



A reduced toluene reference fuel chemical kinetic mechanism for combustion and polycyclic-aromatic hydrocarbon predictions



Hu Wang^{a,b,*}, Mingfa Yao^b, Zongyu Yue^a, Ming Jia^c, Rolf D. Reitz^a

^a Engine Research Center, University of Wisconsin-Madison, 1500 Engineering Drive, Madison, WI 53705, USA

^b State Key Laboratory of Engines, Tianjin University, No. 92 Weijin Road, Nankai District, Tianjin 300072, China

^c School of Energy and Power Engineering, Dalian University of Technology, Dalian 116024, China

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ABSTRACT

A reduced toluene reference fuel (TRF, *n*-heptane, *iso*-octane and toluene)-polycyclic-aromatic hydrocarbon (PAH) chemistry mechanism with 109 species and 543 reactions is proposed for combustion, PAH and soot formation predictions. The mechanism has been validated with shock tube ignition delays, laminar flame speeds, species profiles in premixed flames, and with homogeneous charge compression ignition (HCCI) and direct injection compression ignition (DICI) engine combustion data. Sensitivity and reaction pathway analyses were used to identify the important reactions and reaction pathways for PAH formation for both non-aromatic and aromatic fuels. The results show that the mechanism yields good agreement under all validation conditions. The PAH species concentrations are well predicted for eight flame configurations (C_2H_4 , *n*-heptane, *iso*-octane, benzene ($C_6H_6-A_1$) and toluene). For the non-aromatic fuels, reactions related to C_2H_4 , C_2H_3 and C_2H_2 show the highest sensitivity for PAH formation, while with the aromatic fuel, PAH formation depends highly on reactions related to the ring structure. Benzene (A_1) is mainly produced through the combination of $C_4 + C_2$ and two C_3 radicals for non-aromatic fuels, and for aromatic fuels A_1 mostly comes from the fuel molecule (toluene). The formation pathways of higher PAH species are quite similar for both non-aromatic and aromatic fuels, including $C_5H_5 + C_5H_5 = A_2 + 2H$, the hydrogen abstraction acetylene addition (HACA) scheme, addition reactions between radicals and molecules and reactions between aromatic radicals and molecules. The mechanism is also capable of capturing combustion and emissions in HCCI and DICI engine simulations. The toluene content greatly enhances the PAH and soot formation with TRF fuels. However, improving mixing with TRF fuels due to their longer ignition delay also favors soot oxidation, and the final soot emissions of TRF fuels can be lower than diesel. The good agreement in the predictions of PAH species and soot emissions with the various fuels suggests that the current mechanism can be used reliably for combustion and PAH predictions for surrogate fuels of practical interest.

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1. Introduction

Fuel properties, including both physical and chemical properties, are very important parameters that affect the performance and emissions of internal combustion (IC) engines [1]. Due to more-and-more stringent pollutant emission and carbon dioxide (CO_2) legislation, highly premixed combustion concepts have become competitive measures to achieve clean and high efficiency combustion, such as HCCI [2] and reactivity controlled compression ignition (RCCI) [3], which also highlights the importance of

the fuel chemical properties, since the effects of the fuel physical properties are reduced due to the much longer available mixing time. Thus reliable chemical kinetic mechanisms are crucial for advanced engine combustion concepts simulations.

Currently diesel and gasoline are still the most widely used fuels in IC engines. Both are complex compounds of many components with different molecular structures, depending on the origin and refining process of the crude oil. In order to simulate the combustion processes of diesel and gasoline fuels, it would be ideal to apply a detailed kinetic mechanism, which contains all the possible components in the real fuels. However, currently it is still impossible to develop and apply such large mechanisms in computational fluid dynamic (CFD) simulations due to restrictions of computation power. Also, it is desirable to acquire insight into in-cylinder

* Corresponding author at: Engine Research Center, University of Wisconsin-Madison, 1500 Engineering Drive, Madison, WI 53705, USA.

E-mail address: gwrets@gmail.com (H. Wang).

information from simulations to guide the development of combustion technologies. Thus, simplified surrogate mechanisms have been proposed to represent diesel and gasoline fuels by including the most important components in the fuels. For example, *n*-heptane and *iso*-octane, have been used as single surrogates for diesel and gasoline due to their similar ignitibilities [4]. But the drawbacks are also obvious since no other components are considered in these simplified approaches.

Many researchers have also pointed out that aromatics play important roles in soot formation processes, and the aromatic content in diesel and gasoline fuels is usually around 25–35% [5]. Thus, more realistic multi-component surrogate models, which take the aromatic components into consideration, have been suggested and proposed for both diesel and gasoline fuels. For example, a four component surrogate model including *n*-decane, *iso*-octane, methylcyclohexane and toluene has been suggested by Farrell et al. [6] as a diesel surrogate, while for gasoline fuel, a three component TRF surrogate model, including *n*-heptane, *iso*-octane and toluene, is a widely used surrogate [7,8]. Toluene is present in both diesel and gasoline surrogate models, which confirms the importance of the toluene component for the development of reliable surrogate models. Since the ignition delays of paraffins from C₇ to C₁₆ are quite similar [5], it is possible to replace the *n*-decane component in diesel fuel surrogates with *n*-heptane, a simpler paraffin to reduce the complexity of the surrogate model. Therefore, the TRF model (*n*-heptane/*iso*-octane/toluene) can be regarded as a foundation for the development of more realistic and reliable surrogate models. In addition, since PAH species are considered as soot formation precursors in many soot modeling approaches [9], and the ring structure in the toluene molecule greatly affects the formation of PAH, it is also desirable to include toluene for better PAH and soot predictions.

Experimental and kinetic studies have been conducted to study the oxidation processes of primary reference fuels (PRF, mixture of *n*-heptane and *iso*-octane) and detailed and reduced PRF mechanisms are available from the literature [4,8,10–19]. The general oxidation reaction pathways proposed by Curran et al. [10,11] have been adopted in many kinetic studies. Currently mechanism validation has been shifting from solely predicting ignition delays to studying laminar flame speeds, and species predictions in various combustion devices to improve the prediction accuracy and application range of the mechanisms. The authors have also developed a reduced PRF mechanism [20] based on the detailed gasoline surrogate mechanism developed by Mehl et al. [8], which has been extensively validated with various experimental data. This reduced PRF mechanism is also used as the base mechanism for the development of the current TRF-PAH mechanism.

Although it has been recognized that toluene is an important component for diesel and gasoline surrogate models, the availability of toluene-related experiments and mechanisms is not as rich as for the PRF mechanism. Reduced toluene mechanisms have been validated against ignition delays under high temperature conditions and little attention has been paid to the predictions of laminar flame speed and species profiles in flames, which are important when a toluene sub-mechanism is applied for soot prediction. Therefore, in recent years many kinetic modeling and experimental studies related to toluene and TRF fuels, including ignition delays [21–23], laminar flame speeds [24,25], flames [16–18,26] and HCCI [27] combustion, have been conducted, and many detailed kinetic mechanisms have been proposed based on these studies. Andrae et al. [27–29] proposed several TRF mechanisms. The latest one consisted of 137 species and 635 reactions and was based on their previous studies and the works of Sakai et al. [15]. It has been validated with ignition delays, flame speeds and also species profiles in flow reactors and jet stirred reactors (JSR). Zhong et al. [19] proposed a chemical kinetic mechanism consisting of 89

species and 355 reactions to predict the ignition and oxidation behavior of a five component gasoline surrogate model, including *iso*-octane, *n*-heptane, ethanol, toluene and *di*-*iso*-butylene. Although the ignition behavior in shock tubes was well predicted by the mechanism, large discrepancies could be seen in HCCI combustion simulation, i.e., much higher combustion rates (pressure rise rate) compared to the experiments. Wang et al. [30] proposed an *n*-heptane/toluene/PAH mechanism based on the reduced PRF and toluene mechanisms developed by Ra et al. [4,31]. The mechanism has been validated with ignition delays, important species related to PAH and soot formation in *n*-heptane and toluene flames, and also against HCCI and DICI engine combustion and soot emissions data. However, flame speed validation was not considered at that time, and an *iso*-octane sub-mechanism was also not included in the mechanism. The detailed gasoline surrogate mechanism developed by Mehl et al. [8] for *n*-heptane, *iso*-octane, toluene and C₅–C₆ olefins contains more than 1300 species and has been validated with experimental data from shock tubes, stirred reactors and rapid compression machines (RCM). However, such a large mechanism is even very difficult to apply for zero dimensional (0-D) simulations. Thus, mechanism reduction is inevitable before it can be applied in engine combustion simulations.

The inclusion of toluene not only accounts for important fuel components, but also for PAH and soot formation. Thus, it is also very important to study the effects of toluene/benzene on the PAH formation process. The detailed PAH mechanism developed by Slavinskaya et al. [32,33] was reduced and incorporated in the *n*-heptane/toluene mechanism to study the effects of toluene addition on the PAH and soot formation processes under direct injection spray conditions by Wang et al. [30,34]. It was found that the addition of toluene greatly promotes the formation of PAH and soot, but the longer ignition delay of toluene also extends the available mixing time and thus reduces the locally rich regions and enhances soot oxidation. Raj et al. [7] developed a detailed TRF mechanism for gasoline surrogate fuels and PAH prediction, which contains around 230 species and 1350 reactions. This mechanism has been validated for premixed laminar flames of *n*-heptane, *iso*-octane, benzene and ethylene and also for counter-flow diffusion flames of *iso*-octane/toluene and *n*-heptane/toluene mixtures. The major PAH formation pathways were also identified and discussed in their study. However, their mechanism is still too large to be applied in engine CFD simulations and no ignition delay and flame speed validations were presented in their study.

In the present study a reduced TRF-PAH mechanism is proposed for application in engine combustion, PAH and soot emission predictions. The major PAH formation pathways for different fuels (non-aromatic and aromatic fuels) are analyzed and discussed. The paper starts with the assessment of a previous *n*-heptane/toluene mechanism, followed by the formulation and validation of the current TRF-PAH mechanism, including ignition delays, laminar flame speeds, species profiles in flames and HCCI and DICI engine combustion and emission data. Sensitivity and reaction pathway analyses with respect to PAH formation for the various fuels are also extensively discussed.

2. Mechanism development

2.1. Assessment of a previous *n*-heptane/toluene mechanism

The reduced *n*-heptane/toluene/PAH mechanism proposed by Wang et al. [30] showed good agreement in predictions of ignition delays and PAH species profiles, and HCCI combustion of *n*-heptane/toluene mixtures was also well predicted. Figure 1 shows comparisons of *n*-heptane and toluene laminar flame speeds between experiments and predictions with the mechanism (the

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