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Thermal Effects of CO₂ on the NO_x Formation Behavior in the CH₄ Diffusion Combustion System

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Abstract:

The objective of the present study is to numerically investigate the quantitative effects of CO₂ replacement of N₂ in the oxidizer side on NO_x formation in CH₄ diffusion flames established in counterflow configuration at atmospheric pressure. The mole fraction of O₂ in the oxidizer was kept constant at 21%. Calculations were conducted at different stretch rates and different percentage of CO₂ in the oxidizer. Calculations were also carried out with and without radiation to quantify the effects of radiation heat transfer. For this simulation, a modified CHEMKIN code and a radiation code developed at the Combustion Group of ICPET were used. Mainly due to its much higher specific heat, replacement of nitrogen in air by carbon dioxide significantly lowers the temperature of the flame, leading to much lower NO concentrations. For a specified stretch rate, there exists a maximum percentage of CO₂ in the oxidizer beyond which flame extinction occurs. The value of the maximum percentage of CO₂ in the oxidizer decreases as the stretch rate increases. Effect of radiation heat transfer becomes more important as the stretch rate decreases. Replacement of N₂ by CO₂ in the oxidizer is an effective way to control NO_x formation in CH₄ diffusion flames mainly due to its thermal effect and secondly due to its chemical and radiative effects.

Key words: CH₄ Diffusion Flame; CO₂ replacement; NO_x formation; stretch rate; thermal effects; radiative effects.

1. Introduction

Combustion generated NO_x (represents NO, NO₂ and also N₂O) are major air pollutants and also

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contribute, along with other species (unburned hydrocarbons, CO and CO₂), to global warming through the green-house effect. Various techniques have been developed to reduce the formation of NO_x in flames, including the popular flue gas recirculation (FGR) in furnace application or exhaust gas recirculation (EGR) in engine application. It is important to understand from a fundamental point of view the mechanisms for the reduction of NO_x when FGR or EGR is employed. Since CO₂ is a major component in the combustion products, the present study is concerned with the effect of CO₂ addition to air (through replacement of N₂ by CO₂ while keeping the O₂ concentration constant) on NO_x formation in CH₄ counterflow diffusion flames.

In the open literatures, there are some researches have been recently carried out for the effects and effectiveness of CO₂ addition in reducing flame temperature and NO_x emission [1-3], primarily involving its thermal effects of high heat capacity and radiation loss, and chemical effects of participation in reaction [4,5].

Due to these potential effects, the extinction characteristic is an interesting topic for flames diluted with carbon dioxide [6-8]. Qiao et al. [9] numerically quantified the chemical effect of CO₂ on flame suppression of premixed methane flame in microgravity. The results indicate the decrease of flames temperature and radiative heat losses by diluent most likely lead to the flame extinction. Lock et al. [10] demonstrates the extinction characteristics of methane-air partially premixed and non-premixed flames. The fuel dilution is more effective than the air dilution for flame extinction with decreasing the level of partial premixing. The coflow and counterflow flames exhibit similarity.

Considering that a high CO₂ concentration in the application of Oxy-fuel combustion technology [11, 12], Song et al. [13] investigated the negative impacts of CO₂ on combustion temperature. The nonlinear variation of chemical effects of CO₂ on temperature with fraction of O₂ is also given. Sabia et al. [14] found the dynamic behavior of temperature oscillations. Especially for the fuel-rich mixtures diluted with carbon dioxide, it significantly alters both the CH₄ oxidation and CH₃ recombination to ethane which mainly induces the instabilities.

It is also well known that at high and low stretch rates flame extinction occurs, called stretch extinction and radiation extinction respectively. The present study shows that there exists a maximum amount CO₂ in the oxidizer at a given stretch rate beyond which steady state combustion cannot be established. This type of flame extinction may be termed “thermal extinction” which is caused by flame temperature reduction through increased heat capacity of the combustion products. It has been shown

by previous studies [15, 16] (among several other studies) that radiation heat transfer becomes more important as the stretch rate decreases.

The more recently developed GRI-Mech 3.0 mechanism (optimized for natural gas combustion) was used in this study. The results of this study were compared to the previous numerical studies [15,16] based on GRI-Mech 2.1 to demonstrate the differences between these two versions of GRI-Mech mechanism in the prediction of NO_x in counterflow CH₄ diffusion flames.

2. Numerical Model

In this study numerical calculations were carried out to model CH₄ diffusion flames formed by two coaxial jets of fuel and air streams at atmospheric pressure, as shown in Fig.1. Although the system is 2D (axisymmetric), the problem can be transformed into a system of ordinary differential equations (1D) valid along the centerline [17]. The ordinary differential equations of mass, momentum, species, and energy are given as [17].

$$\frac{dV}{dx} + 2a\rho f' = 0 \quad (1)$$

$$\frac{d}{dx} \left(\mu \rho \frac{df'}{dx} \right) - V \frac{df'}{dx} - a (f')^2 - a \rho_\infty = 0 \quad (2)$$

$$-\frac{d}{dx} (\rho W_k V_k) - V \frac{dY_k}{dx} - \omega_k W_k = 0 \quad (3)$$

$$\frac{d}{dx} \left(\lambda \rho \frac{dT}{dx} \right) - c_p V \frac{dT}{dx} - \sum_{k=1}^K Y_k V_k c_{pk} \frac{dT}{dx} - \sum_{k=1}^K W_k h_k - q_r = 0 \quad (4)$$

where $V = \rho u$ is the mass flux, $f' = v/v_\infty$ is the stream function or the nondimensional velocity in the radial direction, a is the stretch rate (such that the free stream velocities at the edge of the boundary layer are given as $v_\infty = ay$ and $u_\infty = -2ax$), ρ density, μ viscosity, W_k the molecular weight of the k th species, Y_k the mass fraction of the k th species, ω_k the molar rate of production of the k th species per unit volume, h_k the specific enthalpy of the k th species, V_k the diffusion velocity of the k th species, c_p the specific heat of the mixture at constant pressure, c_{pk} the specific heat of the k th species, and q_r the source term due to radiation heat transfer. The system of equations is closed by the ideal gas state equation.

The radiation source term was calculated using the discrete-ordinates method (DOM) coupled with the statistical narrow-band correlated-k (SNBCK) method for the absorption coefficients of CO,

CO₂, and H₂O [18].

The oxidizer jet is located at an axial position of -2.2 cm and the fuel jet is located at 1.3 cm. The reaction mechanism used in the calculations is GRI-Mech 3.0 containing 53 species and 325 reactions. The calculations were conducted for four stretch rates of 4, 10, 25 and 50 s^{-1} . The oxidizer consists of O₂, N₂, and CO₂. The mole fraction of CO₂ is from 0% (standard air as oxidizer) to 60% in the oxidizer. The mole fraction of O₂ in the oxidizer was kept constant at 21%. The fuel is pure CH₄.

Fig.1 Schematic of a counterflow diffusion flame setup and locations of flame and stagnation plane

3. Results and discussion

3.1. Effects of CO₂ and stretch rate on the temperature

The flame temperature is studied for a stretch rate of 10 m^{-1} in Fig. 2. The calculated peak flame temperatures decrease with the increase of the percentage of CO₂. This temperature decrease is a direct consequence to the value of the heat capacity of the carbon dioxide. CO₂ has a high heat capacity compared to the air. The more CO₂ is added in the air side, the more CO₂ takes the heat. Consequently, the more CO₂ is added, the less is the temperature peak flame.

Figure 2. Comparison of the flame temperatures obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 10 s^{-1} .

The flame temperature is studied for a stretch rate of 10 m^{-1} in Fig. 2. The calculated peak flame temperatures decrease with the increase of the percentage of CO₂. This temperature decrease is a direct consequence to the value of the heat capacity of the carbon dioxide. CO₂ has a high heat capacity compared to the air. The more CO₂ is added in the air side, the more CO₂ takes the heat. Consequently, the more CO₂ is added, the less is the temperature peak flame.

In Fig. 3, the calculations have converged with a stretch rate of 25 m^{-1} easier than with 10 m^{-1} . The more the stretch rate is low, the more the convergence is difficult to have because the air and the fuel have not enough velocity to give a good combustion in the flame. These results are interesting because they give more precision on the effect of the CO₂ percentage. The peak temperature decreases regularly with the increase of the CO₂ percentage as shown in Fig. 2. But what is interesting, is to see that for a percentage of 60%, the peak temperature is 1644 K for an abscissa around -0.886 cm whereas for 0%, the peak temperature is 2036 K for $x = -0.625 \text{ cm}$. The dramatic decrease of temperature show that for a percentage higher than around 60%, the temperature of the flame is too low, the combustion is not possible. These results show that it is not possible to make calculations with a high percentage of CO₂ and with a high stretch rate. The position of the flame shifts regularly on the oxidizer side. The position of the case with 50% is because of a flow rate of 0.095 l/s whereas all the other cases have a flow rate of 0.065 l/s.

Figure 3. Comparison of the flame temperatures obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 25 m^{-1} .

The Fig. 4 confirms the results of the Fig. 3. The flame cannot appear with both high stretch rate and high CO₂ percentage. The difference between 0% and 10% without radiation for a stretch rate of 10 m^{-1} is 79 K and for 25 m^{-1} , it is 78 K. So, the decrease of the temperature is not caused by the stretch rate but by the percentage of CO₂. There is no relation for the temperature between the percentage and the stretch rate. It is difficult to compare this point for the radiation because the data do not correspond exactly but it seems to be the same evolution. But all the results without radiation have the same evolution as those with radiation. Consequently, it shows that the radiation undergo the same effects of CO₂ and the stretch rate as without radiation.

Figure 4. Comparison of the flame temperatures obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 50 m⁻¹.

3.2. Effects of CO₂ and stretch rate on the NO formation

Fig. 5 shows clearly that the percentage of CO₂ has a really consequence on the flame and the formation of NO. The quantity of NO decreases dramatically with the increase of the quantity of CO₂. This result is not surprising because it is well known that CO₂ is added in industrial furnaces in order to decrease the pollution and the formation of pollutants like NO in the combustion. But the Fig. 6 shows that the quantity of NO is more important with a higher stretch rate. The dramatic decrease is the same as Fig. 5 but for all the percentages, there are more NO with a high stretch rate than with a low stretch rate. That is because the combustion is better with a low stretch rate. With a high stretch rate, the combustion has not enough time to be completed, that is why the NO formation is more important. For a high percentage, the NO mass fraction is very low. It is not because the pollution is at the minimum but it is because of the flame which is going to be put out. The curve for 50% is shifted because of the flow rate. All these results are confirmed for a stretch rate of 50 m⁻¹ with Fig. 7.

Figure 5. Comparison of mass fractions of NO obtained with and without radiation for different percentages of CO_2 and for a stretch rate of 10 m^{-1} .

Figure 6. Comparison of mass fractions of NO obtained with and without radiation for different percentages of CO_2 and for a stretch rate of 25 m^{-1} .

Figure 7. Comparison of mass fractions of NO obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 50 m^{-1} .

3.3. Effects of CO₂ and stretch rate on the NO₂ and N₂O formation

Fig. 8, 9 and 10 present the same results for the NO₂ formation as for the NO formation presented before except for radiation. All the calculations with radiation for the NO₂ formation show that the NO₂ formation is higher than without radiation contrary to the stretch rate of 10 m^{-1} . This result is normal because a way of the NO₂ formation is the reaction between NO and HO₂ in the low-temperatures regions of flame [19]. And as shown in Fig. 2, 3 and 4, the temperatures decrease with radiation, that is why it is normal to find more low-temperatures regions with the calculations of radiation.

Figure 8. Comparison of mass fractions of NO₂ obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 10 m⁻¹.

Figure 9. Comparison of mass fractions of NO₂ obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 25 m⁻¹.

Figure 10. Comparison of mass fractions of NO₂ obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 50 m⁻¹

Figure 1. Comparison of mass fractions of N₂O obtained with and without radiation for different percentages of CO₂ and for a stretch rate of 10 m⁻¹.

As it has already been shown and according to Fig. 11, when the percentage of CO₂ decreases, the formation of pollutants like N₂O decreases too. And it is the same for all the stretch rate (Fig. 12 and

13). And when the stretch rate increase but stay low, the value of the peak formation increase a bit. It is probably for the same reason as for NO_2 . But for a high stretch rate (between 25 and 50 m^{-1}), this evolution is lower.

Figure 12. Comparison of mass fractions of N_2O obtained with and without radiation for different percentages of CO_2 and for a stretch rate of 25 m^{-1}

Figure13. Comparison of mass fractions of N_2O obtained with and without radiation for different percentages of CO_2 and for a stretch rate of 50 m^{-1} .

4. Conclusion

A numerical study was carried out with CHEMKIN to investigate NO_x formation behavior of CH_4

diffusion flame with CO₂ addition. Numerical results of the present study show that it is not possible to maintain sustainable combustion with either high CO₂ or high stretch rate. For the CH₄ diffusion flame, the thermal effect of CO₂ is more significant than its chemical and radiative effects. The flame temperature significantly decreases with the increase of CO₂ percentage, correspondingly reduce the NO_x formation. Although the stretch rate has very little impact on temperature, there are more NO with a high stretch rate, due to lack of sufficient combustion time. Radiation increases the NO₂ formation as a result of more low-temperatures region. In addition, effect of radiation heat transfer becomes more important as the stretch rate decreases.

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