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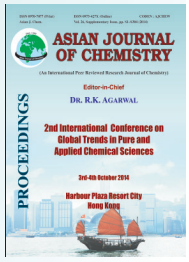

Reduced Chemical Mechanism of *n*-Heptane for Combustion and NO_x Emission Prediction Under Diesel Engine

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Based on chemical kinetics, a reduced chemical reaction mechanism was developed for simulation of combustion process for *n*-heptane, by temperature sensitivity analysis, composition and reaction rate analysis. The final mechanism consists of 43 species and 63 elementary reactions. The reduced mechanism was validated by comparing with the detailed mechanism on the concentration variation of reactants, major intermediates and the final product of combustion. The difference between temperature and pressure in cylinder was also considered. The results show that the analysis is reliable and practical.

Keywords: *n*-Heptane, Reduced mechanism, NO_x, Diesel engine.

INTRODUCTION

The reduction of pollutant emissions is an important guarantee for the protection of the atmospheric environment and human health. The emissions regulations become moreover increasingly stringent, so the use of the necessary measures to control emissions from an internal combustion engine and to improve the combustion process is significant. With the development of computer technology and the advances of chemical reaction mechanism, the simplified model for multidimensional CFD calculations is urgently needed that can describe a diesel engine ignition and the process of combustion. At the same time, the diesel fuel's cetane number is relatively large and its viscosity is high, so the formation of mixed gas and the ignition control is difficult. In a word, there is a large number of theory and technical difficulties for diesel engine cylinder combustion process to be resolved[1].

EXPERIMENTAL

There are many ways to build simplified mechanism now, mainly including the following: Reaction sensitivity analysis, the main component analysis, automatic generation method, a quasi-steady-state approximation and constraints balance method controlled by reaction rate.

Sensitivity analysis method of a chemical reaction is based on perturbation theory, researching the response of the entire system for each disturbance factors. Given the environmental conditions, operating conditions and engine parameters, each of the small perturbation of the reaction rate parameters affect the entire combustion system in quantitative kinetics, including the components, temperature, reaction rate, *etc*., and the influence value for which is called the sensitivity coefficients. The sensitivity coefficients solved by a set of partial differential equations can determine the degree of influence of each element in the entire combustion system derived by comparing the size of the sensitivity coefficients of the reaction. If the sensitivity coefficient is little, the reaction can be omitted, thereby simplified mechanism can be obtained[2].

The reaction system consists of S species composition and R reactions. The reaction rate can be expressed as:

$$\frac{dc_i}{dt} = F_i(c_1, \cdots c_S; k_1, \cdots, k_R)\ c_i\Big|_{t=t_0} = c_i^0, i = 1,2,\cdots,S \quad (1)$$

The eqn. 1 is determined by two factors: The initial conditions and system parameters. Changes of k_R has a certain influence on the value c_i, in order to accurately describe the size of the degree of influence, the degree which the value of c_i depends on of value k_R is defined as the sensitivity coefficient. In fact, the analytical solution of the sensitivity coefficient can not be obtained substantially. Generally it can be analyzed by using numerical methods, namely taking partial differential of the eqn. 1 to obtain a group of differential equations on sensitivity analysis.

$$\left.\begin{aligned}
&\frac{\partial}{\partial k_r}\left(\frac{\partial c_i}{\partial t}\right)=\frac{\partial}{\partial k_r}F_i(c_1,\cdots c_S;k_1,\cdots,k_R)\\
&\frac{\partial}{\partial t}\left(\frac{\partial c_i}{\partial k_r}\right)=\left(\frac{\partial F_i}{\partial k_r}\right)_{c_1,k_{1\neq r}}+\sum_{n=1}^{S}\left[\left(\frac{\partial F_i}{\partial c_n}\right)_{c_{1\neq n},k_1}\left(\frac{\partial c_n}{\partial k_r}\right)_{k_{1\neq j}}\right]\\
&\frac{\partial}{\partial t}E_{i,r}=\left(\frac{\partial F_i}{\partial k_r}\right)_{c_1,k_{1\neq r}}+\sum_{n=1}^{S}\left[\left(\frac{\partial F_i}{\partial C_n}\right)_{C_{1\neq n},k_1}E_{n,r}\right]
\end{aligned}\right\} \quad (2)$$

Since the group of eqn. 2 is a group of linear equations, it can be solved numerically by simultaneous the formula (1). When the various data of reaction system is given, the sensitivity coefficients of individual reaction for the reaction system can be calculated and determined by numerical calculation, then through comparing the magnitude, complex mechanism can be simplified by omitting minor reaction.

The main component analysis method is that through the calculation for the concentration of each component in reaction mechanism, the component which has higher concentration and a longer residence time in the reaction process can be regarded as a main component of the reaction mechanism. In addition, a certain component and the primitive reaction participated can also be removed. And then those components which have a significant impact on the results of the reaction may also be considered as a major component by comparing the results, but this selecting method need large quantity of calculation. In practical application, the main component analysis method is usually associated with the reaction rate of component[3].

RESULTS AND DISCUSSION

Sensitivity analysis results are shown in Fig. 1, the corresponding chemical reaction equations are shown in Table-1.

TABLE-1
TEMPERATURE SENSITIVE EQUATION

R278: $^{\bullet}OOC_7H_{14}OOH => {}^{\bullet}OC_7H_{13}OOH + OH^{\bullet}$
R272: $C_7H_{15}OO^{\bullet} = {}^{\bullet}C_7H_{14}OOH$
R253: $C_7H_{16} + OH^{\bullet} => C_7H_{15\bullet} + H_2O$
R252: $C_7H_{16} + OH^{\bullet} = C_7H_{15\text{-}1\bullet} + H_2O$
R160: $H_2O_2 + OH^{\bullet} = H_2O + HO_{2\bullet}$
R102: $C_3H_6 + OH^{\bullet} = C_3H_{5\bullet} + H_2O$
R55: $C_2H_4 + OH^{\bullet} = C_2H_{3\bullet} + H_2O$
R49: $H_2O_2(+m) = OH^{\bullet} + OH^{\bullet} (+m)$
R47: $HO_{2\bullet} + OH^{\bullet} = H_2O + O_2$
R6: $CO + OH^{\bullet} = CO_2 + H^{\bullet}$

As can be seen from Fig. 1, the sensitivity coefficients have positive value and negative value. The positive sensitivity coefficient indicates that the occurrence of this reaction will make the system's temperature go up. On the contrary, a negative sensitivity coefficient indicates that this reaction will make the system's temperature decrease. The larger the absolute value of the sensitivity coefficient is, the greater the reaction impact on the temperature of system. Fig. 1 shows that these reactions No. 253, No. 49 and No. 47 have significant influence on the changes of temperature.

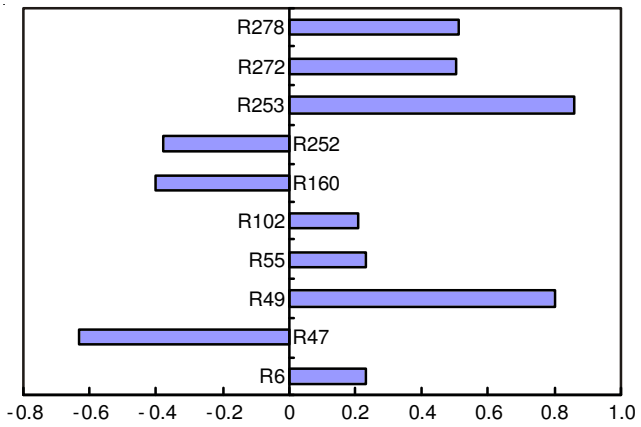

Fig. 1. Sensitivity coefficients

The simplified reaction path of *n*-heptane can be seen from Fig. 2 by the main component analysis method.

Combined with the characteristics of diesel engine cylinder, seven equations has been added to predict NOx emissions based on zeldovich mechanism, making the NOx emission model more complete.

The 7 NO_x formation equations is as follows:

$$N_2O \rightleftharpoons N_2 + O^{\bullet} \quad (3)$$

$$N_2O + O^{\bullet} \rightleftharpoons N_2 + O_2 \quad (4)$$

$$N_2O + O^{\bullet} \rightleftharpoons NO + NO \quad (5)$$

$$N_2O + N^{\bullet} \rightleftharpoons N_2 + NO \quad (6)$$

$$N_2 + HC \rightleftharpoons HCN^{\bullet} + N^{\bullet} \quad (7)$$

$$HCN^{\bullet} + OH^{\bullet} \rightleftharpoons HCO^{\bullet} + H_2 \quad (8)$$

$$HCO^{\bullet} + O^{\bullet} \rightleftharpoons HO + CO \quad (9)$$

The contrast calculation between simplified mechanism and detailed comparison is applied on a single-cylinder diesel engine with the parameters as follows: The initial cylinder temperature is 343 K, the initial cylinder pressure is atmospheric pressure, the cylinder wall temperature is 403 K, the equivalent ratio is 0.54 and the calculation starts from -150 °CA to 120 °CA. The detailed mechanism is Lu model.

The comparison of pressure and temperature curves by calculation is shown in Fig. 3. It can be seen through the curve that the ignition timing of detailed model and a simplified model agrees well. In addition, the two curves have basically the same trend, suggesting that the simplified model can be a

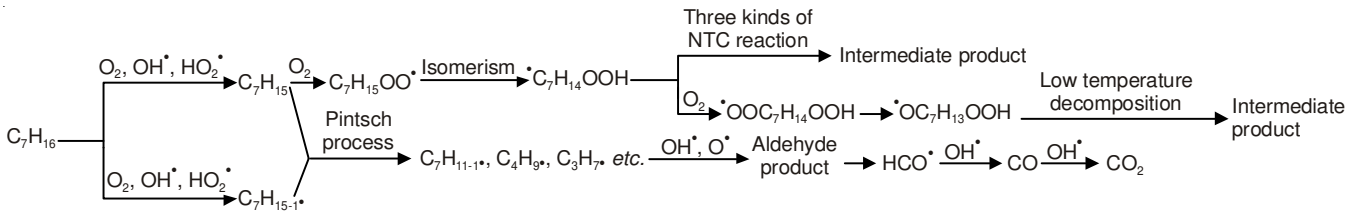

Fig. 2. Simplified reaction path of *n*-heptane

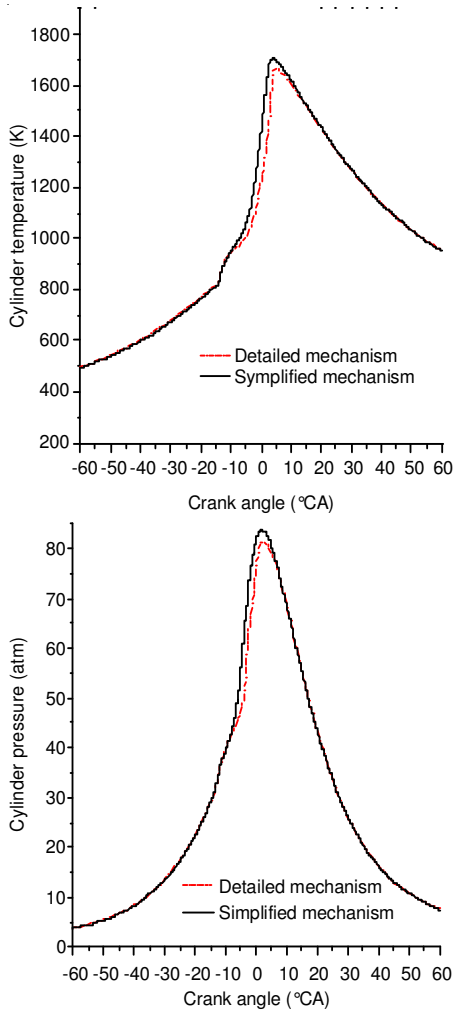

Fig. 3. Comparison of temperature and pressure in cylinder

good description of *n*-heptane combustion in cylinder, including the parameters pressure and temperature.

Conclusions

During the combustion process of *N*-heptane, free radicals involved in the dehydrogenation reaction are mainly $HO_2^{\bullet}$ and $OH^{\bullet}$, of which, $HO_2^{\bullet}$ mainly comes from two initial reaction of *n*-heptane, $OH^{\bullet}$ mainly comes from the scission reaction of H_2O_2, the maindehydrogenation products are $C_7H_{15\text{-}1}\cdot$ and $C_7H_{15}\cdot$.

This paper builds a simplified model for *n*-heptane combustion that contains 43 kinds of components and 63 elementary reactions and, greatly reducing the workload of calculation for diesel engine combustion and emissions. It's found that ignition timing, pressure and temperature in-cylinder agree well by the comparison between simplified model and a detailed model.

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