Coupling of the Chemical Effects of CO and CO2 on Soot Formation in C2H4 Diffusion Flame in O2-CO2 Atmosphere

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Abstract. Previous studies found that the chemical effect of CO (CE-CO) enhances the formation of soot in laminar coflow C2H4/air diffusion flames, while the chemical effect of CO2 (CE-CO2) inhibits soot formation. The coupled CE-CO and CE-CO2 on soot formation characteristics is investigated numerically in O2-CO2 atmosphere through blending fuel flow rate with 10%, 30% and 50% CO and virtual CO (FCO) in a laminar C2H4 diffusion flame. The results show that CE-CO increases the flame temperature, while CE-CO2 is opposite; the CE-CO promotes soot formation attributed to soot oxidation process which decreases the mole fraction of OH by OH+CO$\leftrightarrow$H+CO2, while the CE-CO2 inhibits the formation of soot ascribed to the increase of OH and O2 concentration promoting soot oxidation rate and the decrease of flame temperature, mole fractions of C2H2 and H inhibiting surface growth rate. Moreover, the chemical promotion effect of CO decreases in O2-CO2 atmosphere, and the coupled CE-CO and CE-CO2 suppresses soot formation.

Keywords: Laminar C2H4 diffusion flame; O2/CO2 atmosphere; Soot; Dopant.

1. Introduction
Soot emissions not only reduce the fuel efficiency, but also are harmful to human health and global warming [1,2]. CO is one of the important intermediates of hydrocarbon combustion and is a major component of syngas. Du et al. [3] observed a monotonic decline in soot emissions by adding CO into C2H4/air flame, but its chemical effects promoted soot formation. The simulation results of Guo et al. [4] further found that the chemical promotion effect of CO on soot formation was through the chemical reaction:

\[ \text{OH} + \text{CO} \leftrightarrow \text{H} + \text{CO}_2 \] (1)

producing more H and consuming more OH. For the research on the effect of CO2 addition on soot formation, Liu et al. [5] found that adding carbon dioxide to C2H4 could reduce the formation of soot by its chemical effect, but it becomes more obvious when adding CO2 to the oxidizer side. As discussed by Guo and Smallwood [6], CE-CO2 suppresses soot formation by expanding H radical through the backward reaction of R1. In summary, previous studies have proved that both CO and CO2
can suppress soot formation by the thermal and dilution effect. However, it remains unclear if there is an interaction or coupling between the chemical effects of CO and CO2.

A numerical study was carried to investigate the coupling between the chemical effects of CO added to fuel and CO2 in oxidizer on soot formation characteristics in a laminar coflow C2H4 diffusion flame through applying CoFlame [7]. Therefore, the coupling between the chemical effects of CO added to fuel and CO2 in the oxidant stream is a main concern of this study, since it has not been investigated by far.

2. Numerical Model and Computational Details

A detailed description about the numerical models applied in this research was introduced in our previous studies [1,8]. The further validation of the flame model showed that the simulation results of the flame model described above agree well with the experimental results of Santoro et al. [9] for both the temperature and SVF distributions. Therefore, the model is considered suitable for studying the CE-CO and CE-CO2 on soot formation in axisymmetric laminar coflow C2H4 diffusion flames. Figure 1 and Figure 2 displays the meshing and boundary conditions and the schematic of C2H4 diffusion flame, respectively. And the simulation cases are displayed in Table 1. It should be noted that the difference between the simulated results of CO and FCO addition to fuel reveals the CE-CO. Similarly, the difference in results between CO2 and FCO2 atmospheres quantifies CE-CO2.

3. Results and Discussion

3.1. SVF and Temperature Distributions

Figure 3 displays SVF distributions for C-pure, C-30%CO and C-30%FCO, respectively, $f_{v_{max}}$ represents the maximum SVF, while Figure 4 shows the effects of CO and FCO addition and CE-CO on $f_{v_{max}}$ with increasing the percentage of CO (FCO) addition. The value of $f_{v_{max}}$ of C-30%CO-FCO2...
and C-30%FCO-FCO2 is 11.73 ppm and 11.32 ppm, which is not shown in Fig. 4. We can see that \( f_{v\text{max}} \) decreases monotonically with increasing addition of CO or FCO. Furthermore, adding CO is slightly less effective than FCO, confirming the CE-CO. The difference in \( f_{v\text{max}} \) (i.e., chemical effect) between CO and FCO at 10%, 30%, and 50% addition is 0.058 ppm, 0.133 ppm, and 0.184 ppm (as shown in Fig. 4), respectively. It can be summarized that although CE-CO gradually increases with increasing CO addition, the growth rate of CE-CO gradually decreases. Moreover, comparing the difference between CO and FCO at 10%, 30%, and 50% addition is 0.058 ppm, 0.133 ppm, and 0.184 ppm (as shown in Fig. 4), respectively. It can be summarized that although CE-CO gradually increases with increasing CO addition, the growth rate of CE-CO gradually decreases. Moreover, comparing the difference between C-30%FCO and C-30%FCO-FCO2 (4.518 ppm) and the difference between C-30%FCO and C-30%CO (0.133 ppm), it can be found that the O2-CO2 atmosphere significantly inhibits soot formation.

### Figure 4. The effect of CO, FCO and CE-CO on \( f_{v\text{max}} \).

The maximum soot nucleation rate, surface growth rate and SVF are examined at \( HAB = 0.32, 2.8 \) and 3.5 cm. Figure 5 shows the radial temperature distribution at these three axial heights for C-30%CO, C-30%FCO, C-30%CO-FCO2 and C-30%FCO-FCO2, respectively. It can be seen that, in all three axial heights, the maximum temperature \( (T_{\text{max}}) \) in C2H4 diffusion flames with FCO addition is lower than that with FCO addition and \( T_{\text{max}} \) in O2-CO2 atmosphere is lower than O2-FCO2 atmosphere. Therefore, CE-CO increases the flame temperature through taking part in heat release process, while CE-CO2 is opposite. Furthermore, as the axial height increases, the difference of \( T_{\text{max}} \) between C-30%CO and C-30%FCO-FCO2 gradually decreases due to CE-CO2 while there is almost unchanged between C-30%CO and C-30%FCO because of CE-CO.

### Figure 5. Temperature radial distributions.

3.2. **CE-CO in C2H4/(O2-CO2) Flames and C2H4/(O2-FCO2) Flames**

To further explore CE-CO, CE-CO2 and their coupling, the results of adding 30% CO and 30% FCO are analyzed for the processes of nucleation, surface growth and oxidation. Figures 6 and 7 compare the radial distributions of soot nucleation rate and mole fractions of A1 and A4 at \( HAB = 0.32 \) cm in O2-CO2 and O2-FCO2 atmosphere, respectively. And CE-CO suppresses the nucleation rate of soot. As shown in Fig. 7, CE-CO suppresses the mole fraction of A4, and has little effect on the mole fraction of A1, although CE-CO increases \( T_{\text{max}} \) promoting the formation of PAHs. Through further analysis, the reason is that CE-CO suppresses the H mole fraction near the maximum soot nucleation rate (see Fig. 8 below), thereby suppressing the formation of A4 by the HACA mechanism. Therefore, soot nucleation rate is not the reason of CE-CO for promoting soot formation.

Soot surface growth process is a key factor affecting SVF. Figure 9 shows the two-dimensional distribution of surface growth rate when 30% CO and 30% FCO addition to C2H4. It can be seen that CE-CO suppresses soot surface growth rate, although the increases of \( T_{\text{max}} \) can promote the HACA rate...
due to CE-CO. As shown in Fig. 8, adding CO results in the decrease of H mole fraction at the maximum surface growth rate at HAB = 3.5 cm. Therefore, soot surface growth process is also not the reason for the chemical promotion effect of CO on soot loading.

Finally, the effect of CO addition on soot oxidation is analyzed. Soot oxidation process is mainly ascribed to the attack of OH and O2 on soot particles [4]. Figures 10 and 11 show the radial distributions of OH and O2 at HAB = 0.32, 2.8, and 3.5 cm in the flames of 30%CO and 30%FCO addition, respectively. The results show that in all regions relevant to soot formation, either the nucleation area, surface growth area, or the area of fVmax, CE-CO consistently reduces the mole fractions of OH and O2, thereby suppressing the soot oxidation rate, which in turn results in higher SVFs.

Table 2 displays the calculated maximum forward and reverse rates of main reaction steps involving the oxidation process of CO in the extended ABF mechanism. It is found that the maximum forward rate of R1 is actually the largest in all the six main reaction steps in O2-FCO2 atmosphere, consistent with the finding of Guo et al. [4]. Moreover, in O2-FCO2 atmosphere, R1 is still the most important reaction in the soot oxidation process and CE-CO also inhibits the maximum forward reaction rate of R1 and, ultimately, reduces soot oxidation rate and causes higher SVF.

### Table 2. Calculated maximum forward and reverse reaction rates of main reaction steps. (mol·m⁻³·s⁻¹)

| Reaction step | C-30%CO | C-30%FCO | C-30%CO-FCO2 | C-30%FCO-FCO2 |
|---------------|---------|----------|--------------|--------------|
|               | min     | max      | min          | max          |
| R1: CO+OH↔CO2+H | /       | 3.22     | 3.34         | -9.49        |
| R2: O2+CO↔O+CO2 | -1.24   | 2.82     | -1.41        | 2.44         |
| R3: O+HCO↔CO+OH | /       | 9.37     | 8.51         | 8.49         |
| R4: O+HCO↔CO+OH | /       | 9.37     | 8.51         | 8.49         |
| R5: CH2+O2↔OH+H+CO | /       | 9.37     | 8.51         | 8.49         |
| R6: HCCO+O2↔OH+2CO | /       | 9.37     | 8.51         | 8.49         |

Although it has been studied by Guo et al. [4] that reaction R1 has a dominant role in suppressing soot oxidation by CE-CO, it is necessary to explore if this finding still holds in O2-FCO2 atmosphere.
Therefore, whether in O₂-CO₂ atmosphere or O₂-FCO₂ atmosphere, CE-CO promotes soot formation through the reduced soot oxidation process, which is attributed to the reduced OH mole fraction, rather than soot nucleation or surface growth process.

### 3.3. The Chemical Effect of CO₂ Addition to the Oxidizer in C₂H₄/(O₂-CO₂) Flames and C₂H₄/(O₂-FCO₂) Flames

CE-CO₂ suppresses soot formation in C₂H₄ diffusion flame. However, Figs. 6 and 7 display that CE-CO₂ promotes the A₄ formation and the soot nucleation rate by comparing the results of C-30%FCO and C-30%FCO-FCO₂ although it decreases $T_{\text{max}}$ in Fig. 5. Therefore, soot nucleation process is not the factor responsible for CE-CO₂ suppressing soot formation.

As shown in Fig. 9, the surface growth rate of C-30%FCO is significantly lower than C-30%FCO-FCO₂. Therefore, CE-CO₂ suppresses soot formation by reducing surface growth rate in C₂H₄ flames. Through further analysis, CE-CO₂ reduces the flame temperature, which inhibits the pyrolysis reaction of C₃H₄:

$$
\text{C}_3\text{H}_4 + (M) \leftrightarrow \text{C}_2\text{H}_2 + \text{H} + (M)
$$

(2)

Lower flame temperature and lower mole fractions of H and C₂H₂ decrease the formation of soot in C₂H₄ flames through the HACA surface growth mechanism. Moreover, CE-CO₂ increases mole fraction of OH and O₂ promoting the soot oxidation rate, thereby further suppressing soot formation.

Therefore, CE-CO₂ in the oxidizer of C₂H₄/(O₂-CO₂) flames and C₂H₄/(O₂-FCO₂) flames inhibits the formation of soot attributed to soot surface growth and soot oxidation process. Firstly, CE-CO₂ reduces the flame temperature and mole fractions of H and C₂H₂ which inhibits the soot growth rate in C₂H₄ flames by the HACA mechanism. Secondly, a large amount of CO₂ increases mole fraction of OH and O₂ and promotes chemically the soot oxidation rate.

### 3.4. The Coupling Chemical Effect of CO and CO₂

Through the above discussion, CE-CO significantly reduces the mole fractions of OH and O₂ in O₂-FCO₂ atmosphere and O₂-CO₂ atmosphere, thereby reducing the soot oxidation rate and promoting SVF. However, the chemical effect of a large amount of CO₂ in the oxidant inhibits the formation of soot in C₂H₄ flames, which is attributed to the suppression of soot surface growth through HACA mechanism and enhancement of the mole concentration of OH by reaction R1 in O₂-CO₂ atmosphere. Therefore, it is necessary to carry on a further analysis on if there is coupling between the CE-CO and CE-CO₂.

**Figure 12** displays cross-sectional area integrated SVF $F_v(z)$ distributions along HAB in C₂H₄ diffusion flames with 30% CO and 30% FCO addition. The total amount of soot $S_T$ in the four flames is 3.489 ppm cm⁻³ (C-30%CO), 3.247 ppm cm⁻³ (C-30%FCO), 9.291 ppm cm⁻³ (C-30%CO-FCO₂) and 8.516 ppm cm⁻³ (C-30%FCO-FCO₂), respectively. The chemical promotion effect of CO in O₂-FCO₂ atmosphere is calculated to be 0.775 ppm cm⁻³, which is greater than 0.242 ppm cm⁻³ in O₂-CO₂ atmosphere.

As shown in Table 2, R1 is the important chemical reaction in the coupling between the CE-CO and CE-CO₂. And we can found that the maximum forward reaction rates of R1 in the flames of C-30%CO, C-30%FCO, C-30%CO-FCO₂, and C-30%FCO-FCO₂ are $3.22 \times 10^{-5}$, $3.34 \times 10^{-5}$, $1.28 \times 10^{-3}$, and $1.46 \times 10^{-3}$ mol/(m³s), respectively. Obviously, R1 is least in the C-30%CO flame. Therefore, the chemical promotion effect of CO in O₂-FCO₂ atmosphere is suppressed by the chemical reaction R1, and the coupling of CE-CO and CE-CO₂ suppresses soot formation in C₂H₄ diffusion flames. Based on the above analysis, we guess that the reason for the coupling of chemical effects is that the presence of a large amount of CO₂ in the oxidizer not only significantly reduces the flame temperature in O₂-CO₂ atmosphere inhibiting the rate of R1, but also shifts the chemical reaction R1 to the reverse direction reducing the mole fraction of OH consumption rate.

### 4. Conclusions

A numerical research on soot formation has been conducted in laminar coflow C₂H₄ diffusion flames with addition of CO and FCO in O₂-CO₂ atmosphere and O₂-FCO₂ atmosphere to understand the
CE-CO and CE-CO$_2$ and their coupling. The CE-CO, CE-CO$_2$ and their coupling have been investigated systematically. The following conclusions are obtained:

1. The CE-CO promotes soot loading by reducing the soot oxidation rate as a result of suppressed OH mole fraction by the forward reaction of R1 whether in O$_2$-CO$_2$ atmosphere or O$_2$-FCO$_2$ atmosphere.
2. The CE-CO$_2$ added to the oxidizer in C$_2$H$_4$/(O$_2$-CO$_2$) flames inhibits the formation of soot attributed to reducing surface growth and enhancing soot oxidation.
3. The chemical promotion effect of CO weakens in O$_2$-CO$_2$ atmosphere and the coupling between the CE-CO and CE-CO$_2$ further suppresses soot formation in C$_2$H$_4$ diffusion flames. The reason for the coupling of chemical effects is that the presence of a large amount of CO$_2$ in O$_2$-CO$_2$ atmosphere not only significantly reduces the flame temperature and hence inhibiting the rate of R1, but also shifts R1 to the reverse direction to reduce the mole fraction of OH consumption rate.

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