Kinetic modeling study of hydrogen addition to premixed dimethyl ether-oxygen-argon flames

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**ABSTRACT**

The chemical composition of flames was examined systematically for a series of laminar, premixed low-pressure Dimethyl ether (DME)-oxygen-argon flames blended with hydrogen. The effects of hydrogen addition to the DME base flame were seen to result in interesting differences. The flame is analyzed with a comprehensive kinetic model that combines the chemistries of hydrogen and DME combustion. The results indicated that the reduction of CH₃OCH₃ mole fraction in the blend is the dominant factor for the reduction of CH₃OCH₃ and CO mole fractions in the flame. The rate of the primary reactions related to CH₃OCH₃ and CO increases obviously with the addition of hydrogen. When the volume fractions of H₂ to the total of DME and H₂ exceeds 40%, H₂ will change from an intermediate species to a reactant, which means the effect of H₂ on the premixed combustion will be more significant. The free radicals in the radical pool, such as H, O and OH radicals, increase as hydrogen is added, which promote the combustion process. The mole fraction of CH₂O is decreased as hydrogen is added. Less soot precursors (acetylene (C₂H₂)) were produced with the addition of H₂.

**1. Introduction**

With increasing concern about fossil fuel shortage and stringent emission regulations, researches on alternative fuels gain more and more attention in the field of internal combustion engines [1,2]. As renewable energy sources with excellent characteristics, dimethyl ether and hydrogen have received considerable attention and are regarded as the most promising alternative fuels. DME is one of the most promising alternative automotive fuel solutions among the various ultra clean, renewable, and low-carbon fuels under consideration worldwide. DME can be derived from many sources, including renewable materials (biomass, agricultural products and waste) and fossil fuels (coal and natural gas). Only modest modifications are required to convert a diesel engine to run on DME [3,4]. H₂ is also being extensively studied as an excellent alternative fuel and fuel additive to spark ignition engines for its low required ignition energy, wide flammability range, high flame speed, high thermal efficiency, and low emissions [5–9].

H₂ has been used in DME homogeneous charge compress ignition (HCCI) engine to control the ignition timing and expand the load range [10]. Experimental and numerical studies of DME/air [11–13] or H₂/air premixed flames have been extensively carried out [14,15]. In the previous research, Chen et al. measured the species mole fraction profiles of DME-hydrogen-oxygen-argon laminar premixed flames by using the tunable synchrotron vacuum ultraviolet (VUV) photoionization combined with molecular-beam sampling mass spectrometry techniques [16]. Mole fraction profiles of four intermediate species including methyl radical (CH₃),
The reactants mole fractions of the calculated combustion with hydrogen addition will be discussed.

However, constrained by the measuring technologies, only limited intermediate radicals were reported in few studies. Moreover, the combined chemical kinetics of DME and H₂ was not well understood. Since the oxidation mechanism of both DME and hydrogen are reasonably well understood, the combustion process can be simulated using chemical kinetics calculation to get comprehensive information. The objective of this study is to simulate the DME-H₂-O₂ premixed flame with detailed chemical reaction mechanism and analyze the chemical kinetics effect of hydrogen addition on the blended fuel combustion. The potential of emission reduction of DME combustion with hydrogen addition will be discussed.

2. Mechanism validation and computational methods

The detailed reaction mechanism of DME was well developed by Curran et al. [17,18]. It consists of 351 elementary chemical reactions with associated rate coefficient expressions and thermo chemical parameters for the 79 species. The detailed combustion reaction mechanism for hydrogen was included in DME oxidation mechanism.

In this study, the PREMIX code of CHEMKIN II program with detailed DME oxidation mechanism was used to calculate the DME-hydrogen-O₂ freely propagated laminar premixed flames. The PREMIX code adopts finite difference approximations and Newton algorithm technique with adaptive meshes and mixture averaged transport parameters to solve the steady-state mass, species and energy conservation equations of the calculated flames. The withdraw differencing on both convective and diffusion terms was used in the calculation. The gradient and curvature was set to be both 0.9 to control the adaptive grid. The calculation domain was from 0.0 cm at the upstream to 10.0 cm at the downstream, and this is sufficiently long to achieve the adiabatic equilibrium in the downstream. In order to compare with Chen’s experiment, the initial conditions are as follows: the initial temperature is 298 K and the pressure is 4 kPa, the reactants mole fractions of the initial conditions are as follows: the initial temperature is 298 K and the pressure is 4 kPa, the reactants mole fractions of the initial conditions are as follows: the initial temperature is 298 K and the pressure is 4 kPa, the reactants mole fractions of the initial conditions are as follows: the initial temperature is 298 K and the pressure is 4 kPa. The initial guessing values of the position is set to be 400 K. Initial guessing values of the temperature with that of Chen’s experiment [11].

In order to simulate and interpret the effect of hydrogen addition on DME-O₂ premixed flame by using chemical reactions, the chemical kinetics used in the calculation must be capable of simulating pure DME and DME-hydrogen fuel blends. The comparison of the measured flame temperature of the DME-hydrogen-O₂ mixtures with the calculated results of DME oxidation mechanism is presented in Fig. 1. As the PREMIX code did not consider the heat losses (by definition) and the temperature was computed from the energy equations, the computed flame temperature is higher than that of the experiment results. As shown in Fig. 1, the flame temperature was decreased with the addition of H₂. The same effect of hydrogen addition in methane flame temperature was proven by Sepman et al. [19]. Due to the volume calorific value of H₂ was much lower than that of DME, the unit volume heat release of the mixture will decrease with the increase of hydrogen fraction. The calculation results successfully capture this behavior. This shows that the DME oxidation mechanism can well reproduce the flame temperature of DME-hydrogen-O₂ mixtures over a wide range of equivalence ratios and hydrogen fractions.

3. Results and discussions

By using detailed chemical reaction mechanism, the mole fraction profiles and rate of production of all the flame species can be derived from the calculation results. Fuel-rich (φ = 1.5) DME-oxygen (O₂)-argon (Ar) premixed flames with different hydrogen fractions (volume fractions of H₂ to the total of DME and H₂ were 0%, 40% and 80%) were investigated in this study. Some representative species including the major species CH₃OCH₃, H₂, CO, the free radicals H, O, OH and C1, C2 intermediate species CH₃O and C₂H₂ are selected to analyze the effect of hydrogen addition on the DME chemical reaction. As the mole fraction of DME is decreased with the addition of hydrogen. The calculated mole fraction of carbon-related species in the flames will be affected by this. In this study, the normalized mole fraction of the carbon-related species is used through the following formula:

\[ \frac{Y_{i,DME}}{Y_{i,DME}} = \frac{Y_{i,DME}}{Y_{i,DME}} \]

Table 1 – The reactants mole fractions of the calculated flames.

<table>
<thead>
<tr>
<th>Flame no.</th>
<th>R(H₂)(%)</th>
<th>DME</th>
<th>H₂</th>
<th>O₂</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>0.1637</td>
<td>0.109</td>
<td>0.36365</td>
<td>0.36365</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>0.0857</td>
<td>0.343</td>
<td>0.28565</td>
<td>0.28565</td>
</tr>
</tbody>
</table>

Fig. 1 – Comparison of the calculated premixed flame temperature with that of Chen’s experiment [11].

acetylene (C₂H₂), formaldehyde (CH₂O), ethylene (C₂H₄) were measured and the effect of hydrogen addition on the combustion reaction of DME flames was analyzed.
where the \( Y_{DME1} \) is the mole fraction of DME in flame 1 and \( Y_{DME}^{n} \) refers to that in flame \( n \). \( Y_i \) is the mole fraction or the rate of production of the carbon-related species \( i \) in flame \( n \) and \( Y_i^{\text{C}} \) refers to its corresponding C normalized value.

### 3.1. Mole fraction and rate of production of major flame species

Fig. 2 gives the mole fraction profiles and the rate of production of CH\(_3\)OCH\(_3\) in the flames. The CH\(_3\)OCH\(_3\) is completely consumed at about 5.0 mm from the upstream cold boundary. There are two reasons for reducing the mole fraction of DME. First, the initial mole fraction of DME is lower. And second, more DME was consumed when hydrogen is added. As the C normalized CH\(_3\)OCH\(_3\) mole fraction is almost no change at different hydrogen fractions, it indicates that the reduction of CH\(_3\)OCH\(_3\) mole fraction in the blend is the dominant factor for CH\(_3\)OCH\(_3\) mole fraction decrease in the flame. Actually, the C normalized CH\(_3\)OCH\(_3\) mole fraction in the preheating zone (from 0.0 mm to 2.0 mm) is increased slightly with the increase of hydrogen fraction.

The primary reactions associated with CH\(_3\)OCH\(_3\) can be recognized from the rate of production analysis as follows:

\[
\begin{align*}
\text{CH}_3\text{OCH}_3 & \rightarrow \text{CH}_3 + \text{CH}_3\text{O} \\
\text{CH}_3\text{OCH}_3 + \text{OH} & \rightarrow \text{CH}_3\text{OCH}_2 + \text{H}_2\text{O} \\
\text{CH}_3\text{OCH}_3 + \text{H} & \rightarrow \text{CH}_3\text{OCH}_2 + \text{H}_2 \\
\text{CH}_3\text{OCH}_3 + \text{O} & \rightarrow \text{CH}_3\text{OCH}_2 + \text{OH} \\
\end{align*}
\]

The main consumption reactions of CH\(_3\)OCH\(_3\) in the flame are the unimolecular decomposition reaction and the H abstraction reactions attacked by H, O and OH. The rate of the unimolecular decomposition reaction decreases as hydrogen is added. But the rate of the H abstraction reactions increases, which means that the production of H, O and OH radicals was promoted with the addition of H\(_2\). It is also can be seen that the peak reaction rate of these reactions moved to the upstream cold boundary with the increase of H\(_2\) fraction, which is caused by the reaction promotion effect and the high flame speed of H\(_2\).

The mole fraction and the rate of production of H\(_2\) in the flames are shown in Fig. 3. The dominant reactions related to H\(_2\) are as follows:

\[
\begin{align*}
\text{H}_2 + \text{O} & \rightarrow \text{H} + \text{OH} \\
\text{H}_2 + \text{OH} & \rightarrow \text{H} + \text{H}_2\text{O} \\
\text{CH}_2\text{O} + \text{H} & \rightarrow \text{HCO} + \text{H}_2 \\
\text{CH}_3\text{OCH}_3 + \text{H} & \rightarrow \text{CH}_3\text{OCH}_2 + \text{H}_2 \\
\end{align*}
\]

The rates of these reactions increase with the addition of H\(_2\), especially the reactions of R5 and R6. This is also due to the increase of the O, H and OH radicals with the addition of H\(_2\). These reactions all moved to the upstream side. It is interesting to note that H\(_2\) will change from an intermediate species to a reactant when hydrogen fraction exceeds 40%, which means the effect of H\(_2\) addition on the combustion will be more obvious. The same trend was seen in H\(_2\)/methane flames [20].

![Fig. 2](image-url) – Mole fraction and rate of production of CH\(_3\)OCH\(_3\) in the fuel blends flames.
The mole fraction and rate of production of CO are plotted in Fig. 4 with different H₂ fractions. The experiment data from Chen’s experiment are also presented in this figure. The calculation result gives trends comparable to that of the experiment. With the increase of hydrogen fraction, CO mole fraction is decreased; while the C normalized CO mole fraction is increased. This indicates that the production of CO is promoted with the addition of hydrogen, but less CH₃OCH₃ participate in the reaction result in less production of CO. This can be clearly observed from the rate of production of the dominant reactions contributing to CO increase remarkably as hydrogen is added.

The main CO reaction pathways are:

\[
\begin{align*}
\text{CO} + \text{OH} &= \text{CO}_2 + \text{H} & \text{(R9)} \\
\text{HCO} + \text{M} &= \text{H} + \text{CO} + \text{M} & \text{(R10)} \\
\text{HCO} + \text{H} &= \text{CO} + \text{H}_2 & \text{(R11)} \\
\text{HCO} + \text{CH}_3 &= \text{CH}_4 + \text{CO} & \text{(R12)} \\
\text{HCO} + \text{O}_2 &= \text{CO} + \text{HO}_2 & \text{(R13)}
\end{align*}
\]

It is clearly that the CO is mainly produced by the H abstraction reactions from HCO and consumed by OH radical to produce CO₂.
3.2. **Mole fraction and rate of production of free radicals**

The free radicals such as H, O and OH are extremely active due to the presence of unpaired electrons and are short-lived during the combustion. As the radical pool becomes established, these free radicals play the most important role in the chain branching and chain propagating reactions. Fig. 5 presents the mole fraction and rate of production of H, O and OH with the addition of H₂. It is clearly that the H, O and OH mole fractions are all increased with the increase of hydrogen mole fraction. With the increase of these radicals, the premixed combustion was promoted.

The major reactions related to H are:

\[
\begin{align*}
O + H_2 & \rightarrow H + OH \quad (R5) \\
OH + H_2 & \rightarrow H + H_2O \quad (R6) \\
\text{CH}_2O + H & \rightarrow \text{HCO} + H_2 \quad (R7) \\
\text{HCO} + M & \rightarrow H + CO + M \quad (R10) \\
H + O_2 & \rightarrow O + OH \\ 
\end{align*}
\]

![Fig. 5 – Mole fraction and rate of production of H, O and OH in the fuel blends flames.](image-url)
\[ \text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H} \quad \text{(R15)} \]

The main reactions of O radical are reaction R5, R14 and R15, and the primary reactions of OH are reaction R5, R6 and R14.

3.3. Mole fraction and rate of production of CH2O and C2H2 species

Formaldehyde is a colorless gas with a characteristic pungent odor and it is the simplest aldehyde. Formaldehyde can be allergenic and carcinogenic. It is highly toxic to humans. CH2O is an intermediate combustion product, and it decreases sharply when the temperature reaches over a certain value.

Fig. 6 gives the mole fraction and rate of production of CH2O for DME-hydrogen flames with different hydrogen fractions. The Chen’s experiment data are also shown in this figure. The compute CH2O concentration trends are consistent with that of the experiment. The mole fraction of CH2O is decreased with the addition of H2, while its C normalized value is increased. The dominant reactions associated with CH2O are:

\[ \text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2 \quad \text{(R7)} \]
\[ \text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H} \quad \text{(R15)} \]
\[ \text{CH}_2\text{O} (+\text{M}) = \text{CH}_2\text{O} + \text{H} (+\text{M}) \quad \text{(R16)} \]
\[ \text{CH}_3\text{OCH}_2 = \text{CH}_2\text{O} + \text{CH}_3 \quad \text{(R17)} \]

Except reaction R16, all the other reactions are promoted by the addition of hydrogen. Most of the CH2O transformed to HCO, which is the main precursor of CO. The decrease of CH2O through hydrogen addition indicates that the CH2O emission in DME combustion can be decreased.

It is well known that soot is formed in fuel-rich regions under high temperature conditions. The precursors of soot are unsaturated hydrocarbons such as acetylene (C2H2), ethylene (C2H4) and propargyl (C3H3). The proportion of fuel carbon forming soot precursors has been found to decrease with increased oxygen content and with decreased number of C–C bonds in the fuel [21].

The mole fraction and rate of production of C2H2 for DME-hydrogen flames with different hydrogen fractions are given in Fig. 7. The experiment data from Chen’s experiment are also plotted in this figure. The calculation result gives trends comparable to that of the experiment. The mole fractions of C2H2 decrease with the increase of hydrogen fraction, and its normalized value changes little.

The primary reactions contribute to C2H2 are:

\[ \text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO} \quad \text{(R18)} \]
\[ \text{C}_2\text{H}_3 + \text{O}_2 = \text{C}_2\text{H}_2 + \text{HO}_2 \quad \text{(R19)} \]
\[ \text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H} \quad \text{(R20)} \]

The rate of production of C2H2 is decreased with the increase of hydrogen fraction. This shows the potential in reducing soot emission in DME combustion as hydrogen is added.

Fig. 6 – Mole fraction and rate of production of CH2O in the fuel blends flames.
4. Conclusions

The DME-hydrogen-O₂ freely propagated laminar premixed flames were calculated by using PREMIX code of CHEMKIN II program with detailed DME oxidation mechanism. The mole fraction profiles and the rate of production of the primary reactions related to the major species were achieved. The chemical effect of hydrogen addition on DME/H₂ premixed combustion was evaluated by the mole fraction and rate of production analysis of the selected major species. The main results are summarized as follows:

(1) When the volume fractions of H₂ to the total of DME and H₂ exceeds 40%, H₂ will change from an intermediate species to a reactant, which means the effect of H₂ on the premixed combustion will be more significant.
(2) The free radicals in the radical pool, such as H, O and OH radicals, increase as hydrogen is added, which promote the combustion process.
(3) The mole fraction of CH₂O is decreased as hydrogen is added.
(4) Less soot precursors were produced with the addition of H₂.

Fig. 7 – Mole fraction and rate of production of C₂H₂ in the fuel blends flames.

REFERENCES


