Supercritical fluid properties are implemented in a one-dimensional counterflow flame simulation code using the Soave-Redlich-Kwong equation of state and modifying the transport properties for high-pressure, low-temperature conditions. Examination of a \( \text{GH}_2/\text{LOX} \) diffusion flame at supercritical pressure reveals an extremely fine structure at the edge of the oxygen diffusion layer, indicating that a DNS-like approach to simulation of such flames is not practical in the near term, and flame modeling must be used. To investigate flamelet table construction, we compare simulations that use supercritical fluid and standard temperature and pressure (STP) gas properties. Both types of simulations are shown to produce almost identical flame structures when we parameterize the flame with the scalar dissipation rate at its stoichiometric position. The results show that the use of STP gas property simulation is expected to be an effective means of greatly reducing the computational cost of constructing flamelet tables at supercritical pressures.

Key Words:  Supercritical Pressure, 1D Counterflow Flame, Flamelet Table

1. Introduction

During the history of the development of rocket engine combustion chambers, combustion instability has been a critical factor that can cause enormous increases in development cost and time that must be overcome.\(^1\) To understand and suppress this phenomenon, and to reduce the number of sub- and full-scale tests required, unsteady numerical simulation of combusting flow that can deal with the coupling of combustion heat release and acoustics in a combustion chamber is expected to be an effective analytical tool. Such coupling results in high amplitude pressure oscillations that can lead to the destruction of the chamber.

In many practical cases, rocket propulsion systems use liquids for the fuel and oxidizer. Simulation of liquid combustion is quite difficult because the complex processes of atomization, vaporization, diffusion and chemical reactions have to be taken into account to simulate the chemically reacting two-phase flow. However, it may be possible to adopt an easier approach for the simulation of combustion at supercritical pressures (higher than the critical pressure), which are often utilized in high-power booster engine combustors. At supercritical pressure conditions, the surface tension and latent heat of vaporization disappear.\(^2\) It has been reported that under such conditions, the liquid break-up process is not observable\(^3\) and the mixing of fuel and oxidizer likely takes place in the same way as in the single-phase gaseous diffusion. This hypothesis is supported by various analyses of experimental data.\(^4\) Consequently, it may be possible to apply gaseous single-phase flow simulation techniques to the simulation of combusting flows in a chamber at supercritical pressure.

Even if the difficulties of two-phase flow are removed, however, simulating a single-phase combusting flow is much harder than simulating gas mixtures at atmospheric pressure. The development of computer resources has enabled simulations of laboratory-size atmospheric flames with detailed chemistry and transport properties, but the full-scale simulation of a combustion chamber is not yet possible. Simulation at supercritical pressures is an even more formidable challenge. The theoretical estimate of the reacting layer thickness at 100 atm pressure, for example, is approximately one-tenth of that at normal atmospheric pressure, requiring \(10^4\) times greater computational power. As a result, numerical simulation with detailed chemistry and transport properties is not practical in the near term, and a means of reducing the computational load is required, such as flame modeling. Some approaches have been proposed and applied to the injector combustion flows, in Reynolds-averaged Navier-Stokes (RANS)\(^9,10\) and large eddy simulation (LES)\(^11,12\) contexts, and have obtained a certain level of success.

One successful flame model is the laminar flamelet concept, which assumes a very thin reaction layer within which there is a balance between chemical reaction and molecular diffusion. Based on this concept, the flow calculation can be separated from the chemical reaction calculation, and the chemical reaction calculation is altered by look-up tables prepared from detailed one-dimensional (1-D) simulations. For a rocket engine combustor injector, the flame configuration is expected to have a diffusion flame-like structure which is attached to the injector. In this case, as is well...
known, the flame may be described by a simple formulation based on the fuel mixture fraction and its dissipation rate, and the look-up table is usually constructed based on 1-D counterflow diffusion flame computations. In the case that the flame is detached from the injector, such a simple approach is not applicable; more complicated formulations, for example, the combined use of the mixture fraction and the progress variable, are required. In such cases, the chemical table will be constructed by 1-D counterflow flame simulations of various configurations. Moreover, when the organized flame structure does not exist, the flamelet concept is no longer applicable; for example, in the ignition dominant situations, and when the turbulent eddies are so small that they can penetrate into the reaction layer.

1-D counterflow flame simulation has been widely used for studying flame structures of various configurations also from the fundamental viewpoint and has made considerable contributions to the progress of combustion research. Regarding the H2/O2 diffusion flame, Ribert et al. discussed the flame properties from subcritical to supercritical conditions, and showed that the heat release rate is proportional to the square root of the pressure multiplied by the flame strain rate, while the flame thickness is inversely proportional. However, there have been no studies reported on flame table construction at supercritical pressures or on computational cost reduction.

In this study, we implement the properties of a high-density cryogenic fluid in terms of the equation of state (EOS), enthalpy and transport properties in a 1-D counterflow flame computation code. We discuss the detailed flame structure of a GH2/LOX diffusion flame at supercritical pressure, and then investigate the flame properties mainly from the viewpoint of reducing the computational cost of constructing the flamelet look-up tables.

2. Counterflow Diffusion Flame

The flame configuration studied here is a counterflow diffusion flame as shown in Fig. 1. The fuel and oxidizer are injected from opposite directions to produce a 1-D plane diffusion flame between the two jets. In this paper, the axisymmetric configuration is studied. The fuel is pure hydrogen and the oxidizer is pure oxygen.

3. Physical Model

3.1. Chemical reaction

The reaction mechanism for the hydrogen/oxygen system in this study is the 8-species (H2, O2, OH, H2O, H, O, H2O2, HO2) and 21-reaction model developed by Li et al. which has been validated at up to 87 atm. The elementary reactions are listed in Table 1.

3.2. EOS

When a fluid is very dense, the effects of inter-molecular repulsive force should be taken into account in the EOS. In this study, the Soave-Redlich-Kwong (SRK) EOS is employed.

\[
\rho = \frac{R_u T}{M_m V - b} - \frac{a}{M_m V(M_m V + b)},
\]

where \(R_u\) is the universal gas constant, \(M_m\) is the mean molar weight of the mixture and \(V\) is the specific volume. The parameters \(a\) and \(b\) are calculated from the critical properties of each component as

\[
a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}, \quad b = \sum_i x_i b_i,
\]

\[
a_i = \left(1 + n_i \left[1 - \left(\frac{T}{T_{ci}}\right)^2\right]\right)^2,
\]

\[
n_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2,
\]

\[
\omega_i = \frac{R_u T_{ci}^2}{\rho_{ci}}, \quad b_i = 0.08664 \frac{R_u T_{ci}}{\rho_{ci}},
\]

where \(x_i, T_{ci}, \rho_{ci}\), and \(\omega\) are respectively the mole fraction, critical temperature, critical pressure and acentric factor of species \(i\). The critical properties used in this study are listed in Table 2, where \(T_c\) and \(p_c\) are quoted from Ref. 14, and \(\omega\)
is taken from Ref. 2). For species whose acentric factor is unclear, \( \omega \) is set to zero.

The estimated densities of the major species are shown as functions of the temperature at a pressure of 60 atm and are compared with NIST data\(^{18} \) in Fig. 2. The estimation shows a good agreement with NIST data for \( \text{H}_2 \) and \( \text{O}_2 \) (Fig. 2(a) and (b)) but the agreement is poor for \( \text{H}_2\text{O} \) (Fig. 2(c)). Although this discrepancy for \( \text{H}_2\text{O} \) can be removed by impromptu modification of the critical temperature of \( \text{H}_2\text{O} \), such an ad hoc fix is not used in this study.

3.3. Enthalpy and specific heat

The enthalpy of the chemical species should be modified according to the SRK EOS. The molar enthalpy can be derived from the SRK EOS and Maxwell’s equations of thermodynamics as

\[
h(T, p) = h^0(T) + pV - \frac{R_u}{M_m}T + \frac{1}{M_mb} \left( T \frac{\partial a}{\partial T} - a \right) \ln \left[ \frac{M_mV + b}{M_mV} \right].
\] (2)

The constant pressure specific heat of the mixture is obtained by partially differentiating the enthalpy with respect to temperature as follows

\[
c_p(T, p) = c_p^0(T) = \sum \gamma_i c_{p,i}(T)
\]

\[
+ p \left( \frac{\partial V}{\partial T} \right)_p - \frac{R_u}{M_m} + \frac{T}{M_mb} \frac{\partial a}{\partial T} \ln \left[ \frac{M_mV + b}{M_mV} \right] - \frac{1}{M_mV(M_mV + b)} \left( \frac{\partial V}{\partial T} \right)_p.
\] (3)

In this study, the thermophysical properties at standard temperature and pressure (STP) conditions, namely \( h^0 \) and \( c_p^0 \), are taken from the CHEMKIN library.\(^{19} \) See Appendix A.1 for details of the derivation of the enthalpy and specific heat.

The enthalpies and specific heats at constant pressure of the major species are shown as functions of temperature at a pressure of 60 atm and are compared with NIST data\(^{18} \) in Figs. 3 and 4, respectively. Our adopted method shows quite good agreement with NIST data in the \( \text{H}_2 \) and \( \text{O}_2 \) properties, and the estimates for \( \text{H}_2\text{O} \) are reasonable. However, the estimates for intermediate species have not been validated due to lack of measurement data.

### Table 2. Critical properties\(^ {2,14} \)

| \( p_c \) (atm) | \( T_c \) (K) | Acentric factor (\( \omega \)) |
|-----------------|--------------|-------------------------------|
| \( \text{H}_2 \) | 12.8 | 33.25 | -0.216 |
| \( \text{O}_2 \) | 49.7 | 155.15 | 0.021 |
| \( \text{OH} \) | 85.7 | 443.7 | — |
| \( \text{H}_2\text{O} \) | 218.3 | 647.35 | 0.344 |
| \( \text{H} \) | 88.2 | 404.3 | — |
| \( \text{O} \) | 76.0 | 367.4 | — |
| \( \text{H}_2\text{O}_2 \) | 93.5 | 544.3 | — |
| \( \text{HO}_2 \) | 82.8 | 487.3 | — |

Fig. 2. Densities of major species at 60 atm: (a) \( \text{H}_2 \), (b) \( \text{O}_2 \) and (c) \( \text{H}_2\text{O} \).

Fig. 3. Enthalpies of major species at 60 atm: (a) \( \text{H}_2 \), (b) \( \text{O}_2 \) and (c) \( \text{H}_2\text{O} \).
3.4. Transport properties

At extremely dense cryogenic conditions, the transport properties should be modified to match experimental observations. The diffusion speeds of momentum and heat increase, and that of mass decreases. Viscosity and heat conductivity are modified based on Chung’s method. This method shows fairly good agreement with NIST data for H\(_2\) and O\(_2\) as shown in Figs. 5(a) and (b) and 6(a) and (b), but the agreement for H\(_2\)O is rather poor (Figs. 5(c) and 6(c)). The H\(_2\)O transport coefficients can be improved by the modification of the critical temperature but such an ad hoc fix is not used as mentioned in section 3.2. See Appendix A.2 for details of Chung’s correction method.

Instead, we estimate the diffusion coefficient using the number density of molecules calculated from the SRK EOS. This method provides reduced diffusivities at cryogenic conditions which are almost identical to those estimated using Takahashi’s method, which is based on an empirical database of dense cryogenic fluids (Fig. 7). See Appendix A.3 for details of Takahashi’s correction method.

4. Governing Equations

The base simulation code is a modified version of CHEMKIN PREMIX for counterflow flame simulation at standard pressure. The supercritical fluid properties explained in the previous section are implemented on top of this base code.

The governing equations are given as follows for axisymmetric configurations.
Mass conservation

\[ G(x) + \frac{dF(x)}{dx} = 0, \quad (4) \]

where,

\[ G(x) = -\frac{\rho u}{r}, \quad F(x) = \frac{\rho u}{2} \]

Momentum conservation

\[ H = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{FG}{\rho} \right) = \text{constant}. \quad (5) \]

\[ H - \frac{2}{d} \frac{d}{dx} \left( \frac{FG}{\rho} \right) + 3G^2 + \frac{d}{dx} \left( \frac{\mu}{d} \frac{d}{dx} \left( \frac{G}{\rho} \right) \right) = 0. \quad (6) \]

Energy conservation

\[ \rho u c_p \frac{dT}{dx} - \frac{d}{dx} \left( \frac{4}{d} \frac{dT}{dx} \right) + \sum \rho c_m Y_i V_i \frac{dT}{dx} + \sum h_i \omega_i = 0. \quad (7) \]

Species conservation

\[ \rho u \frac{dY_i}{dx} + \frac{d}{dx} (\rho Y_i V_i) - \omega_i M_i = 0, \quad (8) \]

where \( x \) and \( r \) are the axial and radial coordinates, and \( \rho, T, \lambda \) and \( c_p \) are, respectively, the density, temperature, thermal conductivity and the constant pressure specific heat of the mixture, and \( u \) and \( v \) are the axial and radial velocity components. \( Y_i, h_i, c_{mi}, V_i, \omega_i \) and \( M_i \) are, respectively, the mass fraction, molar enthalpy, constant pressure specific heat, molecular diffusion velocity, production rate and molar weight of chemical species \( i \).

The governing equations are solved using Newton’s method with the help of time marching integration. See Refs. 19) and 22) for details.

5. Results and Discussions

5.1. Flame structure

In this study, a single injector experiment performed at DLR23) is chosen as the reference and the fluid conditions were taken from the experiment. The fuel and oxidizer are gaseous hydrogen and liquid oxygen. The injection temperatures of the hydrogen and oxygen are 125 K and 127 K, respectively. The chamber pressure is 60 atm, which is higher than the critical pressures of hydrogen and oxygen. The fuel and oxidizer properties are listed in Table 3.

First, a condition which is far from flame extinction is simulated. The distance between the opposing jets \( L \) is 1 cm, and the hydrogen and oxygen injection velocities are \( u_{H_2} = 625 \text{ cm/s} \) and \( u_{O_2} = 175 \text{ cm/s} \), respectively. An atmospheric flame is initially created and then temperature is reduced and pressure is increased gradually until the injection conditions are satisfied.

We now discuss the structure of the counterflow diffusion flame. The profiles of the mass fractions of the major species and the density are shown in Fig. 8(a). The profiles of minor species, shown in Fig. 9 with a half-scale abscissa, are thinner than those of major species. In particular, \( H_2O_2 \) has two peaks, the smaller of which is located at the edge of the oxygen diffusion layer and is very narrow, with a width of approximately

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Table 3. Fuel and oxidizer.

| Compo. | \( p \) (atm) | \( T \) (K) | \( u \) (m/s) |
|--------|--------------|-------------|-------------|
| Fuel   | \( \text{H}_2 \) | 60.0         | 125.0       | 6.25        |
| Oxidizer | \( \text{O}_2 \) | 60.0         | 127.0       | -1.75       |

Fig. 7. Diffusivity of \( \text{O}_2 \) compared with estimation by Takahashi’s using21) at 60 atm.

Fig. 8. Flame structure computed with supercritical fluid properties at the conditions listed in Table 3: (a) major species and density, and (b) temperature and heat release rate.

Fig. 9. Profiles of minor species.
Detailed analysis of the elementary reactions reveals that the peak is produced by R16, which starts production of $\text{H}_2\text{O}_2$ ahead of other $\text{H}_2\text{O}_2$-related elementary reactions (Fig. 10).

Figure 8(b) shows the temperature and heat release rate profiles. The heat release layer extends over almost the entire flame, and the so-called diffusion layers, in which convection and molecular diffusion are balanced, are not well structured. The heat release layer profile has two peaks, one of which is located on the fuel side and the other on the oxidizer side. Figure 11 shows the contributions of elementary reactions to the heat release rate, where reactions which are not so important for the formation of the two-peak profile are removed for legibility. The major proportion of the heat release rate is due to R8, which contributes to the formation of the fuel-side peak. The oxidizer-side peak is formed by the heat releases from R9, 13, 16 and 21, each of which takes place in a very narrow layer.

One of the most distinctive properties of a supercritical fluid is the sharp change in enthalpy around the critical temperature, which leads to an extremely peaky profile of specific heat at constant pressure $c_p$. Figure 12 shows the profiles of $c_p$, temperature and enthalpy per unit mass at the edge of the oxygen diffusion layer, where the $c_p$ profile is presented with a mark on each computational grid point. The $c_p$ profile has an extreme peak where the temperature of the mixture passes through the vicinity of the critical temperature of $\text{O}_2$, 155.15 K. The enthalpy profile, accordingly, has an inflectional aspect. These profiles require a very fine grid resolution and make the computation very stiff. More than 2,000 grid points are located within the computational domain of 1 cm. The profile of $c_p$ indicates that we need a resolution of approximately 40 nm to reproduce the structure using the direct numerical simulation (DNS) approach. This is far worse than we expected from the flame theory described in the introduction of this paper. When we deal with flames of larger strain rates, even higher resolution is required. This means that the DNS approach is not practical in the near term, and that we need to use flame modeling. In addition, extremely fine spatial resolution used in the large strain rate computations would conflict with the assumption of continuum fluid. In the largest strain rate computation in this study, which is presented later, the width of the $c_p$ peak is approximately 15 nm and the grid resolution in the vicinity of the peak is 3 nm, while the mean free path of gaseous $\text{O}_2$ at 60 atm is roughly estimated to be 1 nm using STP properties. Then the Knudsen number based on the $c_p$ peak width is 0.067, and that based on the cell size is 0.33. We have to recognize this possibility when we simulate flames of even larger strain rates with supercritical fluid properties.

5.2 Effects of fluid properties at supercritical pressure

To investigate the effects of supercritical fluid properties, the flame structure is compared with two reference computations: case A with STP gas properties and case B with SRK EOS and STP gas transport properties. In both cases the pressure, temperatures and injection velocities are the...
same as those used in the computation with the full supercritical fluid properties.

Figure 13 presents the flame structure of case A, while Fig. 14 shows that of case B. The use of SRK EOS thins the flame and increases the maximum heat release rate (Fig. 13). This is simply because the strain rate is increased due to the increase of injection fluid density, especially on the oxygen side. The modification of transport properties produces a slight reduction in heat release rate (Fig. 14), which results from the increase of viscosity and thermal conductivity, and a decrease of diffusivity on the low-temperature oxygen side. The diffusivity decreases by approximately one-fifth in the oxygen diffusion layer and the viscosity and thermal conductivity increase drastically in the cryogenic region as shown in Fig. 15. Although the changes of transport coefficients are drastic at the edge of the oxygen diffusion layer, the change of heat release rate is slight, indicating that the change in the flame structure is not so significant. The effects of modification of transport properties on flame structure are discussed later.

A further remarkable point is the cusp in the profile of density at the edge of oxygen diffusion layer shown in Fig. 14(a). This cusp results from the existence of H$_2$O in a region where the temperature is lower than its boiling point. The pressure is lower than the critical pressure of H$_2$O in this study, thus H$_2$O is found in the liquid phase there. Although H$_2$O is produced in the hot region, it diffuses toward the low-temperature side by molecular diffusion and eventually a small amount reaches a region where the temperature is lower than its boiling point. In the simulation with transport property modification, the cusp is not visible (Fig. 8(a)) by chance, but liquid H$_2$O exists. The effect of liquid H$_2$O on the flame structure may not be significant, but we have to bear in mind that the validity of the physical model is violated locally, although the affected region is small.

5.3. Discussion from the viewpoint of flamelet table construction

In the previous section, we observed that the effects of supercritical fluid properties are not so significant in the reacting region and that the drastic changes of transport properties in the cryogenic region do not greatly affect the chemical reactions in the reacting region. These observations indicate the possibility of flamelet table construction by simulations with STP gas properties. We investigate this possibility in the following.
When we construct the flamelet tables of diffusion flames, the variables are often tabulated as functions of the local mixture fraction \( Z \), the scalar dissipation rate of the fuel mixture fraction \( \chi \), and variation of the mixture fraction

\[
Z = \frac{1}{1/M_{H_2} + 2/M_{O_2}} \left[ \frac{1}{M_{H_2}} \cdot \left\{ (Y_{H_2} + Y_{H_2O} + Y_{H_2O_2})M_{H_2} + (Y_{OH} + Y_{H} + Y_{H_2O})M_{H} \right\} - \frac{2}{M_{O_2}} \cdot \left\{ (Y_{O_2} + Y_{H_2O_2} + Y_{H_2O})M_{O_2} + (Y_{OH} + Y_{H} + Y_{H_2O})M_{O} \right\} \right]
\]

where \( M_i \) denotes the molecular weight of species \( i \). The scalar dissipation rate \( \chi \) is defined as

\[
\chi = 2D|\nabla Z|^2, \tag{10}
\]

where the diffusivity of mixture fraction \( D \) is given as \( D = \lambda/\rho c_p \).

The flame can be approximately characterized using these two parameters: \( Z \) is equivalent to the fuel mass fraction when the burnt mixture is turned back to the unburnt state, and \( \chi \) presents the mixing time scale; In other words, the degree of non-equilibrium. Figure 16 shows the profiles of major species and temperature have peaks around the mixture fraction equivalent to the stoichiometric condition \( Z_{st} \) (\( =2M_{H_2}/(M_{O_2}+2M_{H_2}) \approx 0.11 \)). From this kind of mapping, combustion characterizing quantities, such as the mass fractions of components, can be estimated. The mapping depends on the strain imposed on the flame. Figure 17 shows the changes in flame maximum temperature and maximum heat release rate with the change of strain imposed on the flame. By changing the distance \( L \), the strain is controlled and the resulting scalar dissipation rate at the stoichiometric position \( \chi_{st} \) is chosen as the abscissa. The condition of the previously shown flame (Fig. 16) is indicated by a \( \triangle \) symbol (\( \chi_{st} = 1.5 \times 10^2 \) s). The maximum temperature decreases and the maximum heat release rate increase with the increase of \( \chi_{st} \); that is, with the increase in degree of non-equilibrium in the range of \( \chi_{st} \) shown in the figure. As expected from the rapid drop of maximum temperature in the range of \( \chi_{st} > 10^4 \) s, the flame goes toward extinction when \( \chi_{st} \) increases more. Thus, \( \chi_{st} \) defines the flame global structure and \( Z \) is used to determine the local values of variables.

Considering the above, the flame structures are compared between simulations with supercritical fluid properties and with STP gas properties at identical \( \chi_{st} \)'s. Three typical conditions of \( \chi_{st} \) marked in Fig. 17 are chosen for comparison: \( \triangle \) very far from flame extinction; \( \bigcirc \) temperature starts to fall; and \( \bigotimes \) flame is about to extinguish. Again, the case \( \triangle \) corresponds to the flame whose structure was previously shown in Figs. 8 and 15, and \( \chi_{st} = 1.5 \times 10^2 \) s. The \( \chi_{st} \)'s of \( \bigcirc \) and \( \bigotimes \) are \( 1.0 \times 10^4 \) and \( 4.0 \times 10^4 \) s, respectively. The distance \( L \) is adjusted to match \( \chi_{st} \) as shown in Table 4, and differs between the two types of simulations.

The flame structure of \( \chi_{st} = 1.5 \times 10^2 \) s simulated with STP gas properties is shown in Fig. 18. The profiles of chemical species, heat release rate and temperature are almost identical to those shown in Fig. 8. The flame structures of \( \chi_{st} = 1.0 \times 10^4 \) s are presented in Fig. 19 simulated with supercritical fluid properties and in Fig. 20 with STP gas properties. The flame structures of \( \chi_{st} = 4.0 \times 10^4 \) s are shown in Figs. 21 and 22. Comparison of the two rather high dissipation rate conditions also shows that the flame internal structures are almost identical for the two types of simulations.

The distribution of compressibility factor (\( =p/\rho RT \)) is shown in Fig. 23 for the \( \chi_{st} = 4.0 \times 10^4 \) s case. The factor is almost unity in the flame, indicating that the effects of SRK EOS are quite small. The effects of transport properties on the flame structure are estimated by varying the transport coefficient from STP to supercritical properties.
via parameter $a$ varying from 0 to 1: that is, $k = a k^{sc} + (1 - a) k^{STP}$, where $k$ is each transport coefficient, and superscripts $sc$ and $STP$ stand for supercritical and STP properties, respectively. The profile shapes of chemical species mass fractions, temperature and heat release rate are defined in terms of their peak values $P$ and one-tenth peak width $W$. $P$ and $W$ are normalized by the values at $a = 1$, and their sensitivities on $a$, $\partial P/\partial a$ and $\partial W/\partial a$, are estimated by linear fitting. The results are summarized in Table 5. The sensitivity is generally low; for example, the peak and the width of the $Y_{OH}$ profile decreases 1.2 and 0.17%, respectively, when the transport properties change from STP to supercritical. However, only $Y_{H_2O_2}$ is exceptional and the sensitivity is high. It peaks at the edge of the oxygen diffusion layer, but the amount is quite small as shown in Fig. 22(b) and the impact on the entire flame structure is not significant. $H_2O_2$ plays a key role at low temperature through R16 in Table 1 and the sensitivity may be a problem at igniting and extinction events, but may not be a problem when the so-called flame structure is established; that is, within the range of the laminar flamelet concept application. In fact, in rocket engine combustor conditions, the chemical reaction is so fast that the diffusion flame is expected to be far from its extinction condition.

These observations indicate that we can construct flamelet tables with acceptable accuracy using STP gas property sim-

| $x_a$ (1/s) | $L$ (cm) for supercritical simulation | $L$ (cm) for STP simulation |
|------------|-------------------------------------|---------------------------|
| 1.5 $\times 10^2$: $\triangle$ | 1.0000 | 0.8530 |
| 1.0 $\times 10^4$: $\diamond$ | 0.0225 | 0.0150 |
| 4.0 $\times 10^4$: $\bigcirc$ | 0.0078 | 0.0046 |

Fig. 18. Flame structure computed with STP gas properties at $x_a = 1.5 \times 10^2$ 1/s: (a) major species and density, (b) minor species, and (c) temperature and heat release rate.

Fig. 19. Flame structure computed with supercritical fluid properties at $x_a = 1.0 \times 10^4$ 1/s: (a) major species and density, (b) minor species, and (c) temperature and heat release rate.
Simulations with supercritical fluid properties require extremely high spatial resolution and therefore require a lot of time. The use of simulations with STP gas properties may be an effective short-cut in flamelet table construction.

5.4 Flame structure dependency on chemical kinetics

The validity of chemical kinetics for the very high pressure condition is still controversial and there has not been a definitive kinetics so far. In this section, another well-known kinetic model developed for high-pressure condition is tested and the flame structure is compared to determine the impact of chemical kinetics. The model proposed by Shimizu et al. is employed here.

The flame structures of $\chi_a = 1.0 \times 10^4$ $\text{l/s}$ are presented in Fig. 24. The distributions of the major species, temperature and heat release rate are almost identical to those calculated with Li’s kinetics. Slight differences are observed in the distributions of minor species, especially in the $\text{H}_2\text{O}_2$ distribution. The difference is not large in the scope of this study and the impact of the difference between the two kinetic models is not significant in the range investigated in this study.

6. Conclusion

Supercritical fluid properties were implemented in a 1-D counterflow flame simulation code. The internal flame structure of the $\text{GH}_2$/LOX diffusion flame was investigated and compared with the flame structure simulated with STP gas properties. The following conclusions were obtained.

- Fluid properties derived from SRK EOS and Chung’s method reproduced to a fairly good extent, the fluid properties at supercritical pressure conditions.
- A $\text{GH}_2$/LOX diffusion flame at supercritical pressure had...
two peaks in the profiles of H$_2$O$_2$ mass fraction and the heat release rate. The oxygen side peaks were very narrow and resulted from the combined contributions of elementary reactions.

*The flame had a very fine structure at the edge of the oxygen diffusion layer. The profile of $c_p$ was extremely narrow and a grid resolution of the order of 10 nm was needed to fully reproduce the flame structure.*

*It was not realistic in the near term to simulate the flame structure via the DNS approach, especially in multi-dimensional analysis; therefore, flame modeling was necessary for the practical simulation of combustion at supercritical pressure.*

*When we parameterized the flames by the scalar dissipation rate at their stoichiometric positions, simulation with STP gas properties produced an almost identical flame internal structure to that of simulations with supercritical fluid properties for the computational conditions tested in this paper.*

*The use of STP gas property simulations is expected to be an effective means of greatly reducing computational
cost in the construction of flamelet tables at supercritical pressure.

The above conclusions were obtained when we relied on the computational model described in section 3. As mentioned in section 5.2, the validity of the physical model may have been violated regarding the property of H\textsubscript{2}O. In addition, some physical constants for intermediate species are unknown, leading to the lack of validation of fluid properties. These issues require careful attention and the ways to overcome them should be explored.

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Appendix

A.1. Enthalpy and specific heat

The enthalpy of dense fluid is derived from the SRK equation of state and Maxwell’s equations of thermodynamics. In this paper, we start from the following relationship regarding the internal energy \( u \),

\[
\frac{du}{dv} = c_v dT + \left( T \left( \frac{dp}{dT} \right)_V - p \right) dV. \tag{A.1}
\]

At a given temperature, the deviation of \( u \) from its STP value \( u^0 \) is obviously

\[
\Delta u = u - u^0 = \int_0^v \left( T \left( \frac{dp}{dT} \right)_V - p \right) dV. \tag{A.2}
\]

The integrand of the right hand side of Eq. (A.2) is

Table 5. Sensitivities of profile shapes of mass fractions, temperature and heat release rate on transport property modification.

|   | \( \frac{\partial Y_{OH}}{\partial \alpha} \) | \( Y_{H,O} \) | \( Y_H \) | \( Y_O \) | \( Y_{H,O} \) | \( Y_{H,O} \) | \( T \) | HRR |
|---|---|---|---|---|---|---|---|---|
| \( \frac{\partial P}{\partial \alpha} \) | \(-1.21 \times 10^{-2}\) | \(8.74 \times 10^{-4}\) | \(-1.72 \times 10^{-2}\) | \(-2.88 \times 10^{-2}\) | \(1.78 \times 10^{-1}\) | \(-1.43 \times 10^{-2}\) | \(-2.23 \times 10^{-3}\) | \(1.96 \times 10^{-2}\) |
| \( \frac{\partial W}{\partial \alpha} \) | \(-1.73 \times 10^{-3}\) | \(9.41 \times 10^{-3}\) | \(2.30 \times 10^{-3}\) | \(-4.79 \times 10^{-3}\) | \(-8.55 \times 10^{-2}\) | \(-5.62 \times 10^{-3}\) | \(-4.23 \times 10^{-3}\) | \(-7.00 \times 10^{-4}\) |
\begin{align}
T \left( \frac{\partial p}{\partial T} \right)_V - p &= T \left( \frac{R_u}{M_m V - b} - \frac{1}{M_m V(M_m V + b)} \left( \frac{\partial a}{\partial T} \right)_V \right) \\
&- \left\{ \frac{R_u T}{M_m V - b} - \frac{a}{M_m V(M_m V + b)} \right\} \\
&= \frac{1}{b} \left[ \frac{1}{M_m V} - \frac{1}{M_m V + b} \right] \left( \frac{\partial a}{\partial T} \right)_V - a - \left( \frac{\partial a}{\partial T} \right)_V T. 
\end{align}

Then \( \Delta u \) is calculated as

\begin{equation}
\Delta u = \frac{1}{M_m b} \ln \left( \frac{M_m V + b}{M_m V} \right) \left( \frac{\partial a}{\partial T} \right)_V T - a. 
\end{equation}

Using the relationship of \( h = u + pV \), the deviation of enthalpy is

\begin{equation}
\Delta h = pV - \frac{R_u T}{M_m} + \Delta u \\
= pV - \frac{R_u T}{M_m} + \frac{1}{M_m b} \ln \left( \frac{M_m V + b}{M_m V} \right) \left( \frac{\partial a}{\partial T} \right)_V T - a,
\end{equation}

which yields Eq. (2). The specific heat at constant pressure \( c_p \) is obtained by partially differentiating Eq. (2) with respect to \( T \), which yields Eq. (3).

The term \( \partial V/\partial T \)_\( p \) in Eq. (3) is obtained in the following manner. When we employ the SRK EOS, the density \( \rho \) or the specific volume \( V (=1/\rho) \) is obtained by solving the cubic equation below,

\begin{equation}
V^3 + c_1 V^2 + c_2 V + c_3 = 0, 
\end{equation}

which yields

\begin{equation}
\left( \frac{\partial V}{\partial T} \right)_p = \frac{\left( \frac{\partial c_1}{\partial T} \right)_p V^2 + \left( \frac{\partial c_2}{\partial T} \right)_p V + \left( \frac{\partial c_3}{\partial T} \right)_p}{3V^2 + 2c_1 V + c_2}. 
\end{equation}

\textbf{A.2. Chung’s correction method}

The correction of the viscosity and thermal conductivity is made by use of Chung’s method\textsuperscript{20} in the following formulations.
Viscosity

\[ \mu = \mu_s + \mu_p, \]
\[ \mu_s = \mu_0[1/G_2 + A_6 Y], \]
\[ \mu_p = [36.344 \times 10^{-6}(M_m T_C)/\sqrt{V_C^2}]/A_7 Y^2 G_2 \exp(A_k + A_9/T^* + A_{10}/T^{*2}), \]
\[ Y = \rho V_C/6, \]
\[ T^* = T/T_C \times 1.2593, \]
\[ G_1 = (1.0 - 0.5Y)/(1.0 - Y)^3, \]
\[ G_2 = [A_1[1.0 - \exp(-A_4 Y)]/Y + A_2 G_1 \exp(A_5 Y + A_5 G_1)/(A_1 A_4 + A_2 + A_3). \]

Thermal conductivity

\[ \lambda = \lambda_s + \lambda_p, \]
\[ \lambda_s = \lambda_0[1/G_2 + B_6 Y], \]
\[ \mu_p = [3.039 \times 10^{-4}(T_C/M_m)/\sqrt{V_C^2}]/B_7 Y^2 G_2 \exp(B_1 + B_2 T_T^{1/2}), \]
\[ T_T = T/T_C, \]
\[ G_1 = (1.0 - 0.5Y)/(1.0 - Y)^3, \]
\[ H_2 = [B_1[1.0 - \exp(-B_2 Y)]/Y + B_2 G_1 \exp(B_3 Y + B_3 G_1)/(B_1 B_4 + B_2 + B_3). \]

Here, \( \mu_0 \) and \( \lambda_0 \) are the viscosity and conductivity at STP condition, respectively, which are estimated using CHEMKIN library in this study.\(^{[19]} \) The coefficients \( A_i \) (\( i = 1, 10 \)) and \( B_i \) (\( i = 1, 7 \)) are given in Eqs. (A.10) and (A.11).

\[ A_i = a_0(i) + a_1(i)\omega + a_2(i)\mu_T + a_3(i)\kappa \quad i = 1, 10, \quad (A.10) \]
\[ B_i = b_0(i) + b_1(i)\omega + b_2(i)\mu_T + b_3(i)\kappa \quad i = 1, 7, \quad (A.11) \]

where \( \omega, \mu_T \) and \( \kappa \) are, respectively, the acentric factor, reduced dipole moment and association parameter of the mixture which are defined by Chung’s method.\(^{[20]} \) The dipole moment and the association parameter are taken into account only for \( H_2O \) in this study. The coefficients in Eqs. (A.10) and (A.11), \( a_i \) (\( i = 1, 10 \)) and \( b_i \) (\( i = 1, 7 \)) are shown in Tables A.1 and A.2.\(^{[20]} \)

### A.3. Takahashi’s correction method

Takahashi’s method corrects the diffusivity for dense fluid in the following way. The ratio of the product of diffusivity and pressure to that at atmospheric condition is given by the following relationship:\(^{[20]} \)

\[ (Dp)/(Dp)^0 = (Dp)_0\exp(AT_T^{-B}(1 - f)), \quad (A.12) \]

where \( f = CT_T^{-E} \).

The parameters in Eq. (A.12) are interpolated using the parameters listed in Table A.3 as functions of \( p_r = p/p_c \).