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# Thermal Effects of CO<sub>2</sub> on the NO<sub>x</sub> Formation Behavior in the CH<sub>4</sub> Diffusion Combustion System

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## **Abstract:**

The objective of the present study is to numerically investigate the quantitative effects of CO<sub>2</sub> replacement of N<sub>2</sub> in the oxidizer side on NO<sub>x</sub> formation in CH<sub>4</sub> diffusion flames established in counterflow configuration at atmospheric pressure. The mole fraction of O<sub>2</sub> in the oxidizer was kept constant at 21%. Calculations were conducted at different stretch rates and different percentage of CO<sub>2</sub> 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 CO<sub>2</sub> in the oxidizer beyond which flame extinction occurs. The value of the maximum percentage of CO<sub>2</sub> in the oxidizer decreases as the stretch rate increases. Effect of radiation heat transfer becomes more important as the stretch rate decreases. Replacement of N<sub>2</sub> by CO<sub>2</sub> in the oxidizer is an effective way to control NO<sub>x</sub> formation in CH<sub>4</sub> diffusion flames mainly due to its thermal effect and secondly due to its chemical and radiative effects.

**Key words:** CH<sub>4</sub> Diffusion Flame; CO<sub>2</sub> replacement; NO<sub>x</sub> formation; stretch rate; thermal effects; radiative effects.

## **1. Introduction**

Combustion generated NO<sub>x</sub> (represents NO, NO<sub>2</sub> and also N<sub>2</sub>O) are major air pollutants and also

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contribute, along with other species (unburned hydrocarbons, CO and CO<sub>2</sub>), to global warming through the green-house effect. Various techniques have been developed to reduce the formation of NO<sub>x</sub> 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<sub>x</sub> when FGR or EGR is employed. Since CO<sub>2</sub> is a major component in the combustion products, the present study is concerned with the effect of CO<sub>2</sub> addition to air (through replacement of N<sub>2</sub> by CO<sub>2</sub> while keeping the O<sub>2</sub> concentration constant) on NO<sub>x</sub> formation in CH<sub>4</sub> counterflow diffusion flames.

In the open literatures, there are some researches have been recently carried out for the effects and effectiveness of CO<sub>2</sub> addition in reducing flame temperature and NO<sub>x</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> concentration in the application of Oxy-fuel combustion technology [11, 12], Song et al. [13] investigated the negative impacts of CO<sub>2</sub> on combustion temperature. The nonlinear variation of chemical effects of CO<sub>2</sub> on temperature with fraction of O<sub>2</sub> 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 CH<sub>4</sub> oxidation and CH<sub>3</sub> 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 CO<sub>2</sub> 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<sub>x</sub> in counterflow CH<sub>4</sub> diffusion flames.

## 2. Numerical Model

In this study numerical calculations were carried out to model CH<sub>4</sub> 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].

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

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

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

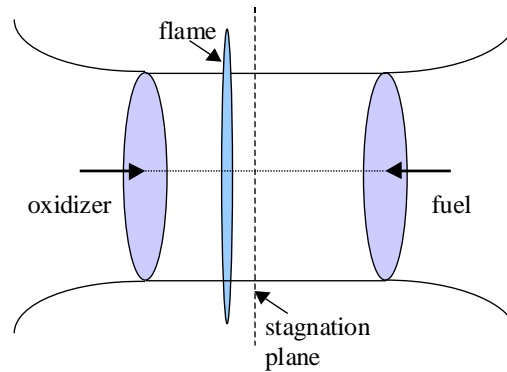
$$\frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) - e_p V \frac{dT}{dx} - \sum_{k=1}^K \sum_{p=1}^K Y_k V_k c_{pk} \frac{dT}{dx} - \sum_{k=1}^K W_k h_k + q_r = 0 \quad (4)$$

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  $u_\infty = -2ax$ ),  $\rho$  density,  $\mu$  viscosity,  $W_k$  the molecular weight of the  $k$ th species,  $Y_k$  the mass fraction of the  $k$ th species,  $\omega_k$  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,

CO<sub>2</sub>, and H<sub>2</sub>O [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<sup>-1</sup>. The oxidizer consists of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>. The mole fraction of CO<sub>2</sub> is from 0% (standard air as oxidizer) to 60% in the oxidizer. The mole fraction of O<sub>2</sub> in the oxidizer was kept constant at 21%. The fuel is pure CH<sub>4</sub>.



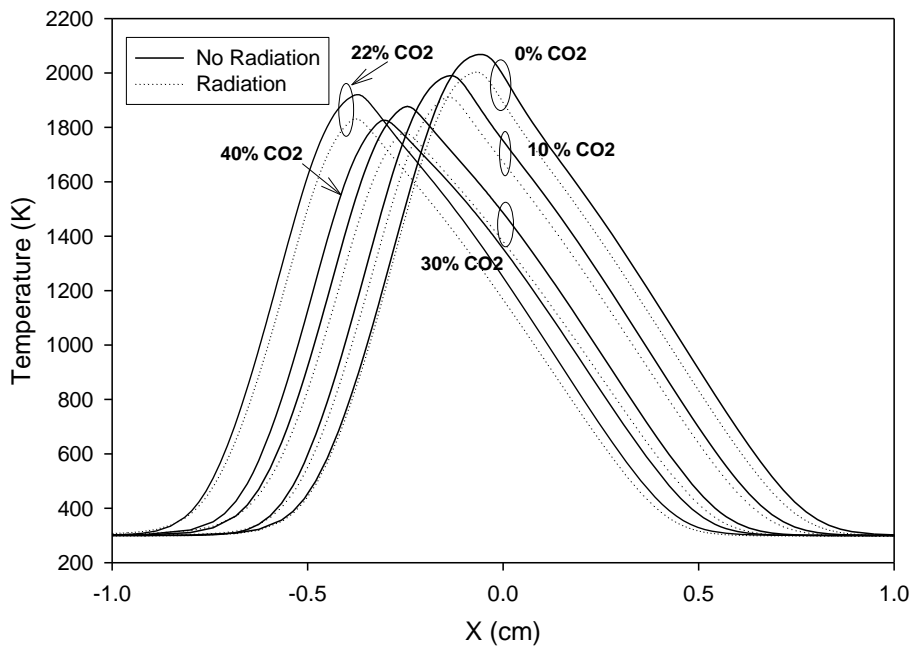
**Fig.1 Schematic of a counterflow diffusion flame setup and locations of flame and stagnation plane**

### **3. Results and discussion**

#### **3.1. Effects of CO<sub>2</sub> and stretch rate on the temperature**

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

### CH4 Flame - Stretch Rate = $10 \text{ m}^{-1}$

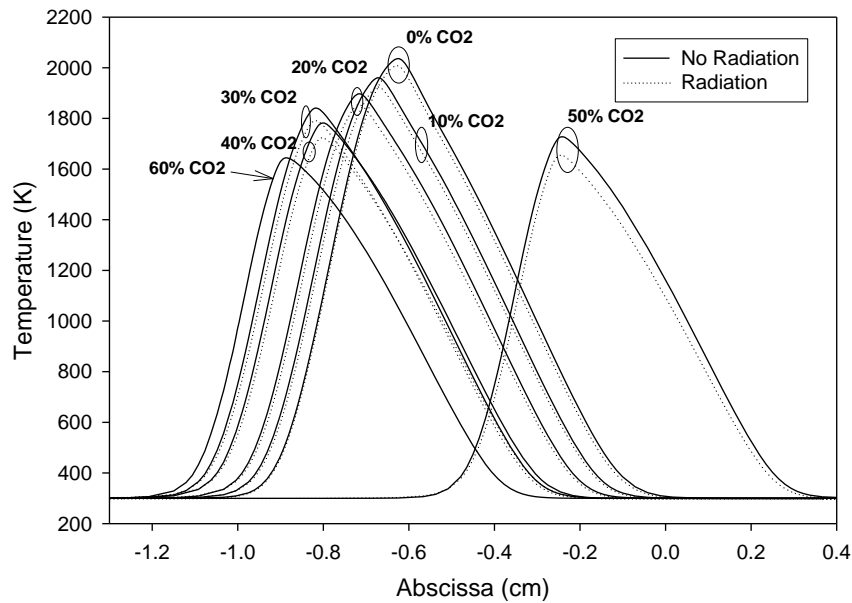


**Figure 2. Comparison of the flame temperatures obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of  $10 \text{ s}^{-1}$ .**

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

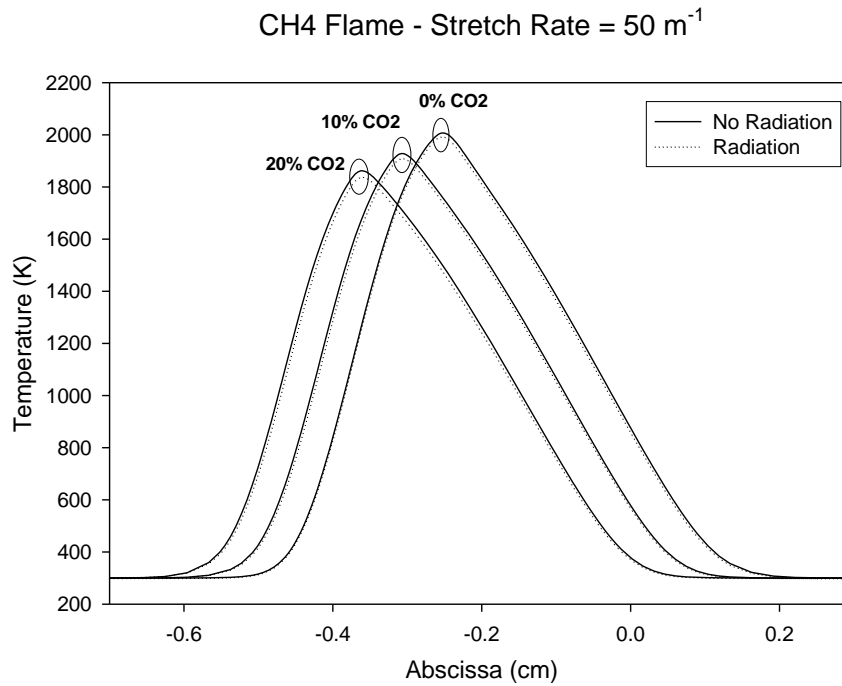
In Fig. 3, the calculations have converged with a stretch rate of  $25 \text{ m}^{-1}$  easier than with  $10 \text{ m}^{-1}$ . The more the stretch rate is low, the more the convergence is difficult to have because the air and the fuel have not enough velocity to give a good combustion in the flame. These results are interesting because they give more precision on the effect of the CO<sub>2</sub> percentage. The peak temperature decreases regularly with the increase of the CO<sub>2</sub> 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 CO<sub>2</sub> 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.

### CH<sub>4</sub> Flame - Stretch Rate = 25 m<sup>-1</sup>



**Figure 3. Comparison of the flame temperatures obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of 25 m<sup>-1</sup>.**

The Fig. 4 confirms the results of the Fig. 3. The flame cannot appear with both high stretch rate and high CO<sub>2</sub> percentage. The difference between 0% and 10% without radiation for a stretch rate of 10 m<sup>-1</sup> is 79 K and for 25 m<sup>-1</sup>, it is 78 K. So, the decrease of the temperature is not caused by the stretch rate but by the percentage of CO<sub>2</sub>. 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 CO<sub>2</sub> and the stretch rate as without radiation.



**Figure 4. Comparison of the flame temperatures obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of  $50 \text{ m}^{-1}$ .**

### 3.2. Effects of CO<sub>2</sub> and stretch rate on the NO formation

Fig. 5 shows clearly that the percentage of CO<sub>2</sub> 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 CO<sub>2</sub>. This result is not surprising because it is well known that CO<sub>2</sub> 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  $50 \text{ m}^{-1}$  with Fig. 7.



CH<sub>4</sub> Flame - Stretch Rate = 10 m<sup>-1</sup>

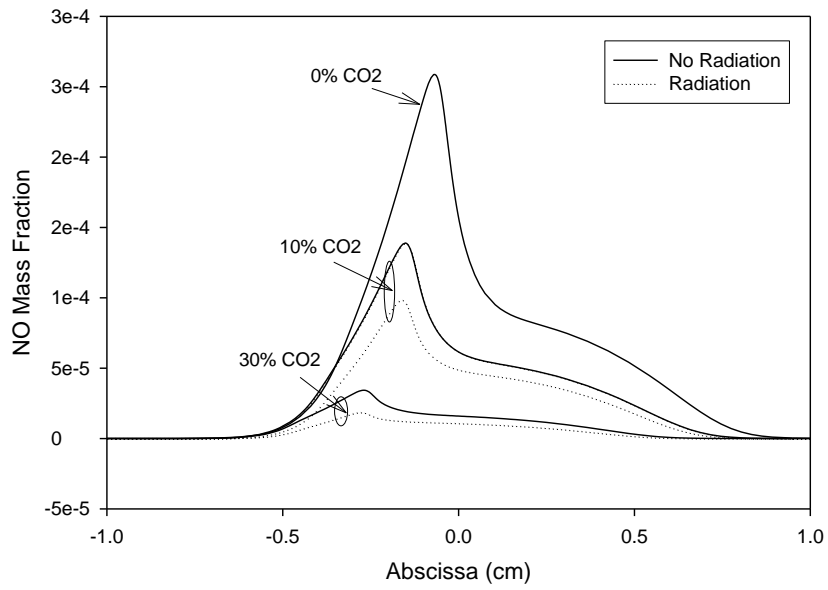


Figure 5. Comparison of mass fractions of NO obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of 10 m<sup>-1</sup>.

CH<sub>4</sub> Flame - Stretch Rate = 25 m<sup>-1</sup>

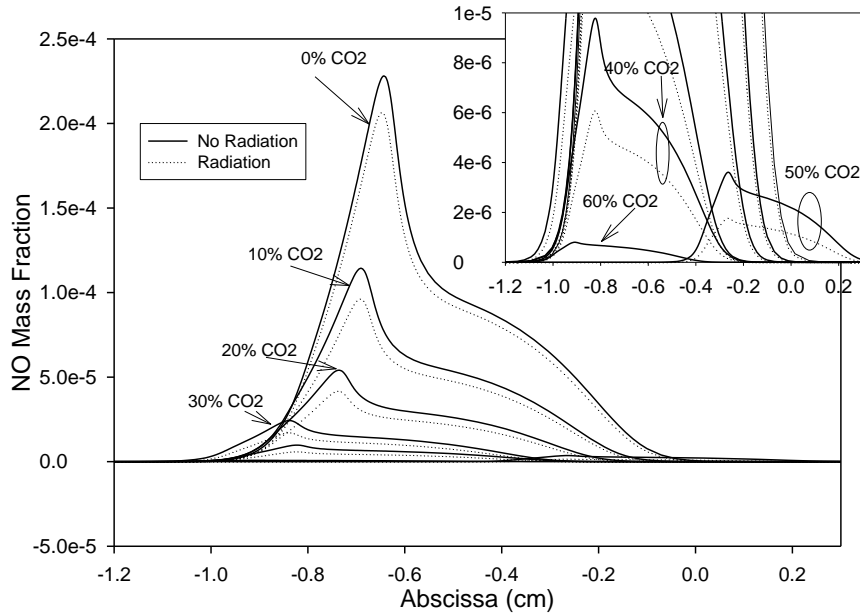
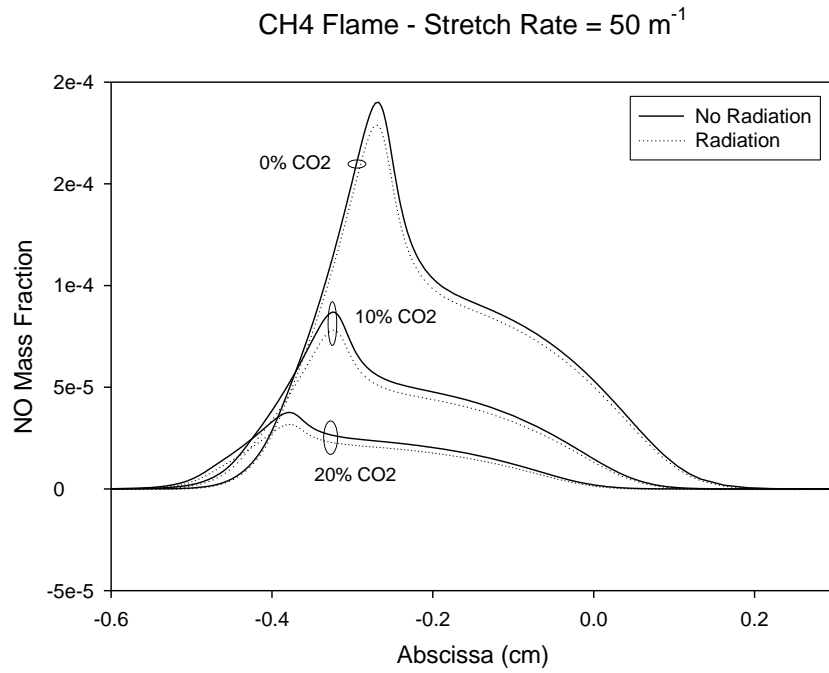


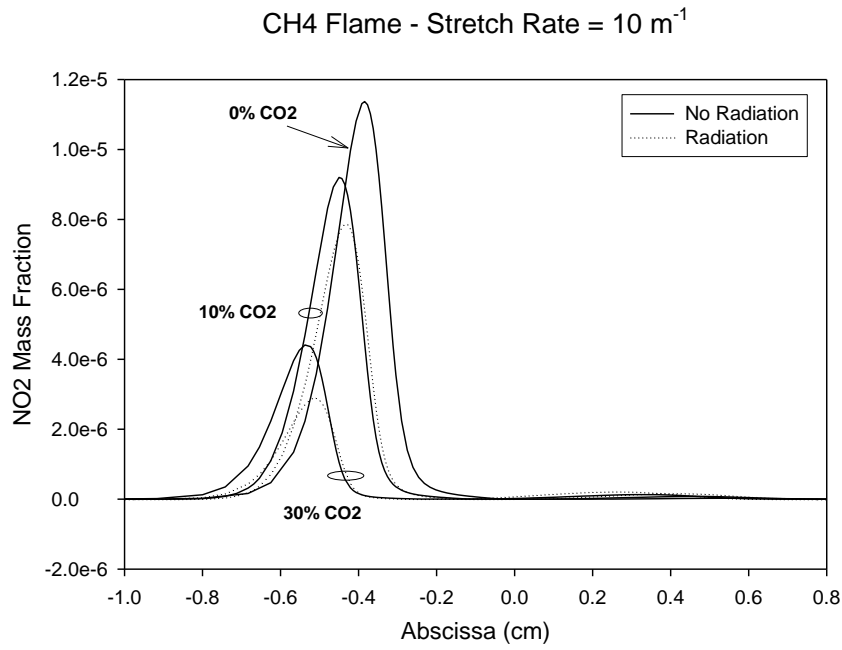
Figure 6. Comparison of mass fractions of NO obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of 25 m<sup>-1</sup>.



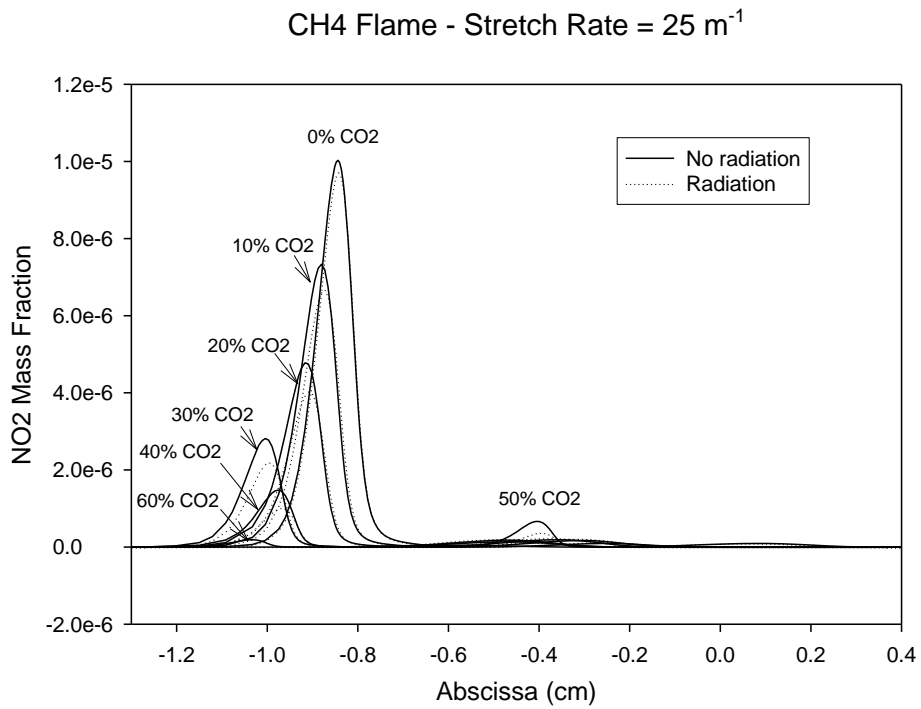
**Figure 7. Comparison of mass fractions of NO obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of 50 m<sup>-1</sup>.**

### ***3.3. Effects of CO<sub>2</sub> and stretch rate on the NO<sub>2</sub> and N<sub>2</sub>O formation***

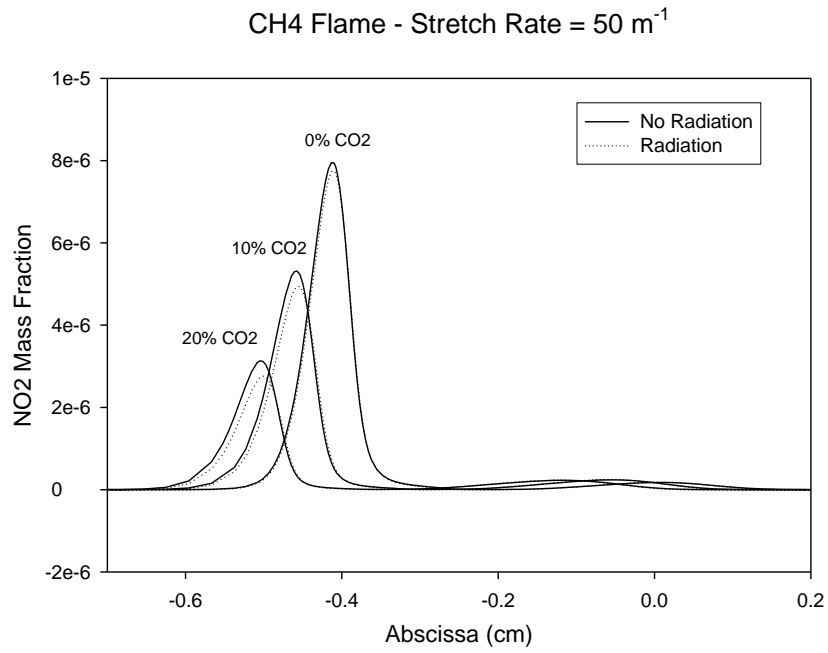
Fig. 8, 9 and 10 present the same results for the NO<sub>2</sub> formation as for the NO formation presented before except for radiation. All the calculations with radiation for the NO<sub>2</sub> formation show that the NO<sub>2</sub> formation is higher than without radiation contrary to the stretch rate of 10 m<sup>-1</sup>. This result is normal because a way of the NO<sub>2</sub> formation is the reaction between NO and HO<sub>2</sub> 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.



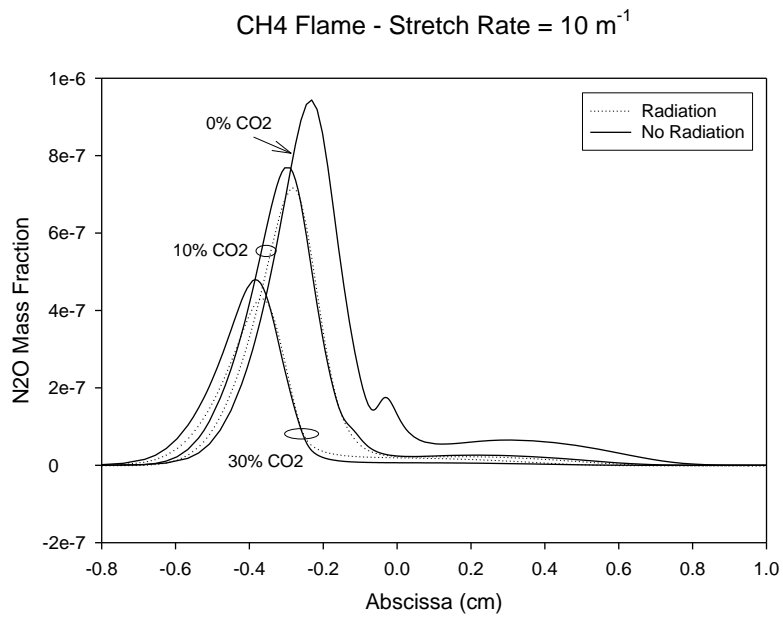
**Figure 8. Comparison of mass fractions of  $\text{NO}_2$  obtained with and without radiation for different percentages of  $\text{CO}_2$  and for a stretch rate of  $10 \text{ m}^{-1}$ .**



**Figure 9. Comparison of mass fractions of  $\text{NO}_2$  obtained with and without radiation for different percentages of  $\text{CO}_2$  and for a stretch rate of  $25 \text{ m}^{-1}$ .**



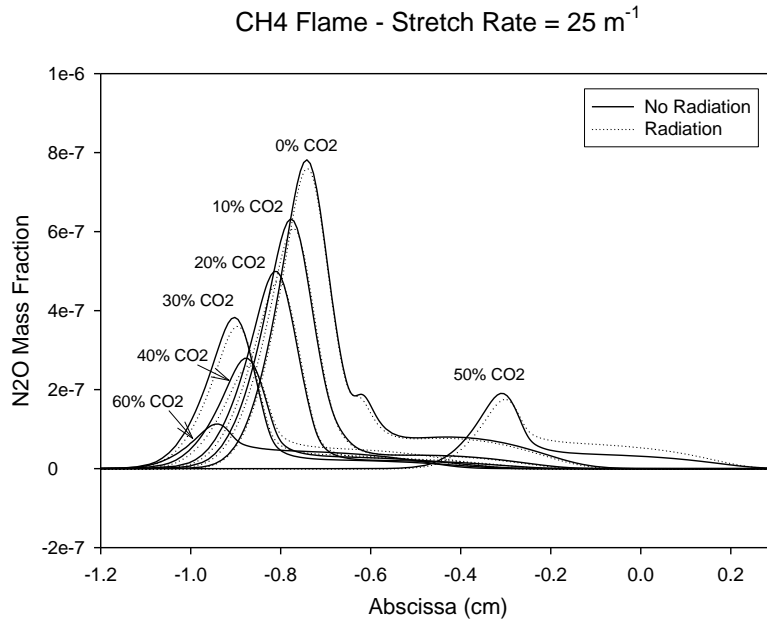
**Figure 10. Comparison of mass fractions of NO<sub>2</sub> obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of 50 m<sup>-1</sup>**



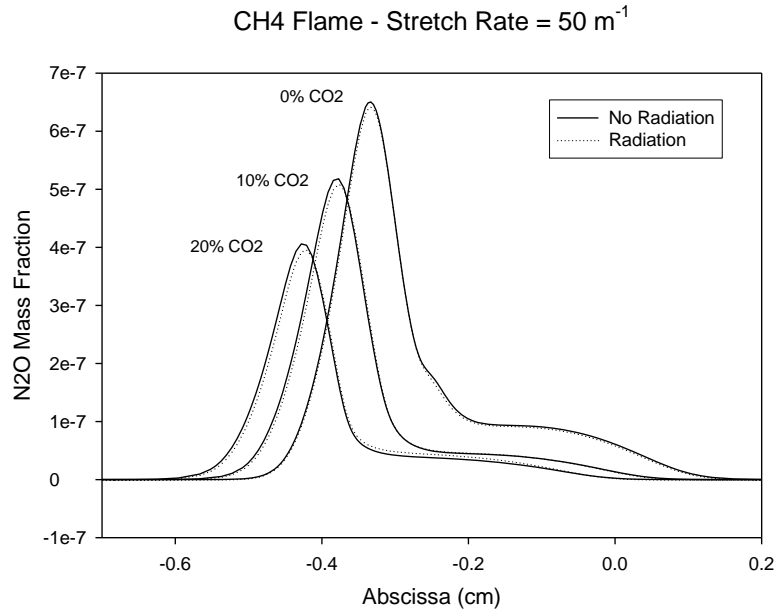
**Figure 1. Comparison of mass fractions of N<sub>2</sub>O obtained with and without radiation for different percentages of CO<sub>2</sub> and for a stretch rate of 10 m<sup>-1</sup>.**

As it has already been shown and according to Fig. 11, when the percentage of CO<sub>2</sub> decreases, the formation of pollutants like N<sub>2</sub>O 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  $\text{NO}_2$ . But for a high stretch rate (between 25 and  $50 \text{ m}^{-1}$ ), this evolution is lower.



**Figure 12. Comparison of mass fractions of  $\text{N}_2\text{O}$  obtained with and without radiation for different percentages of  $\text{CO}_2$  and for a stretch rate of  $25 \text{ m}^{-1}$**



**Figure13. Comparison of mass fractions of  $\text{N}_2\text{O}$  obtained with and without radiation for different percentages of  $\text{CO}_2$  and for a stretch rate of  $50 \text{ m}^{-1}$ .**

#### 4. Conclusion

A numerical study was carried out with CHEMKIN to investigate  $\text{NO}_x$  formation behavior of  $\text{CH}_4$

diffusion flame with CO<sub>2</sub> addition. Numerical results of the present study show that it is not possible to maintain sustainable combustion with either high CO<sub>2</sub> or high stretch rate. For the CH<sub>4</sub> diffusion flame, the thermal effect of CO<sub>2</sub> is more significant than its chemical and radiative effects. The flame temperature significantly decreases with the increase of CO<sub>2</sub> percentage, correspondingly reduce the NO<sub>x</sub> 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 NO<sub>2</sub> formation as a result of more low-temperatures region. In addition, effect of radiation heat transfer becomes more important as the stretch rate decreases.

### References

- [1] Park, Jeong, et al. "NO emission behavior in oxy-fuel combustion recirculated with carbon dioxide." *Energy & fuels* 21.1: 121-129(2007).
- [2] Min, Jiesheng, et al. "Impact of CO<sub>2</sub>/N<sub>2</sub>/Ar addition on the internal structure and stability of nonpremixed CH<sub>4</sub>/Air flames at lifting." *Combustion Science and Technology* 182.11-12: 1782-1804(2010).
- [3] Liu, Dong. "Chemical Effects of Carbon Dioxide Addition on Dimethyl Ether and Ethanol Flames: A Comparative Study." *Energy & Fuels* 29.5: 3385-3393 (2015).
- [4] Park, Jeong, et al. "Flame characteristics in H<sub>2</sub>/CO synthetic gas diffusion flames diluted with CO<sub>2</sub>: effects of radiative heat loss and mixture composition." *international journal of hydrogen energy* 33.23 (2008): 7256-7264.
- [5] Park, Jeong, et al. "A study on H<sub>2</sub>-air counterflow flames in highly preheated air diluted with CO<sub>2</sub>." *Energy & fuels* 19.6: 2254-2260 (2005).
- [6] Min, Jiesheng, and Françoise Baillet. "Experimental investigation of the flame extinction processes of nonpremixed methane flames inside an air coflow diluted with CO<sub>2</sub>, N<sub>2</sub>, or Ar." *Combustion and Flame* 159.12: 3502-3517 (2012).
- [7] Xing Li, Li Jia, Takakazu Onishi. Study on stretch extinction limits of CH<sub>4</sub>/CO<sub>2</sub> versus high temperature O<sub>2</sub>/CO<sub>2</sub> counterflow non-premixed flames, *Combust. Flame* 161.1526–1536 (2014).
- [8] Chen, Zheng, et al. "Studies of radiation absorption on flame speed and flammability limit of CO<sub>2</sub> diluted methane flames at elevated pressures." *Proceedings of the Combustion Institute* 31.2: 2693-2700 (2007).

- [9] Qiao, L., et al. "Extinction of premixed methane/air flames in microgravity by diluents: Effects of radiation and Lewis number." *Combustion and Flame* 157.8: 1446-1455(2010).
- [10] A. Lock, et al. "Lift off and extinction characteristics of fuel- and air-stream-diluted methane-air flames." *Combustion and Flame* 149: 340–352(2007)
- [11] Glarborg, Peter, and Line LB Bentzen. "Chemical effects of a high CO<sub>2</sub> concentration in oxy-fuel combustion of methane." *Energy & Fuels* 22.1: 291-296(2008).
- [12] Al-Abbas, Audai Hussein, and Jamal Naser. "Effect of chemical reaction mechanisms and NO<sub>x</sub> modeling on air-fired and oxy-fuel combustion of lignite in a 100-kW furnace." *Energy & Fuels* 26.6: 3329-3348(2012).
- [13] Song, Yu, et al. "The chemical mechanism of the effect of CO<sub>2</sub> on the temperature in methane oxy-fuel combustion." *International Journal of Heat and Mass Transfer* 86: 622-628 (2015).
- [14] Sabia, Pino, et al. "Dynamic Behaviors in Methane MILD and Oxy-Fuel Combustion. Chemical Effect of CO<sub>2</sub>." *Energy & Fuels* 29.3: 1978-1986 (2015).
- [15] Wang, J., and Niioka, T., "The effect of radiation reabsorption on NO formation in CH<sub>4</sub>/air counterflow diffusion flames, " *Combust. Theory Modelling* 5:385-398 (2001).
- [16] Lee, C. E., Lee, S. R., Han, J. W., and Park, J., "Numerical study on effect of CO<sub>2</sub> addition in flame structure and NO<sub>x</sub> formation of CH<sub>4</sub>-air counterflow diffusion flames, " *International Journal of Energy Research* 25:343-354 (2001).
- [17] Smooke, M. D., Puri, I. K., and Seshadri, K., "A comparison between numerical calculations and experimental measurements of the structure of a counterflow diffusion flame burning diluted methane in diluted air, " *Proc. Combust. Inst.* 21:1783-1792 (1986).
- [18] Liu, F., Smallwood, G. J., and Gülder, Ö. L., "Radiation heat transfer calculations using the SNBCK method," 33rd Thermophysics Conference, 28 June- 1 July 1999, Norfolk, VA, AIAA 99-3679.
- [19] Rortveit, G. J., Hustad, J. E., Li, S. C., and Williams, F. A., "Effects of diluents on NO<sub>x</sub> formation in hydrogen counterflow flames, " *Combustion and Flame* 130:48-61 (2002).