



Comprehensive chemical kinetic modeling of toluene reference fuels oxidation

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HIGHLIGHTS

- ▶ Kinetic model for oxidation of toluene reference fuels developed.
- ▶ Predicts ignition delay time and laminar burning velocity of real gasoline.
- ▶ May be used in CFD simulations and in further development studies.

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ABSTRACT

Important reactions in the toluene sub-mechanism of a chemical kinetic model for toluene reference fuels oxidation have been revised based on recent measurements and quantum chemical calculations. The revised model has been checked for validity against a wide range of experimental data including ignition delay in shock tube and rapid compression machine, species profiles in flow- and perfectly stirred reactors and laminar burning velocity. The model which consists of 635 reactions among 137 species, improves overall model predictions, especially at lean fuel–air ratios and flow- and perfectly stirred reactor conditions for both neat toluene and toluene in fuel blends. By using an appropriate gasoline surrogate fuel composition, the model has shown to successfully predict ignition delay times and laminar burning velocity for real gasoline at engine-relevant conditions. This suggests that mixtures with toluene and primary reference provide enough complexity for practical purposes.

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1. Introduction

Due to concerns regarding the greenhouse effect and limitations on carbon dioxide emissions, the possibility of a next-generation combustion mode for internal combustion engines that can simultaneously reduce exhaust emissions and substantially improve thermal efficiency has drawn increasing attention.

The most prominent characteristic of new combustion modes, such as Homogenous Charge Compression Ignition (HCCI), Stratified Charge Compression Ignition (SCCI), and Low Temperature Combustion (LTC), is that the combustion process lacks a direct method for the control of ignition timing and combustion rate, which are instead controlled primarily by chemical kinetics and, to a lesser extent, by turbulence and mixing [1]. Because of the significant impacts of fuel physical–chemical properties on the ignition and combustion process, fuel design and management has become the most common approach for the control of ignition timing and combustion rate in such advanced combustion modes [2].

An important part of the fuel design work is detailed modeling of combustion in engines by Computational Fluid Dynamic (CFD)

calculations. Due to the high complexity of commercial fuels such as gasoline, these models need kinetic reaction mechanisms for the combustion of simple surrogate fuels including representative hydrocarbons [3]. The main objectives of these models are to be able to correctly simulate ignition delay of representative surrogate fuels at engine-relevant conditions. Although several kinetic models and fuel mixtures have been suggested to mimic real gasoline [e.g. 4–8], it was shown recently that a three-component mixture including the fuels *n*-heptane, *iso*-octane and toluene is sufficient for practical purposes to represent non-oxygenated real gasoline [9].

Generally detailed kinetic models (with several hundreds to thousands of species) are too large to be utilized effectively, even in one-dimensional applications that couple transport and chemistry such as laminar flame speed simulations. For practical purposes it is desirable to reduce the number of species and reactions without losing accuracy. An alternative way to reduce the detailed mechanism is to make use of semi-detailed models and optimize reaction rate constants of selected reactions [10–12]. These models could be made up of sparse (lumped) chemical kinetic information for sub-mechanisms where there is greater overall knowledge of the underlying chemistry, and detailed reaction kinetics for sub-mechanisms that are more uncertain and the knowledge is less well known.

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The semi-detailed model for Toluene Reference Fuels (TRFs) in [10] consists of detailed toluene kinetic sub-set and skeletal mechanisms for *iso*-octane and *n*-heptane. The toluene sub-set in the TRF-model was mainly developed and tested for validity against high-pressure ignition delay data from shock tubes and to a much lesser extent species profiles. The most sensitive reaction in the mechanism was found to be the benzylperoxy radical decomposition, $C_6H_5CH_2OO\cdot \rightarrow C_6H_5CHO + OH\cdot$, and it was tuned for best fits to shock tube ignition delay data for toluene in [10]. The reaction has high sensitivity to the ignition because it is a main source of OH instead of the branching reactions $H_2O_2 + M = OH + OH + M$ and $H + O_2 = O + OH$. It was further shown that this reaction was also very sensitive in the chemical kinetic model developed for ethylbenzene self-ignition as it was an important source for consumption of benzyl radicals at high pressure [13].

Overall, the semi-detailed model was found to be very predictive for global model parameters such as ignition delay at engine-like conditions. However, it was not extensively tested for validity against measured species profiles in well defined reactor conditions, and this particular aspect of the validation process may make the model less reliable for predicting non-global parameters. Moreover, uncertainties regarding the benzylperoxy chemistry and updating rate constants for other important reactions in the toluene sub-mechanism further motivate search for improvements through revision and validation of the semi-detailed model.

Therefore, in this work a revision of some of the key reactions in the toluene sub-set has been conducted mainly based on quantum chemical calculations involving the benzylperoxy radical ($C_6H_5CH_2OO\cdot$) by Murakami et al. [14] and the kinetic model by Sakai et al. [15]. The revised model has been tested for validity against a wide variety of data including ignition delay obtained in shock tube, rapid compression machine and HCCI engine, species profiles in flow- and perfectly stirred reactors, and laminar flame speeds. When the revised model is compared with the previous one, it is shown that the revised model improves model predictions, especially for species profiles at lean conditions and high temperature.

2. Chemical kinetic model and numerical solution method

The starting mechanism for model development was a semi-detailed chemical reaction mechanism for toluene reference fuels [10] involving 137 species and 633 reactions. It consists of a detailed reaction mechanism for toluene, and skeleton mechanisms for the combustion of the primary reference fuels *iso*-octane (2,2,4-trimethylpentane) and *n*-heptane.

Table 1 shows the changes made to the toluene sub-set in this work based on the work by Murakami et al. [14] and Sakai et al. [15]. No changes were made to the skeletal mechanisms of the primary reference fuels. A new feature of the revised toluene model is the description of reaction (33–36), where rate constants are both temperature and pressure dependent and have been fitted to the rate data by Murakami et al. to be used as ordinary and modified Arrhenius rate constants. The rate constant for reaction (35) fitted based on data from quantum chemical calculations is significantly lower than the one used in the previous model ($k_{\text{forward}} = 3.00 \times 10^{9.7} T^{1.1} e^{-29500 \text{ cal/mol}/RT}$). Moreover, a new reaction (36) has been included in the revised toluene mechanism. The rate of this reaction is much lower than the competing reaction (35) for benzylperoxy decomposition. Other important revisions include the initiation reaction (3) where the rate constant by Oehlschlaeger et al. [16] is employed, and reaction (27) where the rate was increased from 2.00×10^{12} to 1.00×10^{13} based on the work by da Silva and Bozzelli [17] and Metcalfe et al. [18].

Thermodynamic- and transport data were taken from the work in [13] and simulations were performed with the CANTERA software package [19].

3. Results

3.1. Model validation for toluene sub-model

3.1.1. Shock tube ignition delay in shock tube and rapid compression machine

When modeling shock tube and rapid compression ignition delay data, a homogeneous adiabatic reactor was assumed with a constant internal energy, constant volume constraint. Ignition was assumed to be accomplished when the temperature had increased 400 K from the initial temperature. Similar ignition delay time is achieved when having an ignition criterion as the time when the hydroxyl radical (OH) reaches its maximum concentration.

Figs. 1 and 2 show model comparison against shock tube ignition delay for toluene in air by Shen et al. [28]. Both the revised model and the model in [10] relatively well capture the ignition delay dependence on pressure, temperature and mixture strength. However, the revised model shows a more accurate temperature dependence (higher global activation temperature) and also better prediction at the leanest fuel–air ratio ($\phi = 0.25$).

Fig. 3 shows model comparisons with the rapid compression machine (RCM) data from Mittal and Sung [29]. To account for post-compression heat loss in the RCM, a volume expansion term was introduced as $dV/dt = 0.25 \text{ m}^3/\text{s}$ to fit the measured pressure trace (Fig. 2 in [29]) for non-reactive mixtures. Both kinetic models can predict that the ignition delay time decrease as the fuel–air ratio (ϕ) decrease. The differences in ignition delay time slope between the models as shown in Figs. 1 and 2 are even more pronounced in the simulated RCM results. The revised model in this work predicts longer ignition delay times than the old model for decreased temperatures. This is also a result of a larger sensitivity to heat losses at temperatures below 1000 K. No ignition at all could be observed below 957 K.

3.1.2. Species profiles in a high pressure single pulse shock tube

Sivaramakrishnan et al. [30] used a high-pressure single pulse shocktube (HPST) to study the oxidation of toluene at reflected shock pressures from 22 to 550 bar and temperatures from 1210 to 1480 K. Experiments were performed for dilute (8–85 ppm toluene) stoichiometric and rich ($\phi = 5$) reagent mixtures. Stable species were analyzed using gas chromatography and gas chromatography/mass spectrometry. Selected experiments at $\phi = 1.0$ from the study above were used to check the validity of the revised model to predict stable species profiles for toluene oxidation at high pressure and temperature as shown in Figs. 4 and 5. A zero-dimensional, adiabatic, constant pressure reactor was used to simulate the experiments. The revised model shows a satisfactory prediction for fuel consumption and major species CO and CO₂, although it is somewhat more reactive than the model in [10] as seen in the toluene consumption and CO production.

3.1.3. Species profiles in a variable pressure flow reactor

Metcalfe et al. studied toluene oxidation in a variable pressure flow reactor (VPFR) [18]. A zero-dimensional, adiabatic, constant pressure reactor was used to simulate the experiments, and Fig. 6 shows model predictions and measurements of intermediate species at near stoichiometric conditions, 12.5 atm, and a constant temperature of 920 K, with a varying residence time. Both the revised- and old model significantly overestimates the rate of toluene consumption, although the revised model could predict the

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