



Ignition delay time measurements of primary reference fuel blends



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ABSTRACT

Ignition delay times of four different primary reference fuels (PRF), mixtures of n-heptane and iso-octane, were measured behind reflected shock waves in a high-pressure shock tube facility. The PRFs were formulated to match the RON of two high-octane gasolines (RON 95 and 91) and two prospective low-octane naphtha fuels (RON 80 and 70). Experiments were carried out over a wide range of temperatures (700–1200 K), pressures (10, 20, and 40 bar) and equivalence ratios (0.5 and 1). Kinetic modeling predictions from four chemical kinetic mechanisms are compared with the experimental data. Ignition delay correlations are developed to reproduce the measured ignition delay times. Brute force sensitivity analyses are carried out to identify reactions that affect ignition delay times at specific temperature, pressure and equivalence ratio. The large experimental data set provided in the current work will serve as a benchmark for the validation of chemical kinetic mechanisms of primary reference fuel blends.

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1. Introduction

The autoignition phenomenon is critical in improving the efficiency of combustion processes in spark ignition (SI) and compression ignition (CI) engines. For internal combustion engine design, efficiency and emissions are the two most important design parameters [1]. An obvious way to increase an engine's efficiency is to operate the engine at higher compression ratio. However, this results in increased probability of knocking, as the pressure and temperature of the end gas increase with an increase of the compression ratio. Knocking has been a key factor in limiting the improvement of efficiency in high compression ratio spark ignition engines for more than 60 years [2,3]. The presence and absence of knocking in a given engine depend mainly on the anti-knock quality of the fuel [4], which is conventionally defined by the fuel's octane number. Fuels with varying octane numbers may provide varying knock-limited compression ratios for an engine. Fuel chemistry and auto-ignition characteristics play an even greater role in modern engine designs such as homogeneous charged compression ignition (HCCI), partially premixed compression ignition (PPCI), and reactivity controlled compression ignition (RCCI). These engines are based on low-temperature operation and lean/stratified combustion to minimize soot and NO_x emissions while simultaneously increasing the engine efficiency [5].

Fuel auto-ignition quality is commonly specified by research and motor octane numbers, RON and MON, respectively. These are determined by comparing the ignition of a given fuel with primary reference fuel (PRF), n-heptane/iso-octane, blends in standard knock tests. Gasoline consists of a large number of components, and its composition varies depending on the fuel's source and production history. Therefore, ignition characteristics of automotive fuels are often represented using surrogate fuels comprising of two or more components. One of the simplest surrogates that can be considered is a PRF blend. Practical fuels are very different from PRFs because they are complex mixtures of paraffins, aromatics, olefins, naphthenes and oxygenates. However, under certain conditions, the oxidation processes of PRFs can adequately represent the ignition and combustion characteristics of real fuels [6–8]. Although complex surrogates containing three or more components have been proposed in literature and can better represent chemical and physical characteristics of practical fuels, PRF blends remain the first choice of engine community for modeling real fuel properties [9–12]. This is due to the fact that the number of species and reactions increase tremendously for multi-component surrogates, making those impractical for use in computation fluid dynamic (CFD) simulations. Additionally, kinetic mechanisms of PRFs serve as the base mechanisms in the formulation of large multi-component chemical kinetic models. As a result, development of fully validated chemical kinetic mechanism of PRFs is critical for engine modeling.

There have been several experimental and modeling efforts on the ignition characteristics of neat n-heptane and iso-octane

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Table 1Previous experimental studies of pure n-heptane, pure iso-octane, pure toluene and toluene blends. ^(a)TPRF refers to iso-octane/n-heptane/toluene blends.

S/N	Reference	Fuel	Temperature	Pressure	Equivalence ratio
1	Vermeer et al. [13]	n-Heptane and iso-octane	1200–1700 K	1–4 bar	1
2	Coats et al. [14]	n-Heptane	1300–2000 K	1–2 bar	0.5–4
3	Ciezkowski et al. [15]	n-Heptane	660–1350 K	3.2–42 bar	0.5–3
2	Davidson et al. [16]	iso-Octane	855–1269 K	14–59 bar	0.5, and 1
3	Mansfield et al. [17]	iso-Octane	740–1125 K	3–30 bar	0.25, and 1
4	Gauthier et al. [18]	n-Heptane, gasoline, and TPRF ^a	850–1280 K	15–25, and 45–60 bar	0.5, 1, and 2
5	Hartmann et al. [19]	Toluene, iso-octane and toluene/ n-heptane	700–1200 K	40 bar	0.5, and 1
6	Minetti et al. [20]	n-Heptane	630–880 K	2.7–4.5 bar	1
7	Herzler et al. [21]	n-Heptane	720–1100 K	50 bar	0.1–0.4
8	Dagaut et al. [22]	n-Heptane, and iso-octane	550–1150 K	10 bar	0.3–1.5
9	Shen et al. [23]	n-Heptane	786–1396 K	9–58 bar	0.25, 0.5, and 1
10	Davidson et al. [24]	n-Heptane and iso-octane	1100–1460 K	1.6–2 bar	Oxidation ($\phi = 1$) and pyrolysis
11	Davidson et al. [25]	n-Heptane	1300–1600 K	2 bar	1
12	Sakai et al. [26]	n-heptane/ toluene, iso-octane/ toluene and TPRF ^a blends	1200–1600 K	2.5 bar	1
13	Javed et al. [27]	TPRF ^a blends	650–1250 K	10, 20, and 40 bar	0.5, and 1

Table 2

Previous and current experimental ignition delay studies of PRF blends.

S/N	Reference	Fuel	Temperature	Pressure	Equivalence ratio
1	Fieweger et al. [3]	PRF 0, 60, 80, 90 iso-Octane	700–1200 K 700–1250 K	40 bar 13–40 bar	1 0.5, 1, and 2
2	Sarathy et al. [28]	PRF 84	715–1500 K	10, 20, and 40 bar	0.5, and 1
3	This work	PRF 70, 80, 91, 95	700–1200 K	10, 20 and 40 bar	0.5 and 1

Table 3Previous chemical kinetic mechanisms of pure n-heptane, pure iso-octane, pure toluene and their blends. ^(a) TPRF refers to iso-octane/n-heptane/toluene blends.

S/N	Reference	Model	Number of species / reactions
1	Westbrook et al. [29] (1989)	Detailed chemical kinetic reaction mechanism for the oxidation of iso-octane, n-heptane and their mixtures (PRF)	212/765
2	Ranzi et al. [30,31] (1995 & 1997)	Semi-detailed kinetic scheme for n-heptane oxidation	145/2500
3	Curran et al. [32] (1998)	Detailed chemical kinetic mechanism for n-heptane oxidation	550/2450
4	Curran et al. [33] (2002)	Detailed chemical kinetic mechanism for iso-octane oxidation	860/3600
5	Tanaka et al. [34] (2003)	Reduced chemical kinetic mechanism for PRF blends.	32/55
6	Jia et al. [35] (2006)	Skeletal Chemical kinetic for iso-octane oxidation	38/69
7	Agafonov et al. [36] (2007)	Chemical kinetic mechanism for soot formation during the pyrolysis and oxidation of toluene and n-heptane.	210/2250
8	Ahmed et al. [37] (2007)	Comprehensive and compact chemical mechanisms for n-heptane oxidation	246/2309
9	Kirchen et al. [38] (2007)	Skeletal chemical kinetic mechanism for PRF blends	58/120
10	Ogura et al. [39] (2007)	Detailed chemical kinetic mechanism for the oxidation of PRFs in the presence of ethyl-tert-butyl-ether (ETBE) and ethanol	634/2390
11	Andrae et al. [40] (2008)	Detailed chemical kinetic model of gasoline surrogate fuels consisting of iso-octane, n-heptane, toluene, di-isobutylene and ethanol	1121/4961
12	Andrae et al. [41] (2008)	Semi-detailed chemical kinetic mechanism for PRF oxidation	137/ 633
13	Ra et al. [42] (2008)	Reduced chemical kinetic mechanism for PRF oxidation	41/130
14	Sakai et al. [43] (2009)	Detailed chemical kinetic model for TPRF ^a	783/2883
15	Lee et al. [44] (2010)	Reduced chemical kinetic mechanism for TPRF ^a	48/67
16	Mehl et al. [45] (2011)	Detailed chemical kinetic model for gasoline surrogate components	1550/6000
17	Liu et al. [46] (2012)	Skeletal chemical kinetic models for PRF oxidation	41/124
18	Wang et al. [47] (2013)	Reduced mechanism for PRF combustion	73/296
19	Cai et al. [48] (2015)	Kinetic model for PRF blends based on the optimization of reaction rate rules developed previously by Curran et al. [33]	314/2327

oxidative mixtures. However, blends of n-heptane and iso-octane, PRFs, have not been studied as extensively. Experimental ignition delay studies of pure n-heptane, pure iso-octane, pure toluene and toluene blends are listed in Table 1, whereas experimental studies of PRF blends are listed in Table 2. In addition, relevant modeling studies are listed in Table 3. We would like to emphasize that despite the development of these many models for n-heptane/iso-octane, the validation data on the reactivity of PRF blends are quite limited.

In the current work, we have measured ignition delay times of lean and stoichiometric PRF blends over a wide range of pressures (10–40 bar) and temperatures (700–1200 K). The data encompass the negative temperature coefficient (NTC) region of the studied

fuel blends. Four PRF blends are studied in this work. PRF 91 and 95 represent research octane numbers (RON) of common gasolines used in the US, Europe and Middle East. PRF 70 was chosen to represent light naphtha – a fuel that can potentially be used in gasoline compression ignition (GCI) engines. Finally, PRF 80 was chosen as an intermediate mixture to provide a range of n-heptane/iso-octane mixture fractions that can be used to validate and improve chemical kinetic mechanisms of PRF blends.

2. Experimental details

Ignition delay times of primary reference fuel blends were measured using the high-pressure shock tube (HPST) facility at King

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