction under these conditions are generalizable, Figures 7 and 8 exhibit the peak NO mole fraction at different strain rates (from 20 to 100 s\(^{-1}\)) and inlet temperature (from 400 to 600 K), and very similar trends can be found among the displayed lines. However, the detailed analyses of how strain rates and inlet temperature affects the NO formation are beyond this paper’s scope.

Figure 9 displays the individual effects of 20% H\(_2\)O and 20% CO\(_2\) dilution on the peak NO mole fraction. The dilution effects on NO reduction in the air-side are stronger than those in the fuel-side, same as the influence on flame temperature, Figure 4. In Figure 9, the chemical effect of H\(_2\)O dilution exerts a decreasing impact on NO emission despite promoting the flame temperature in Figure 4. This

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**Figure 4:** The overall and individual effects of 20% CO\(_2\) and 20% H\(_2\)O dilution on the peak flame temperature of CH\(_4\)/air counterflow diffusion flame: \( a_i = 50 \text{ s}^{-1}, L = 2 \text{ cm}, 400 \text{ K} \).
can be easily understood from the distribution of CH radical shown in Figure 6. Although the flame temperature is enhanced slightly by H2O dilution, the CH concentration is reduced more considerably, which results in more significant NO reduction through the prompt NO route than the prompting effect on NO through the thermal NO route.

3.4. NO Formation Mechanism. Figure 10 displays the emission index of NO via different formation routes as introduced in Section 2.3. The emission index of NO was calculated using equation (3), which has been widely utilized in previous studies, such as [10, 30].

$$\text{EINO} = \frac{\int_0^L \omega_{\text{NO}} M_{\text{NO}} dx}{-\int_0^L \omega_F M_F dx}$$  \hspace{1cm} (3)

where $\omega_{\text{NO}}$ and $\omega_F$ are the NO production rate and fuel consumption rate, respectively, and $M_{\text{NO}}$ and $M_F$ are the molecular weight of nitric oxide and fuel, respectively.

Firstly, it can be observed that the effects of H2O and CO2 dilution in the air- or fuel-side on EINO correlate well
with those on the peak NO mole fraction shown in Figures 5 and 9, namely, air-side CO$_2$ dilution $>$ air-side H$_2$O dilution $>$ fuel-side H$_2$O dilution $>$ fuel-side CO$_2$ dilution. This is because that CH$_4$ flow rate was kept constant for all the cases, and EINO was calculated over the entire computational domain in this study. Secondly, the prompt route plays the dominant role in NO formation, followed by the NO-reburning and NNH route, while the thermal and N$_2$O-intermediate routes contribute negligibly. For clarity, the percentages of reduction of total NO, prompt NO, NNH NO, and NO-reburning for 20% H$_2$O and 20% CO$_2$ dilution are also marked in Figure 10. For example, 18.8% means adding 20% CO$_2$ into the fuel stream (Case 6) reduces 18.8% NO emission than the no-dilution case (Case 1). It can be observed that the order of NO reduction percentage through the prompt NO route and NO-reburning for different dilutions totally agrees well with that through the full chemistry, i.e., air-side CO$_2$ dilution $>$ air-side H$_2$O dilution $>$ fuel-side H$_2$O dilution $>$ fuel-side CO$_2$ dilution. However, H$_2$O and CO$_2$ dilution’s influence on the third most important NO formation route (NNH pathway) does not follow the above order. Even so, it can still be concluded that the relative importance of H$_2$O and CO$_2$ dilution to NO formation reduction is determined by the dilution impact on the prompt NO formation and NO-reburning routes under the conditions of this study.

Using the method proposed by Revel et al. [32], the elemental fluxes of N through some critical reactions were calculated, and the pathways of NO formation based on the full chemistry of the GRI-Mech 2.11 for Case 1, Case 3, Case 6, Case 9, and Case 12 are demonstrated in Figure 11. It is worth pointing out that N’s elemental fluxes were calculated along with the whole computational domain rather than just at the flame front, indicating the average value over the entire combustion process. In Figure 11, the arrow shows the progress direction of a certain conversion, from the reactants to the products. The values on each arrow indicate the N flux over the entirely computational domain (from the fuel nozzle exit to the oxidizer nozzle exit with a distance of 2 cm in this study), and the width of each arrow distinguishes the magnitude of the N flux. The percentage after the value means the ratio of the N flux reduction relative to the baseline case (Case 1) through the reaction after it in parentheses. The pathway map in Figure 11 covers the five NO formation/destruction routes, and the conversion paths can be briefly highlighted as the thermal route (N$_2$ $\rightarrow$ N $\rightarrow$ NO), prompt route (N$_2$ $\rightarrow$ HCN $\rightarrow$ CN, NCO, NH, N, and HNO $\rightarrow$ NO), NNH route (N$_2$ $\rightarrow$ NNH

Figure 8: The peak NO mole fraction of CH$_4$/air counterflow diffusion flames with different inlet temperatures: $T = 400$ K (black), 500 K (red), and 600 K (blue). $a_i = 50$ s$^{-1}$, $L = 2$ cm.

Figure 9: Peak NO mole fractions of CH$_4$/air counterflow diffusion flame with and without 20% H$_2$O and 20% CO$_2$ dilution: $a_i = 50$ s$^{-1}$, $L = 2$ cm 400 K.
Figure 10: The percentages of EINO reduction by 20% H$_2$O and 20% CO$_2$ dilution in the air and fuel side of CH$_4$/air counterflow diffusion flame: $a_t = 50$ s$^{-1}$, $L = 2$ cm, 400 K.

Figure 11: Continued.
Figure 11: NO formation pathways for (a) no dilution (Case 1). (b) 20% CO₂ dilution in fuel (Case 6). (c) 20% CO₂ dilution in air (Case 12). (d) 20% H₂O dilution in fuel (Case 3). (e) 20% H₂O dilution in air (Case 9).
as follows:

(\(\rightarrow \text{NH}\)) \(\rightarrow\) NO), \(\text{N}_2\text{O}\)-intermediate route (\(\text{N}_2\) \(\rightarrow\) \(\text{N}_2\O\) \(\rightarrow\) \(\text{NO}\)), and part of NO-reburning route (\(\text{N}_2\) \(\rightarrow\) HCN, HCNO \(\rightarrow\) CN, NCO, NH\(_3\), NH\(_2\), NH \(\rightarrow\) \(\text{N}_2\O\), NO, and \(\text{N}_2\)).

By comparing Figures 11(b) and 11(c) with Figures 11(a), 11(d) and 11(e) with Figure 11(a), it can be found that the air-side dilution and fuel-side dilution affect the NO formation pathway similarly in general. To be specific, the nitrogen elemental fluxes in Figure 11(a) are the highest among all the five presented cases, indicating that the CH\(_4\) flame without dilution produces the highest amount of NO. The fuel-side dilution weakens the nitrogen elemental fluxes to a lesser degree than the air-side dilution for both H\(_2\O\) and CO\(_2\) diluents. Besides, as a more detailed illustration than Figure 10, Figure 11 shows that the NO formation through the thermal route, NNH route, and \(\text{N}_2\O\)-intermediate route is much less influenced than that through the prompt route, and the less affected reactions include R204 to R210 (NNH route), R178 (thermal route), and R185, R183, R182, and R199 (\(\text{N}_2\O\)-intermediate route).

However, differences do exist between the effects of the two diluents. When the flame is diluted with CO\(_2\), the NO formation pathway, NO \(\rightarrow\) HCN \(\rightarrow\) HNCO \(\rightarrow\) NH\(_2\) \(\rightarrow\) NH \(\rightarrow\) N \(\rightarrow\) NO (the N flux and its reduction percentage, as well as the involved reactions, are distinguished in blue), is most affected. While for H\(_2\O\) dilution, the most affected pathway is NO \(\rightarrow\) HCN \(\rightarrow\) NCO \(\rightarrow\) NH \(\rightarrow\) N \(\rightarrow\) NO. Besides, another remarkable change for H\(_2\O\) dilution can be observed for the conversion of NO \(\rightarrow\) HNO. When H\(_2\O\) is added to the fuel-side, the nitrogen elemental flux of R212 (from the NNH NO formation route) is decreased mainly by 48.56%. This degree far exceeds that of other NO formation pathways (with reduction percentages of 14.74%–39.93%). As for H\(_2\O\) dilution on the air-side, the direction of the conversion between NO and HNO is even reversed. This shift of the progress direction of R212 correlates well with the highest NO reduction percentage of air-side H\(_2\O\) dilution in Figure 8. All the abovementioned phenomena show that H\(_2\O\) dilution has more complex influences on flame structure and NO formation reduction than CO\(_2\) dilution.

4. Conclusions
Motivated by the widespread utilization of dilution combustion in many advanced technologies, this work systematically compared the effects of up to 40% H\(_2\O\) and CO\(_2\) dilutions to the fuel- and air-side on NO emissions in N\(_2\) diluted CH\(_4\)/air counterflow diffusion flames. This numerical study was performed using the OPPDIF code in conjunction with the GRI-Mech 2.11 kinetics mechanism at varying strain rates (20–100 s\(^{-1}\)) and inlet temperatures range from 400 K to 800 K, 1 atm. The dilution was also realized by replacing N\(_2\) with either CO\(_2\) or H\(_2\O\) in the oxidizer and the fuel stream to maintain the fuel and oxygen concentration constant. Several important findings are listed as follows:

1. The dilutions with H\(_2\O\) and CO\(_2\) in the oxidizer and fuel-side all decrease the flame temperature and NO formation. Dilutions by H\(_2\O\) and CO\(_2\) lower the peak flame temperature nearly linearly as the dilution ratio increases. The reduction rate of peak NO mole fraction displays a decreasing trend with increasing the dilution ratio, especially when the dilution takes place on the oxidizer side. The differences between the results based on the adiabatic treatment, the optically thin approximation, and the discrete-ordinates method coupled with the statistical narrow-band based correlated-k radiative property model decrease with increasing the dilution ratio.

2. The chemical effects of CO\(_2\) dilution lower both the flame temperature and NO emissions while the chemical effect of H\(_2\O\) dilution exerts a slightly promoting impact on the flame temperature but a suppression influence on NO formation. The apparently conflicting chemical effect of H\(_2\O\) dilution on the flame temperature and NO formation is attributed to the considerably suppressed CH radical, which results in more significant NO reduction through the dominant prompt NO route than the NO promotion through the thermal NO route.

3. The importance of effects of H\(_2\O\) and CO\(_2\) dilution in the air- and fuel-side on NO reduction follows the order of air-side CO\(_2\) dilution > air-side H\(_2\O\) dilution > fuel-side H\(_2\O\) dilution > fuel-side CO\(_2\) dilution, and the prompt NO route always plays the dominant role under the current investigation conditions.

4. Pathway analysis shows that the air-side dilution and fuel-side dilution affect the NO formation pathway similarly in general, but H\(_2\O\) dilution still differs from CO\(_2\) dilution. When the flame is diluted with CO\(_2\), the most affected NO formation pathway is NO \(\rightarrow\) HCN \(\rightarrow\) HOCN \(\rightarrow\) HCN \(\rightarrow\) N \(\rightarrow\) NO. However, when the flame is diluted with H\(_2\O\), the most affected pathway is NO \(\rightarrow\) HCN \(\rightarrow\) N \(\rightarrow\) NO.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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