Combustion and Evolution of the Polycyclic Aromatic Hydrocarbons in Diesel Engine

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1. Introduction

The soot particle constitutes the main respirable particulate matter in diesel and poses a serious threat to human health. Its intermediate product----polycyclic aromatic hydrocarbon (PAH) in particular, is believed to carry carcinogenic substance. Therefore, for the past decades developed countries have paid great attention to the detailed reaction kinetic mechanism of the formation of the soot. According to the previous researches, it was found that in the condition of high temperature and hypoxia, fuel hydrocarbons would pyrolyze and oxidize to generate hydrocarbons whose molecular weight is smaller. Then from the aliphatic hydrocarbons would originate the first aromatic component, which, after the adding of the smaller alkyl components and other aromatic components, would be further dehydrogenized and cyclized to end in the PAHs form. There is a consensus that PAHs would continue to grow into the initial soot particle, often referred to the simple precursor of soot particle [1], which has an important role to play in the soot formation mechanism. However, the formation mechanism of soot and PAHs is far complex than this. There is no simple correlation between PAHs and soot formation even in a simple flame structure as laboratory-scale burner. So, in this paper, author devolops a enthalpy computation module of species in KIVA3V [2], and uses detailed chemical reaction of n-Tetradecane developed by A.Durán et al [3], simulates formationa and evolution of PAHs in diesel cylinder, analyzes formation mechanisms and evolution regulation of PAHs.

2 Chemical reaction kinetic mechanisms

In this paper, the chemical mechanisms including small molecular mass PAHs (4 rings and under 4 rings) in A.Durán's mechanism [3] (92 chemical species, 230 chemical reactions) is used.

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3 Computational Models

The thermodynamic functions of substances are involved in the kinetic simulation, such as the enthalpy, the entropy, the heat capacity at constant pressure, etc. In this paper, the enthalpy computation module of chemical composition is added into KIVA3V program and the thermodynamic database of corresponding chemical compositions is built. This database uses NASA chemical equilibrium code [4]. The molar heat capacity at

constant pressure can be expressed as:
$$\frac{C_{pk}^o}{R} = \sum_{N=1}^N a_{nk} T_k^{(n-1)}$$

The superscript *o* refers to the state under standard atmospheric pressure. For perfect gases, however, the heat capacities vary with pressure, and the standard-state value is the mean value. Other thermodynamic properties are given in terms of integrals of the molar heat capacities. First, the standard molar enthalpy can be expressed as:

$$H_k^o = \int_{298}^{T_k} C_{pk}^o dT + H_k^o (298),$$

So that

$$\frac{H_{k}^{o}}{RT_{k}} = \sum_{n=1}^{N} \frac{a_{nk}T_{k}^{(n-1)}}{n} + \frac{a_{N+1,k}}{T_{k}}$$

Where, the parameter $a_{N+1\,k}R$ represents the standard heat formed at 298 K.

This paper's database is designed to work with the thermodynamic data form used in the NASA chemical equilibrium code, so the above equations (12-14), which are in the form of arbitrary-order polynomials, need to be tailored to meet this requirement. In this case, seven coefficients are needed for each of two temperature ranges. These fits take the following form, where the temperatures are in Kelvin:

$$\frac{C_{pk}^{o}}{R} = a_{1k} + a_{2k}T_{k} + a_{3k}T_{k}^{2} + a_{4k}T_{k}^{3} + a_{5k}T_{k}^{4}$$
,
$$\frac{H_{k}^{o}}{RT_{k}} = a_{1k} + \frac{a_{2k}}{2}T_{k} + \frac{a_{3k}}{3}T_{k}^{2} + \frac{a_{4k}}{4}T_{k}^{3} + \frac{a_{5k}}{5}T_{k}^{4} + \frac{a_{6k}}{T_{k}}$$

The lowest temperature, intermediate temperature and highest temperature for every chemical composition are given in NASA thermodynamic data, and thus two temperature ranges can be determined (low temperature range and high temperature range). The values of a_{1k} , a_{2k} , a_{3k} , a_{4k} , a_{5k} , a_{6k} are determined in different temperature ranges. Different coefficients are selected to calculate the standard-state molar enthalpy and molar heat capacity of chemical compositions, depending on different temperatures. So the molar enthalpy at other temperature can be obtained according to the first law of thermodynamics [5]:

$$H = H_k^o + \Delta H = H_k^o + \int_{T_o}^T C_p dT$$

Often, specific thermodynamic properties are needed in mass units (per gram) rather than in molar units (per mole). The conversion is made by dividing the property in molar units by the molecular weight. The specific

properties are thus
$$h_k = \frac{H_k}{W_k}$$
, With the above equations, the enthalpy of any chemical composition involved in

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detailed chemical reaction mechanism can be derived so as to execute a three-dimensional numerical simulation of the chemical reaction progress of the combustion in diesel cylinder.

4 Other Computational Models [6]

In the present study, many other computational models were used: The modified RNG k- ε model, The wave breakup model (also referred to as Kelvin-Helmholtz (KH) breakup model), "Shell" model, The laminar and turbulent characteristic time model, Belardini et al [7] soot model.

5 Computation and Boundary Conditions

Туре	Single-cylinder, DI
Bore	100 mm
Stroke	115 mm
Con-rod length	190 mm
Displacement	903 cm3
Rate power	9.5kW
Speed	1600 rpm
Intake valve closure	-131° ATDC
Compression ratio	17.4
Type of injector	4 holes $\times 0.30$ mm
Swirl ratio	1.3
Start of Injection	25 BTAC
Injection duration	20 °
Fuel injected	140mg/cycl
chamber	Direct port ω

Table 1: Specifications of the Tested Engine





Figure 1. computation mesh of combustion chamber



6 Evolution of PAHs and Soot in the Cylinder



Figure 3. Change tendency of benzene mass with crank angle



Figure 5. Change tendency of acenaphthylene mass with crank angle



Figure 7. Change tendency of pyrene mass with crank angle



Figure 9. Change tendency of styrene mass with crank angle





Figure 8. Change tendency of phenylacetylene mass with crank angle



Figure 10. Change tendency of acenaphthene mass with crank angle



with crank angle



Figure 2. to Figure 10. show the formation and evolution process of PAHs produced by per gram fuel in diesel combustion. As can be seen from these figures, the fuel ignites and combusts near top dead center. The mass of aromatic and polycyclic aromatic hydrocarbons in cylinder rapidly increases, and peaks at about 10 °CA ATDC. This shows a high formation rate of PAHs at initial stage, a stage where the soot particle-induced process also begins. As the combustion process continues, the mass of PAHs tends to decrease dramatically due to the oxidation, and finally reaches a steady value after the rapid combustion stage is ended. Consider the yield of 8 PAHs at the final stage of combustion before exhaust valves are opened, benzene yield is highest, followed successively by phenanthrene, phenylacetylene, naphthalene, styrene, acenaphthylene, pyrene, The emission of acenaphthene is lowest. The soot computation model proposed by Belardini [7] is used here to simulate the mass of soot emission in cylinder of diesel engine, and the soot mass varying with crank angle is shown in Fig.11. Through the computation of soot model, it is found that the mass of aromatic and polycyclic aromatic hydrocarbon generated would have great effect on the soot emission. And among all the PAHs generated, the emission amount of benzene, phenanthrene, phenylacetylene and naphthalene is comparatively large, making them the main contributor to the formation of soot emission. According to simulation for different inject timings, it is found that soot and NO emissions are best in -20° ATDC in present study (Figure 12.).

7 **PAHs Distribution in the Cylinder**

Figure 13. to Figure 15. Show Combustion happened firstly in the piston bowl, and then happened in other positions of the combustion chamber with the developing of combustion (develop clockwise along the piston bowl), and PAHs distribute in the top of cylinder in the end of combustion.

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