

Analysis of the Trade-off between Soot and Nitrogen Oxides in Diesel-Like Combustion by Chemical Kinetic Calculation

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ABSTRACT

This study makes use of the detailed mechanisms of n-heptane combustion, from gas reactions to soot particle formation and oxidation, and a two-stage model based on the CHEMKIN reactor network is developed and used to investigate the trade-off between soot and NOx emissions. The effects of the equivalence ratio, EGR, ambient pressure and temperature, and initial particle diameter are observed for various residence times. The results show that high rates of NOx formation are unavoidable under conditions where high reduction rates of soot particles are obtained. This suggests that suppression of the amount of soot during the formation stage is essential for simultaneous reductions in engine-out soot and NOx emissions.

CITATION: Li, T. and Ogawa, H., "Analysis of the Trade-off between Soot and Nitrogen Oxides in Diesel-Like Combustion by Chemical Kinetic Calculation," *SAE Int. J. Engines* 5(2):2012, doi:10.4271/2011-01-1847.

INTRODUCTION

In conventional diesel combustion, soot particles are generated in the fuel-rich zones and mostly burnt off at high-temperature near-stoichiometric reaction zones with entrainment of ambient air, while the formation of nitrogen oxides (NOx) emissions and this emission component is unavoidable with the high temperature zones where soot particles are being burnt off. Therefore, there is a trade-off between soot and NOx emissions in diesel engines. For instance, when strategies such as exhaust gas recirculation (EGR) or retardation of fuel injection timing are employed to reduce NOx emissions, the temperatures and residence times that are necessary to burn off soot particles are reduced, and soot emissions usually increase, and vice versa.

Premixed (also termed partially premixed) low temperature diesel combustion (LTC) can deliver simultaneous reductions in soot and NOx emissions and have attracted much attention from research institutions worldwide [1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18]. However, at present most of LTC is limited to relatively low load operations. In almost all the LTC concepts, large quantities of cooled EGR are generally conducted to lower flame temperatures and then reduce NOx emissions. Non-sooting combustion can be realized as long as the temperature is sufficiently low, which can be obtained by ultra-high EGR, but this is at the expense of dramatic increases in unburned hydrocarbon (UHC) and carbon monoxide (CO) emissions,

and unacceptable deteriorations in combustion efficiency [2, 13, 14, 15, 17-18]. Recent research has demonstrated that a promotion of fuel-air mixing before ignition at relatively high intake oxygen concentrations or low EGR rates is necessary for non-sooting LTC with relatively high thermal efficiency [14-15, 17-18]. At higher loads, however, more fuel has to be injected into the cylinder where it then needs longer premixing times, while reductions in NOx need more EGR (lower intake oxygen) owing to the higher in-cylinder temperatures. As a result, it is very difficult to achieve a non-sooting and low NOx combustion at higher loads.

The equivalence ratio - temperature (ϕ - T) diagram was initially proposed by Kamimoto and Bae [19], and it can be established with reaction kinetic calculations [2, 20, 21, 22] and has been widely used in the analysis of diesel combustion [7, 15]. Figure 1 shows a schematic of ϕ - T diagram. Recently, it was reported that as suggested by the ϕ - T diagram, soot may be burnt off at $1800 < T < 2200$ K where there is little formation of nitrogen oxides (NOx) [23-24], and that non-sooting, low-NOx diesel combustion could be possible with moderate rates of EGR, and without severe deterioration in combustion efficiency at these temperatures. Accordingly, non-sooting, low-NOx combustion could be realized at relatively higher loads. However, a complete burning-off of soot particles needs both sufficiently high temperatures and the long residence times that would induce NOx formation, and while the zones at $1800 < T < 2200$ K in the ϕ - T diagram indicate conditions without soot formation,

they are not necessarily the conditions for soot particle burning off. Therefore, a careful examination of the kinetics of soot particle oxidation and NO_x formation processes is necessary to understand the situation here in more detail.

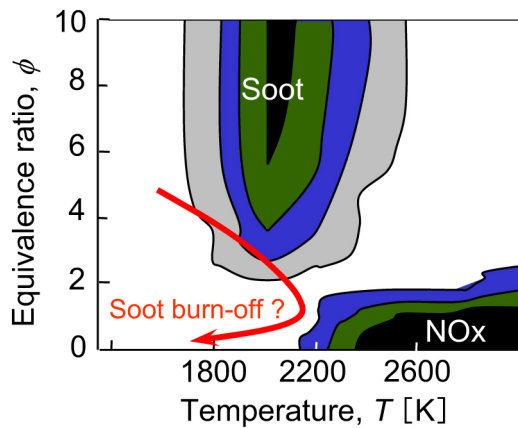


Fig. 1. A schematic of ϕ - T diagram for soot and NO_x formation region

In this study, the detailed mechanisms of n-heptane, from gas reactions to soot particle formation and oxidation are employed, and a two-stage model based on the CHEMKIN reactor network is developed and used to investigate the trade-off between soot and NO_x emissions. The effects of the equivalence ratio, EGR, ambient pressure, and temperature, as well as of the initial particle diameter are examined for a range of residence times.

MODEL FORMULATION

GAS REACTIONS

The detailed n-heptane reaction mechanism developed by Curran et al. [25] was used as the basic reactions, the formation mechanism of soot precursors by Wang and Frenklach [26] and the NO_x chemistry in GRI-Mech 3.0 [27] were added to generate a combined reaction mechanism comprised of 647 species and 3078 elemental reactions. Figure 2 shows a comparison between the ignition delays of shock tube experiments [28] and the calculated values with the combined mechanism in this study. The calculations were carried out with the Perfectly-Stirred Reactor (PSR) of CHEMKIM-pro. The calculated ignition delays agree very well with the experimental values. Since a similar good agreement can also be obtained with the original mechanism of n-heptane reactions, the results show that the effects of the addition of the parameters for the soot precursors and NO_x mechanisms are negligible.

SOOT MODELS

In this study, the formation, growth and oxidation processes of soot particles were simulated by the Particle Tracking Feature (PTF) of CHEMKIN-pro. The PTF employs the method of moments developed by Frenklach and

coworkers [29,30,31,32]. Here only a brief description on the method of moments is given, detailed information can be found in the papers and book by Frenklach et al. [29,30,31,32] or the CHEMKIN Theory Manual [33].

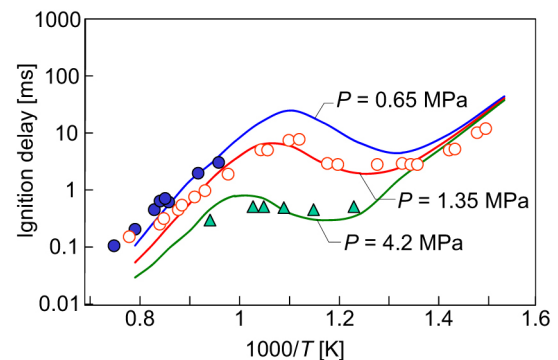


Fig. 2. Ignition delay of calculations (lines) and experimental results with shock tube [28] (symbols) for three ambient pressures ($\phi=1.0$, n-heptane/air mixture)

The method of moments tracks the evolution of an aerosol system by moments rather than the actual form of the particle-size distribution, and it can provide overall properties such as number density, total particle volume fraction, and average particle diameter. In the simulation of sooting processes, the r -th moment is defined as

$$M_r = \sum_{i=1}^{\infty} m_i^r N_i \quad (1)$$

where m_i and N_i are the number of carbon atoms and number density of soot particles of size class i , respectively. It can be seen from Eq. (1) that the zero-th moment M_0 yields the total particle number N of the population, as shown by

$$N = M_0 = \sum_{i=1}^{\infty} N_i \quad (2)$$

Similarly, the first moment M_1 is the total number of carbon atoms in the soot particles. Thus, the total volume of soot particles can be calculated as

$$V = \frac{m_c}{\rho_B} M_1 \quad (3)$$

where m_c is the mass of a carbon atom and ρ_B is the bulk density of soot particles ($\rho_B = 1.8 \text{ g/cm}^3$ in this study). Assuming spherical particles, the average particle diameter can be obtained as

$$d_p = \left(\frac{6m_c}{\pi\rho_B} \frac{M_1}{M_0} \right)^{1/3} \quad (4)$$

In the method of moments, the dynamics of the sooting processes are described as

$$\frac{dM_r}{dt} = R_r + G_r + W_r \quad (5)$$

Where R_r , G_r , and W_r are the nucleation, coagulation, and surface rate terms at the r -th moment of the particle-size distribution function, respectively. In this study, the particle nucleation is assumed to be due to the coalescence of two pyrene (four ring aromatics) molecules, and the particle surface growth due to both the H-abstraction and acetylene-addition (HACA) mechanism and the surface condensation of polycyclic aromatic hydrocarbons (PAH). Soot particle oxidation by molecular oxygen and OH radicals is taken into account in this study. A list of the reaction mechanism can be found in the references [30,31,32].

Figure 3 shows a comparison between the experimental results with the shock tube by Kellerer et al. [34] and the predicted values with the above-mentioned model of the dependence of particle average diameter (d_p), number density (N), and soot volume fraction (f_v) on the ambient pressure. In the experiments, initially, the pressure would increase rapidly due to the compression by the reflected shockwave, and then stabilize at the target values. The experimental data are from 1.5 ms after the appearance of the first particles, probably occurring during the rapid compression period. Further, the first particles refer to those determined in the optical extinction and scattering measurements, and there are likely to be particles formed earlier at other zones, but detailed information is lacking in the paper [34]. Calculations were conducted with a perfectly-stirred reactor under constrained pressure and temperature conditions, and it is difficult to determine the exact moment where comparison with the experimental data here is optimum. In Fig. 3, the calculated data at the time of the peak of the particle number density are used for the comparison. Here one has to multiply the simulated results by the numbers given (e.g. 2.5 for N) to get the lines presented in the figure. It can be seen from the figure that although the simulation significantly underestimates the experimental results for all the three parameters: d_p , N , and f_v , the simulation does show very good agreement with the experimental results in the trend of the pressure dependence.

Figure 4 shows the results of the shock tube experiments by Kellerer et al. [35] and the calculated results of the dependence of soot yield on the ambient temperature. Here the soot yield is defined by the percentage of the number of carbon atoms in the soot particles (C_{soot}) and in the fuel (C_{fuel}). Although the calculated results are only half the

experimental results, qualitatively, the agreement in the trend between the experimental and calculated results is very encouraging. That is, for both cases, with the temperature decreasing, the soot yield initially increases, reaches a peak around 1800 K, and then decreases.

Based on the above comparisons, it is concluded that the model is reasonably accurate for use in evaluating the relative soot reduction rates in this study.

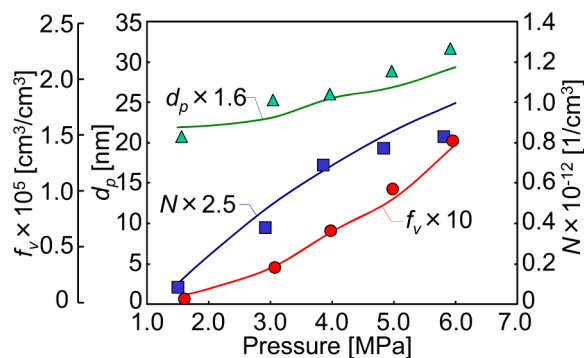


Fig. 3. Dependence of particle diameter (d_p), number density (N), and soot volume fraction (f_v) on ambient pressure. The experimental data (symbols) taken 1.5 ms after the appearance of the first particles by Kellerer et al. [34]; the calculated data (lines) at the time of the number density peak ($\phi = 5$, n-heptane / air mixture, Ar = 99%, $T = 1820$ K)

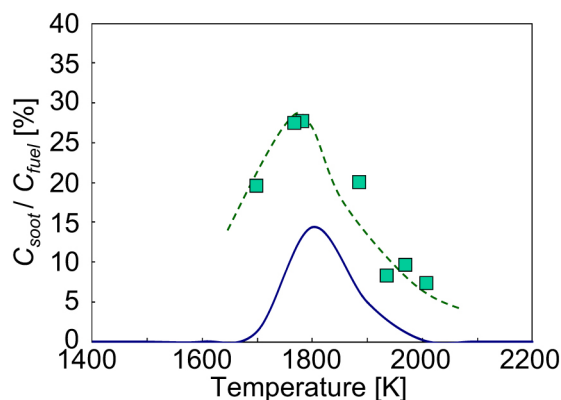


Fig. 4. Dependence of soot yield (C_{soot} / C_{fuel}) on ambient temperature by the experiments (dashed line) adapted from the shock tube experiments by Kellerer et al. [35] and from calculations (solid line) ($\phi = 5$, n-heptane / air mixture, $t = 1.5$ ms, Ar = 99.5%, $P = 4.0$ MPa)