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Ignition studies of *n*-heptane/*iso*-octane/toluene blends

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ABSTRACT

Ignition delay times of four ternary blends of *n*-heptane/*iso*-octane/toluene, referred to as Toluene Primary Reference Fuels (TPRFs), have been measured in a high-pressure shock tube and in a rapid compression machine. The TPRFs were formulated to match the research octane number (RON) and motor octane number (MON) of two high-octane gasolines and two prospective low-octane naphtha fuels. The experiments were carried out over a wide range of temperatures (650–1250 K), at pressures of 10, 20 and 40 bar, and at equivalence ratios of 0.5 and 1.0. It was observed that the ignition delay times of these TPRFs exhibit negligible octane dependence at high temperatures ($T > 1000$ K), weak octane dependence at low temperatures ($T < 700$ K), and strong octane dependence in the negative temperature coefficient (NTC) regime. A detailed chemical kinetic model was used to simulate and interpret the measured data. It was shown that the kinetic model requires general improvements to better predict low-temperature conditions and particularly requires improvements for high sensitivity (high toluene concentration) TPRF blends. These datasets will serve as important benchmark for future gasoline surrogate mechanism development and validation.

1. Introduction

Commercial transportation grade gasoline is widely used for light duty vehicles, and is a complex mixture of hundreds of hydrocarbons, primarily spanning C_4–C_{10}, including linear and branched paraffins, naphthenes, olefins and aromatics [1]. The composition of gasoline may vary considerably depending on its origin and refining/upgrading process [2]. State-of-the-art advanced combustion engine (ACE) technologies, such as homogeneous charge compression ignition (HCCI), reactivity controlled compression ignition (RCCI), gasoline compression ignition (GCI), premixed charged compression ignition (PCCI) and their variants, are expected to be more efficient [3,4], and will have a reduced environmental footprint associated with hydrocarbon combustion [5]. Fuel reactivity and ignition characteristics are the fundamental parameters controlling ignition in these ACE technologies [6–8]. Therefore, the development and validation of chemical kinetic mechanisms for gasoline-like fuels is very important. Due to the complex composition of gasoline, or any real fuel for that matter, it is an arduous task to assemble a chemical kinetic mechanism for all of the constituents. This difficulty is overcome by formulating a simple surrogate fuel which emulates the target properties of the real fuel. Generally, these target properties include the desired combustion properties (ignition delay, flame speeds, etc.) and/or physical properties (molecular weight, H/C ratio, viscosity, density, distillation curve, etc.). However, it should be noted that a given surrogate may not be able to emulate all of the targets and, therefore, care must be taken in selecting a particular surrogate. Good accounts on surrogate fuel formulation strategies can be found in [8–14].

Primary reference fuel (PRF) surrogates are among the simplest surrogates employed to emulate gasoline ignition. A PRF is a bicomponent mixture of *n*-heptane (octane number defined to be 0) and *iso*-octane (octane number defined to be 100), with PRF xx meaning xx% *iso*-octane and 1 − xx% *n*-heptane by volume. Gasoline fuels are knock rated, having both a Research Octane Number (RON) and a Motor Octane Number (MON), based on comparisons with PRF blends in a cooperative fuels research (CFR) engine. Due to the traditional use of *n*-heptane and *iso*-octane as gasoline surrogate components, several experimental [15–17] and modeling efforts [18–21] are available in the literature describing the ignition of *n*-heptane and *iso*-octane. A few chemical kinetic modeling and experimental studies have also focused on describing the ignition of PRF blends [16,22–27].

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It has been shown that a PRF surrogate captures the ignition of a high-paraffinic content gasoline reasonably well at temperatures above 850 K [28]. Sarathy et al. [28] showed that for two highly paraffinic gasoline fuels, FACE (Fuels for Advanced Combustion Engines; Conoco Philips) gasoline A and C, a PRF surrogate was more reactive at low temperatures (<850 K) compared to the gasoline fuels. Commercial gasoline fuels generally have high aromatic content (~20–30%) and some other non-paraffinic (~5–10%) components [1]. Consequently, such fuels tend to have a high sensitivity (S = RON – MON) which can be thought of as a measure of the non-paraffinic content of the fuel. A PRF surrogate by definition has zero sensitivity and will not be able to emulate the ignition behavior of a real gasoline fuel. Kalghatgi and coworkers [13,14] demonstrated that PRF surrogates cannot be used to rate a gasoline based on the primitive RON and MON testing methods. This discrepancy is due to the fact that real gasoline, due to its high sensitivity (S ~10), matches different PRF blends at different engine operating conditions. They proposed the use of toluene/*n*-heptane [14] and toluene/*n*-heptane/*iso*-octane [13] blends as more suitable gasoline surrogates. Kalghatgi et al. [13] developed correlations to calculate the composition of a toluene/*n*-heptane/*iso*-octane surrogate to match the RON and sensitivity of a target gasoline for a wide range of octane numbers. By matching both RON and sensitivity, the surrogate is expected to capture the real fuel reactivity over a wide range of conditions.

There have been a few fundamental ignition studies of surrogates comprising three or more components. Gauthier et al. [29] studied the auto-ignition characteristics of *n*-heptane/air, RD387 gasoline/air, and ternary surrogate/air (63% *iso*-octane/20% toluene / 17% *n*-heptane by volume) mixtures in a shock tube facility. They showed that the auto-ignition behavior of the RD387 gasoline was well-reproduced by the ternary surrogate. Vanhove et al. [23] studied an *iso*-octane/1-hexene/toluene ternary blend in a rapid compression machine, interestingly preferring 1-hexene over *n*-heptane to produce low-temperature reactivity. Kukkadapu et al. [30] measured ignition delay times of RD387 in a rapid compression machine and the results agreed well with the work of Gauthier et al. [29]. In further studies, Kukkadapu et al. [31,32] reported better agreement of a four component (*iso*-octane/*n*-heptane/toluene/2-pentene) surrogate with ignition delay times of RD387 at lower temperatures compared to the ternary surrogate proposed by Gauthier et al. [29]. Sarathy et al. [28] used five- (*n*-butane/*iso*-pentane/2-methylhexane/*n*-heptane/*iso*-octane) and six- (*n*-butane/*iso*-pentane/2-methylhexane/*n*-heptane/toluene/*iso*-octane) component surrogates to simulate low-temperature ignition of FACE gasolines A and C, respectively.

Previous work has thus shown that ternary blends of toluene/*n*-heptane/*iso*-octane (henceforth referred to as TPRF) can serve not only as adequate gasoline surrogate candidates on their own but may also be major constituents of the more complex multi-component surrogates. This is because TPRF surrogates can emulate the aromatic, *n*-paraffinic and *iso*-paraffinic content present in a real gasoline, where these three classes represent >90% of the chemical content of commercially available distillate gasoline fuels. However, wide-ranging fundamental studies of TRPF ignition and chemical kinetic development are not available in the literature. The objective of the current work is to provide a large dataset of experimental ignition delay times of TPRF blends for use in the refinement and development of surrogate kinetic models. Here, ignition delay times of four TPRF mixtures (RON = 70, 80, 91 and 97.5; S = 4, 5.7, 7.6 and 10.9) have been measured in a shock tube (ST) and in a rapid compression machine (RCM). These measurements were performed at pressures of 10 (RCM), 20 and 40 bar (RCM and ST) in the temperature range 650–1250 K and at equivalence ratios of 0.5 and 1.0. The TPRF mixtures were formulated to match the RON and sensitivity of two certified gasoline and two prospective naphtha-like fuels. These data are the first of their kind and will form highly valuable dataset for future gasoline surrogate mechanism development and validation.

2. Methods

2.1. TPRF surrogate formulation

Several methodologies have been proposed in the literature to formulate TPRF surrogates for gasoline fuels [13,33,34]. Morgan et al. [33] developed a second-order volume-based model to derive TPRF surrogate composition corresponding to the RON and MON of the target fuel. Kalghatgi et al. [13], on the other hand, proposed a second-order method on molar basis. Both works relied on engine octane data to optimize the correlations. Pera et al. [34] used octane ratings and the carbon, hydrogen and oxygen content of the target gasoline (ULG 95) to optimize the TPRF surrogate. However, they used linear by volume blending method which can potentially introduce errors in determining surrogates composition [33]. The TPRF surrogates studied in this work were formulated based on the correlations developed by Kalghatgi et al. [13]. These correlations calculate the TPRF surrogate composition required to emulate the RON and sensitivity the target fuel. The surrogates tested in this work were formulated over a wide range of octane numbers (RON: 70–97.5) with varying degrees of sensitivity (S: 4–11). The RON and MON values of the TPRF surrogates were experimentally measured at the Saudi Aramco Research and Development Center in their cooperative fuel research (CFR) engine following the ASTM D6733 (RON) and D6730 (MON) standards. These surrogates are listed in Table 1. It can be seen that the measured and estimated (from [13]) RON and MON values are in very good agreement with each other which further fortifies the use of the correlations developed by Kalghatgi et al. [13]. For brevity, the surrogate blends henceforth will be referred as TPRF xx where xx represents the RON of the surrogate blend.

2.2. Experimental details

The experiments reported in this study were performed in the high-pressure shock tube (HPST) facility at King Abdullah

Table 1
TPRF surrogates investigated in this work. See Table S1 (Supplementary material) for compositions in mole fractions.

Surrogate	*iso*-Octane[a]	*n*-Heptane[a]	Toluene[a]	RON estimated[b]	RON measured[c]	MON estimated[b]	MON measured[c]	Sensitivity[d]
TPRF 70	42.48	36.23	21.29	70	70	66	66	4
TPRF 80	39.85	28.58	31.57	80	80.4	74.3	75.3	5.7
TPRF 91	36.58	19.31	44.1	91	92	83.4	84.3	7.6
TPRF 97.5	11.52	18.04	70.44	97.5	98	86.6	87.1	10.9

[a] % volume.
[b] RON and MON estimated using correlations developed by Klaghatgi et al. [13].
[c] RON and MON measured in a CFR engine using ASTM standards.
[d] Sensitivity S = RON – MON (estimate).