Numerical Analysis of Extremely-rich CH₄/O₂/H₂O Premixed Flames at High Pressure and High Temperature Considering Production of Higher Hydrocarbons*

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Abstract
Numerical analysis of CH₄/O₂/H₂O laminar premixed flame under various conditions of pressure, equivalence ratio and steam concentration was performed using GRI-Mech 3.0 and the mechanism proposed by Davis and Law, which consists of C1 to C6 hydrocarbons in addition to GRI-Mech 3.0. The pressure dependence of laminar burning velocity and flame structure under fuel-rich conditions was focused on. Effects of the formation of higher hydrocarbons under fuel-rich conditions were also clarified using the mechanism proposed by Davis and Law. Results showed that for extremely fuel-rich conditions, laminar burning velocity increases as pressure increases for both mechanisms. The increase of laminar burning velocity is caused by the shift of the oxidation pathway of CH₃ radical from the C2 Route to the C1 Route. The formation of C3-C6 hydrocarbons has only a small effect on laminar burning velocity. Under fuel-rich conditions, super-adiabatic flame temperature (SAFT) occurs and its pressure dependency was clarified.

Key words: Fuel-rich Premixed Flames, Pressure Effect, Steam Dilution Effect, Super-adiabatic Flame Temperature, Higher Hydrocarbons

1. Introduction
Oxy-fuel combustion is one of the most promising combustion technologies which are advantageous for obtaining a high temperature for extensive radiation heat transfer, no NOx emission and low levels of flue gas and is also applicable to carbon capture and storage (CCS). As for chemical processes, oxy-fuel combustion can be considered as an elementary process of the auto-thermal reformer (ATR) for production of synthesis gases for Gas-To-Liquids (GTL) plants. In ATR using methane in natural gas, the following overall oxidation reaction and partial oxidation reaction occur under fuel-rich conditions:

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]
\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \]
which are exothermic reactions and have relatively large reaction rates. The steam
reforming reaction,
\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2, \]
which is endothermic and has a relatively small reaction rate, also occurs using the heat
generated by the above-mentioned oxidation reaction and partial oxidation reaction. The
differences of the reaction rate and the heat of reaction between these three reactions cause
a temperature decrease in the products, i.e., hydrogen and carbon monoxide. Hydrogen is
further produced by the following water gas shift reaction:
\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2. \]
Accordingly, steam in combination with oxy-fuel combustion plays a significant role in
ATR.

To increase hydrogen yield, ATR with higher water vapor concentration is operated at a
high pressure of around 3.0 MPa and a high temperature of about 500 K, and the optimum
equivalence ratio is much higher than unity, i.e., close to 3.0. In the case of oxy-fuel
combustion, the flammability limits are much wider and burning rate is higher than those of
ordinary fuel-air combustion. To design safety ATR systems, therefore, information on the
combustion characteristics in such an extreme condition is required. Among the combustion
characteristics, laminar burning velocity, which is the most fundamental one, is important
because it is necessary to determine the residence time of the reactants in the reforming
catalyst embedded in practical reformers.

In addition to the practical viewpoints mentioned above, characteristics of laminar
burning velocity and the effect of the reaction mechanism under such an extreme condition
are interesting. Raghu et al. [1] have performed calculations and experiments for
\( \text{CH}_4/\text{C}_2\text{H}_6/\text{O}_2/\text{NO} \) flames under the conditions of equivalence ratio of 1.5 at pressure of 1.0
MPa in jet stirred reactor (JSR). In their calculations, the detailed mechanism proposed by
Tranter et al. [2] based on GRI-Mech 3.0 [3] was used. They reported that the experimental
results for concentration profile in JSR were relatively good agreement with calculation.
However, they didn't validate about laminar burning velocity.

premixed flames at pressures of 0.5 to 20 atm and for equivalence ratios of 0.6 to 1.5. He
found that the overall reaction order of laminar burning velocity does not change
monotonically with increasing pressure and has a minimum value in the case of \( \text{CH}_4/\text{air} \)
flames. He also concluded that the initial decrease of the overall reaction order is related to
the competition between the following two reactions, R38 and R52, in GRI-Mech 3.0 [3]:
\[ \text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH} \quad \text{(R38)} \]
\[ \text{H} + \text{CH}_3 (+\text{M}) \leftrightarrow \text{CH}_4 (+\text{M}) \quad \text{(R52)} \]
and that the increase of the overall reaction order at higher pressure is predominated by
R119 in GRI-Mech 3.0 [3] :
\[ \text{HO}_2 + \text{CH}_3 \leftrightarrow \text{OH} + \text{CH}_3\text{O} \quad \text{(R119)} \]
However, the increase of laminar burning velocity was not seen in their results under the
conditions of high pressure nor under fuel-rich conditions. Rozenchan et al. [5] measured
and calculated the laminar burning velocity of \( \text{CH}_4/\text{air} \) and \( \text{CH}_4/\text{O}_2/\text{He} \) flames under
conditions of pressure up to 20 atm and 60 atm, respectively, with equivalence ratios of 0.6
to 1.4 for both flames. They used GRI-Mech 3.0 [3] for \( \text{CH}_4/\text{air} \) flames and GRI-Mech 1.2
[6] and GRI-Mech 3.0 [3] for \( \text{CH}_4/\text{O}_2/\text{He} \) flames. In their numerical results at 20 atm,
GRI-Mech 3.0 [3] overpredicted the laminar burning velocity for both flames in the
fuel-rich region. At higher pressures of 40 and 60 atm, both GRI-Mech 1.2 [6] and
GRI-Mech 3.0 [3] further overpredicted under all calculation conditions of the equivalence
ratio. No examination of the difference between the results of measurement and numerical
simulation was done.

In the previous study by our research group [7], the laminar burning velocity of
CH$_4$/O$_2$/H$_2$O mixture was evaluated using GRI-Mech 3.0 [3] under the conditions of pressures of 0.1 to 3.0 MPa, equivalence ratios of 0.4 to 3.0 and steam mole fractions of 0.0 to 0.5. It was found that the laminar burning velocity increased as pressure increased. In oxy-fuel combustion with a large number of H$_2$O molecules, a three-body recombination reaction, R35;

$$H + O_2 + H_2O \leftrightarrow HO_2 + H_2O \quad (R35)$$

was enhanced as pressure increased. HO$_2$ generated from R35 prompts R119. It was concluded that R119 prompted by R35 enhanced the direct oxidation of CH$_4$ to CO$_2$ and the laminar burning velocity increased as pressure increased in the case of a high equivalence ratio. In addition to the interesting variations of laminar burning velocity, super-adiabatic flame temperature (SAFT) [8-11] was observed under certain conditions of pressures and equivalence ratios.

As for the phenomenon of SAFT, Liu and Gülder [10, 11] reported in their papers on numerical analysis using GRI-Mech 3.0 [3] for CH$_4$/air flames that the reactions R38 and R52 play significant roles in SAFT. They also concluded that the effects of exothermic and endothermic reactions, R35 and R119, respectively, become significant at high pressure.

In all the above-mentioned recent research studies, the laminar burning velocity and SAFT were evaluated by GRI-Mech 1.2 [6], GRI-Mech 2.11 [12] and GRI-Mech 3.0 [3]. However, under fuel-rich conditions at high pressure, the production of higher hydrocarbons as a precursor of soot can be expected, while GRI-Mech 1.2 [6] and GRI-Mech 2.11 [12] and the minimum reaction set of C3 hydrocarbons in GRI-Mech 3.0 [3] can be used for evaluation up to C2 hydrocarbons because GRI-Mech 2.11 [12] and GRI-Mech 3.0 [3] are intended to quantify NOx generation intrinsically. Namely, the effects of higher hydrocarbon on the laminar burning velocity and SAFT phenomenon in the case of CH$_4$/O$_2$/H$_2$O premixed flames under high pressure and high equivalence ratio should be clarified using another chemistry which includes higher hydrocarbons with aromatics as a soot precursor seed, something which has not been previously done.

Peter et al. [13, 14] proposed detailed mechanism for CH$_4$/O$_2$ and CH$_4$/C$_2$H$_6$/O$_2$ flames with or without nitrogen monoxide under the conditions of equivalence ratio of approximately 100 at high pressure up to 10.0 MPa. They validate their mechanism using approximate plug flow reactor. Moreover, laminar burning velocity was validated at atmospheric pressure. However, they didn't validate laminar burning velocity for the effects of high pressure and steam dilution. In addition, no discussion was done about the effect of higher hydrocarbons at extremely fuel-rich composition.

In the present study, to clarify the characteristics of oxy-fuel combustion including ATR conditions and features of elementary reactions, numerical simulations of CH$_4$/O$_2$/H$_2$O laminar premixed flame were performed under various conditions of pressure, equivalence ratio and steam dilution ratio. The dependence of laminar burning velocity on pressure was first focused on under the condition of high equivalence ratio, as well as higher steam concentration conditions. Two reaction mechanisms, i.e., GRI-Mech 3.0 [3], which is validated by using experimental data under the various conditions, and the mechanism proposed by Davis and Law [15], which has higher hydrocarbons including benzene, were employed and compared in terms of higher hydrocarbons under ATR conditions. Two types of SAFT phenomenon were also found and examined based on the elementary reactions.

2. Numerical method

Numerical simulations of one-dimensional premixed flame were performed using CHEMKIN-II [16] and PREMIX [17]. The thermodynamic data were taken from the study of Burcat and Rusci [18]. The thermodynamic and transport properties were calculated by CHEMKIN-II [15]. In this work, the effect of radiation heat loss was not considered. To
clarify the role of higher hydrocarbons at high equivalence ratios, as mentioned in the introduction, the detailed reaction mechanism proposed by Davis and Law [15] (denoted by DA Mech [15] in the following) was used as the detailed reaction mechanism. DA Mech [15] consists of 71 chemical species and 469 elementary reactions. The chemical species up to C6 hydrocarbons are included. The numerical results using GRI-Mech 3.0 [3] were compared with the results evaluated by DA Mech [15]. In the present work, nitrogen, nitrogen oxide and its related reactions were not considered.

Sensitivity analysis of laminar burning velocity and reaction path analysis and integral reaction flow analysis suggested by Warnatz [19] were performed in this study.

The calculation conditions of the present numerical simulations cover wide ranges of pressures, $P$, 0.1 to 3.0 MPa, equivalence ratios, $\phi$, 0.4 to 3.0 and steam dilution ratios, $Z_{H2O}$, i.e., steam mole fractions of 0.0 to 0.5. The upstream temperature of the premixed gas, $T_0$, was fixed at 500 K. The equivalence ratio, $\phi$, was defined by $\phi = ([\text{CH}_4]/[\text{O}_2])/([\text{CH}_4]/[\text{O}_2])_{st}$, where the index ‘st’ denotes the stoichiometric composition; the O atom in the steam molecule was not considered. Zero gradient condition for all physical quantities was considered at the outlet of the calculation domain.

3. Results and Discussion

3.1. Effects of dilution ratio and pressure on laminar burning velocity and flame structure

Figure 1 shows the relationship between pressure and laminar burning velocity under conditions of steam dilution ratios of 0.1 to 0.5 and equivalence ratios of 0.4, 1.0 and 3.0. Figure 2 shows the relationship between equivalence ratio and laminar burning velocity under conditions of steam dilution ratios of 0.1 to 0.5 and pressures of 0.1, 1.0 and 3.0 MPa. In Figs. 1 and 2, the solid and broken lines denote laminar burning velocity evaluated by GRI-Mech 3.0 [3] and DA Mech [15], respectively. In both mechanisms, laminar burning velocity decreases as pressure increases under fuel-lean and stoichiometric conditions. However, under extremely fuel-rich condition, such as the equivalence ratio of 3.0 in Fig. 1 (c), the laminar burning velocity increases as pressure increases. This tendency is significant as the steam dilution ratio increases. Without steam dilution, i.e., for the steam dilution ratio of 0.0, the laminar burning velocity once decreases in the range of pressure of 0.1 to 0.7 MPa, and then increases up to 3.0 MPa. In the case of a steam dilution ratio lower than 0.3, the laminar burning velocity has a minimum value as the pressure increases. At a steam dilution ratio higher than 0.4, the laminar burning velocity increases under all pressure conditions. In the comparison of laminar burning velocity evaluated by GRI-Mech 3.0 [3] and DA Mech [15], the laminar burning velocity evaluated by DA Mech [15] is lower than that evaluated by GRI-Mech 3.0 [3] for steam dilution ratios higher than 0.3. At the equivalence ratio of 3.0, the laminar burning velocity evaluated by DA Mech [15] is lower than that evaluated by GRI-Mech 3.0 [3] in all steam dilution ratio cases. For the equivalence ratio of 3.0, while the difference of laminar burning velocity in both mechanisms is lower as the steam dilution ratio increases, it becomes greater as pressure increases. For the equivalence ratio of 0.4 at low steam dilution ratios such as 0.0 and 0.1, the laminar burning velocity evaluated by DA Mech [15] is higher than that evaluated by GRI-Mech 3.0 [3]. For the equivalence ratio of 0.4 at low steam dilution ratios such as 0.0 and 0.1, the difference of laminar burning velocity in both mechanisms also becomes greater as pressure increases.
To clarify the mechanism of the increase of laminar burning velocity under high pressure and extremely fuel-rich conditions, sensitivity analysis for the laminar burning velocity was performed. Figure 3 shows the reactions which have higher sensitivity coefficients for the steam dilution ratio of 0.5 and equivalence ratios of 0.4, 1.0 and 3.0 respectively. In Fig. 3, the reaction numbers denote those in DA Mech [15]. In the following, the reaction numbers also denote the numbers in DA Mech [15]. At equivalence ratios of 0.4 and 1.0, the following reaction has the highest sensitivity coefficient of all reactions in DA Mech [15]:

\[
H + O_2 \leftrightarrow O + OH \quad (R1)
\]

At pressures of 0.1 to 1.0 MPa for the equivalence ratio of 3.0, R1 also has the highest sensitivity coefficient. This reaction is the main chain-branching reaction predominant for laminar burning velocity. At equivalence ratios of 0.4 and 1.0 with higher steam dilution ratios, because the three-molecule recombination reaction

\[
H+O_2+H_2O \leftrightarrow HO_2+H_2O \quad (R14)
\]

and R1 are competitive for the H radical, R14 has a large negative sensitivity coefficient and is one of the elementary reactions which decreases laminar burning velocity.
Fig. 3  Sensitivity coefficients of elementary reactions using DA Mech in CH$_4$/O$_2$/H$_2$O premixed gas under conditions of Z$_{H_2O}$ = 0.5 and T$_0$ = 500 K: (a) $\phi = 0.4$; (b) $\phi = 1.0$; (c) $\phi = 3.0$.

It resembles CH$_4$/air or H$_2$/air flames where R14 has a large negative sensitivity coefficient. However, for the equivalence ratio of 3.0, R14 has a positive sensitivity coefficient. R14 also has a positive sensitivity coefficient when GRI-Mech 3.0 [5] is used. [7] While the sensitivity coefficient for R1 decreases drastically as pressure increases, R14 and the following chain-branching reaction, R93,

$$\text{CH}_3 + \text{HO}_2 \leftrightarrow \text{CH}_3\text{O} + \text{OH}, \quad (R93)$$

have a larger positive sensitivity coefficient than that for R1 at a pressure of 3.0 MPa. Under all conditions of pressure for the equivalence ratio of 3.0, the following fall-off reaction has the highest negative sensitivity coefficient:

$$2\text{CH}_3 (+\text{M}) \leftrightarrow \text{C}_2\text{H}_6 (+\text{M}) \quad (R101)$$

The chain-termination reaction,

$$\text{CH}_3\text{H} (+\text{M}) \leftrightarrow \text{CH}_4 (+\text{M}), \quad (R85)$$

also has a high negative sensitivity coefficient. The sensitivity coefficients for R101 and R85 decrease as pressure increases. Under the conditions where laminar burning velocity increases as pressure increases such as that at high pressure and for a high equivalence ratio, the same tendency of the results of sensitivity analysis was observed. This implies that the reaction pathway changes as pressure increases and, therefore, laminar burning velocity increases.

To elucidate the reaction mechanism based on highly sensitive reactions for laminar burning velocity, reaction path analysis was conducted with the post-flame region being
excluded to eliminate the effect of the steam reforming reactions which slowly proceeds in the post-flame region.

Figures 4 (a) and (b) show the reaction pathway for the steam dilution ratio of 0.5 and the equivalence ratio of 3.0 at pressures of 0.1 MPa and 3.0 MPa, respectively. The thickness of arrows indicates the relative amount of species formation. First, CH₄ is oxidized to CH₃ by following reaction:

\[
\text{CH}_4 + \text{OH} \leftrightarrow \text{CH}_3 + \text{H}_2\text{O} \quad \text{(R120)}
\]

This reaction is important for the oxidation of CH₄ and has high sensitivity, as shown in Fig. 3. CH₃ is converted to CH₄, CH₃O and C₂H₆, respectively, by three competitive reactions of CH₃ in R85 and the following two reactions which have high sensitivity:

\[
\text{CH}_3 + \text{HO}_2 \leftrightarrow \text{CH}_3\text{O} + \text{OH} \quad \text{(R93)}
\]

\[
2\text{CH}_3 (+\text{M}) \leftrightarrow \text{C}_2\text{H}_6 (+\text{M}) \quad \text{(R101)}
\]

R85 decreases laminar burning velocity because it prevents CH₄ oxidation. CH₃O formed by R93 is finally oxidized to CO₂ through various C₁ hydrocarbons. The reaction pathway through C₁ hydrocarbons denotes the C₁ Route in Fig. 4. C₂H₆ formed by R101 is also finally oxidized to CO₂ through various C₂ hydrocarbons. The reaction pathway through C₂ hydrocarbons denotes the C₂ Route in Fig. 4. Because the C₂ Route consists of many slower reactions of C₂H₆ decomposition, the oxidation to CO₂ through the C₂ Route is slower than that through the C₁ Route, namely, laminar burning velocity decreases. Thus, in the reaction pathway which leads to oxidation to CO₂, the competition of R93 and R101 is predominant for the branching to the C₁ Route, and the C₂ Route has a significant influence on the laminar burning velocity. In Figs. 4 (a) and (b), C₁ hydrocarbons react with C₂ hydrocarbons to form C₃ hydrocarbons and then form the C₃ Route. Moreover, in Fig. 4 (a), C₃ hydrocarbons can be seen to react with C₁ hydrocarbons to form C₄ hydrocarbons and then they form the C₄ Route. Comparison of Fig. 4 (a) with Fig. 4 (b) shows that at a higher pressure of 3.0 MPa, the C₄ Route disappears and the main reaction pathway shifts to a lower hydrocarbon route from the C₂ Route to the C₁ Route.

To understand the mechanism of the shift from C₁ Route to C₂ Route, reaction rate analysis was performed. Figures 5 (a) and (b) show the reaction rate profiles for highly sensitive reactions for an equivalence ratio of 3.0 and a steam dilution ratio of 0.5 at pressures of 0.1 MPa and 3.0 MPa, respectively. In Fig. 5, highly sensitive reactions shown in Fig. 3 are located before the post-flame region, indicating the validity of performing reaction path analysis before the post-flame region shown in Fig. 4. At both pressures, chain propagating reaction R120 is the fastest reaction in the reaction zone.

As shown in Fig. 4 (a), at a pressure of 0.1 MPa and under fuel-rich conditions, the C₂ Route is more predominant than the C₁ Route. CH₃ forms C₂H₆ through R101 and finally oxidizes to CO₂. Because R101 and R85 are fall-off reactions, the reaction rate constants approach a constant value, i.e., there is a high pressure limit as pressure increases. Thus, the reaction rate is relatively slower than those of the other highly sensitive reactions at high pressure. As shown in Fig. 4, under fuel-rich conditions, the three-molecule recombination reaction R14 and the chain-propagating reaction R93 have faster reaction rates than those of other highly sensitive reactions as pressure increases. More HO₂ is formed by the three-molecule recombination reaction R14, which is enhanced by the pressure increase, and prompts R93. Thus, for a high equivalence ratio, the reaction pathways from CH₃ to CH₄ and C₂H₆ are weakened and then the reaction pathway from CH₃ to CH₃O is enhanced. Namely, the main reaction route shifts from the C₂ Route to the C₁ Route and laminar burning velocity increases as pressure increases. This shift of the main oxidation reaction pathway to a lower hydrocarbon route causes the disappearance of the reaction pathway for higher hydrocarbon routes such as the C₄ Route, as shown in Fig. 4. In the range where laminar burning velocity decreases as pressure increases for the equivalence ratio of 3.0, as shown in Fig. 1, the reaction rate of R101 becomes larger compared with that of R93 as
pressure increases, while it is not shown in Fig. 4. This is because R101 is a fall-off reaction with a strong pressure dependency and because the rate constant of R101 greatly increases as pressure increases. Consequently, the shift of reaction path from the C1 Route to the C2 Route is promoted as pressure increases. Moreover, the reaction rate of the fall-off reaction R85 also increases as pressure increases, leading to the consumption of the H radical and the regeneration of CH₄. Therefore, the laminar burning velocity decreases in the range in which laminar burning velocity is decreased as pressure increases for the equivalence ratio of 3.0.

Fig. 4 Reaction pathway of CH₄/O₂/H₂O premixed gas under conditions of ZH₂O = 0.5, φ = 3.0 and T₀ = 500 K using DA Mech: (a) P = 0.1 MPa; (b) P = 3.0 MPa.
As already shown in Fig. 1, under conditions of high equivalence ratio and high steam dilution ratio, the difference of laminar burning velocity calculated using GRI-Mech 3.0 [3] and DA Mech [15] can be explained by the difference of reaction rate constants of highly sensitive reactions related to CH₃ competition reactions, R85, R93 and R101, in the two mechanisms. In DA Mech [15], the reaction rate constant for R85 (negative sensitivity) and that for R93 (positive sensitivity) are lower, and R101 (negative sensitivity) is higher than those in GRI-Mech 3.0 [3]. Namely, in DA Mech [15], the ratio of passage to the C2 Route is higher than that of GRI-Mech 3.0 [3]. Thus, laminar burning velocity evaluated by DA Mech is lower than that evaluated by GRI-Mech 3.0 [3]. Under conditions of high equivalence ratio and high steam dilution ratio, the difference of reaction rate constants of the fall-off reactions, R85 and R101 between the two mechanisms is greater as pressure increases, so that the difference of laminar burning velocity is greater as pressure increases. Moreover, under the conditions of high equivalence ratio and high steam dilution ratio, the reaction rate constant for R14 in DA Mech [15] is higher than that in GRI-Mech 3.0 [3]. The difference of reaction rate constants between these two mechanisms is greater in the low temperature region such as higher steam dilution conditions. In the case of a higher steam dilution ratio, the HO₂ radical formed by R14 evaluated by DA Mech [15] is greater than that formed by GRI-Mech 3.0 [3]. In DA Mech [15], the reaction rate for R93 prompted by R14 is more greatly enhanced and the ratio of passage to the C1 Route is higher for the higher steam dilution ratio in comparison with GRI-Mech 3.0 [3]. Thus, the difference of laminar burning velocity evaluated by the two mechanisms is smaller as steam dilution ratio increases in the case of high equivalence ratios. Under the conditions where laminar burning velocity evaluated by DA Mech [15] is higher than that evaluated by GRI-Mech 3.0 [3], the C1 Route is predominant because of the low equivalence ratio, and thus, among the above-mentioned CH₃ competitive reactions, R85 is the most predominant for laminar burning velocity because of the low steam dilution ratio. The third body in R85 is a CH₄ molecule which has relatively large collision efficiency. Therefore, for a low equivalence ratio with a low steam dilution ratio, the laminar burning velocity evaluated by DA Mech is higher than that evaluated by GRI-Mech 3.0 [3] and the difference of laminar burning velocity evaluated by the two mechanisms is greater as pressure increases.

3.2. Formation of higher hydrocarbons and the effects on laminar burning velocity on extremely fuel-rich CH₄/O₂/H₂O flames

As already shown in Figure 4, the C3 Route leads to C₆H₆ formation of higher hydrocarbons. In DA Mech [15], C₆H₆ is mainly formed by the following C₃H₃ recombination reaction:

\[ C_3H_3 + C_3H_3 \leftrightarrow C_6H_6 \]  \hspace{1cm} (R313).

Figure 5 shows temperature profiles and the main chemical species profiles calculated using DA Mech [15] in various conditions. For the high equivalence ratio of 3.0, C₆H₆, which is a representative soot precursor, evolves and its maximum mole fraction is about 5000 ppm, as shown in Figs. 6 (g) and (h) on flame structures.

Figure 7 shows the maximum C₆H₆ production rate in flame structure per unit mass of CH₄/O₂/H₂O premixed gas in the condition of the equivalence ratio of 3.0 with a steam dilution ratio of 0.0 to 0.5. In Fig. 6, because the recombination reaction of hydrocarbon is enhanced under high pressure, C₆H₆ production increases as pressure increases. As the steam dilution ratio increases, C₆H₆ production also increases. Higher flame temperature for a lower steam dilution ratio causes C₂H₆ pyrolysis. On the other hand, when the increase ratio of C₆H₆ production rate based on the C₆H₆ production rate at 0.1 MPa from 0.1 to 3.0 MPa in each steam dilution ratio is considered, the ratio decreases to 3.28, 2.54, 2.00, 1.63, 1.37 and 1.19 times at the steam dilution ratios of 0.0-0.5, respectively. This decrease of C₆H₆ increase ratio at the higher steam dilution ratio is caused by the cracking reaction of
the H₂O molecule which has large collision efficiency, indicating another effect of high steam concentration on higher hydrocarbons. From the results of sensitivity analysis shown in Fig. 3, it can be seen that there are no other highly sensitive reactions related to C3 higher hydrocarbons. Although DA Mech indicates that higher hydrocarbons are formed, as shown in the flame structure (Fig. 6) and reaction pathway (Fig. 4), there are no highly sensitive reactions related to C3 and C4 hydrocarbons (Fig. 3). Thus, when the laminar burning velocity is considered for CH₄/O₂/H₂O flames, the effect of the higher hydrocarbons is very small.

![Fig. 5 Profiles of reaction rate and temperature using DA Mech [15] in CH₄/O₂/H₂O premixed gas under conditions of ZH₂O = 0.5, φ = 3.0 and T₀ = 500 K: (a) P = 0.1 MPa; (b) P = 3.0 MPa.](image)

### 3.3. Existence of two types of SAFT phenomenon

As is seen in Fig.6 on flame structures, flame temperature often shows a maximum in the reaction zone and then decreases in the post flame-region. The phenomenon that the maximum temperature is higher than the adiabatic flame temperature is termed the super-adiabatic flame temperature (SAFT). As shown in Figs. 6 (a) and (b), for the equivalence ratio of 0.4, SAFT does not occur under any pressure conditions. H₂ and CO are formed by the partial oxidation reaction and completely consumed in the reaction zone; these species do not exist in chemical equilibrium. As shown in Figs. 6 (c) and (d), for the
Fig. 6 Flame structures using DA Mech [15] in CH₄/O₂/H₂O premixed gas at T₀=500 K under conditions of various pressures, equivalence ratios and steam dilution ratios. Symbol “■” shows adiabatic flame temperature.

Fig. 7 Maximum C₆H₆ production rate of CH₄/O₂/H₂O premixed gas under the condition of φ = 3.0 and T₀ = 500 K as a function of ambient pressure using DA Mech [15].
equivalence ratio of 0.4 and steam dilution ratio of 0.5, SAFT does not occur under pressure conditions, either. H\textsubscript{2} and CO concentration profiles have peaks in the reaction zone and then approach chemical equilibrium. As shown in Fig. 6 (e), under conditions of a pressure of 0.1 MPa, the equivalence ratio of 1.0 and a steam dilution ratio of 0.0, SAFT occurs. The H\textsubscript{2}O mole fraction decreases gradually, that of H\textsubscript{2} increases slightly and the temperature decreases gradually in the post-flame region. However, as shown in Fig. 6 (f), SAFT disappears as pressure increases. As shown in Figs. 6 (g) and (h), under the high equivalence condition, SAFT occurs even at ordinary pressure. At high equivalence ratios, H\textsubscript{2} and CO increase gradually and temperature decreases gradually in the post-flame region. This is due to a steam reforming reaction and a water shift reaction which the reaction rates are smaller than that of partial oxidation and oxidation reaction. Another feature of the flame structures shown in Figs. 6 (g) and (h) is the existence of a significant amount of C\textsubscript{3} higher hydrocarbons such as C\textsubscript{6}H\textsubscript{6}. Figure 8 shows the occurrence of the SAFT conditions systematically. It was found that in the case using GRI-Mech 3.0 [3], SAFT occurred under the same conditions as when using DA Mech. Because DA Mech [15] is a detailed reaction mechanism which has been expanded from GRI-Mech 2.11 [12], it can be understood that SAFT occurs under almost the same conditions.

It is interesting to note that, as shown in Fig. 8, there are two types of SAFT. The first type of SAFT occurs for equivalence ratios of 1.0 to 2.0 and steam dilution ratios of 0.0 to 0.4. In the first type of SAFT, the laminar burning velocity decreases as pressure increases. The second type of SAFT occurs under all pressure conditions at equivalence ratios higher than 2.0 with steam dilution ratios of higher than 0.5 and equivalence ratios of higher than 2.5 with all steam dilution ratio conditions. In the second type of SAFT, laminar burning velocity increases as pressure increases.

According to Liu and Gülder [10, 11], in CH\textsubscript{4}/air flame evaluated by GRI-Mech 3.0 [3], the preferential diffusion of the H radical formed by H\textsubscript{2}O pyrolysis at high temperature from the reaction zone to the preheating zone is the main cause of the first type of SAFT. Even in the case of CH\textsubscript{4}/O\textsubscript{2}/H\textsubscript{2}O flames in the present study, because of the gradual decrease of H\textsubscript{2}O profile shown in Fig. 7 (e), it is reasonable to consider that the first type of SAFT is caused by the preferential diffusion of the H radical. As to the second type of SAFT, they focused on several exothermic reactions in the post-flame region and suggested the following endothermic reaction:

\[
\text{CH}_2 + \text{CO (M)} \leftrightarrow \text{CH}_2\text{CO (M)}, \quad (R60)
\]

which is main cause of the second type of SAFT under high pressure conditions.

Figures 9 (a) and (b) show the heat release rate for major exothermic and endothermic reactions for the equivalence ratio of 3.0, the steam dilution rate of 0.5 and the pressure of 0.1 MPa and 3.0 MPa, respectively. As shown in Figs. 9 (a) and (b), under conditions of an extremely high equivalence ratio, high pressure and high steam dilution ratio, the following endothermic reaction was observed:

\[
\text{C}_2\text{H}_2 + \text{H (M)} \leftrightarrow \text{C}_2\text{H}_3 (M), \quad (R143)
\]

which plays a predominant role in SAFT rather than R60 in the post-flame region. Because R143 is the fall-off reaction, the reaction rate of R143 approaches a constant as pressure increases. Namely, the magnitude of endothermic heat by R143 approaches a constant as pressure increases. On the other hand, as for the exothermic reaction, the heat release rate for the three-molecule recombination reaction R14 is relatively enhanced as pressure increases, as shown in Figs. 9 (a) and (b). Therefore, the difference between the maximum flame temperature and the adiabatic temperature in the SAFT phenomenon is enhanced as pressure increases.
Fig. 8  Region of SAFT occurrence using DA Mech: (a) P = 0.1 MPa; (b) P = 1.0 MPa; (c) P = 3.0 MPa

Fig. 9  Profiles of heat release rates using DA Mech in CH₄/O₂/H₂O premixed gas under conditions of ZH₂O = 0.5, φ = 3.0 and T₀ = 500 K: (a) P = 0.1 MPa; (b) P = 3.0 MPa.
4. Conclusions

Numerical analysis of one-dimensional CH\textsubscript{4}/O\textsubscript{2}/H\textsubscript{2}O premixed flames under conditions of a wide range of pressures from 0.1 to 3.0 MPa was performed for equivalence ratios of 0.4 to 3.0 and steam dilution ratios of 0.0 to 0.5. The initial temperature of premixed gas was fixed at 500 K. GRI-Mech 3.0 and DA Mech were used as the detailed reaction mechanisms.

Laminar burning velocity was evaluated using both of the mechanisms. At steam dilution ratios higher than 0.3, the laminar burning velocity evaluated by DA Mech was lower than that evaluated by GRI-Mech 3.0. This was caused by the difference of reaction rate constants of high sensitivity reactions, chain-branching reaction of CH\textsubscript{3} + HO\textsubscript{2} ⇄ CH\textsubscript{3}O + OH (R93) and the two fall-off reactions of CH\textsubscript{3} + H (+M) ⇄ CH\textsubscript{4} (+M) (R85) and 2CH\textsubscript{3} (+M) ⇄ 2C\textsubscript{2}H\textsubscript{6} (+M) (R101) between the two mechanisms. For the equivalence ratio of 3.0, laminar burning velocity increased as pressure increased. Analysis of the reaction pathway and reaction rate indicated that, as pressure increased, the main oxidation reaction shifted from the C2 Route to the C1 Route, resulting in an increase in the laminar burning velocity at a high equivalence ratio. As pressure increased, the difference of reaction rate constants of the fall-off reactions, R85 and R101, between the two mechanisms was greater and the ratio of passage to the C2 Route was higher. Moreover, as the steam dilution ratio increased, the reaction rate for R93 prompted by the HO\textsubscript{2} radical formed by R14 was further enhanced, and, in DA Mech, as compared with GRI-Mech 3.0, the ratio of passage to the C1 Route was higher at higher steam dilution ratios. Therefore, for an extremely fuel-rich condition such as equivalence ratio of 3.0, while the difference of laminar burning velocity in both mechanisms was lower as the steam dilution ratio increased, it became greater as pressure increased.

From the flame structure at high pressure and high equivalence ratio, C\textsubscript{6}H\textsubscript{6}, which is a representative soot precursor, evolved, its maximum mole fraction being about 5,000 ppm. The increase ratio of the C\textsubscript{6}H\textsubscript{6} production rate based on increasing pressure at each steam dilution ratio was considered, due to the occurrence of a cracking reaction of the H\textsubscript{2}O molecule, which has large collision efficiency, and the increase ratio was shown to decreases as the steam dilution ratio increased.

Although the formation of higher hydrocarbons was confirmed from the flame structure and reaction pathway evaluated by DA Mech, highly sensitive reactions were the same as those evaluated by GRI-Mech 3.0. The sensitivity coefficient of the elementary reactions concerning higher hydrocarbons was low, indicating that the higher hydrocarbon had only a small effect on the laminar burning velocity.

In this work, the range of SAFT occurrence was shown systematically. Under the condition of high equivalence ratio, the difference between the adiabatic flame temperature and the maximum flame temperature increased as pressure increased. This resulted from the heat release rate of the exothermic reaction. The three-molecule recombination reaction of H + O\textsubscript{2} + H\textsubscript{2}O ⇄ HO\textsubscript{2} + H\textsubscript{2}O (R14) was enhanced and the endothermic reaction, i.e., the fall-off reaction of C\textsubscript{2}H\textsubscript{2} + H (+M) ⇄ C\textsubscript{2}H\textsubscript{3} (+M) (R143), approached constant as pressure increased.

References


