

# Ignition Studies of Two Low-octane Gasolines

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## Abstract

Low-octane gasolines (RON ~ 50 – 70 range) are prospective fuels for gasoline compression ignition (GCI) internal combustion engines. GCI technology utilizing low-octane fuels has the potential to significantly improve well-to-wheel efficiency and reduce the transportation sector's environmental footprint by offsetting diesel fuel usage in compression ignition engines. In this study, ignition delay times of two low-octane FACE (Fuels for Advanced Combustion Engines) gasolines, FACE I and FACE J, were measured in a shock tube and a rapid compression machine over a broad range of engine-relevant conditions (650 – 1200 K, 20 and 40 bar and  $\phi = 0.5$  and 1). The two gasolines are of similar octane ratings with anti-knock index,  $AKI = (RON + MON)/2$ , of ~ 70 and sensitivity,  $S = RON - MON$ , of ~ 3. However, the molecular compositions of the two gasolines are notably different. Experimental ignition delay time results showed that the two gasolines exhibited similar reactivity over a wide range of test conditions. Furthermore, ignition delay times of a primary reference fuel (PRF) surrogate (n-heptane/iso-octane blend), having the same AKI as the FACE gasolines, captured the ignition behavior of these gasolines with some minor discrepancies at low temperatures ( $T < 700$  K). Multi-component surrogates, formulated by matching the octane ratings and compositions of the two gasolines, emulated the autoignition behavior of gasolines from high to low temperatures. Homogeneous charge compression ignition (HCCI) engine simulations were used to show that the PRF and multi-component surrogates exhibited similar combustion phasing over a wide range of engine operating conditions.

## Keywords

Low-octane gasolines; naphtha; ignition delay; shock tube; rapid compression machine; surrogates

## 1. Introduction

The transportation sector accounts for around half of global oil consumption and about 23% of global CO<sub>2</sub> emissions [1, 2]. At the 2015 United Nations Climate Change Conference (COP 21, Paris), 196 countries reached an agreement to implement stringent emission regulations and work on strategies that would limit the environmental impact of global warming. The improvements in the transportation sector are necessary to reduce its environmental footprint from the perspective of CO<sub>2</sub> emissions as well as harmful NO<sub>x</sub> / unburnt HC / soot emissions. Due to the higher efficiencies of compression ignition engines, several strategies are being explored to use gasoline-like fuels in these engines. Variants of these engine technologies include gasoline compression ignition (GCI), dual-fuel reactivity controlled compression ignition (RCCI), and partially premixed compression ignition (PPCI). These modes of engine operation offer wide ranging potential to increase engine efficiency while reducing harmful environmental emissions compared to traditional compression ignition engines [3].

Gasoline compression ignition (GCI) engines have several advantages over conventional spark ignition gasoline and compression ignition diesel engines. These engines operate at higher compression ratios thus improving overall thermal efficiency which makes these engines comparable to the compression ignited diesel engines [4]. Several studies have demonstrated that GCI engines can operate optimally with fuels having octane numbers ranging 50 – 70 [5-7]. Utilization of low-octane gasolines eliminates refinery catalytic reforming and isomerization units required for the production of high-octane gasolines. This may significantly reduce the refinery costs and subsequent emissions from refinery processing as compared to the conventional gasolines with higher octane rating. Life cycle analysis [1] of GCI engines employing low-octane fuels predicts about 25% reduction in energy consumption and about 23% reduction in CO<sub>2</sub> emissions compared to the conventional spark ignition engines and gasolines. Moreover, there is growing disparity between the demand of diesel and gasoline fuels resulting in lighter fractions of hydrocarbons being in oversupply [8]. Such imbalance can also be potentially solved by employing GCI engine technologies that operate with lighter hydrocarbon streams and can thereby reduce the operational challenges faced by many refineries around the world.

Combustion phasing in GCI engines are largely governed by chemical kinetics [9]. However, combustion chemistry of low-octane gasolines is relatively less studied as compared to conventional gasolines. The only previous contributions to the chemical kinetics of fully blended

low-octane gasolines are from our group at KAUST [10-13]. Javed et al. [10] studied the ignition delay times and surrogate formulation of light naphtha, a low-octane (RON = 64.5, MON = 63.5) fully blended fuel, in a high-pressure shock tube and rapid compression machine over wide range of test conditions. They showed that at high temperatures and in the negative temperature coefficient (NTC) region, a primary reference fuel (PRF) surrogate (mixture of n-heptane and iso-octane) adequately captured the autoignition of light naphtha; while at low temperatures, a multi-component surrogate better reproduced the ignition behavior of light naphtha. Javed et al. [11] and Abbad et al. [12] provided a wide range of ignition delay data for toluene/PRF (TPRF) and PRF blends with research octane numbers (RON) ranging 70 – 97.5 to model the reactivity of low-to-high octane gasolines.

At the Clean Combustion Research Center (CCRC) of King Abdullah University of Science and Technology (KAUST), significant efforts have been devoted towards formulating surrogates and developing combustion kinetics of gasolines with varying compositions and octane numbers [10, 14-18]. Sarathy et al. [14] studied the ignition delay times of FACE (Fuels for Advanced Combustion Engines) gasolines A and C using shock tubes and rapid compression machines, and developed multi-component surrogates for these gasolines based on detailed hydrocarbon analyses (DHA). The FACE gasolines A and C had similar octane numbers (AKI ~ 84) but contained varying amounts of n-alkanes, iso-alkanes and aromatics. It was shown that these two gasolines exhibited comparable ignition delay times at all experimental conditions and a PRF surrogate adequately captured the ignition requirements of these gasolines with minor discrepancies at low temperatures. Sarathy et al. [15] also studied the ignition behavior and surrogate formulation of FACE gasolines F and (RON = 94.4, MON = 88.8) and G (RON = 96.8, MON = 85.8) having similar antiknock indices (AKI ~ 91.5) but varying octane sensitivities and compositions. They showed that at high temperatures ( $T > 900$  K), ignition delay times of both gasolines were quite similar. However, at low temperatures ( $T < 750$  K), gasoline with lower RON (FACE F) was slightly more reactive compared to the high-RON gasoline (FACE G), and the fuel with low sensitivity (FACE F) showed greater NTC behavior. Finally, gasoline with lower MON (FACE G) was more reactive in 800 – 900 K temperature range. Based on DHA analysis, multi-component surrogates were developed for FACE F and G and it was shown that multi-component surrogate simulations better captured the ignition behavior of high sensitivity gasolines.

The current study aims to continue our efforts of formulating surrogates for wide variety of gasolines and improving the chemical kinetic modeling of these fuels. Specific objectives of the current study are two-fold; first, we aim to provide new ignition delay data for two low-octane FACE gasolines (FACE I and J); second, we wish to provide adequate surrogate formulation guidelines for such low-octane fuels. As mentioned earlier, ignition delay data are scarce for low-octane gasolines, and, hence, the data reported herein serves as valuable benchmark for future studies. The manuscript is structured as follows: fuel characterization using DHA analysis, gasoline properties and the tested surrogates are presented in Section 2, experimental techniques are briefly presented in Section 3, ignition delay results are presented and discussed in Section 4, chemical kinetic analyses are presented in Section 5 to illustrate the reactivity trends, HCCI engine simulations are included in Section 6 to assess how different surrogates affect combustion phasing, and the key findings of this work are summarized in Section 7.

## **2. Fuel characterization and surrogate formulation of FACE gasolines I and J**

The two fully blended gasoline fuels studied in this work, FACE gasoline I and J, were acquired from Conoco Philipps Chemical Company. Fuel compositions and other relevant properties are listed in Table 1 (See also Supplementary Material Table S1-S2 for Detailed Hydrocarbon Analysis, Figure S1-S2 for a comparison between PIONA and ADC of fuels and surrogates). FACE I is highly paraffinic (~ 84 mol %) and has low aromatic (~ 5 mol %) and olefinic (~ 7 mol %) content. FACE J has relatively less paraffinic content (~ 64 mol %) but it contains larger fraction of aromatics (~ 30 mol %). FACE gasolines I and J have relatively low octane sensitivities of 0.7 and 3, respectively. The two fuels, with widely different compositions, have very similar anti-knock index ( $AKI = \frac{RON+MON}{2}$ ) of ~ 70.

Gasoline reactivity is compared against two kinds of surrogates. A binary PRF surrogate, mixture of n-heptane/iso-octane, matching the AKI of the FACE I and J is used as the simplest surrogate. Multi-component surrogate mixtures formulated for FACE I and FACE J, henceforth referred to as FGI-KAUST and FGJ-KAUST, respectively, are shown in Table 1 and Table 2. The FGI-KAUST (seven component) and FGJ-KAUST (five component) mixtures were formulated using the surrogate formulation methodology developed by Ahmed et al. [19]. This methodology is based on optimization of surrogate palette species to match the target properties of the real fuel.

A palette of 10 species has been identified as potential surrogate candidates, where an important selection criteria being the availability of detailed and validated chemical kinetics mechanisms. This surrogate palette includes paraffins (n-butane and n-heptane), i-paraffins (2-methylbutane, 2-methylhexane, i-octane), olefins (1-hexene), naphthenes (cyclopentane, cyclohexane) and aromatics (toluene, 1,2,4-trimethylbenzene). The optimization targets included H/C ratio (governs equivalence ratio and heating value), density (governs viscosity, spray formation, mixing behavior, and heating value), RON and MON (linked to fuel autoignition reactivity), volatility characteristics (governs vaporization and air/fuel mixture formation) [20], carbon type distribution (governs chemical kinetic reactivity) [21], and average molecular weight (governs equivalence ratio, density, and heating value). For the FACE I surrogate (FGI-KAUST), linear-by-mole octane blending rule was used. This methodology has been previously used to formulate multi-component surrogates for FACE gasolines A and C [14], FACE gasolines F and G [15], and has been shown to satisfactorily reproduce the anti-knock quality of these fuels. FACE J, however, is a more complex fuel as it has high aromatic content (~ 30 mol %) despite having relatively low octane rating (RON = 71.8) and low sensitivity ( $S = 3$ ). A linear-by-mole octane blending method was tested for FACE J surrogate formulation but was found to give poor results. This can be attributed to the non-linear blending characteristic of aromatics with paraffins, which are difficult to quantify [22]. Therefore, for FACE J surrogate (FGJ-KAUST) formulation, we decided to use the more detailed octane blending treatment proposed by Ghosh et al. [23]. The RON and MON values for FACE J surrogate components were also taken from [23].

Table 1 and Table 2 show that FGI-KAUST and FGJ-KAUST closely matched various targets of FACE I and FACE J gasolines, respectively, whereas, a simple PRF 70 surrogate only matched the AKI of the fuels. Detailed comparisons of gasoline properties and multi-component surrogates are provided in the Supplementary Material. In subsequent sections of the manuscript, ignition delay times of FACE I and FACE J are compared with the experimentally measured ignition delay times of PRF 70 and with the chemical kinetic simulations of PRF 70, FGI-KAUST and FGJ-KAUST surrogates. The FACE gasoline mechanism [15] is used for ignition delay times simulations using CHEMKIN PRO [24].

Table 1: Properties of FACE gasolines I and J, multi-component and PRF surrogates.  
Hydrocarbon types are given in mole %.

	<b>FACE I</b>	<b>FGI- KAUST surrogate</b>	<b>FACE J</b>	<b>FGJ- KAUST surrogate</b>	<b>PRF 70 surrogate</b>
RON	70.3	70.7	71.8	70.6	70
MON	69.6	68.4	68.8	66.5	70
Sensitivity	0.7	2.3	3	4.1	0
AKI	69.9	69.6	70.3	68.6	70
Avg. mol. wt.	95.5	98.9	100.2	103.2	109.7
<i>n</i> -alkanes	14	12	31.5	35	33
<i>iso</i> -alkanes	70	72	32.4	35	67
Cycloalkanes	4	6	2.4	-	0
Aromatics	5	4	30.6	30	0
Olefins	7	6	0.6	-	0
Unidentified	-	-	2.5	-	-

Table 2: Detailed composition (mole %) of the multi-component and PRF surrogates.

	<b>FGI- KAUST surrogate</b>	<b>FGJ-KAUST surrogate</b>	<b>PRF 70 surrogate</b>
n-butane		10.5	-
2-methylbutane	11	-	-
2-methylhexane	27	23	-
1-hexene	6	-	-
n-heptane	12	24.5	33
iso-octane	34	12	67
cyclopentane	6	-	-
1,2,4 trimethylbenzene	4	30	-

### 3. Experimental details

Ignition delay experiments reported in this work were carried out in the high-pressure shock tube (HPST) and rapid compression machine (RCM) facilities at the King Abdullah University of Science and Technology (KAUST). Experimental conditions spanned a wide range of temperatures (650 – 1200 K), two nominal pressures (20 and 40 bar) and two equivalence ratios (0.5 and 1). To use each device close to its optimum operating regime, we did not report any shock tube experiments with ignition delay times longer than 4 ms, and similarly we did not include any RCM ignition delay times below 3 ms. This allowed the data to be relatively free of potential non-idealities in shock tube (pre-ignition and larger influence of  $dp/dt$ ) and RCM (reactions in the compression stroke). As will be shown in next section, the data from the two facilities complemented each other with some overlapping region. The PRF 70 data used for comparisons with current measurements is taken from our previous work [12]. Additional PRF 70 data, at RCM relevant conditions, is reported in the present study. These facilities have been previously reported in the literature [10, 25]; only a brief account is given here.

The shock tube employed in present study consists of a double diaphragm mid-section to better control the diaphragm burst pressure and hence provides precise control of the thermodynamic conditions behind reflected shock wave. The shock tube is constructed from stainless steel with driven and driver sections being 6.6 m long; both sections have same diameter of 10 cm. The shock tube and mixing tank, along-with the mixing manifold, were heated to 50 °C to avoid fuel condensation. Six pressure transducers, located over the last 3.7 m of the driven section, were used to measure the incident shock speed. One-dimensional shock jump equations were used to calculate the reflected shock temperature and pressure using measured shock speed and thermodynamic parameters of the fuel/oxidizer as inputs. Ignition delay time was determined using pressure and OH\* chemiluminescence measurements through the side-wall and end-wall ports. Estimated uncertainty in in the reflected shock temperature/pressure is < 1% and the uncertainty in the reported ignition delay times is ~ 20%. Gradual pressure rise behind the reflected shock wave,  $dp/dt$ , was found to be between 2 – 3 %/ms; therefore, a 3%  $dp/dt$  was imposed on zero-dimensional kinetic simulations [26], henceforth referred as “shock tube simulations”.

The KAUST RCM has twin opposed piston design which allows better mechanical balance and lower compression times compared to single piston configuration. The reaction chamber is 50.8 mm in diameter with a stroke length of each piston being 169 mm; this results in a

compression ratio of 16.8:1. The pistons are coupled with a fast pneumatic compression system which helps in achieving compression times (final 50%) of  $\sim 3$  ms. A pressure transducer (Kistler 6045) mounted on the combustion chamber was used to monitor the pressure and determine ignition delay times. To avoid vortex formation inside the core of the reaction chamber, creviced pistons having  $\sim 10\%$  of the post-compression volume were employed [27]. Heat loss in the RCM core was accounted for by using non-reactive volume profiles [28] while performing chemical kinetic simulations, henceforth referred as “RCM simulation”. Estimated uncertainty in the RCM ignition delay measurements is  $\sim 15\%$ . Non-reactive RCM volume profiles required for simulations are provided as Supplementary Material.

#### **4. Results and discussion**

Experimentally measured ignition delay times of FACE I, FACE J and PRF 70 are reported in this section. Throughout this section, solid symbols represent ignition delay results from the high-pressure shock tube (HPST) and open symbols represent ignition delay data from the rapid compression machine (RCM). Moreover, ignition delay time simulations for FGI-KAUST, FGJ-KAUST and PRF 70 surrogates are also presented in this section. Solid lines represent “shock tube simulations” and dashed lines represent “RCM simulations”.

##### **4.1. Experimental ignition delay data**

Figure 1 shows ignition delay measurements of FACE I (circles) and FACE J (squares) at 20 and 40 bar for equivalence ratio (fuel/air mixtures) of 1.0 and 0.5. Both fuels exhibit NTC behavior in the temperature range of  $\sim 750 - 850$  K. In general, ignition delay times of the two gasolines, with significantly varying composition but similar octane ratings, are quite similar over the entire temperature range. These results are in line with previous literature findings [10, 14] which have shown that gasolines with similar octane rating and low sensitivity exhibit similar ignition delay times. Small differences in octane numbers (RON and MON) of these two gasolines and their effect on ignition delay times are somewhat evident in these measurements. Mehl et al. [29, 30] have shown that ignition delay times correlates with the AKI of the fuel in the NTC region (825 K, 25 atm), wherein low RON fuels exhibit shorter ignition delay times. Our data at 20 bar and  $\phi = 1$ , Figure 1 (a), show that FACE I with slightly smaller RON (70.3) than FACE J (71.8) has slightly shorter ignition delay times. Sarathy et al. [15] have shown that fuels with high sensitivity

(lower MON) exhibit smaller ignition delay times in the 800 – 900 K temperature range (within the NTC region) compared to low-sensitivity fuels of similar AKI. Our  $\phi = 0.5$  RCM data, Figure 1 (b), exhibit this trend with FACE J (MON = 68.8) being slightly faster than FACE I (MON = 69.6). Nonetheless, it is acknowledged that due to the relatively small octane number differences between these gasolines and due to measurement uncertainties, the variation of ignition delay times with RON/MON are not perfectly evident at all relevant experimental conditions. It should also be pointed that the shock tube and RCM data compare well at the overlapping temperatures and complement each other.

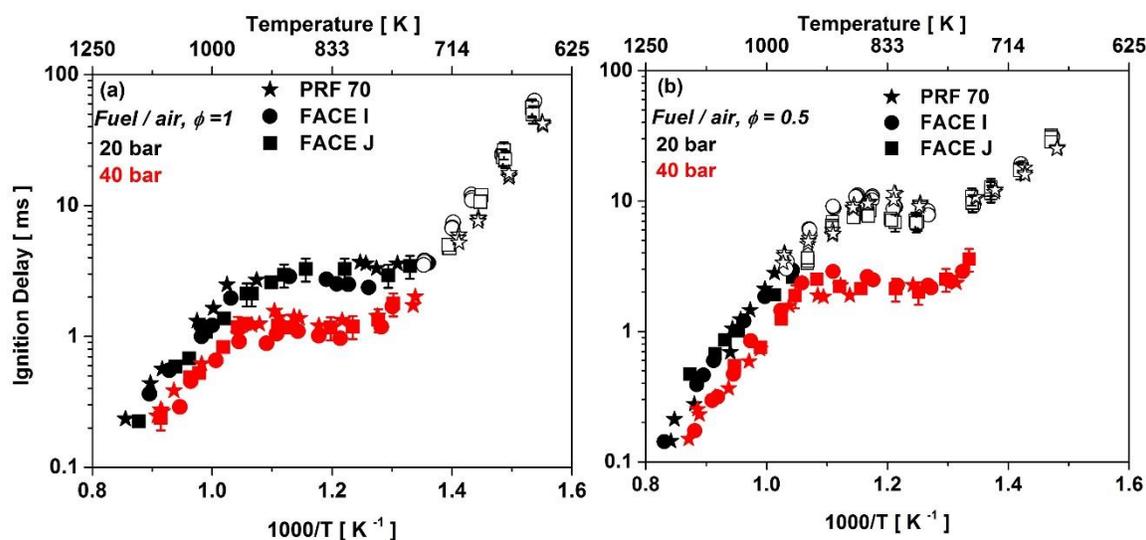


Figure 1: Ignition delay times of PRF 70, FACE I and FACE J at 20 and 40 bar for equivalence ratios of (a) 1.0 and (b) 0.5. Solid symbols are shock tube data and open symbols are RCM data. Note that the RCM measurements were only carried out at 20 bar.

Figure 1 also shows comparison of gasoline ignition delay times of these with a PRF 70 (star symbols) surrogate. The PRF 70 surrogate, matching the AKI of these low-sensitivity gasolines, adequately captures the reactivity trends of FACE I and FACE J. At low-temperature ( $< 700$  K) RCM conditions, PRF 70 is marginally faster ( $\sim 25 - 30\%$ ) than the two gasolines. These findings are consistent with our previous work [10, 14] and further strengthens the effectiveness of a simple bi-component PRF surrogate in capturing the reactivity of low-sensitivity ( $S < 3$ ) gasolines.

## 4.2. *Ignition delay simulations*

Chemical kinetic simulations were carried out for PRF 70 and multi-component surrogates. Comparisons of measured ignition delay times with simulations are shown in Figure 2 and Figure 3. It is observed that PRF 70 simulations (blue lines) capture the experimental ignition delay times of the two gasolines and PRF 70 reasonably well at high ( $T > 900$  K) and low temperatures ( $T < 700$  K). However, the PRF simulations are less reactive in the NTC region ( $T \sim 750 - 850$  K). The FGI-KAUST (black lines) surrogate simulations are quite similar to the PRF 70 simulations. The FGJ-KAUST (red lines) surrogate simulations exhibit good agreement with the experimental data in the NTC and low-temperature regions, especially at 20 bar, but the predicted ignition delay times are larger at high temperatures compared to FACE J (and other fuels).

The FACE gasoline mechanism developed by Sarathy et al. [15] (KAUST, NUIG, LLNL collaboration) has been put together for gasoline surrogate fuels and contains detailed sub-mechanisms for the palette species mentioned in Section 2. This mechanism is continually being upgraded to improve its predictions, and the latest update of iso-octane base chemistry [31] improves the PRF predictions significantly over a wide range of data measured here and other studies from our group [10, 12]. Further improvements in the predictions of FGI-KAUST (7 component) and FGJ-KAUST (five component) simulations are anticipated as improved n-heptane [32], iso-octane [31], cyclopentane [33, 34], 2-methylhexane [35], and 1,2,4-trimethylbenzene mechanisms become adopted in this large mechanism. Here, we use the current mechanism, as it is, to explain some interesting trends where we have good agreement between the simulations and experimental data.

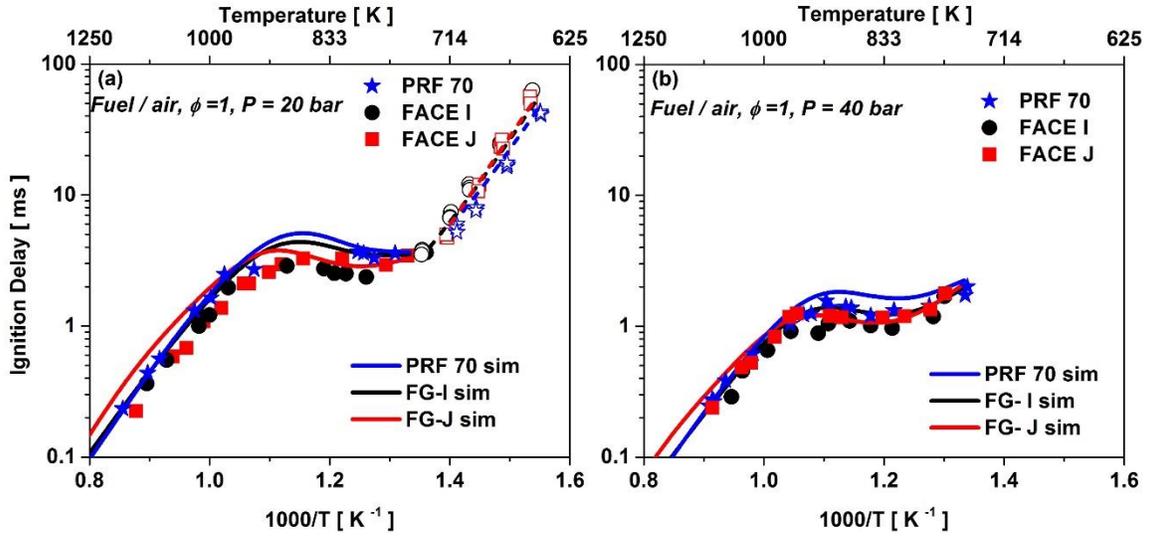


Figure 2: Comparison of experiments (scatter) and simulations (lines) for  $\phi = 1$  at (a) 20 bar and (b) 40 bar. Simulations carried out using FACE gasoline mechanism [15].

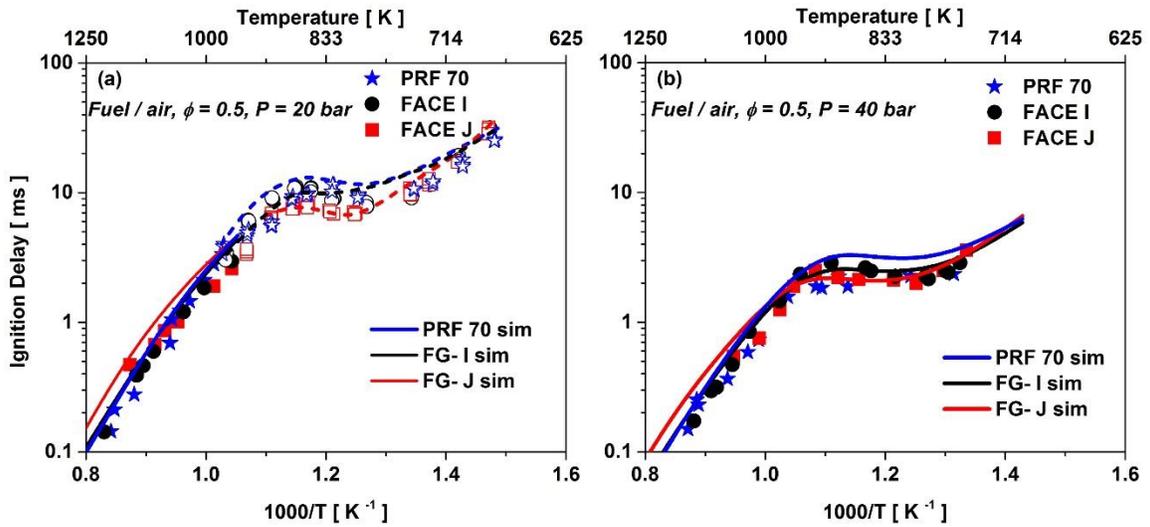


Figure 3: Comparison of experiments (scatter) and simulations (lines) for  $\phi = 0.5$  at (a) 20 bar and (b) 40 bar. Simulations carried out using FACE gasoline mechanism [15].

## 5. Chemical kinetic analyses

It has been shown previously [10, 11, 14, 15, 36] that at high temperatures ( $T > 900$  K), ignition delay times of practical fuels are not sensitive to octane numbers. This is because, at high temperatures, chain branching is controlled through  $\text{H}_2\text{O}_2 (+\text{M}) \leftrightarrow \text{OH} + \text{OH} (+\text{M})$  and  $\text{H} + \text{O}_2 \leftrightarrow \text{OH} + \text{O}$  reactions, and these are favored more or less equally for a wide range of practical fuels and surrogates. In the current study, we have observed likewise (Figure 1) that, at high temperatures, experimentally measured ignition delay times of FACE I, FACE J and PRF 70 are quite similar. Also, the simulations (Figure 2 and Figure 3) adequately capture the high-temperature ignition delay data. One exception is the high-temperature FGJ-KAUST simulations being slower which may be attributed to the slow reactivity of 1,2,4 trimethylbenzene (30 mole% in the surrogate) at high temperatures.

In the NTC region ( $T \sim 750 - 850$  K), Figure 1 (a) and (b) showed that the measured ignition delay times of all fuels are quite similar with some minor differences. The kinetic simulations, however, predict faster ignition delay times for FGJ-KAUST surrogate at 20 bar,  $\phi = 1$  conditions compared to the FGI-KAUST and PRF 70 surrogates. This unexpected trend may be attributed to the deficiencies in the chemical kinetic models of the constituting surrogate palette species. The NTC region is primarily governed by  $\text{HO}_2$  production and consumption. Ignition data may be useful for global validation of the NTC region but detailed optimization of the kinetic mechanism at NTC conditions requires intermediate species measurements using flow reactor type experiments and is beyond the scope of this work. However, as mentioned above, the FACE gasoline mechanism is continuously being updated to take into account such optimizations. The FGJ-KAUST simulation exhibits less NTC behavior compared to the FGI-KAUST simulation. The lesser NTC observed for the FGJ-KAUST simulations is explained by the fact that FGJ-KAUST surrogate has larger predicted sensitivity ( $S = 4$ ) compared to that ( $S = 2.3$ ) of FGI-KAUST surrogate. The same trend was observed in our previous work on FACE F and G [11].

At low temperatures ( $T < 750$  K), the two gasoline fuels (FACE I and J) and the PRF surrogate show quite similar reactivity although their chemical compositions are vastly different (see Table 1). In our previous work on TPRF blends [11], we showed that ignition delay times at low temperatures ( $T < 700$  K) for fuels with low RON and low sensitivity exhibit weak correlation

with octane numbers. The same trend is observed here for FACE I and J gasolines, which have slightly different octane numbers but show very similar low-temperature reactivity.

Here, we utilize the hydroxyl (OH) rate of production (ROP) analysis, following the same procedure as in our previous works [10, 11], to illustrate the reasons for observing similar low-temperature ignition delay times for three fuels with varying composition but similar octane ratings. The ROP analysis is performed at a time corresponding to 2/3 of the first stage OH peak concentration for a representative ignition case at initial conditions of 700 K and 20 bar. It is to be noted that the above indicated time is also quite close to 2/3 of total ignition delay, where temperature rise is negligible. Figure 4 shows the hydroxyl ROP analysis for PRF 70, FGI-KAUST and FGJ-KAUST surrogates. Of all the reactions influencing hydroxyl radical ROP, top 12 reactions were selected for each surrogate. Furthermore, various pathways of a similar reaction class were grouped in a single representative reaction for brevity. For example, secondary hydrogen abstraction of n-heptane ( $\text{NC}_7\text{H}_{16}$ ) by OH can proceed through five secondary sites to produce n-heptyl ( $\text{C}_7\text{H}_{15}$ ) radicals; the effective hydroxyl ROP of all these pathways is shown in Figure 4. For structural representation of all species appearing in the ROP analysis, please refer to the Supplementary Material (Table S3). It may be seen from Figure 4 that hydrogen abstraction by OH to produce n-heptyl radicals ( $\text{NC}_7\text{H}_{16} + \text{OH} \rightleftharpoons \text{C}_7\text{H}_{15} + \text{H}_2\text{O}$ ) is an important consumption (negative ROP) pathway for all fuels. Molecular oxygen ( $\text{O}_2$ ) may add on to these n-heptyl radicals and go through internal isomerizations to produce ketohydroperoxide radicals ( $\text{C}_7\text{H}_{14}\text{OOH(a)-(b)O}_2 \rightleftharpoons \text{NC}_7\text{KET(ab)} + \text{OH}$ ), which further decompose to give OH radicals, and hence complete the low-temperature chain branching process. Because of the presence of 2-methylhexane ( $\text{C}_7\text{H}_{16-2}$ ) in FGI-KAUST and FGJ-KAUST surrogates, these may also consume OH radicals to produce branched heptyl ( $\text{C}_7\text{H}_{15-2}$ ) radicals which follow similar low-temperature chain branching pathways ( $\text{C}_7\text{OOH(a)-(b)O}_2-2 \rightleftharpoons \text{C}_7\text{KET(ab)-2} + \text{OH}$ ). Hence, hydrogen abstraction by OH from the secondary sites of n-heptane (and its isomers) is very important OH consumption pathway for fuels containing n-heptane or 2-methylhexane. The OH consumption by 1,24 trimethylbenzene in FGJ-KAUST to produce resonantly stabilized benzyl radicals is somewhat balanced by OH + isooctane in FGI-KAUST which produces relatively stable intermediates (tertiary isooctyl radical undergoes  $\beta$ -scission to produce stable isopropyl radical and isobutene). The hydroxyl production pathways are primarily from  $\text{C}_7$  ketohydroperoxides and these pathways act similarly for all three fuels. Therefore, the vast differences in the compositions of these fuels do not have much effect

on their reactivity at low temperatures. Combining these findings with those of previous studies [11, 15], we conclude that low-temperature reactivity differences are negligible for low-octane, low-sensitivity fuels.

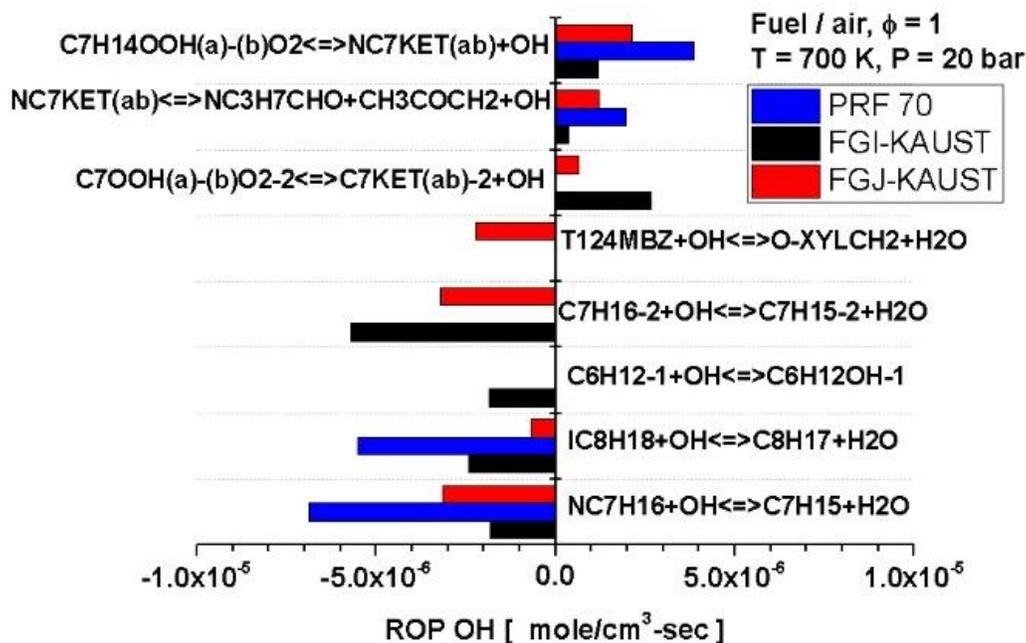


Figure 4: Hydroxyl ROP analysis at  $T = 700 \text{ K}$ ,  $P = 20 \text{ bar}$  and  $\phi = 1$ .

To experimentally verify the above assertion, Figure 5 plots experimentally measured low-temperature ignition delay times of a wide range of fuels at 20 bar and  $\phi = 1$ . It is observed that fuels of low octane (64 – 85) and low sensitivity (0 – 4), e.g., FACE A and C (AKI ~ 84, S ~ 0), PRF 84 (RON = 84, S = 0), TPRF 70 (RON = 70, S = 4), FACE I (AKI ~ 70, S = 0.7), FACE J (AKI ~ 70, S = 3) and PRF 70 (RON = 70, S = 0), exhibit quite similar ignition delay times at these low temperatures. The data presented in Figure 5 are from three different RCM facilities - KAUST (FACE I, FACE J and PRF 70), NUIG (TPRF 70) and UCONN (FACE A, FACE C, PRF 84) – but still support the above assertion. The figure further shows surrogate RCM simulations which reproduce the experimentally observed trends. This points to the fact that for these low-sensitivity fuels, the low-temperature reactivity indeed proceeds through similar channels resulting in similar ignition delay times. The PRF surrogate is marginally faster (~ 25 – 30 %) compared to gasolines which can be explained because of the higher reactivity of n-heptane in PRF surrogates.

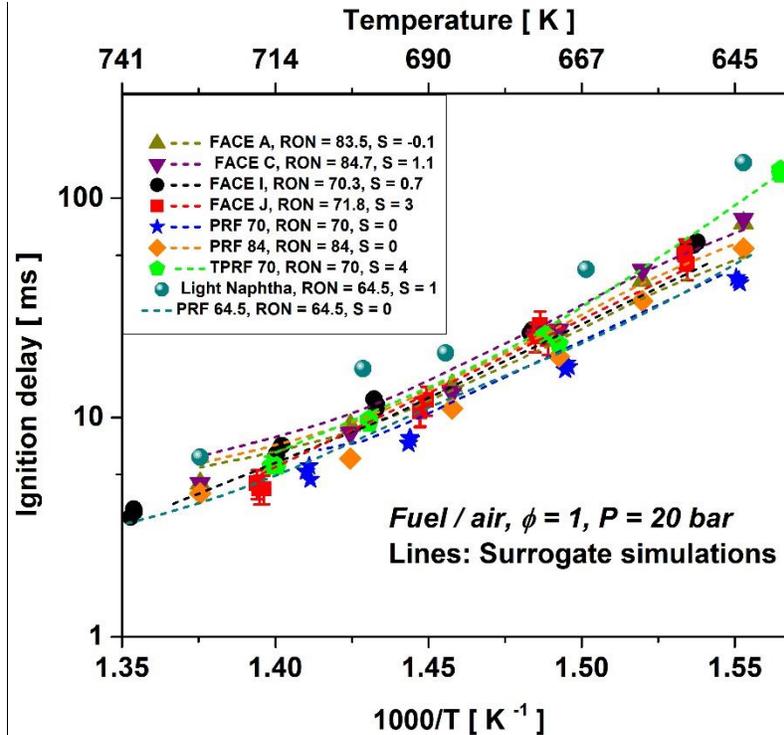


Figure 5: Experimentally measured low-temperature ignition delay data for a wide range of fuels at 20 bar and  $\phi = 1$ . FACE A, FACE C and PRF 84 data taken from [14], TPRF 70 data taken from [11], FACE I, FACE J and PRF 70 (current study), Light Naphtha data taken from [10]. Dashed lines represent RCM simulations using FACE gasoline mechanism [15]. RON and sensitivity ( $S = \text{RON} - \text{MON}$ ) values are given for each fuel.

Figure 5 includes ignition delay data of light naphtha which not only has low octane rating and low sensitivity (RON = 64.5, S = 1) but also has relatively lighter weight (Avg. mol. wt. = 78.4) and contains low boiling range components [10]. Light naphtha exhibits significantly larger ignition delay times compared to the rest of fuels and, particularly, compared to PRF surrogates (e.g., PRF 70 data or PRF 64.5 simulation). These differences are due to the chemical composition of light naphtha that includes significant proportion of smaller chain n-, iso-, and cyclo- paraffins (~ 50% pentane isomers) compared to the PRF surrogate. We further showed [10], both experimentally and from simulations, that a multi-component surrogate, closely matching the chemical composition and molecular structure of light naphtha, was required to adequately capture the ignition delay times of light naphtha at low temperatures.

Therefore, combining these findings, it maybe stated that PRF surrogate works satisfactorily at high and intermediate temperatures for a wide range of low-octane, low-sensitivity gasoline fuels. At low temperatures, PRF surrogate may overpredict the reactivity of such fuels by ~ 25 –

100% depending on the chemical makeup of the target gasoline. A multi-component surrogate can be formulated to capture the reactivity of such gasolines over wide range of temperature. Moreover, multi-component surrogates may be needed to meet a wide range of physical/chemical targets for practical applications.

## 6. HCCI simulations

In order to understand the surrogate requirements for internal combustion engine applications, we carried out zero-dimensional single zone HCCI simulations in CHEMKIN PRO [24] to compare the combustion phasing for the PRF and multi-component surrogates presented in previous sections. Input parameters used for the HCCI simulations are included in Table 3. The parametric study resulted in a wide range of IMEPs (indicated mean effective pressure), we broadly grouped those in two ranges; 4 – 5 bar IMEP are referred to as low-load and 6 – 9 bar IMEP are referred to as mid-load conditions.

Table 3: HCCI simulations parameters

$P_{BDC}$ [ atm ]	1, 1.5 2
$T_{BDC}$ [ K ]	400 - 450
$\phi$	0.3, 0.6
Compression ratio	14.5
Engine speed [RPM]	1500

Figure 6 shows the simulated differences in CA 50 (CAD for 50 % heat release) of PRF and the two multi-component surrogates of FACE I and FACE J gasolines. At low load (black squares), combustion phasing differences are minimal ( $\pm 3$  CAD), indicating that the surrogates behave similarly for these conditions. As the load is increased (IMEP 6 – 9 bar), the differences in combustion phasing start becoming prominent at low initial temperatures, particularly between FG-I KAUST and PRF 70 surrogates. The trends found in ignition delay times (Figure 2, Figure 3) are consistent with the combustion phasing trends observed in Figure 6. Overall, we may state that a PRF surrogate provides reasonable representation of combustion phasing for these low-octane, low-sensitivity gasolines under HCCI conditions. However, a more complex surrogate may be needed to achieve higher chemical fidelity and to match physical characteristics of the target gasoline.

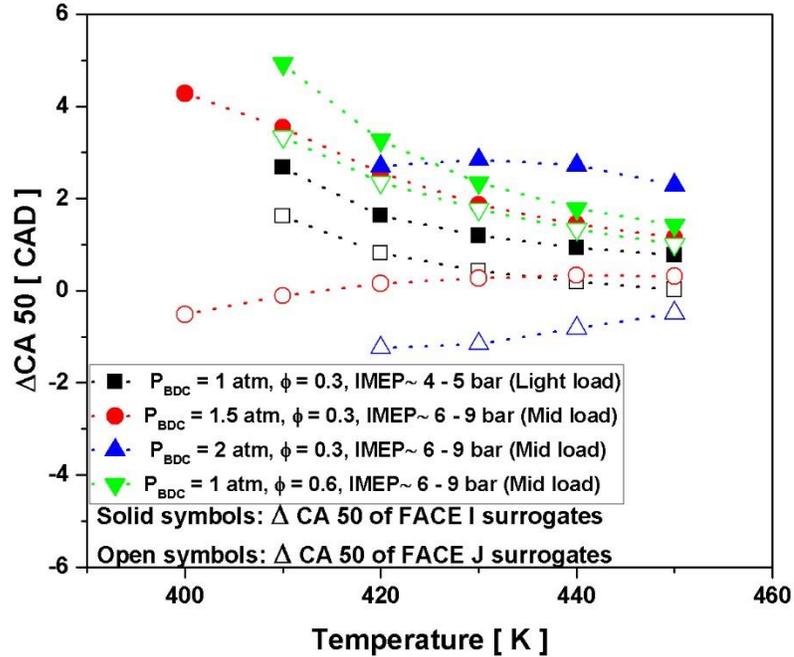


Figure 6: Simulated differences in CA 50 of PRF and multi-component surrogates. Solid symbols are the differences in CA 50 for PRF 70 and FG-I KAUST surrogates. Open symbols are the differences in CA 50 for PRF 70 and FG-J KAUST surrogates.

## 7. Conclusions

Ignition delay times of two low-octane gasolines, FACE I and J, were measured using a shock tube and a rapid compression machine over broad range of test conditions. It was shown that the two gasolines, with large differences in compositions but similar octane ratings, exhibit very similar reactivity. It was further shown that a PRF surrogate, matching the anti-knock index of these gasolines, adequately captures the ignition delay times of these gasolines with some minor differences at low temperatures. Multi-component surrogate simulations illustrate that the two gasolines show negligible differences in low-temperature reactivity because the ignition controlling reactions are quite similar for these gasolines. Using a wide range of low-temperature ignition delay literature data, it was shown that octane and compositional differences have negligible effect on low-temperature reactivity of low-octane, low-sensitivity gasolines. Finally, homogenous charge compression ignition (HCCI) simulations indicated that a PRF surrogate adequately captures combustion phasing trends with some minor deviations at medium-to-heavy loads and at lower initial temperatures. The results of this study can be used to validate and refine gasoline surrogate mechanisms and to develop surrogate formulation strategies for predictive engine modeling.

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