

Effects of Flue Gas Addition on the Premixed Oxy-Methane Flames

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Abstract

This numerical study investigates the flame characteristics of premixed methane with various flue gas additions in order to simulate oxy-fuel or oxy-combustion of hydrocarbon fuels with flue gas recirculation system. In general, a flue gas consists of high concentration carbon dioxide (and water steam) and high gas temperature. The diluent gas in oxy-combustion has been changed compared with air-combustion, so that the flame behavior and combustion characteristics of oxy-fuel must be influenced. The effect of laminar burning velocity and adiabatic flame temperature on flue gas addition has been discussed via using Chemkin-pro simulation. By observing the resultant flame temperature and species concentration profiles, the results indicate the shifts on flame location and concentration distribution of major chemical radicals. It means a change of flame structure and flame chemical reaction paths with flue gas addition. The reaction step R99 ($\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$) of premixed methane flame is significantly reduced due to the flue gas recirculation. Furthermore, sensitivity analysis of burning velocity shows that the important reaction step is R38 ($\text{O}_2 + \text{H} \rightarrow \text{O} + \text{OH}$).

Keywords: Flue gas, flame structure, oxy-fuel, oxy-combustion, laminar burning velocity.

1. Introduction

Owing to the rising of the environmental protection awareness, oxy-combustion in the last decade has been widely discussed [1, 2]. The concept of combined post-combustion emission recycling with carbon dioxide capture has been the most attentive scheme for power generation system in present. Therefore, to retrofit the traditional coal-fire or nature gas-fire power generator to oxy-combustion has become an increasing subject. Oxy-combustion is to recuperate the flue gas as diluent gas to replace nitrogen in air, and to obtain high concentration of carbon dioxide and water steam in downstream flue gas [3, 4]. Nevertheless, carbon dioxide and water steam in hydrocarbon fuel as diluent gas would alter the flame behaviors via three effects, dilution effect, thermal effect and chemical effect. Principally, dilution effect is to reduce the concentration of oxygen in reaction zone and further influence the reaction rate, and thermal effect is caused by the difference in thermal capacity and thermal radiation, and the chemical effect is to increase the radical concentration and further shift the chemical pathway.

Kimura et al. [5] discovered that the ignition delay and flame instability would occur in oxy-combustion condition, and proposed that an increase of gas temperature and oxygen concentration in flue gas can mitigate the combustion instability. Besides, the increasing percentage of water steam in flue gas can improve the combustion efficiency of oxy-fuel flame. Payne et al. [6] use a pilot-scale furnace to compare the gas emission of oxy-combustion with dry and wet flue gas recirculation system. It is noted that the reduction of NO_x emission in dry flue gas recirculation system approaches to 70% while the CO_2/O_2 mole fraction is 2.7. However, NO_x emission in wet flue gas recirculation decreases 83% while the $(\text{CO}_2 + \text{H}_2\text{O})/\text{O}_2$ mole fraction is 3.2. In general, the combustion efficiency of wet flue gas recirculation is prior to that of dry flue gas recirculation. Compared to nitrogen, carbon dioxide and water steam would be pre-dissociated in a high temperature region of oxy-combustion, and lead to shift the chemical pathway. Haler et al. [7] experimentally and numerically investigated the flame behaviors of methane/air in CO_2 -diluent, N_2 -diluent, and CO_2 - N_2 -diluent (71.6% N_2 + 28.4% CO_2). It

found that CO₂-diluent has inherently high thermal capacity compared to N₂-diluent, and induces pre-dissociation phenomenon.

Considered the effect of CO₂-diluent flames in flame reaction rate, Liu et al. [8] used fictitious inert gases (FCO₂), which only possess heat capacity and thermal transport, but do not participate in the chemical reaction, to compare with the real carbon dioxide. It appears that the flame burning velocity with fictitious inert gas is lower than that with real carbon dioxide. It points out that carbon dioxide participates in the chemical reaction by interfering with key chemical step R99, and leads to flame burning velocity reduction. Similarly, Mazas et al. [9] discussed the effect of water steam addition in premixed methane/air flame, and found the chemical effect in flame burning velocity, especially in fuel lean and near-stoichiometric condition.

Accordingly, there are three parameters to influence the combustion efficiency of oxy-fuel, namely CO₂/O₂ mole fraction, temperature of flue gas and water steam content in flue gas. These parameters are crucial in design of oxy-fuel combustor. This study would numerically discuss the effect of flue gas additions in flame burning velocity of methane/oxygen flame. Various dilution concentrations of carbon dioxide, nitrogen, water steam, and flue gas (33%CO₂+67%H₂O) in oxy-combustion are considered. The shift of flame structure in various inert gas dilutions is also investigated.

2. Numerical method

The PREMIX code of Chemkin collection is used to calculate the adiabatic, unstrained, free propagation velocities of the laminar premixed CH₄/air/H₂O₂ flames. It solves the equations governing steady, isobaric, quasi-one-dimensional flame propagation. The equations are written as follows:

Continuity:

$$\dot{M} = \rho u A$$

Energy:

$$\dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^K \dot{w}_k h_k W_k = 0$$

Species:

$$\dot{M} \frac{dY_k}{dx} + \frac{d}{dx} (\rho A Y_k V_k) + A \dot{w}_k W_k = 0 \quad (k = 1, \dots, K_g)$$

Equation of state:

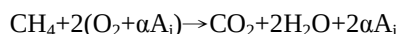
$$\rho = \frac{P M}{R T}$$

In addition, the adiabatic flame temperature is calculated by using the EQUIL code of the Chemkin collection. An initial reactant mixture is specified and equilibrium of constant enthalpy and constant pressure is constrained. To obtain accurate adiabatic flame temperature, besides reactants and products, all radical species that might occur in the flame are also included.

The GRI-Mech 3.0 chemical kinetic mechanism composing of 53 chemical species and 325 reaction steps and detailed transport properties are used without any modifications. The reaction rate constant is represented by the modified Arrhenius expression,

$$k = A T^b \exp\left(\frac{-E_a}{RT}\right)$$

At the cold boundary, the unburned reactants are supplied at 400 K and 1 atm. This temperature is above the boiling temperature of H₂O and it will make all reactants to be in gas phase. The CH₄/O₂ reaction with different gas addition is defined as:



A_i is the gas addition and 2α is the mole number. In the study, the gas addition includes N₂, CO₂, H₂O and flue gas. The number of α is between 0.25 and 3.0. Since the complete reaction of one mole CH₄ produces one mole CO₂ and two moles H₂O, the composition of flue gas is fixed with 33%CO₂ and 67%H₂O.

3. Results and Discussion

3.1. Laminar burning velocity

Figure 1a shows the laminar burning velocities of various inert gas additions ranging from 25% to 300% oxygen. It is noted that carbon dioxide dilution would obviously restrain flame burning velocity compared to

nitrogen dilution. The difference of laminar burning velocity in various inert gas additions causes by heat capacity difference and chemical effect. Depending upon decreasing diluent/oxygen percentage, especially below 150% of diluent/oxygen, laminar burning velocity is significantly increasing. While the ratio of diluent/oxygen is 200, flame burning velocity of carbon dioxide-diluent is approximately 0.39 m/s, which is similar to 0.4 m/s of methane/air stoichiometric flame. Therefore, discussion of flame structure shifts is considered at 200% CO₂-diluent condition.

3.2. Adiabatic flame temperature

Figure 1b indicates the adiabatic flame temperature of various inert gas additions ranging from 25% to 300% oxygen. Similarly, carbon dioxide dilution would obviously restrain flame temperature compared to nitrogen dilution. It is due to heat capacity difference of diluent inert gas. It is well-known that CO₂ (37 J/mol · K) > H₂O (33 J/mol · K) > N₂ (21 J/mol · K). When the diluent/oxygen ratio is 300, the flame temperature difference is large. Depending upon the decreasing diluent/oxygen ratio, flame temperature difference becomes smaller. It is noted that there is only 100K different between various inert gas dilutions when the diluent/oxygen ratio is only 25%, and flame temperatures for all diluents are above 2800K. Nonetheless, according to Fig. 1a, laminar burning velocities among various inert gas dilutions have certainly different. The flame velocity of CO₂-diluent at 25% of diluent/oxygen ratio is 3 m/sec, but that of H₂O is 3.8 m/sec. It means that fuels probably have dissociation phenomenon in high temperature surrounding, and lead to release amount of radicals. These radicals accelerate chemical reaction and influence flame burning velocity.

3.3. Sensitivity analysis of the burning velocity

In order to further understand the effect of chemical reaction on the flame speed of methane flame with various inert gas dilutions, the first-order sensitivity analysis of laminar burning velocity is shown in Fig. 2. R38 is a dominant chain branching reaction step in sensitivity analysis, especially in CO₂-diluent, H₂O-diluent and flue gas-diluent. Besides, R55 is a second prominent reaction step in sensitivity analysis, and is an initiation reaction step of methane in low temperature surrounding. Regarding to R99, it is a key reaction of carbon monoxide oxidation, and it has high exothermicity. In nitrogen-diluent and H₂O-diluent conditions R99 is third prominent reaction step of methane combustion, but R119 would be a third prominent reaction step in a CO₂-diluent and flue gas-diluent condition. In general, the present of R99 can improve the reaction, and enhance the flame speed. R119 is a key reaction step of CH₃ oxidation close to ignition. It appears that high concentration of carbon oxide surrounding would modify the chemical reaction of methane flame.

3.4. Major species and intermediate radicals

Figure 3a displays the numerical results of carbon dioxide production rate along axial direction for various inert gas dilutions. Total rate of production (black line) is coincident with R99 (green line). It appears that R99 in N₂-diluent is larger than others. Then, in CO₂-diluent and flue gas-diluent condition, R99 has apparently decreasing tendency. Especially, the amount of R99 in CO₂-diluent condition is much low than that in N₂-diluent condition. When carbon dioxide is a diluent gas, it would promote the reverse reaction of R99, and decelerate the net reaction rate of R99. Nevertheless, R153 would be enforced as in CO₂-diluent condition.

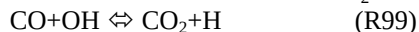


Figure 3b displays the numerical results of water steam production rate along axial direction for various inert gas dilutions. It shows that total rate of production in a N₂-diluent condition is larger than others, and R84 (orange line) is dominant production rate step. In a H₂O-diluent condition R84 would apparently diminish, and R98 (purple line) would be prominent production rate step. However, in a CO₂-diluent condition R98 and R84 become equal. Reason is probably related to radical concentration of H and CH₃. Otherwise, R86 (green line) is primary chain termination, and it would be enlarged in H₂O-diluent condition.

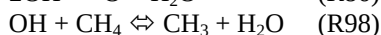
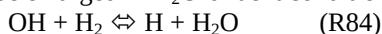


Figure 4a displays the numerical results of carbon monoxide production rate along axial direction for various inert gas dilutions. It shows that in a N₂-diluent condition R284 and R144 are primary production rate step and secondary is R168 and R166. In a H₂O-diluent condition the total rate of production is decreasing, and R166 becomes a primary production rate step, and R284 and R144 are decreasing. In a CO₂-diluent condition the

total production rate is sharply decreasing, but R166 is still a prominent production rate step. As to flue gas dilution, the total production rate is located between H₂O-diluent and CO₂-diluent condition, and R166 is also a dominant production rate step. Besides, due to reverse reaction of R99, CO concentration is increasing in a CO₂-diluent condition.

Figure 4b displays the numerical results of O production rate along axial direction for various inert gas dilutions. In a H₂O-diluent condition R86 becomes a consumption reaction, and yields a lot of OH radicals. It leads to enhance the reverse reaction of R38, and further reduces the concentration of OH radical. In a CO₂-diluent condition the reverse reaction of R99 would be increased and competes with R38 for radical H. It affects the concentration of O and OH radicals, and limits to offer O radicals to R10 and R3. In a flue gas-diluent condition R86 is also a primary consumption reaction step and apparently increased due to water addition.

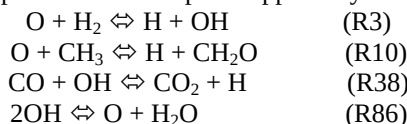


Figure 5a displays the numerical results of H production rate along axial direction for various inert gas dilutions. In a H₂O-diluent condition the total production rate becomes weak, and R166 becomes a primary production reaction, and R84 becomes a secondary production reaction. It appears that adding water in inert gas results in increasing reverse reaction of R84 and both reactions of R166. In a CO₂-diluent condition the total production rate is extensively reducing, and R86 is still a primary production rate step. However, R38 is decreasing due to decreasing OH and H radicals. It causes to reduce the production of H radicals providing from R84. In a flue gas-diluent condition the total production rate is located between H₂O-diluent and CO₂-diluent condition, and R166 becomes a secondary production rate step.

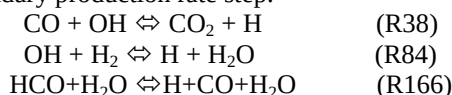


Figure 5b displays the numerical results of OH production rate along axial direction for various inert gas dilutions. In a H₂O-diluent condition the total production rate becomes weak, and R38 becomes a primary production reaction, and R86 replaces R3 to become a secondary production reaction step due to water addition. R98 becomes the primary consumption reaction and R84 becomes a secondary one. In a CO₂-diluent condition the total production rate is extensively reducing, and R38 is still a primary production rate step. However, R98 and R84 are fairly equal due to OH radical competition. In a flue gas-diluent condition the total production rate is located between H₂O-diluent and CO₂-diluent condition, and R38 and R86 are top two production reaction step, while R98 and R84 are top two consumption reaction step.

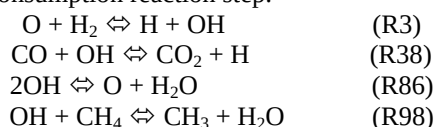
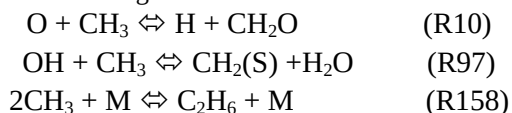


Figure 6 displays the numerical results of CH₃ production rate along axial direction for various inert gas dilutions. Production reaction of CH₃ is related to consumption reaction of CH₄. In a N₂-diluent condition R53 is a primary production reaction step. Nevertheless, in a H₂O-diluent condition R98 becomes a primary production reaction step due to increasing concentration of OH radical. R10 is reduced due to decreasing O radicals. Correspondingly, R158 becomes a prominent production reaction. In a CO₂-diluent condition R98 is primary production reaction step due to H radical limitation from R53. The consumption reaction of R10 and R97 are also influenced by limiting OH and O offering.



4. Conclusions

In this work, we discuss the various inert gas dilutions in methane oxy-combustion, CO₂-diluent, H₂O-diluent, N₂-diluent and flue gas-diluent case, respectively. According to sensitivity analysis, R38 is a dominant chain branching reaction step, while R52 is a prominent reaction step to restrain flame speed. R99 is a third reaction step and provides principal exothermicity for N₂-diluent and H₂O-diluent case, while R119 is a third reaction step for the other two cases. Besides, production rate of major species and intermediate radicals is

further discussed and compared with various inert gas dilutions. Results show the primary production and consumption reaction steps for different inert gas dilution are shifted.

6 Acknowledgements

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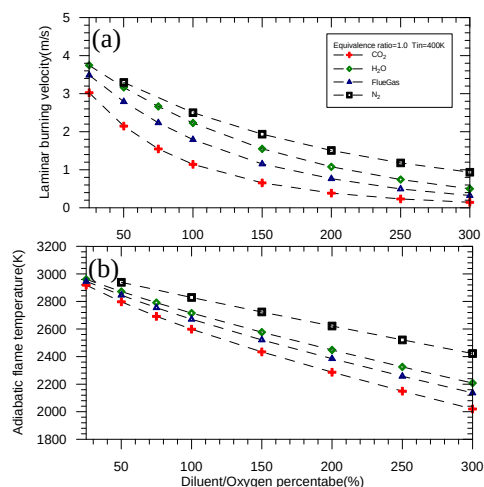


Figure 1. (a) Laminar burning velocity in various inert gas additions; (b) adiabatic flame temperature in various inert gas additions.

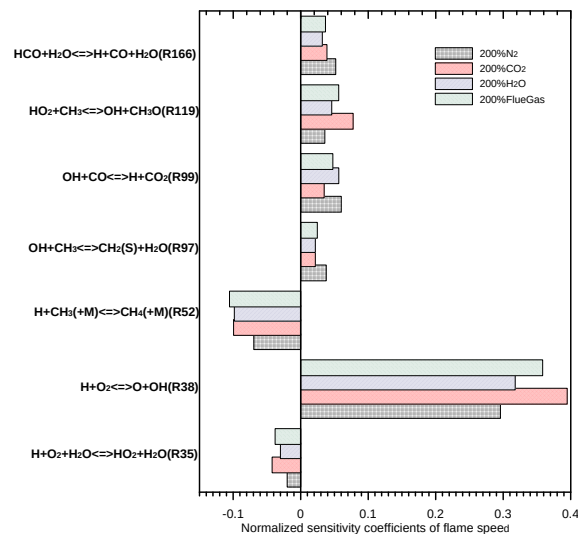


Figure 2. Sensitivity analysis of the laminar burning velocity for various inert gas dilutions

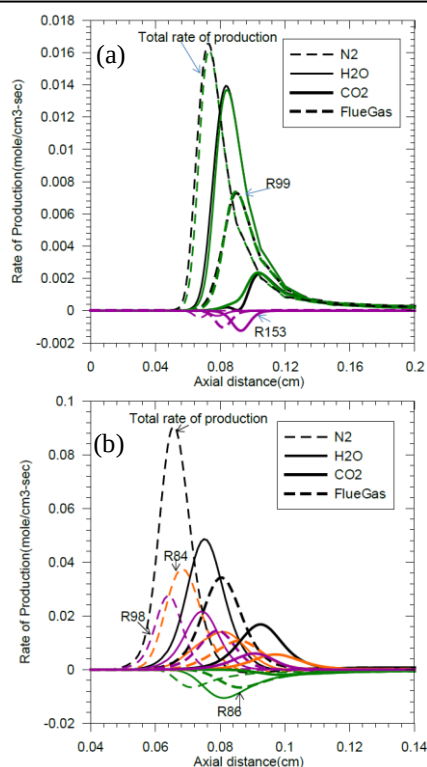


Figure 3. Effect of inert gas dilution on different production rate. (a) CO₂ production rate; (b) H₂O production rate.

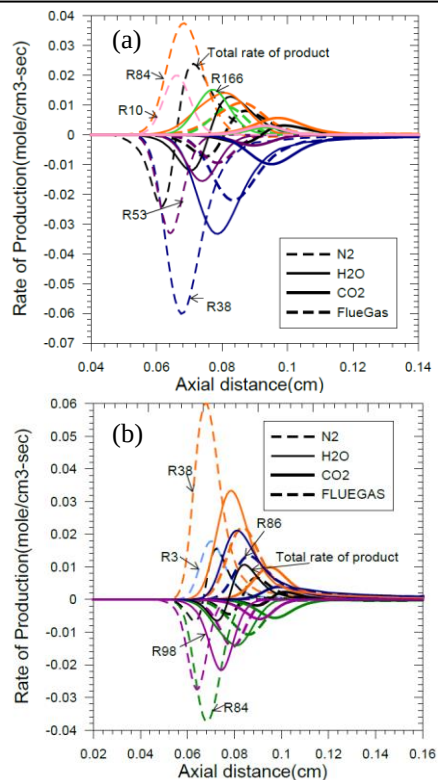


Figure 5. Effect of inert gas dilution on different production rate. (a) H production rate; (b) OH production rate.

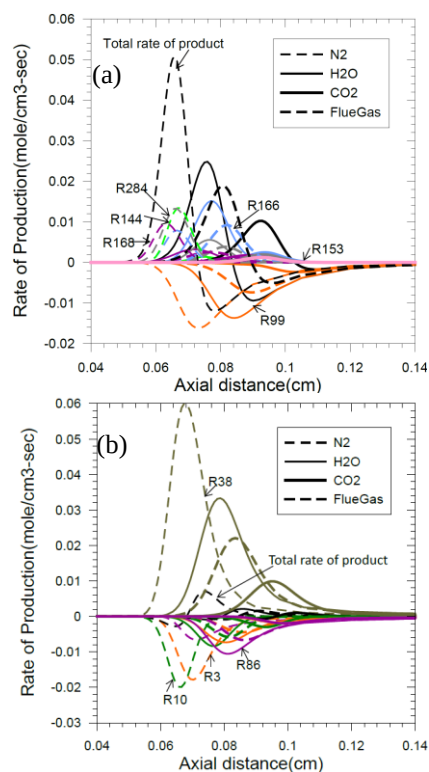


Figure 4. Effect of inert gas dilution on different production rate. (a) CO production rate; (b) O production rate.

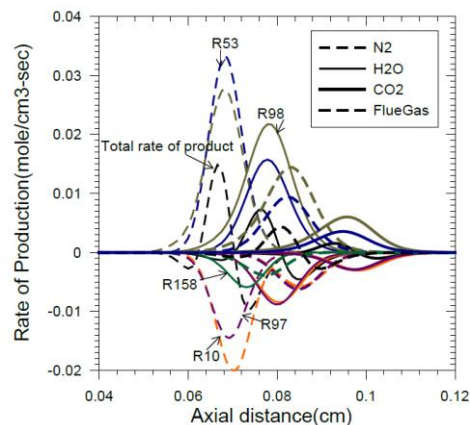


Figure 6. Effect of inert gas dilution on OH production rate.