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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 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.

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	Ciezki 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-hepane/ 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 1. Previous 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	Fieweger et al. [3]	PRF 0, 60, 80, 90	700 – 1200 K	40 bar	1
		iso-Octane	700 – 1250 K	13 – 40 bar	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 2. Previous and current experimental ignition delay studies of PRF 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

Table 3: Previous 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

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 Abdullah University of Science and Technology (KAUST). The shock tube is constructed from stainless steel with an inner diameter of 10 cm. The driven section is 6.6 m long and the driver section has a modular design to vary its length from 2.2 m to a maximum of 6.6 m. The mid-section of the shock tube houses two pre-scored aluminum diaphragms in a double diaphragm arrangement (DDA) which allows better control of the post-reflected shock conditions compared to a single diaphragm arrangement (SDA). The main difference between DDA and SDA is the diaphragm rupture timing. In SDA, gas pressure in the driver section is increased until the diaphragm ruptures. The breaking pressure depends on many variables such as diaphragm thickness, scoring depth, aluminum grade and rate of pressure increase. This makes it hard to precisely control the bursting pressure (P_4) and ultimately provides varying conditions (P_5 and T_5) behind reflected shock wave. In DDA, the mid-section is filled with bath gas pressure that is much lower than the breaking pressure of the diaphragm. Thereafter, the driver section is filled to the desired pressure (P_4). Breaking of the diaphragms is activated by suddenly venting the mid-section. This procedure allows precise control of post-shock conditions and experimental conditions can be easily reproduced.

Incident shock speed was measured by six PCB 113B26 piezoelectric pressure transducers (PZTs) placed in the last 3.7 m of the driven section of the shock tube. Incident shock attenuation rates varied from 0.5 to 1.8 %/m. Shock jump relations and known thermodynamic parameters [49] were used to calculate the post-reflected shock conditions (P_5 and T_5) with an uncertainty of $< 1\%$. Sidewall pressure trace was measured using a Kistler 603B1 piezoelectric pressure transducer located at 1.0 cm from the endwall. Electronically excited OH* chemiluminescence at 307 nm was monitored through sapphire windows at the endwall using UV-intensified Thorlabs PDA36A photo-detectors. A schematic of the shock tube end-section is shown in *Fig. 1*.

Fig. 1. Schematic of the optical configuration for ignition delay time measurements.

Liquid n-heptane and iso-octane were blended volumetrically to prepare the desired PRF blend. For example, PRF 80 consists of 80% iso-octane and 20% n-heptane by volume. Fuel/oxidizer mixtures were prepared in a heated (75 °C) magnetically stirred mixing tank. After vacuuming the mixing tank to pressures less than 1×10^{-2} mbar, liquid fuel blend was injected directly in the heated mixing tank. The injection was made through a septa rubber valve that has high sealing properties. Following the fuel evaporation and pressure stabilization, the pressure was measured using an MKS pressure gauge (0 – 100 Torr range). Nitrogen and oxygen were added slowly to inhibit condensation of fuel that can lead to inaccuracies in the test mixture composition. Mixtures were left in the mixing vessel for at least one hour prior to experiments. High purity (99.9%) n-heptane and iso-octane were purchased from Sigma Aldrich. Research-grade oxygen and nitrogen cylinders (99.999% purity) were purchased from AH Gas Company. A molar ratio of 3.76:1 of $N_2:O_2$ was used to prepare fuel/air mixtures. Helium was used as the driver gas for ignition delay times less than 1.5 ms. Driver gas tailoring (nitrogen in helium) and long length of driver section were used to extend the shock tube test times to more than 10 ms. A gradual pressure rise behind reflected shock wave (dP_5/dt) was observed, which varied from 2.5%/ms to 3.5%/ms.

Ignition delay time is defined as the time between the arrival of the reflected shock wave and the onset of the ignition near the endwall. The arrival of the reflected shock wave was determined by the step rise in pressure at the sidewall (1 cm from endwall) observation location. The onset of ignition was detected by the maximum slope in the sudden increase of pressure or OH^* endwall.

The two methods lead to very similar ignition delay times. Ignition delay data presented in this work were deduced from the pressure signal. Representative ignition delay time measurements are shown in *Fig. 2(a)* (non-tailored driver gas) and *Fig. 2(b)* (tailored driver gas). Uncertainty in the reported ignition delay times is estimated to be about $\pm 15\%$ and comes primarily from the uncertainty in the calculated reflected shock temperature.

Fig. 2. Examples of pressure and OH emission-time histories for (a) non-tailored (He driver gas) shock and (b) tailored (mixture of N_2 and He driver gas) shock.*

3. Results and Discussion

Ignition delay times were measured for four PRF blends (PRF 70, 80, 91, and 95) over a wide range of temperatures (700 - 1200 K), pressures (10, 20 and 40 bar), and equivalence ratios (0.5 and 1.0). Measured ignition delay times are displayed in subsequent sections on Arrhenius-like plots, with the ignition delay on a log scale plotted as a function of reciprocal of reflected-shock temperature (T_5). All experimental data are provided in tabular form in the Supplementary Material (Table S1). In subsequent sections, representative plots are given for the effect of pressure, equivalence ratio and fuel composition.

Ignition delay time simulations were carried out using CHEMKIN-PRO [50] with a homogeneous batch reactor. The gradual pressure rise behind reflected shock wave ($dp_5/dt = 3\% \text{ ms}^{-1}$) is converted to volume history and imposed on the homogeneous calculations. Ignition

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4 delay times from this study are compared with the predictions of four kinetic mechanisms;
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6 detailed gasoline surrogate mechanism of Mehl et al. [45], reduced PRF mechanism of Cai et al.
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8 [48], detailed PRF mechanism of Curran et al. [33], and detailed three-component (n-heptane,
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10 iso-octane, toluene) mechanism of Andrae et al. [40].

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12 The sensitivity analyses presented in this work are calculated using the “brute-force” method.
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14 This involves increasing and decreasing the reaction rate coefficients by a factor of 2 and
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16 calculating the effect on the simulated ignition delay times. The sensitivity coefficient (σ) is
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18 defined as:

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$$\sigma = \frac{\log\left(\frac{\tau_+}{\tau_-}\right)}{\log(4)},$$

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25 where (τ_+) is the ignition delay time when the rate coefficient of the reaction is doubled and (τ_-)
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27 is the ignition delay time when the rate coefficient of the reaction is halved [51]. According to
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29 this definition, a reactivity promoting reaction results in a negative sensitivity coefficient and a
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31 reactivity inhibiting reaction results in a positive sensitivity coefficient. Unless otherwise
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33 specified, sensitivity analyses presented in subsequent sections are performed using the Mehl et
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35 al. [45] mechanism.

36 37 38 39 **3.1 Comparison with Previous Measurements**

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41 *Fig. 3(a & b)* present a comparison among ignition delay times of PRF 80 and 91 from this work
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43 and PRF 80 and 90 from Fieweger et al. [3] and PRF 84 from Sarathy et al. [28]. It should be
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45 emphasized that both of these previous works measured the ignition delay times of PRF blends at
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47 limited ranges of conditions compared to the current work, as illustrated in Table 2. At high
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49 temperatures, there is excellent agreement among the ignition delay time measurements of the
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51 three works. Even at lower temperatures, there is a reasonably good agreement for the 20 bar as
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53 well as 40 bar cases. These comparisons ascertain the accuracy of the current data set.

Fig. 3. Comparison of measured ignition delay times between this work and the data reported by Fieweger et al. [3] and Sarathy et al. [28].

3.2 Ignition Delay Time Correlation

For engine simulations, it is useful to have simple correlations that can represent the fuel autoignition behavior over a wide range of engine operating conditions. In the current work, we have developed ignition delay correlations in three steps. In the first step, we used the three-Arrhenius model proposed by Wiesser et al. [52] for deriving the correlation of ignition delay times of pure iso-octane and n-heptane over 700 – 1300 K and 10 – 40 bar. The Wiesser et al. [52] model correlates ignition delay times separately for the high-, intermediate- and low-temperature reactivity regions. The low and intermediate ignition chemistries occur sequentially giving a two-stage ignition. However, at high temperatures, single ignition chemistry occurs. The ignition process may be illustrated with a simplified system, shown in Fig. 4, and written mathematically as:

$$\frac{1}{\tau_j} = \frac{1}{(\tau_1 + \tau_2)} + \frac{1}{\tau_3} \quad (1)$$

$$\tau_i = A_i * \left(\frac{P}{P_{ref}} \right)^{\beta_i} * \Phi^{\gamma_i} * \exp\left(\frac{T_{ai}}{T}\right), \quad (2)$$

$$i = 1, 2, \text{ and } 3$$

where τ_1 , τ_2 and τ_3 represent the low, intermediate, and high temperature ignition regimes, respectively, and τ_j refers to the overall ignition delay of n-heptane ($\tau_{n-heptane}$) or iso-octane ($\tau_{iso-octane}$). Fitting parameters A_i , β_i , γ_i , and T_{ai} are determined by regression analysis on the measured ignition delay data. Here, the ignition delay times of pure iso-octane and n-heptane were estimated from the available experimental data of the four PRF blends. The four fitting parameters were adjusted to fit the experimental data. The correlation parameters extracted from fitting Eqs. (1) – (2) to the experimental data are listed in *Table 4*. Values of the fitting parameters for the ignition delay time correlation of PRF blends. In the second step, we employed the ignition delay modeling approach proposed by Ma et al. [53] to include the effect of blending:

$$\frac{1}{\tau} = \frac{x_{iso-octane}}{\tau_{iso-octane}} + \frac{x_{n-heptane}}{\tau_{n-heptane}} \quad (3)$$

where $x_{iso-octane}$ and $x_{n-heptane}$ are the molar fractions of iso-octane and n-heptane, respectively, in the PRF blend. In the third step, we used Livengood-Wu [54] integral to account for the temperature/pressure change prior to ignition caused by the gradual pressure rise (dP/dt) behind reflected shock waves:

$$\int_0^{\tau_{ign}} \frac{1}{\tau(T, P)} dt = 1 \quad (4)$$

where τ is the instantaneous ignition delay time as a function of pressure and temperature, and τ_{ign} is the total ignition delay time of the PRF blend. While applying this methodology to engine simulations, pressure and temperature time-histories of piston compression may be used in Eq. (4) to calculate the onset of knock.

Fig. 4. Simplified system employed for the description of ignition process [52]

n-Heptane	τ_1	τ_2	τ_3
A	1.544×10^{-13}	2.15×10^5	1.2×10^{-5}
β	-0.1	-1.9	-1.1
γ	-0.1	-0.8	-0.3
T_a	2.2×10^4	-5×10^3	1.53×10^4
iso-Octane	τ_1	τ_2	τ_3
A	2.21×10^{-13}	2.15×10^6	1.5×10^{-5}
β	-0.1	-1.9	-1.1
γ	0.1	-0.8	-0.3
T_a	2.2×10^4	-5×10^3	1.53×10^4

Table 4. Values of the fitting parameters for the ignition delay time correlation of PRF blends.

Fig. 4 illustrates a comparison between the ignition delay times calculated from the correlations and the experimental data of this work. In general, the developed correlation does a reasonable job of modeling the measured ignition delay times. Such a correlation can be effectively used in simple computational fluid dynamic simulations of PRF blends.

Fig. 4. Comparison between ignition delay time correlation and the experimental data of this work for PRF 70 blend.

3.3 Influence of Pressure on Ignition Delay Times

Ignition delay time measurements of the PRF blends were performed at pressures near 10, 20 and 40 bar. Fig. 5 (a, b and c) present the effect of pressure on PRF 70 ($\phi = 0.5$ and 1) and PRF 91 ($\phi = 1$). As expected, ignition delay times of the PRF blends decrease with increasing pressure. Also, the pressure dependence increases as we move from the high-temperature to the NTC region. Moreover, the turnover temperature, marking the start of NTC region from the high-temperature side, increases with increasing pressure. The NTC is less pronounced at higher pressures due to the increased stability of RO_2 radicals and faster decomposition of H_2O_2 at higher pressures. It can be observed that the pressure dependence is less for lean mixtures compared with stoichiometric mixtures. Fig. 5(c) also shows that larger concentration of isooctane in PRF 91 results in longer ignition delay times and less pronounced NTC reactivity.

Fig. 5. Influence of pressure on ignition delay times. (a) PRF 70 ($\phi = 1$), (b) PRF 70 ($\phi = 0.5$), (c) PRF 91 ($\phi = 1$), (d) brute-force sensitivity analyses for PRF 70 ($\phi = 1$) at 800 K using the Mehl et al. mechanism [45].

Sensitivity analysis was carried out at 800 K and three pressures (10, 20 and 40 bar) to elucidate the effect of pressure on reactions controlling auto-ignition. Critical reactions for stoichiometric PRF 70/air mixture are presented in Fig. 5(d). As pressure increases from 10 to 40 bar, the rate coefficient of the pressure dependent decomposition of hydrogen peroxide ($\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$) becomes very fast and does not need to compete as much with the bimolecular reaction ($\text{H}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{HO}_2$). At lower pressures, these two reactions compete more effectively and thus

the system reactivity decreases as pressure decreases. An interesting observation from sensitivity analysis is that the overall reactivity is more sensitive to the isomerization of RO₂ radicals to QOOH than to the decomposition of hydrogen peroxide at 40 bar.

The pressure dependence exponents, n , have been calculated from the experiments and simulations over a temperature range between 700 and 1400 K. Experimental pressure dependence exponents were calculated from the fitting of the measured ignition delay times. The fitting error was found to be +/- 20% and the variation of the fitting error with respect to temperature, pressure, equivalence ratio and fuel composition is shown in *Fig. S1 (Supplementary Material)*. The pressure exponents were calculated from the 20 and 40 bar data, as follows:

$$n = \frac{\log\left(\frac{\tau_{P=40}}{\tau_{P=20}}\right)}{\log\left(\frac{40}{20}\right)}$$

Figure 7 show a comparison among the pressure exponents derived from the current experiments and the four kinetic models for PRF 70 stoichiometric and lean mixtures. As temperature increases from ~ 850 to 1250 K, experiments show that the pressure exponents of the lean mixtures of PRF 70 decrease more sharply than the stoichiometric mixtures. The pressure exponents calculated from Curran et al. [33] and Andrae et al. [40] mechanisms decrease more gradually as temperature increases from 850 to 1400 K. Cai et al. [48] mechanism shows higher pressure exponents than Curran et al. [33] and Andrae et al. [40]. Interestingly, the exponents calculated from Mehl et al. [45] mechanism decrease from 850 to ~ 1000 K and then increase slightly from ~ 1000 K to higher temperatures. The experiments and simulations show highest exponents in the NTC region due to the increased effect of pressure-dependent reactions such as hydrogen peroxide decomposition. Also, it may be observed that the pressure exponents decrease as we move from the NTC region to lower temperatures. Additional plots of pressure exponents for PRF 80 and 91 are given in the Supplementary Materials (*Fig. S2*).

Fig. 6. Comparison of experimental and simulated pressure dependence exponents for PRF 70.

In order to elucidate the different pressure exponents predicted by the kinetic models at high temperatures, sensitivity analyses were conducted for PRF 70 at 1100 and 1200 K; these analyses are given in Fig. S3 (Supplementary Material). At 1100 K, the overall reactivity is sensitive to the reaction of atomic hydrogen and molecular oxygen to form hydroperoxide radical and the decomposition of hydrogen peroxide to form two hydroxyl radicals. At 1200 K, the sensitivity coefficients of these reactions are smaller than at 1100 K. Among the four models, Mehl et al. [45] and Cai et al. [48] mechanisms shows higher sensitivity to these reactions than Curran et al. [33] and Andrae et al. [40] mechanisms at 1200 K. In other words, as temperature increases from 1100 to 1200 K, the sensitivity coefficients of the pressure-dependent reactions decrease more for Curran et al. [33] and Andrae et al. [40] mechanisms compared to Mehl et al. [45] and Cai et al. [48] models. As a result, Curran et al [33] and Andrae et al. [40] exhibit lower pressure exponents at higher temperatures.

Variation of pressure exponents with fuel composition is shown in Fig. S4 (Supplementary Material) at 1100 K. The experiments and the four mechanisms show an increase in the pressure exponents as we move to PRF blends with higher iso-octane concentration. This is due to the larger pressure dependence of iso-octane reactions compared with n-heptane at high temperatures (see sensitivity analysis in Fig. S5, Supplementary Material).

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4 Preceding analyses were based on the pressure exponents calculated from 40 and 20 bar data.
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6 Additional simulations were carried out to see how these exponents vary at lower pressures. *Fig.*
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8 *S6 (Supplementary Material)* shows that in the intermediate temperature (850 – 1000 K) region,
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10 the pressure exponents calculated from 40 and 20 bar data are larger than those calculated from
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12 20 and 10 bar data. The trend is reversed at low temperatures (< 850 K) where pressure
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14 exponents are larger for 20 and 10 bar data. This behavior could be explained based on the
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16 variation in pressure-dependent reactions across the two temperature regimes.
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21 **3.4 Influence of Equivalence Ratio on Ignition Delay Times**

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23 Ignition delay times for all PRF blends were measured at fuel lean ($\phi = 0.5$) and stoichiometric
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25 conditions. *Figure 8(a)* shows a representative case for the effect of equivalence ratio for PRF 70
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27 at a nominal pressure of 40 bar. The effect of equivalence ratio is strongest in the intermediate
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29 temperature range where reactivity increases as ϕ increases. At higher and lower temperatures,
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31 ignition delay times exhibit weak dependence on equivalence ratio. Sensitivity analyses were
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33 carried out for PRF 70 at 800 K and 40 bar for lean and stoichiometric mixtures. At moderate
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35 temperatures, hydroperoxyl radical chemistry plays very important role. At lean conditions, the
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37 reaction of hydrogen peroxide with oxygen plays strong inhibiting role. Also, the sensitivity
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39 coefficients of the important reactions inhibiting the reactivity are higher for lean mixtures
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41 compared to the stoichiometric mixtures – illustrating the observed smaller reactivity for lean
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43 mixtures.
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(a)

(b)

Fig. 8. Influence of equivalence ratio on ignition delay times. (a) PRF 70 at 40 bar, (b) brute force sensitivity analysis for PRF 70 at 40 bar and 800 K.

Equivalence ratio dependence exponents, m , have been calculated from the experiments and kinetic models at 40 bar according to the following equation:

$$m = \frac{\log\left(\frac{\tau_{\phi=1}}{\tau_{\phi=0.5}}\right)}{\log\left(\frac{1}{0.5}\right)}$$

Fig. 7 shows comparison among the equivalence ratio exponents calculated from experiments and simulations. In general, the equivalence ratio exponents calculated from the experiments are found to be smaller than those from the simulations. The experiments and simulations show that the exponents are highest at intermediate temperatures (~ 850 K) and decrease as we go to high temperatures or to low temperatures. For fuel/air mixtures, the variation in equivalence ratio results in varying fuel concentration and almost constant oxygen concentration. At high temperatures, the overall reactivity is controlled by competition between $\text{H} + \text{O}_2$ branching reaction and $\text{CH}_3 + \text{CH}_3$ termination reaction, as seen in the sensitivity analysis presented in Fig. S7 (Supplementary Material). As temperature increases in this region, the $\text{H} + \text{O}_2$ reaction becomes more dominant compared to the fuel-dependent methyl recombination reaction and thus

the dependence on equivalence ratio decreases. At very high temperatures ($> \sim 1350$ K), the $H + O_2$ reaction is fully dominant and a ‘cross-over’ is observed where lean mixtures start to become more reactive than rich mixtures. As we go from intermediate to low temperatures, the oxygen addition steps forming RO_2 and O_2QOOH control the system reactivity and thus varying the fuel concentration (or equivalence ratio) has less effect on system reactivity in this temperature region.

Equivalence ratio exponents are observed to vary as a function of pressure. *Figure S8* (Supplementary Material) shows that the equivalence ratio exponents at 40 bar are larger than at 20 and 10 bar for high temperatures; however, at intermediate to low temperatures the equivalence ratio exponents become higher for lower pressures. These trends may be explained from the variation in pressure-dependent and fuel-dependent reactions across these different temperature regimes.

Fig. 7. Comparison between the equivalence ratio dependence exponents (m) calculated from experiments and simulations

3.5 Influence of Composition on Ignition Delay Times

Fig. 8(a) illustrates the variation in ignition delay times for PRF 70, 80, 91 and 95. Results show that ignition delay times are almost independent of composition in the high-temperature region. In other words, at fixed pressure and equivalence ratio, the ignition delay times for PRF 70, 80,

91 and 95 are quite similar at high temperatures. However, the composition does have an appreciable effect at intermediate temperatures ($\sim 700 - 900$ K). Increasing the iso-octane fraction (PRF 70 to PRF 95) results in a decrease of overall reactivity and consequently longer ignition delay times. At further lower temperatures (< 700 K), ignition delay times are less sensitive to fuel composition.

Fig. 8. Influence of fuel composition on ignition delay times. (a) comparison among the four PRF blends at 40 bar and $\phi = 1$, (b) brute force sensitivity analysis comparison for the four blends at 20 bar, $\phi = 1$ and 800 K. The inset in (a) shows ignition delay times on a linear scale to illustrate the composition dependence.

Fig. 8(b) presents the sensitivity analyses of PRF 70, 80, 91, 95 at 20 bar and 800 K for stoichiometric mixture. It can be observed that H-abstraction reactions of n-heptane and iso-octane compete for the hydroxyl radicals. The inhibiting effect of iso-octane increases as the fraction of iso-octane increases in the fuel blend which results in overall decreased the reactivity of the system.

3.6 Comparison with Chemical Kinetic Models

Fig. 9(a) presents comparison between the four kinetic models and the experimental data for PRF 70 at $\phi = 1$ and pressures of 10, 20 and 40 bar. At temperatures higher than 1000 K, experimental data agree well with all mechanisms except Cai et al. [48] which appears to be slightly faster. At lower temperatures and in the NTC region, the agreement between

measurements and models varies. For example, the 20 bar data agree quite well with the predictions of Mehl et al. [45] models. On the other hand, the 40 bar data agreed well with the predictions of the optimized model of Cai et al. [48].

Fig. 9(b) compares experimental data and model predictions for PRF 70 at pressure of 40 bar and two equivalence ratios ($\phi = 0.5, 1$). At high temperatures, in contrast to all models, the experimental data exhibit very weak equivalence ratio dependence. At lower temperatures, stoichiometric PRF 70 data compare very well with the predictions of Cai et al. [48] mechanism. Ignition delay times for lean mixture seem to be overestimated by all mechanisms in the NTC and low-temperature region.

The performance of various mechanisms in predicting fuels of varying composition is shown in *Fig. 9(c)*, which plots data for PRF 70 and 95 at pressure of 40 bar and $\phi = 1$. In the high-temperature region, experimental data agree quite well with the four mechanisms. However, in the NTC and low-temperature region, the experimental data agree better with the prediction of Cai et al. [48] model.

Fig. 9. Comparison of measured ignition delay times with the predictions of four kinetic mechanisms: Mehl et al. [45], Cai et al. [48], Curran et al. [33], Andrae et al. [40].

In general, the mechanism by Cai et al. [48] shows better agreement with experimental data over a broader range of conditions. This is due to the fact that this model is developed by optimizing rate coefficient rules with the help of literature ignition delay data of n-heptane, iso-octane and PRF mixtures. Further detailed comparisons of our experimental ignition delay times and model predictions are provided in Fig. S9 (a – x) of the Supplementary Material.

Ignition delay time sensitivity analyses were conducted for the four kinetic mechanisms at 800 K and 20 bar for PRF 70 stoichiometric mixture; results for the top five reactions are plotted in Fig. 10. The selected condition falls in the NTC region. The mechanisms place varying levels of importance to the critical reactions. The competition between hydrogen peroxide (H_2O_2) decomposition and the reaction of hydrogen peroxide with oxygen dictates the reactivity of the system. H-abstraction by OH from n-heptane promotes reactivity while H-abstraction from iso-octane inhibits reactivity. This competition for hydroxyl radicals is important in all mechanisms except Cai et al. [48]. On the other hand, Cai et al. [48] model places much greater emphasis on the isomerization of RO_2 radicals to QOOH.

Fig. 10. Ignition delay times sensitivity analyses for the four chemical kinetic models.

3.7 Pre-ignition Energy Release

Shock tube ignition delay data at relatively long ignition delay times may be affected by non-ideal phenomena such as gradual pressure increase behind reflected shock wave and pre-ignition energy release. Davidson et al. [16] observed pre-ignition energy release in iso-octane/air and toluene/air mixtures and considered this behavior to be due to a chemical kinetic process not predicted by the chemistry models. Mittal et al. [55] presented additional data on toluene/air ignition in a rapid compression machine and showed no evidence of pre-ignition activity. They speculated that wall contamination might be responsible for pre-ignition phenomena. Vasu et al. [56] re-examined toluene ignition delays and concluded that contamination was not the source of the pre-ignition observed by Davidson et al. [16]. They conclude that pre-ignition phenomena can be connected to mild, strong, and mild-to-strong ignition regimes. This conclusion is consistent with the observation of localized ignition in the mild and transition regimes in other shock tube studies. Recently, Troutman et al. [57] used high speed OH* chemiluminescence imaging to study pre-ignition during the combustion of n-heptane and attributed pre-ignition to the shock tube wall contamination and shock / boundary-layer interactions.

In the current work, all pressure profiles were analyzed in detail to alleviate any shortening of ignition delay times by pre-ignition energy release. At the low temperatures of the current work, some pressure and OH* emission-time profiles did exhibit evidence of pre-ignition energy release. However, further analyses revealed that such pre-ignition energy release had negligible

effect on the ignition delay time data reported here. As a representative illustration, *Fig. 11(a)* presents pressure time-histories of two ignition delay time measurements for stoichiometric mixture of PRF 80 at ~ 10 bar. The two pressure profiles exhibit varying amounts of pre-ignition energy release with the green trace showing relatively small pressure rise before autoignition (exponential pressure rise) and the black solid trace showing considerably larger pressure rise before bulk ignition. These measurements points are marked correspondingly in the Arrhenius plot in *Fig. 11(b)*. The expected placement of the two ignition delay time data points along the high-temperature Arrhenius line indicates that these measurements were negligibly affected by the pre-ignition energy release.

Fig. 11. Pre-ignition effect on igniting delay time. (a) Pressure- time history with and without evidence of weak pre-ignition energy release for stoichiometric mixture of PRF 80 at ~ 10 bar. (b) Ignition delay times for stoichiometric mixture of PRF 80 at ~ 10 bar.

4. Conclusions

Ignition delay times for PRF 70, 80, 91 and 95 were measured over a wide range of temperatures, pressures and two equivalence ratios. The extensive measurements provide detailed validation targets for testing the fidelity of the chemical kinetic mechanisms of n-heptane/iso-octane blends. Measured ignition delay times from this study were compared to the predictions of four different kinetic mechanisms: Mehl et al. [45], Cai et al.[48], Curran et al. [33], and Andrae et al. [40]. Overall, good agreement among the data and models was observed

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4 at high and moderate temperatures. However, the agreement varies in the NTC and low-
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6 temperature regions based on the pressure, composition and equivalence ratio. Pressure appears
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8 to have a significant effect on the ignition delay times and this effect is amplified in the NTC
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10 region compared to the high and low temperatures. The effect of equivalence ratio and
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12 composition on the ignition delay time is also larger in the NTC region. Ignition delay time
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14 correlations were developed to fit the measured ignition delays over the wide range of
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16 experimental conditions. Such correlations can be quite useful in the simulation-based design of
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18 modern engines. We believe that the extensive reactivity data obtained in this work will serve as
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20 a benchmark for detailed and reduced gasoline surrogate models.
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23 24 **Acknowledgement**

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Supplementary Material

Table S1. Measured ignition delay times and corresponding conditions. All data were measured in fuel/air mixtures.

Fig. S1 (a – x). Additional comparisons of measured ignition delay times with predictions of four kinetic mechanisms.

Fig. S1. Error between fitted and measured ignition delay times.

Fig. S2 (a – b). Comparison between the pressure dependence exponents (n) calculated from experiments and simulations.

Fig. S3 (a – b). Temperature sensitivity analyses for stoichiometric mixture of PRF 70 at 1100 and 1200 K.

Fig. S4. Comparison between the pressure exponents of the four PRF blends at 1100 K.

Fig. S5. Temperature sensitivity analysis for stoichiometric mixtures of PRF 70 and 95.

Fig. S6 (a – d). Pressure dependence exponents for stoichiometric mixture of PRF 70 at 10 – 20 bar and 20 – 40 bar pressure ranges.

Fig. S7. Temperature sensitivity analysis of lean and stoichiometric mixtures of PRF 70.

Fig. S8 (a – d). Equivalence ratio exponents for stoichiometric mixture of PRF 70 at 10, 20 and 40 bar.

Fig. S9 (a – x). Additional comparisons of measured ignition delay times with the predictions of four kinetic mechanisms.

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