Pressurized MILD and oxy-fuel combustion in counter-flow configuration: Emissions of NO and CO

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1 Abstract

Both the MILD combustion and oxy-fuel combustion technologies have received significant attention as clean combustion technologies. However, the majority of previous investigation is limited at atmospheric pressure condition. This paper systematically investigates the effect of pressure on the NO and CO emissions from counter-flow combustion under MILD and oxy-fuel conditions. After comprehensive validation of the modeling, the effects of pressure on the formation of nitrogen oxides (NO_x) and CO are investigated in detail. Note that the terms "T-N2", "T-CO2", "MILD-N2" and "MILD-CO2" combustion adopted hereafter represent the traditional combustions diluted by N₂ and CO₂, and MILD combustions diluted by N₂ and CO₂, respectively. As the pressure increases from 1 atm to 10 atm under $T-N_2$ or $T-CO_2$, the temperature raises by approximately 300 K and the NO emission drastically increased by 10 times. However, for MILD-N₂ or MILD-CO₂, the temperature raises by only 150 K. More interestingly, although both the pressure and reaction temperature increase, the NO emission from MILD combustion first increases but then decreases with the peak NO emission obtained at 3 atm, regardless of N_2 or CO_2 dilution. This unexpected NO reduction phenomenon at high pressure is caused by the competition between the chain reaction (H+O₂ \rightleftharpoons O+OH) and recombination reaction (H+O₂(+M) \rightleftharpoons HO₂(+M)). Further analysis found that the prompt NO route controls the NO formation in pressurized MILD-N₂ combustion, while the N₂O-intermediate route dominates the NO production in pressurized MILD-CO₂ combustion. The importance of N₂O-intermediate route increases significantly when the strain rate is lower than 10 s⁻¹ at 5 atm.

Keywords: MILD combustion, oxy-fuel combustion, pressurized combustion, NO emission

2 Introduction

The control of NO_x emission is a major goal for the clean utilization of fossil fuel. Moderate or intense low oxygen dilution (MILD) combustion has significant potential for suppressing NO_x emission. Moreover, semi-uniform thermal distribution and high thermal performance can be achieved under the MILD condition. As a high-efficiency and clean combustion technology, the MILD combustion has been successfully adopted in gas turbines, steel and metallurgy industries and other fields. The MILD combustion can be established not only with O_2/N_2 as oxidant, but also with O_2/CO_2 (oxy-fuel), which is termed as MILD-N₂ and MILD-CO₂ combustion, respectively. In oxy-fuel combustion, the CO₂ level in the exhaust gas can be significantly increased, which is suitable for carbon capture. The MILD-CO₂ combustion can further increase the thermal performance and simultaneously reduce NO_x emission of the combustion system, relative to the traditional high temperature oxy-fuel combustion.

The MILD combustion has been extensively investigated at atmospheric pressure. However, to our best knowledge, a small number of the studies are in pressurized conditions. Sohn et al.¹ investigated the effects of pressure (1~20 atm) on NO formation in CH₄ counter-flow diffusion flames of high-temperature and diluted-air conditions. They found that NO emissions are lower and dilution effect on NO reduction is

enhanced with pressure increasing. Ye et al². experimentally investigated the characteristics of MILD combustion of liquid fuels (ethanol, acetone and n-heptane) at different pressure (1, 2.5, 5 bar). They found that the NO_x emission is increased with pressure rise, which is caused by increased flame temperature and residence time. On the oxy-fuel combustion side, majority of the investigations on oxy-fuel combustion are also in atmospheric pressure conditions. To further increase the system efficiency, the oxy-fuel combustion can be extended to elevated pressure condition. To our best knowledge, the detailed formation NO_x and CO formation path at pressurized oxy-fuel combustion are not explored. Meanwhile, the characteristics of MILD-CO₂ combustion at elevated pressure are also not addressed. Therefore, the effect of pressure on NO and CO emissions of MILD-N₂ and MILD-CO₂ combustion are investigated through counter-flow combustion.

3 Methodology



Figure 1. Structure of the counter-flow diffusion combustion.

The schematic diagram of counter-flow model is shown in Figure 1. The counter-flow model has been widely adopted in the investigations of MILD combustion, oxy-fuel combustion and pressurized combustion. The OPPDIFF code is applied to solve the equations of the counter-flow model.

| Mechanisms | Species | Reactions |
|----------------------------|---------|-----------|
| GRI-Mech 2.11 | 49 | 279 |
| GRI-Mech 3.0 | 53 | 325 |
| USC-Mech II-2.11 NO_x | 128 | 886 |
| USC-Mech II-3.0 NO_x | 128 | 890 |
| USC-Mech II-mod-3.0 NO_x | 129 | 900 |
| GDF-Kin 3.0 | 77 | 591 |

Table 1. Six chemical mechanisms for methane combustion and NO_x formation

Table 1 summarizes the six detailed reaction mechanisms compared and validated in the present study. USC-Mech II-2.11 NO_x means USC-Mech II coupled with NO_x sub-mechanism from GRI-Mech 2.11. USC-Mech II-3.0 NO_x means the USC-Mech II together with NO_x sub-mechanism from GRI-Mech 3.0. USC-Mech II-mod-3.0 NO_x means USC-Mech II with the modified NO_x sub-mechanism³ of GRI-Mech 3.0. From Figure 2, the predictions of NO formation from USC-Mech II-2.11 NO_x agree well with the experiment. This detailed mechanism is adopted in the present study.

The present study employs the density-weighted strain rate (instead of global strain rate) to isolate the chemical effect of pressure variation from the physics effect. The density-weighted strain rate is defined as

$$k' = \frac{P_c}{P_{ref}}k$$
(1)

where P_c is the chamber pressure, P_{ref} is the reference pressure (1 atm), k is the global strain rate. The global strain rate (k) is defined as

Pressurized MILD and oxy-fuel combustion

Kai Wang

$$k = \frac{2}{L} \left(u_f + u_o \sqrt{\frac{\rho_o}{\rho_f}} \right)$$
(2)

where L (= 1.5 cm) is the distance between the fuel and the oxidizer inlets, ρ_f and ρ_o are the density of fuel and oxidizer respectively, u_f and u_o are the velocity of fuel and oxidizer exit respectively. Detailed conditions settings are listed in Table 2.



Figure 2. Validation of six chemical mechanisms with experiments of (a) counter-flow combustion with N_2 dilution at atmospheric pressure; (b) counter-flow air-combustion at elevated pressure

| condition | Fuel | Oxidizer | $T_f(\mathbf{K})$ | $T_{ox}(\mathbf{K})$ |
|----------------------|--|---|-------------------|----------------------|
| T-N ₂ | $X_{CH4} = 0.2$ $X_{N2} = 0.8$ | $X_{O2} = 0.43$ $X_{N2} = 0.57$ | 300 | 300 |
| T-CO ₂ | $X_{CH4} = 0.28$ $X_{CO2} = 0.72$ | $X_{O2} = 0.559$ $X_{CO2} = 0.366$ $X_{N2} = 0.075$ | 300 | 300 |
| MILD-N ₂ | $X_{CH4} = 0.07$ $X_{N2} = 0.93$ | $X_{O2}^{N2} = 0.29$ $X_{N2} = 0.71$ | 300 | 1200 |
| MILD-CO ₂ | $X_{CH4} = 0.104$ $X_{CO2} = 0.896$ | $X_{02}=0.4$ $X_{C02}=0.525$ $X_{N2}=0.075$ | 300 | 1200 |

Table 2. Initial parameters for the four typical combustion conditions with $\Phi = 1$ and $k' = 90 \text{ s}^{-1}$

For removing the differences caused by dilution levels and reliably comparing the emissions from different conditions, the emission index of pollutants Y (NO, CO), EIY (g-Y/kg-CH4) is severally defined in Equation (3):

$$EIY = \frac{\int_{0}^{L} \omega_{\gamma} M_{\gamma} dx}{-\int_{0}^{L} \omega_{CH_{\gamma}} M_{CH_{\gamma}} dx} \times 1000$$
(3)

Where ω and M respectively mole fraction and molecular weight of species.

4 Results and Discussion

4.1 Basic cases at atmospheric pressure condition

Pressurized MILD and oxy-fuel combustion

Figure 3 shows the profiles of temperature and heat release, as well as emissions of NO and CO of the four base cases at atmospheric pressure condition. The difference between temperature peak and oxidizer temperature is set as ΔT , In Figure 3a, according to the definition⁶ of MILD combustion: oxidizer temperature $T_{ox}>T_{si}$, $\Delta T<T_{si}$, both MILD-N₂ and MILD-CO₂ in present work satisfy the definition of MILD combustion. The peak temperature of atmospheric MILD combustion whether under N₂ or CO₂ dilution are kept at constant. Shown in Figure 3b, whether under conventional or MILD combustion, heat release rate in CO₂ dilution case is greater. In Figure 3c, compared to conventional combustion, oxy-fuel combustion and MILD combustion can obviously reduce NO emissions. MILD-CO₂ can reduce NO emissions in the further step. The NO emissions is lower than 1/100 of that in T-N₂ case. Due to MILD-CO₂ diluted by CO₂, CO emissions is higher than that in MILD-N₂, but just half of that in oxy-fuel combustion. It is found that MILD-CO₂ has comprehensive advantages on NO and CO reduction.



Figure 3. Combustion and emission characteristics of four kinds of combustion mode (T-N₂, T-CO₂, MILD-N₂, MILD-CO₂) at atmospheric pressure: (a) temperature profiles; (b)heat release rate profiles; (c) EINO; (d) EICO

4.2 Effect of pressure on NO and CO emissions in four modes



Figure 4. Effect of pressure on T_{max}, EICO and EINO

Figure 4 displays the dependence of T_{max} , EICO and EINO on pressure. In Figure 4a, for four kinds of combustion mode, elevated pressure promote temperature increasing. However, MILD-N₂ and MILD-CO₂ can reduce temperature rise at elevated pressure. Temperature rise in MILD cases is just 153 K, which is lower than that in conventional cases (314 K) when pressure is increased from 1 atm to 10 atm.

Found in Figure 4b, CO emissions are decreased by about 2/3 in MILD-N₂ and MILD-CO₂ when pressure is increased from 1 to 10 atm. In MILD conditions, the key reaction controlling CO consuming is CO+OH \rightleftharpoons CO₂+H. Under MILD conditions, as pressure increases, H radicals are consumed through H+O₂ \rightleftharpoons OH+O.

Rate of CO+OH \rightleftharpoons CO₂+H on CO consuming gradually increases. However, under T-N₂ and T-CO₂ conditions, CO emissions decrease at first and then increase, reaching the minimum value at 3 atm. In T-N₂ case, in high pressure (*P* >3 atm), CH₂CO(+M) \rightleftharpoons CH₂+CO(+M), CH₂CO+H \rightleftharpoons CH₃+CO increases with pressure increasing, promoting CO formation. In T-CO₂, except for factors in T-N₂, elevated pressure enhances CH₂*+CO₂ \rightleftharpoons CH₂O+CO, strengthening CO emissions.

For NO emissions, elevated pressure promotes NO emissions in traditional conditions. NO is increased by 10 times when pressure increases from 1 to 10 atm. This is due to thermal-NO path controlling NO formation. However, interestly, in MILD-N₂ and MILD-CO₂, with pressure increasing, EINO firstly increases and then decreases. And the maximum EINO are obtained at $P \approx 3$ atm for both the N₂ and CO₂ dilution. Through sensitivity analysis for NO, chain raction H+O₂ \rightleftharpoons O+OH plays the most significant role in the reduction of NO. Recombined reaction H+O₂(+M) \rightleftharpoons HO₂(+M) plays the most significant role in the reduction of NO. In previous work on MILD, lower than critical pressure (3 atm), H+O₂ \rightleftharpoons O+OH is stronger than H+O₂(+M) \rightleftharpoons HO₂(+M). Elevated pressure promotes NO emissions. However, when higher than critical pressure, the recombined reaction is stronger than chain reaction. Then, more NO is produced with pressure increasing.



4.3 Effect of pressure on relative importance of NO formation and destruction

Figure 5 Calculated absolute and relative importance of NO formations and reductions via thermal, prompt, N₂O-intermediate and re-burning routes of counter-flow diffusion model using USC Mech II-2.11NO_x mechanism under different combustion mode and different pressure

Figure 5 displays the effect of pressure on absolute and relative importance of NO formations and reductions through thermal, prompt, NNH, N₂O-intermediate and re-burning routes with USC-Mech II-2.11 NO_x under different combustion mode. In conventional combustion modes (T-N₂ and T-CO₂), thermal-NO play the first important role. However, as for MILD-N₂ and MILD-CO₂, due to the lower peak temperature, thermal-NO are obviously suppressed, through pressure is increased up to 10 atm. In these two modes, thermal-NO nearly can be neglected. Due to different diluents, MILD-N₂ and MILD-CO₂ have different controlling mechanism. In MILD-N₂ case, prompt and N₂O-intermediate path control NO formation in the meanwhile, both contribution ratios are about 40 %, through contribution ratio of prompt path is slightly higher at low pressure (lower than 7 atm). With pressure increasing, in MILD-N₂, NO formation through prompt-NO increases at first and then decreases. The peak prompt-NO formation occurs at about 3 atm. This is due to reaction rate of key steps of prompt path in MILD-N₂: N+OH \rightleftharpoons NO+H, CH+N₂ \rightleftharpoons HCN+N increasing at

lower than 3 atm and decreasing at higher than 3 atm. In MILD-CO₂, the contribution ratio of prompt path is obviously reduced. N₂O-intermediate path controls NO formation, contributing to higher than 60 % NO formation. With pressure increasing, N₂O-intermediate path increases at first and then decreases. The NO formation peak of N₂O-intermediate occurs at 3 atm. This is due to reaction rate of key steps of N₂Ointermediate path: N₂+O(+M) \rightleftharpoons N₂O(+M), N₂O+H \rightleftharpoons NH+NO, NH+O \rightleftharpoons NO+H increasing when lower than 3 atm and decreasing at higher 3 atm. Whether under MILD-N₂ or MILD-CO₂, with pressure increasing, contribution ratio of NO-reburning is gradually enhanced. This is mainly due to reaction rate of key step of NO-reburning: NO+HCCO \rightleftharpoons HCNO+CO, increasing with pressure. Even when higher than 5 atm, higher than 50% NO can be reduced through NO-reburning path. At different pressure, contribution ratio of NOreburning path in N₂ diluent is about 20 % higher than that in CO₂ diluent case. This is mainly due to CH and CH₂(s) consumed in CO₂ diluent. Less CH and CH₂(s) weakens reactions of CH, CH₂(s) and NO:CH+NO \rightleftharpoons HCN+O,CH+NO \rightleftharpoons H+NCO,CH+NO \rightleftharpoons N+HCO,CH₂(s)+NO \rightleftharpoons H+HNCO,CH₂(s)+NO \rightleftharpoons OH +HCN, CH₂(s)+NO \rightleftharpoons H+HCNO. Therefore, NO-reburning in MILD-CO₂ is weaker than that in MILD-N₂.

5 Conclusions

In the present work, effects of pressure on temperature, NO and CO emissions are emphatically discussed in counter-flow flame. Four conclusions can be made after detailed validations as follow:

(1) At elevated pressure, for same kind of diluent (N_2 or CO_2), MILD combustion (MILD- N_2 or MILD- CO_2) can obviously reduce CO emissions by up to 88% and NO emissions by up to 90%, compared to traditional combustion (T- N_2 or T- CO_2 , respectively).

(2) Under traditional combustion (T-N₂ and T-CO₂), NO emissions are obviously increased by 10 times when pressure is increased from 1 to 10 atm. However, interestingly, NO emissions in MILD combustion (MILD-N₂ and MILD-CO₂) increase at first and then decrease, reaching the peak at 3 atm.

(3) Promote path controls NO formation in pressurized MILD-N₂ case, while N₂O-intermediate dominates NO formation in pressurized MILD-CO₂ case.

(4) The peak of NO formation occurs at 3 atm, due to the competition between chain reaction (H+O₂ \rightleftharpoons O+OH) and recombination reaction (H+O₂(+M) \rightleftharpoons HO₂(+M)).

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