

Testing the validity of a mechanism describing the oxidation of binary n-heptane/toluene mixtures at engine operating conditions

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Introduction

Efficient and clean combustion of hydrocarbons has always attracted the attention of the scientific community. The two most common types of Internal Combustion Engines (ICEs) namely Spark Ignition (SI) and Compression Ignition (CI) make use of gasoline and diesel fuels, respectively. These fuels are complex mixtures of several hydrocarbon families [1] and hence, fuel surrogates are used to emulate their properties. The most common fuel surrogates for the combustion of gasoline and diesel fuels are the so-called primary reference fuels (PRFs), i.e. mixtures of iso-octane and n-heptane. As engine development has moved towards low-temperature combustion (LTC) operating modes, PRF blends proved to be inadequate to describe the actual fuel's behavior [2]. In an effort to capture the behavior of real fuels in engines operating under LTC modes, PRF fuels were blended with toluene, the simplest methylated aromatic species, creating the so-called Toluene Reference Fuels (TRF) [3, 4].

In the context of engines studies, ignition delay time (IDT) is an important parameter. IDTs, defined as the time interval between the initiation of a combustion process and the first energy release, belong to the global reactivity measurements, provide modeling targets and are used for engine optimization [5]. Toluene's IDTs have been widely studied as a fuel component (in blends with n-heptane, iso-octane, etc.) [6-9].

Accurate predictions of toluene oxidation remains challenging; most literature models are unable to satisfactorily reproduce experimental IDT data at lower temperatures. In this context, the present study, like others before [6-10], focuses on blending toluene with a very reactive and well characterized fuel as is n-heptane, to increase mixture's reactivity and to extend the available experimental data to a wider range of conditions.

The present contribution is a summary of the work recently published by the authors in [11].

Approach

The study provides novel experimental ignition delay time data both at low temperatures and high toluene concentrations, in an attempt to fill the relevant gap in the literature. Measurements include three mixtures (50%, 75% and 90% vol. by toluene

concentration) at lean ($\phi=0.5$), stoichiometric ($\phi=1.0$) and rich ($\phi=2.0$) conditions at 10 and 30 bar over the temperature range of 650–1450 K. The experiments were carried out in the high-pressure shock tube (HPST) and rapid compression machine (RCM) at the National University of Ireland, Galway (NUIG). The devices have been used in a complementary way in order to cover the desired temperature range. The experimental setups of the devices have been described previously [HPST in [12] and RCM in [13]. Further, in order to investigate the synergies of toluene and n-heptane in the reactivity of the TRF mixtures, the LLNL TRF detailed kinetic mechanism is utilized, in both its original version [14] as well as in its recently updated one [15]. The model includes 1426 species and 6128 reactions. Simulations were carried out in CHEMKIN-PRO [16] with constant volume conditions. Heat loss effects in the RCM experiments are taken into consideration in simulations, as described in [17].

Results and discussion

The measured IDTs for all conditions have been plotted in Fig. 1 allowing for a comparison of many different variables. Each row contains measurements for a certain equivalence ratio with an ascending order ($\phi=0.5$ in the top row, $\phi=1.0$ in the middle and $\phi=2.0$ in the bottom row). Accordingly, the columns present measurements for mixtures with respect to their toluene content in ascending order, i.e. toluene/n-heptane ratio of 50/50(left), 75/25 (middle) 90/10 (right).

A comparison along the y-axis (vertically) shows that the IDTs in the 10 bar measurements are almost insensitive to variations in equivalence ratio at temperatures above 1150 K. This behavior is less pronounced as pressure increases and can be observed at temperatures only above 1250 K. Increasing the toluene concentration enhances this effect as data are sensitive to temperature for $T > 1050$ K for the low-pressure measurements. As temperatures decrease beyond these thresholds the fuel-lean cases have the longest IDTs. Another important observation can be made for the 90/10 mixture ratio at 10 bar, where the IDT for the fuel-lean and the stoichiometric cases coincide, while the fuel-rich mixtures have significantly longer IDTs at low pressures. At 30 bar, the fuel-rich and stoichiometric mixtures coincide, while the fuel-lean mixture has notably shorter IDTs.

A comparison of the results in the x-direction (horizontally (a) \rightarrow (c), (d) \rightarrow (f) and (g) \rightarrow (i)) shows an increase in IDTs with increasing toluene content. This increase is more pronounced at lower temperatures and as the equivalence ratio (ϕ) increases.

Regarding the performance of the mechanisms, Fig. 1a shows that the current mechanism predicts longer IDTs in the low pressure case yielding improved performance against experimental data at lower temperatures. Both HPST and RCM data are satisfyingly captured. Increasing the toluene concentration in the mixture to 75% naturally leads to longer predicted IDTs, as expected (Fig. 1b). The current mechanism version predicts longer IDTs, compared to the original one, at lower temperatures and reproduces better the ignition delay time data in this regime. In the NTC region, the updates cause the model to predict longer IDT with negative impact on the agreement. Modeling agreement at 30 bar is not affected by the mechanism modifications. In general, the modifications have resulted only in a small change of mechanism performance at high pressure, leading to improved predictions.

Figs. 1(d)–(f) show the stoichiometric measurements for all three mixture ratios. The current model predicts longer IDTs than the original one, showing improved agreement against the reported data at temperatures below 1000 K. In the high temperature regime,

no difference in the performance of both models is observed. Both mechanisms, however, fail to capture the NTC behavior of the 75/25 mixture ratio (Fig. 1e), predicting shorter IDTs. The 90/10 mixtures were not measured in the RCM due to repeatability issues and therefore only HPST data are presented in Figs. 1(g)–(i). For the 50/50 and the 75/25 mixture the agreement is very good for all measurements.

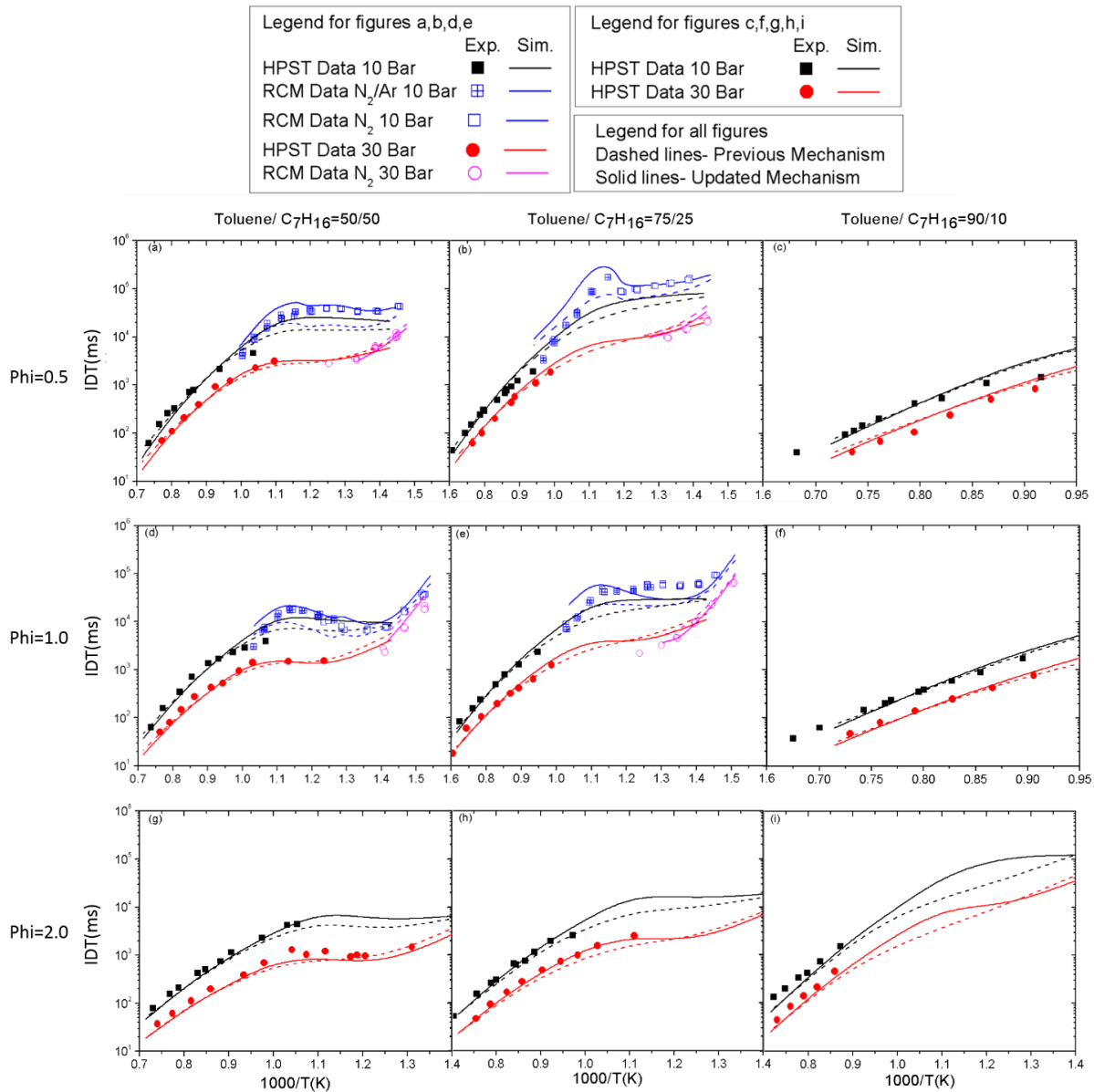


Figure 1: Experimentally determined HPST (closed symbols) and RCM data (open symbols) versus simulations using the original LLNL TRF mechanism (dashed lines) and the current one (solid lines) Square symbols refer to experiments at 10 bar and circle symbols to those at 30 bar.

Conclusions

Experimental data have revealed that IDTs were insensitive to changes in equivalence ratio at higher temperatures. This behavior was less pronounced at higher pressures, starting at higher temperatures, but was enhanced when the toluene content increased. At low temperatures, the fuel-lean mixtures showed the longest IDTs. The opposite was observed for higher temperatures, where the lean mixtures posed increased reactivity.

Computations have proved the improved agreement of the updated LLNL model on the current dataset; the updated model reproduces the experimentally observed longer IDTs in the low and intermediate temperature regime, presenting an overall improved performance, while it retains the original model's good performance in the high temperature regime.

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