



Development of a PAH (polycyclic aromatic hydrocarbon) formation model for gasoline surrogates and its application for GDI (gasoline direct injection) engine CFD (computational fluid dynamics) simulation



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ABSTRACT

To elucidate the evolution process of PAHs (polycyclic aromatic hydrocarbons) in GDI (gasoline direct injection) engines, a reduced chemical model with 17 species and 40 reactions for PAHs formation was developed and integrated into a skeletal TRF (toluene reference fuels) oxidation mechanism to predict PAHs emissions. The final mechanism consisted of 85 species and 232 reactions. The new mechanism was validated for ignition delays and laminar flame speeds for gasoline/air and TRF/air mixtures under engine-like conditions, and good agreement was obtained for most of the experiments. Laminar pre-mixed flames were simulated to validate the small species related to PAHs formation, as well as PAHs profiles up to A4 in flames, and the experimental trends were reproduced well. The combustion processes of GDI engines can be reproduced well using the new mechanism. PAHs were sampled from exhaust and analyzed by GC–MS, and PAHs with more than four rings were primary observed in particulate matter, while two and three ring polyaromatic hydrocarbons mainly existed in the vapor-phase PAHs. The vapor-phase PAHs released from the exhaust pipe were predicted, and the results indicated that the current mechanism could be used as a valuable tool to meet the needs of CFD (computational fluid dynamics) simulation for PAHs evolution in GDI engine combustion.

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1. Introduction

GDI (Gasoline direct injection) spark ignition engines are of particular interest because they can effectively reduce CO₂ emissions from gasoline-powered vehicles. However, GDI engines cause high particulate numbers (PN) in the nucleation mode (~10–100 nm). Furthermore, GDI engine vehicular traffic is a major source of both gaseous and particulate emissions of toxic species such as benzene and PAHs (polycyclic aromatic hydrocarbons). These particulates can seriously affect human health, and higher PN emissions generated from GDI engines will be strictly limited by increasingly stringent Euro VI regulations. This limitation has prompted a growing number of researchers to study soot

precursors and the soot formation processes of GDI engine combustion [1–3]. Jesús et al. [1] studied the impact of in-cylinder gas density and oxygen mass concentration on the mixing and oxidation processes and the final soot emissions in diesel engine. They pointed out that oxygen molecular concentration had a strong effect on both mixing and oxidation processes while gas density principally affected the mixing process. Both the two parameters had an influence on the final soot emissions. Olawole et al. [2] investigated the impact of spray and gas entrainment characteristics of different fuels on the soot formation processes. They used the LIF–PIV (laser induced fluorescence–particulate image velocimetry) technique to obtain information about the combustion processes. Karavalakis et al. [3] studied the regulated gaseous emissions and particulate emissions from two GDI engines fueled with different ethanol and iso-butanol blend fuels. The two GDI engine are spray-guided and wall-guided configuration respectively. The results showed that the particulate mass, particle number and soot mass

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emissions were significantly decreased with higher ethanol and butanol blends in injection process. To date, PAHs have not been included in automobile emission regulations as a strictly limited pollutant [4–6]. PAHs are emitted into the atmosphere either in the vapor phase or as particulate-bound PAHs. Totton et al. [7] studied the clusters assembled from PAHs and found that the resulting geometries of the TEM-style projections were similar to small soot particles. Mosbach et al. [8] developed a detailed soot model for internal combustion engines using PAHs, such as pyrene, as a soot precursor species for the soot particle inception process. These researchers studied aggregate size distributions as well as time evolution through simulation and obtained satisfactory agreement for the simulations. Vander et al. [9] studied PAHs using electron microscopy and noted that the stacking of planar PAHs led to the formation of soot particles, and the edges of soot particles were surrounded by PAHs. Therefore, PAHs are generally known to be the precursors of soot particulates, even though they are not yet considered as toxic emission.

CFD (computational fluid dynamics) simulation coupled with a chemical mechanism for in-cylinder combustion could provide accurate fuel oxidation and pollutant formation processes, especially for the formation of PAHs. Recently, Raj et al. [10] developed a detailed chemical mechanism (226 species and 2121 reactions) for single component gasoline surrogate fuels, including PAH formation, and updated the rate constants for several PAH reactions using density functional theory and transition state theory. However, this mechanism is only suitable for high temperature conditions ($T > 1000$ K). Based on the Raj mechanism, the author's group developed a semi-detailed TRF (toluene reference fuels) mechanism (219 species and 1229 reactions) that included the sub-mechanisms for PAHs growth [11]. However, it is highly time-consuming and computationally expensive to couple GDI engine combustion simulation with a detailed chemical mechanism. This is because the intake and exhaust processes need to be considered for GDI in-cylinder simulation; the effects of chemistry need to be considered at each CFD calculation time step (Δt); each computational cell is treated as a single zone 0D reactor model, then the CFD code calculates the source terms for the species transport equations and the enthalpy equation. To implement the simulation of the in-cylinder combustion and to also reduce the computational costs, many researchers used reduced gasoline surrogate mechanisms to represent real gasoline. Andrae [12] proposed a semi-detailed TRF oxidation mechanism (137 species and 633 reactions) and validated it for ignition delays, flame velocities and concentrations of major species. Machrafi et al. [13] proposed a skeletal TRF chemical model including 49 species and 62 reactions and studied the auto-ignition process under different engine conditions. However, no PAH formation reactions were considered in these reduced mechanisms. Pang et al. [14] developed a skeletal PAHs mechanism for PRF (primary reference fuel). This mechanism was validated for the species profiles in a flow reactor and jet-stirred reactor. Wang et al. [15] developed a reduced n-heptane chemical mechanism and embedded the skeletal PAH reactions to predict the formation of PAHs in soot emissions. However, these mechanisms are more suitable for diesel engine combustion.

To elucidate PAHs formation and the PAHs evolution process in GDI engines, a reduced gasoline surrogate mechanism that includes PAH formation reactions and can be coupled with CFD simulation urgently needs to be developed. The objective of this paper was to develop a reduced TRF mechanism (defined as "PAN mechanism") that includes modified the sub-mechanisms for PAH growth. Furthermore, the new mechanism was validated for ignition delays, laminar flame velocities and mole fractions of PAHs in pre-mixed flames. Finally, the in-cylinder pressure and PAHs emissions from GDI engine exhaust pipes were simulated to

ensure the reliability of the application of the new mechanism to GDI engine simulation.

2. Development of the reduced chemical mechanism

As mentioned previously, Pang [14] and Wang [15] developed two mechanisms that could not be used to predict the formation of PAHs in GDI engines. The presently proposed reduced chemical mechanism was based on the Pang model, and several reactions were modified to improve the model-predicted gasoline oxidation and PAH formation. The specific development process is presented in the following section.

The high temperature reactions were obtained from the Pang model and were retained in the PAN mechanism. The low temperature reactions (H-abstraction, peroxide formation, peroxide isomerization and decomposition, formaldehyde formation that relates to the cool flame and the NTC phenomenon) of n-heptane and iso-octane were updated and modified from the Pang and Tsurushima [16] models. Fig. 1 shows the major reaction branches of n-heptane and iso-octane (R' denotes C5 or C6 alkyl radicals) [11]. The modifications of n-heptane and iso-octane mainly focus on the intermediates, olefins, aldehydes and beta-scission of alkyl radicals that relate to the low-temperature reactions, as shown in Tables 1 and 2.

Toluene is one of the major aromatic components in real gasoline and is frequently used as a fuel additive because of its high anti-knock rating and high energy density [17]. The basic toluene mechanism was retrieved from the Pang model and some of the reactions selected from the author's semi-detailed model [11] were also added into the PAN mechanism ($C_6H_5CH_2 \rightarrow C_{10}H_{10} \rightarrow A2$ and $C_6H_5CH_2 + C_9H_7 \rightarrow A4$). The toluene mechanism consists of two parts; one part is the toluene oxidation decomposition process to form benzyl ($C_6H_5CH_2$) and phenyl (C_6H_5) groups, as shown in the blue box in Fig. 2, which has been studied by Oehlschlaeger et al. [18], Bounaceur et al. [19] and Qi et al. [20]. After these reactions, the subsequent reactions of toluene go through the benzene sub-mechanism, as shown in the green box in Fig. 2.

To ensure that the newly developed mechanism could be used to predict PAH emissions, several reactions for PAH formation that go beyond benzene with up to four rings were added into the PAN mechanism. The reactions involving chemical species (Fig. 3 shows the structures of the PAHs) were mainly obtained from the Raj mechanism and the ABF mechanism [21].

The formation of benzene is notably very important in the process of PAH formation. The subsequent H-abstraction– C_2H_2/C_4H_4 -addition (HACA) is also conducted based on benzene. The author's group had previously confirmed the pathways of benzene formation and consumption [11]. At the low temperature stage, the key benzene formation reactions include R25 and R26:



In the middle temperature stage, the influence of toluene, allene and allylene on benzene formation becomes increasingly prominent. In the T-G-C model [22], the kinetics of diacetylene (C_4H_2) and naphthalene were selected to serve as descriptions of the pre-particle gas-phase chemistry for the determination of soot particle nucleation rates. Therefore, the reactions related to n- C_4H_5 and C_4H_2 were taken from the Wang [15] model, which contains the C3–C4 species reactions, including C_3H_3 , C_4H_2 , C_4H_4 , C_4H_5 and C_5H_5 formation reactions, and were added to the PAN mechanism (see the mechanism files in supplementary material 01). The benzene consumption pathway mainly includes the H-abstraction reactions

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