

Analysis of chemical-induced irreversibility in premixed counterflow CH₄/CO/air flame

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1 Introduction

Due to the energy crisis concerned in recent years, there are more and more researches focused on gasified biomass. As a kind of alternative to fossil fuel, its sustainability, reliability, and waste reduction attract researchers' attention. The composition of gasified biomass mainly consists of methane, carbon monoxide, hydrogen, and nitrogen, but it depends on the fuel sources and manufacturing process on a case-by-case basis. The concern about flame characteristics of CO addition on premixed CH₄/air flame was studied by many researchers, and these studies emphasized the importance of studying the CH₄/CO/air flame[1, 2]. The non-equilibrium second law of thermodynamics, as an analysis method compared with the First law of thermodynamics one, can investigate the energy not only in quantity but also in quality in the point of view of exergy, which introduced the energy degradation and cannot be studied by the First law of thermodynamics[3]. Recent studies mainly focused on the exergy loss induced by chemical reactions, heat conduction, mass diffusion, and viscous dissipation[4, 5, 6], but seldom discuss the detail for each effect. In the present study, the characteristics of chemical-induced irreversibility, as known as exergy loss, are discussed in the room temperature and atmosphere. The irreversibility caused by each chemical reaction can be found. In addition, an empirical formula was concluded. By this formula, the irreversibility caused by the chemical reaction can be evaluated easily. In conclusion, this study hopes to give biomass combustion a more comprehensive understanding and application.

2 Methodology

In this study, the numerical simulation was calculated by Chemkin 2020 R1 coupled with San Diego mechanism[7], which has been applied in many studies and the results noted that the simulation result fitted the experiment one appropriately[8]. Laminar burning velocity was calculated using the PREMIX code. The chemical-induced irreversibility was studied using counterflow flame with OPPDIF package, and the distance between the two nozzles was set as 20 mm. The ambient pressure and initial gas temperature were set as 1 atm and 298K for each case. By the feature of premixed symmetric counterflow flame, only one side of flame was discussed in the following content.

Background theory

The non-equilibrium local irreversibility generation caused by each chemical reaction[9] can be modified as following form:

For forward reaction, the chemical-induced entropy for species i in reaction j can be expressed as following form:

$$s_{F,j} = -\sum_i \frac{\mu_{F,i} \varepsilon_{F,i} \dot{\omega}_{F,i}}{T} - \sum_i \frac{\mu_{R,i} \varepsilon_{R,i} (-\dot{\omega}_{R,i})}{T}$$

For reverse reaction, the chemical-induced entropy for species k in reaction j can be expressed as following form:

$$s_{R,j} = -\sum_k \frac{\mu_{F,k} \varepsilon_{F,k} (-\dot{\omega}_{F,k})}{T} - \sum_k \frac{\mu_{R,k} \varepsilon_{R,k} \dot{\omega}_{R,k}}{T}$$

where the subscript F and R were the abbreviation of forward and reverse reaction.

The chemical potential for the specific species i or k in reaction j , written as μ , can be presented as following form:

$$\mu_{i(k),j} = h_{i(k)}(T) + Ts_{i(k)}(T) + RT \ln\left(\frac{X_{i(k)} P}{P_0}\right)$$

where h , s , T , R , X_k , P and P_0 were the enthalpy formation, entropy, temperature, gas constant, mole fraction for species i or k , pressure and standard atmospheric pressure, respectively.

Then the irreversibility can be written as

$$i = T_0 s$$

To get the overall irreversibility in the whole reaction zone, an intergal formula was used here.

$$i_{overall} = \int_x (i_F + i_R) dx$$

3 Results and discussions

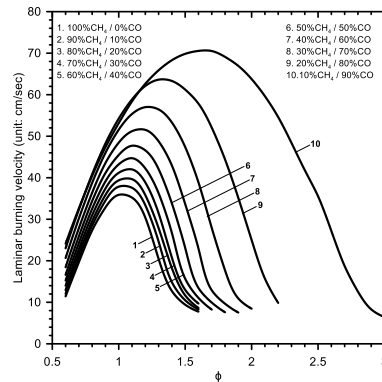


Figure 1: Computed laminar burning velocity of CH₄/CO/air flames versus equivalence ratio with different CO content from 0% to 90% in the fuel mixture.

As Figure 1 shown, for each case, the flammability range increases gradually as the CO content increases. It is worth noting that the laminar burning velocity increases gradually from 0% to 80% CO content then decreases slightly at 90% CO content when the equivalence ratio equals 1.

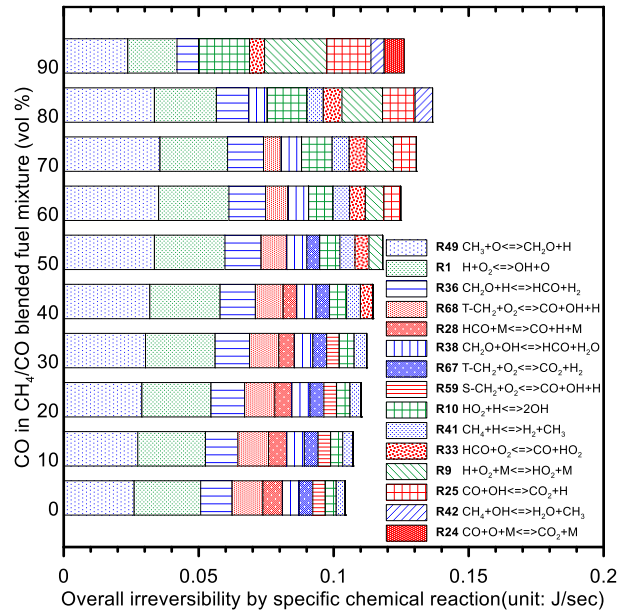


Figure 2: Chemical-induced irreversibility for top 10 contributed reactions in various CO content in fuel. The equivalence ratio and stretch rate were set as 1 and 200(1/s).

The irreversibility caused by the chemical reaction was illustrated in Figure 2. To observe the main irreversibility caused by specific chemical reaction precisely, only the top 10-generated irreversibilities were listed. As shown in the figure, the CO content increased, the irreversibility caused by chemical reaction increased between 0% to 80% CO content but decreased slightly when the CO content was at 90%. A similar tendency could be observed as laminar burning velocity. Another issue was that the irreversibility was mainly caused by R49($\text{CH}_3+\text{O} \rightleftharpoons \text{CH}_2\text{O}+\text{H}$), R1($\text{H}+\text{O}_2 \rightleftharpoons \text{OH}+\text{O}$), and R36($\text{CH}_2\text{O}+\text{H} \rightleftharpoons \text{HCO}+\text{H}_2$) regardless of the CH₄ content. R25($\text{CO}+\text{OH} \rightleftharpoons \text{CO}_2+\text{H}$) appeared only when CO content was higher than 60%, and R24($\text{CO}+\text{O}+\text{M} \rightleftharpoons \text{CO}_2+\text{M}$) only appeared when CO content was as high as 90%. R68($\text{T-CH}_2+\text{O}_2 \rightleftharpoons \text{CO}+\text{OH}+\text{H}$) decreased as the CH₄ content decreased and finally disappeared when CO content was as high as 80%.

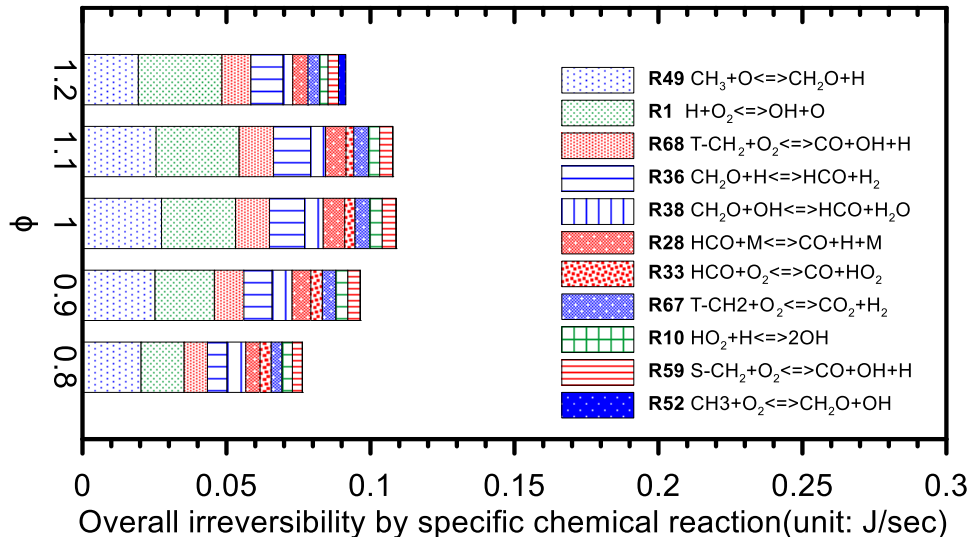


Figure 3: Chemical-induced irreversibility for top 10 contributed reactions in different equivalence ratio. The CO content in fuel and stretch rate were set as 0% and 100(1/s).

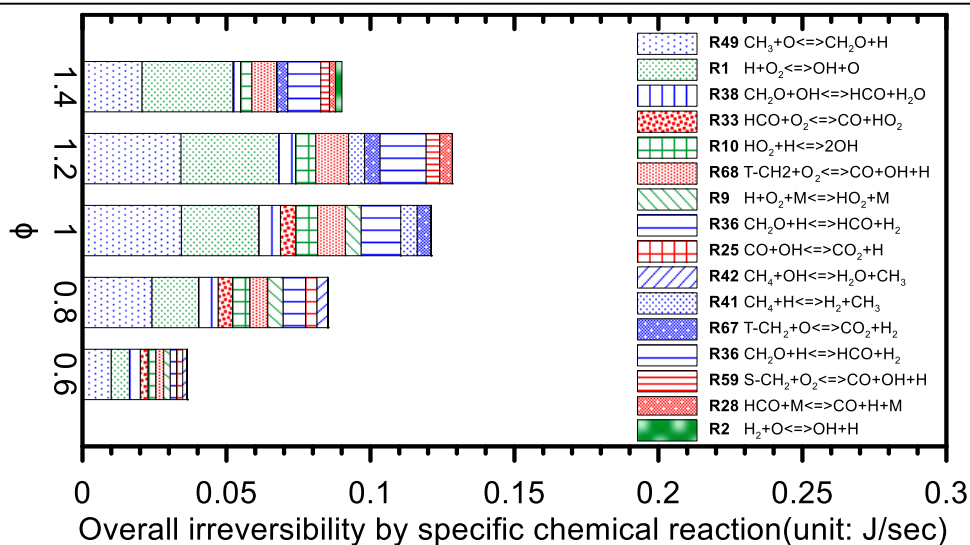


Figure 4: Chemical-induced irreversibility for top 10 contributed reactions in different equivalence ratio. The CO content in fuel and stretch rate were set as 50% and 100(1/s).

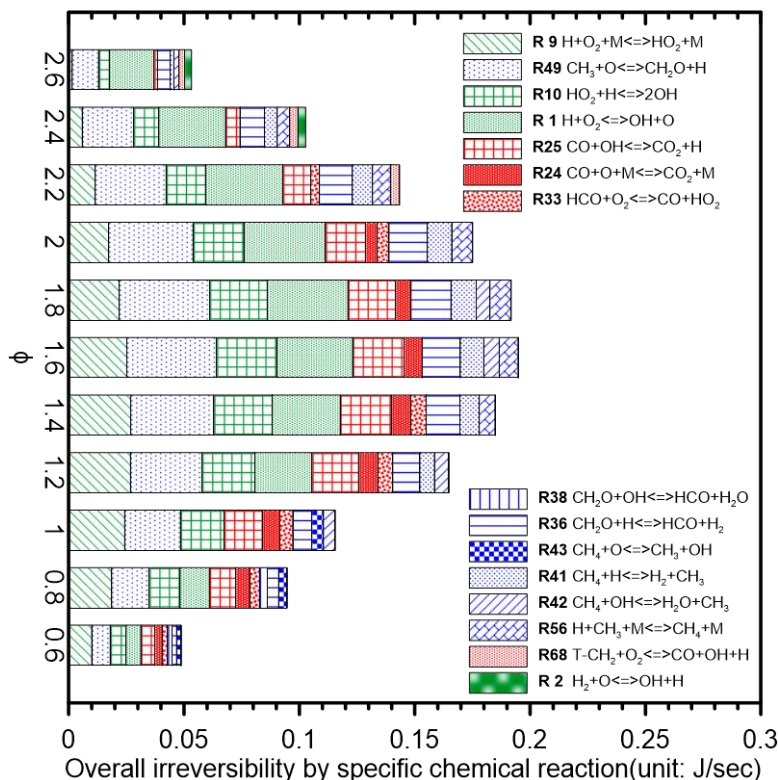


Figure 5: Chemical-induced irreversibility for top 10 contributed reactions in different equivalence ratio. The CO content in fuel and stretch rate were set as 90% and 100(1/s).

As shown in Figure 3, Figure 4, and Figure 5, the tendency of irreversibility caused by chemical reaction versus equivalence ratio was much the same as the laminar burning velocity shown in Figure 1. A compelling finding was that the irreversibility caused by R9($\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$) and R10($\text{HO}_2 + \text{H} \rightleftharpoons 2\text{OH}$) increased obviously when CO content was as high as 90%. The irreversibility caused by R24($\text{CO} + \text{O} + \text{M} \rightleftharpoons \text{CO}_2 + \text{M}$) and R25($\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$) were not obvious when CO content was 50%, and they became slightly higher when CO content was 90%. In conclusion, the irreversibility caused by CO-related reaction was not obvious and was still occupied mainly by R9 and R49.

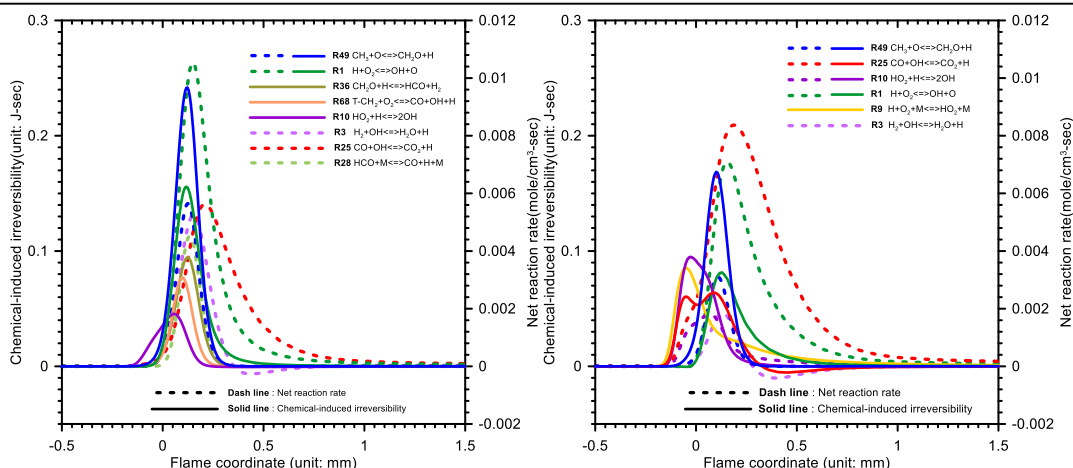


Figure 6: The distributions of irreversibility caused by chemical reaction and net reaction rate for the main five reactions in flame coordinate. The equivalence ratio and stretch rate for each case was set as 1 and 100(1/s). Left: CH₄/CO=50%/50%, Right: CH₄/CO=10%/90%

Figure 6 illustrated the distribution for net reaction rate and chemical-induced irreversibility. To discuss the phenomenon in simplicity, only the main five reactions, for the reaction rate and irreversibility separately, were listed. As the figure on the left-hand side shown, R49(CH₃+O \rightleftharpoons CH₂O+H) contributed the most irreversibility above each reaction, yet the reaction rate was not the largest one upon each reaction. Comparing the reaction rate for R25(CO+OH \rightleftharpoons CO₂+H) in Figure 6, it increased obviously when CO content increased to 90%. However, the irreversibility caused by R25 was not as high as its reaction rate. To conclude, the irreversibility was affected by reaction rate but not the main impact factor. The chemical potential for the species in the reaction should also be taken into consideration.

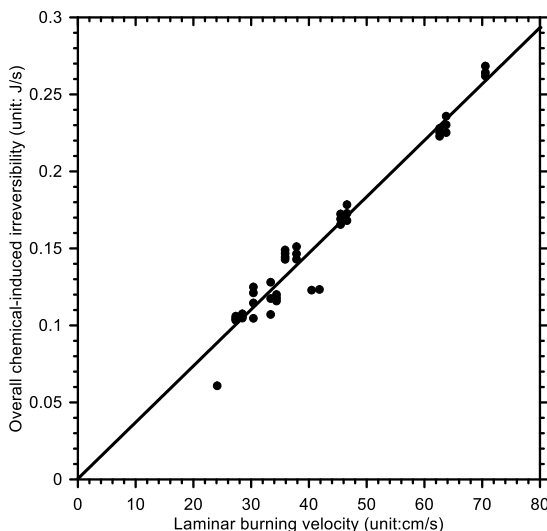


Figure 7: The relationship between laminar burning velocity and chemical-induced irreversibility.

By combing the abovementioned results, a linear empirical formula is summarized. The laminar burning velocity was linearly proportional to overall chemical-induced irreversibility in the room temperature and atmosphere. The empirical formula can be written as:

$$i_{overall} = 0.00366v$$

where v is laminar burning velocity in the units of cm/s .

The irreversibility caused by the chemical reaction can be easily obtained by laminar burning velocity without considering the proportion of CH₄/CO blended fuel.

4 Conclusions

The irreversibility caused by detailed chemical reactions in one-dimensional premixed CH₄/CO binary fuel combustion is firstly discussed. Some comprehensive conclusions can be drawn in the following:

1. The laminar burning velocity is proportional to overall chemical-induced irreversibility.
2. CO-related reactions are not the main-caused irreversibility, Y even when the CO content is as high as 90%.
3. The chemical potential and reaction rate should be considered together for the calculation of the irreversibility caused by the chemical reaction. For the reaction with high reaction rate doesn't necessary mean a high irreversibility.
4. An empirical formula is proposed in this study. The irreversibility caused by the chemical reaction can be obtained easily by laminar flame velocity.

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