Modeling of a Cracking and Auto-Ignition Process in Diesel Combustion

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ABSTRACT

A new reaction model for the diesel ignition is presented considering a cracking process that takes place before ignition in most diesel combustion conditions. It is conceivable that the diesel ignition process is governed by high-temperature oxidation including cracking, unlike the low-temperature oxidation observed in the knocking process of SI engines. This model adopts the Rice-Hezfeld mechanism for the cracking process and supposes that the generation of alkyl radicals at the end of the pyrolysis is represented by notation of the global reaction. The global reaction is coupled with the C2 hydrocarbon oxidation mechanism to characterize the complete reaction system. The global reactions assumed in this study are as follows:

\[ C_{m}H_{n} + M \rightarrow \alpha C_{2}H_{4} + \beta i-C_{2}H_{6} + M \]
\[ n-C_{2}H_{7} \rightarrow C_{2}H_{4} + C_{2}H_{5} \]
\[ i-C_{2}H_{5} \rightarrow C_{2}H_{5} + CH_{3} \]

where, \( \alpha \) and \( \beta \) are constants which are determined by atomic balance. The rate constant for the above global reaction was obtained through comparison with the ignition delay measured in a rapid compression machine. The result shows good agreement between the calculated and measured induction periods at the high temperature oxidation range, which is higher than 1000K. Furthermore, the computed fractions of CH, C2H4, C2H6, and C2H8 during the induction period agree closely with the measurements.

INTRODUCTION

The ignition process of hydrocarbon fuels proceeds via different mechanisms depending on temperature range, as shown in Fig. 1. During high-temperature oxidation, many of the hydrocarbon molecules decompose before they can react directly with oxygen \(^{(1)}\). The weakest bond, C-C, is split in the initiation reaction and olefins and alkyl radicals are produced during the induction period. On the other hand, slow combustion at lower temperatures at the initiation process is considered to involve hydrogen abstraction by oxygen from a hydrocarbon fuel, and undergoes two-stage ignition \(^{(1)}\). Since the compression ignition process in diesel combustion shows instantaneous heat release at ignition and the temperature range is usually higher than 1000 K, a high-temperature combustion mechanism is considered dominant. Characteristics of diesel combustion such as thermal efficiency and NOx formation and emission are strongly affected by the ignition process and heat release process. Furthermore, it is considered that generation of soot is strongly influenced by a decomposed fraction such as acetylene or ethylene \(^{(2,3)}\). However, the detailed reaction mechanisms for higher hydrocarbons such as diesel fuel are complicated, and elementary reactions have not yet been elucidated.

In response to these needs, we present a new reaction model for auto-ignition in diesel combustion based on the high

![Diagram of combustion process of hydrocarbon fuels](image)

Fig.1 Overview of combustion process of hydrocarbon fuels
temperature mechanism special emphasis on the generation of derivatives or decomposed fuel fractions during the induction period.

BASIC CONCEPT

In high-temperature combustion, many of the hydrocarbon molecules decompose before they react directly with oxygen. Rice-Herzfeld postulated a general mechanism based on chain reactions involving atoms and free radicals, which enabled them to explain both the kinetics and the products of paraffin pyrolysis \(^{(1)}\). In their scheme the weakest bond, C-C, is split in the initiation reaction, and termination involves the interaction of two radicals. This scheme can be generalized as follows:

\[
\begin{align*}
\text{RH} & \rightarrow 2\text{R} \\
\text{R} + \text{RH} & \rightarrow \text{products} + \text{R} \\
\text{R} & \rightarrow \text{R} + \text{olefin} \\
\text{R} & \rightarrow \text{H} + \text{olefin} \\
\text{H} + \text{RH} & \rightarrow \text{R} + \text{H}_2 \\
\text{H} + \text{R} & \rightarrow \text{H}_2 + \text{olefin}
\end{align*}
\]

here RH shows the paraffin and R the alkyl radical. The forward reaction (1) is the initiation reaction and shows the split of C-C bond. The reverse direction shows the termination reaction. It is noted that the propagation reactions, not the branching reactions, are dominant in the thermal cracking process.

On the other hand, the Shell model \(^{(2)}\), originally developed to model the two-stage ignition process at low temperature combustion, is adapted for diesel combustion by optimizing the rate constants.

\[
\begin{align*}
\text{RH} + \text{O}_2 & \rightarrow 2\text{R} \\
\text{R} & \rightarrow \text{R} + \text{product} \\
\text{R} & \rightarrow \text{R} + \text{B} \\
\text{R} + \text{O} & \rightarrow \text{R} + \text{B} \\
\text{R} & \rightarrow \text{product} \\
\text{R} & \rightarrow \text{R} + \text{Q} \\
2\text{R} & \rightarrow \text{product} \\
\text{B} & \rightarrow 2\text{R}
\end{align*}
\]

As mentioned above, the thermal decomposition process is not initiated by the direct reaction of fuel with oxygen. Moreover, branching reaction such as R (14) unlikely occurs. Therefore, it is not rational to adapt the Shell model for high temperature mechanism in most diesel combustion conditions.

COMPUTATION

Description of the model

Edelman et al. showed the resemblance among ignition delays in higher paraffins (propane and above) at temperatures higher than 1000 K under the circumstance of oxygen coexistence \(^{(9)}\). They postulated a "quasi-global" scheme that consists of single-step overall reaction to characterize the reactions high up in the chain, and a set of detailed reversible reactions (wet CO mechanism) to characterize the kinetics processes at the lower end of the chain. This scheme is useful for the combustion problem, which relates to only the heat release process. However it cannot represent the thermal cracking process and the generation of fuel derivatives.

In this study, chain reactions for pyrolysis are represented by notation of the global reaction and coupled with the C\(_2\) hydrocarbon oxidation mechanism to characterize the complete reaction system \(^{(6-8)}\). Assuming that alkyl radicals decompose to give lower alkyl radicals and olefins without the shift of a hydrogen atom, we examine the two sets of global reactions R(15) and R(16) ~ R(18) to ascertain the chain reaction of pyrolysis as follows:

\[
\begin{align*}
\text{C}_n\text{H}_m + \text{M} & \rightarrow \alpha \text{C}_2\text{H}_4 + \beta \text{C}_2\text{H}_6 + \text{M} \quad \text{R(15)} \\
\text{C}_n\text{H}_m + \text{M} & \rightarrow \alpha \text{C}_2\text{H}_4 + \beta \text{i-C}_2\text{H}_6 + \text{M} \quad \text{R(16)} \\
\text{i-C}_2\text{H}_6 & = \text{C}_2\text{H}_4 + \text{CH}_2 \quad \text{R(17)} \\
\text{n-C}_2\text{H}_6 & = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \quad \text{R(18)}
\end{align*}
\]

here, \(\alpha\) and \(\beta\) are the constants decided from atomic balance. Reaction (15) assumes \(\text{C}_2\text{H}_4\) and \(\text{C}_2\text{H}_6\) as the products at the end of pyrolysis's chain reaction, while reaction (16) assumes \(\text{C}_2\text{H}_4\) as the final product at the end of the chain. The set of reactions (17) ~ (18), elementally reactions, are the interface between the global reaction and the \(\text{C}_2\) hydrocarbon oxidation mechanism. The \(\text{C}_2\) hydrocarbon mechanism used in this study is listed in Table 1.

Computation and fitting procedure

Computations were carried out by numerically integrating the set of differential equations for chemical species, pressure, and temperature under the constant volume condition using LSODE.

The reaction system was optimized by adjusting the rate constants of either reaction (15) or (16) to fit the calculated ignition delay with that obtained by the experiments carried out by Miwa et al. \(^{(9,10)}\). These experiments were conducted using the free-piston rapid compression machine, having a swirl chamber, to clarify the ignition delay in diesel combustion. Derivatives or decomposed fuel fractions were also analyzed using the rapid reaction-freezing system, which was mounted on the combustion chamber and consisted of a rupture film and an expansion vessel. The model was evaluated by comparing the decomposed fraction calculated by the present model with that of the measured value. Since the complete freezing of the reaction takes several milliseconds, part of mixture reaches combustion during the rapid expansion process in a flammable atmosphere or oxygen coexistence circumstance even if reaction freezing has already started before ignition. The comparison, therefore, is intended for the pyrolysis in a nitrogen atmosphere. Although in the high temperature oxidation process oxygen takes part in the reaction both directly and indirectly, it is conceivable that pyrolysis itself is not strongly influenced by oxygen. Thus, the model can be evaluated by its comparison under a nitrogen atmosphere.

In actual diesel combustion, the diffusion process between fuel and air takes place by turbulent mixing after the fuel injection. The time lag for preparing the mixture, called
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k = A \cdot T^{n-1} \cdot E$</th>
<th>A</th>
<th>n</th>
<th>E</th>
<th>A</th>
<th>n</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C} + \text{OH} \rightarrow \text{CO} + \text{H}$</td>
<td>2.25$ \cdot 10^6$</td>
<td>2.85$ \cdot 10^6$</td>
<td>1.50</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>$\text{C} + \text{O} \rightarrow \text{CO}$</td>
<td>1.00$ \cdot 10^6$</td>
<td>1.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

* The pressure dependence of the rate coefficient was treated based on the SRI form.
physical delay, should be discriminated from that for chemical reactions, called chemical delay. During the experiment, a strong swirl was generated in the combustion chamber to promote mixing and to minimize the physical delay. At the end of the compression the maximum tangential velocity reached almost 100 m/s. In comparison with chemical delay, therefore, the physical delay could be disregarded.

Although the mixing proceeds rapidly, considerable heterogeneity exists during induction period, and since mixing ratio of fuel to air varies locally, calculations are made in a homogeneous local region. Since ignition delay is affected with mixing ratio, the shortest ignition delay, calculated in advance along the various mixing ratios, is compared with that of the measurement value by assuming that ignition takes place at the local region that shows the shortest ignition delay.

The piston is fixed after rapid compression and the pressure and temperature fall off by heat transfer. The fuel is injected when the temperature becomes a specified value. Fig. 2 shows the example of the pressure record in an experiment. In this example, the fuel was injected at bulk average temperature $T_i=800 K$. The conservation of the adiabatic relation between temperature and pressure at the center of the combustion chamber’s core region has been confirmed, although the heat transfer from wall to wall distributes the temperature in a radial direction in the chamber. Thereupon, the calculations were carried out regarding to the core temperature. The fuel temperature in calculations is set 450 K.

RESULTS AND DISCUSSION

First, the calculations were carried out for the case that hypothesized reaction (15) as the global reaction. By assuming C_{18}H_{34} as the representative organization of diesel fuel (assuming the hydrogen/carbon ratio of fuel 2.125), reaction (15) is represented as follows:

$$C_{18}H_{34} + M \rightarrow 6 C_2H_4 + 2 C_2H_5 + M$$

Figure 3 shows the dependency of ignition delay on the equivalence ratio calculated at the core temperature $T_c=996.3 K$ (bulk average temperature $T_i=800 K$). The rate constant is assumed to be $k=2.95 \times 10^{17} \exp(-166/RT)$. From the figure, the shortest ignition delay values at the equivalence ratio around 0.4. This is the result of competition of two contradictory effects. One is the increase of overall reaction rate at the fuel rich region due to the increase in the product of fuel and oxygen concentration, which is proportional to the overall reaction rate. The other is the decrease in mixture temperature at the fuel rich region due to the fuel temperature being lower than that of air.

Next, the comparison of the components of thermal decomposition was conducted in nitrogen atmosphere. Fig. 4 shows the results at the core temperature $T_c=996.3 K$. From the figure, it is noted that ethylene concentration shows much higher than the experimental value and that there is little agreements for another components. Therefore, it is conceivable that R (19) is not appropriate as the global
Calculations were carried out for the case that hypothesized reaction (16) as the global reaction. By assuming \( \text{C}_{15}\text{H}_{34} \) as a representative organization of diesel fuel, reaction (16) is represented as follows:

\[
\text{C}_{15}\text{H}_{34} + \text{M} \rightarrow 4 \text{C}_2\text{H}_4 + 2 \text{i-C}_6\text{H}_{14} + \text{M} \quad \text{R}(20)
\]

In regard to \( \text{R}(17) \sim \text{R}(18) \), the reaction rate constants of these elementary reactions are clarified. The rate constant of reaction (20) was assessed to fit the calculated ignition delay with that obtained at the experiment. Fig.5 shows the dependency of ignition delay on equivalence ratio under the core temperature \( T_c = 996.3 \text{ K} \). The rate constant of R(20) is \( k = 2.95 \times 10^{17} \exp (-158/RT) \). From the figure, ignition delay becomes the minimum at the equivalence ratio \( \phi \) around 1.0. In comparison to the case that used R(19) as a global reaction, the equivalence ratio where ignition delay shows minimum value shifts toward the fuel rich region. This difference may come from the generation of \( \text{CH}_4 \) in R(17) or R(20). \( \text{CH}_4 \) can activate the \( \text{C}_2 \) hydrocarbon reaction mechanism more than \( \text{C}_2\text{H}_4 \). The comparison of the calculated ignition delay's temperature dependence with that obtained in the experiments is shown in Fig.6. From the figure, the measured data show a discontinuity at around 900 K and show negative temperature dependence at lower temperatures. This range is inferred to be the low temperature oxidation range. Calculated data and observed data agree well in the range of temperature \( T > 900 \text{ K} \) (\( T^{-1} < 1.1 \times 10^{-3} \)), which is considered the high temperature oxidation range.

Figure 7 shows the experiment and predicted proportions of decomposed components during the induction period at the core temperature \( T_c = 1121 \text{ K} \). It is noted that they agree well and that agreement of \( \text{CH}_4 \) is improved in comparison with the model that used R(19). This is conceivable because the channel of \( \text{CH}_4 \) formation opened by R(17) or (20) in this model. These results, therefore, demonstrate that present model can rationally depict an actual reaction mechanism.

**CONCLUSION**

A new reaction model for auto-ignition in diesel combustion has been developed based on the high temperature mechanism, emphasizing the generation of derivatives or decomposed fuel fractions during the induction period. The model adopts the Rice-Heizfeld mechanism for the cracking process and supposes that the generation of alkyl radicals and olefins at the lower end of the chain reaction of pyrolysis is represented by the notation of the global reaction. The global reaction is coupled with the \( \text{C}_2 \) hydrocarbon oxidation mechanism to characterize the complete reaction system. By adjusting the rate constants of the global reaction to fit the calculated ignition delay obtained in the experiment, we have optimized the reaction system. The result shows the good agreement of the calculated and measured induction periods at the high temperature oxidation range, which is higher than 1000K. Furthermore, computed fractions of \( \text{CH}_4, \text{C}_2\text{H}_4, \text{C}_6\text{H}_{14}, \) and \( \text{C}_5\text{H}_{12} \) during induction period agree closely to those of the measurements.
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REFERENCES