Exploring gasoline oxidation chemistry in jet stirred reactors

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Abstract

Recent decades have seen increasingly restrictive regulations applied to gasoline engines. Gasoline combustion chemistry must be investigated to achieve a better understanding and control of internal combustion engine efficiency and emissions. In this work, several gasoline fuels, namely the FACE (Fuel for Advanced Combustion Engines) gasolines, were selected as targets for oxidation study in jet-stirred reactors (JSR). The study is facilitated by formulating various gasoline surrogate mixtures with known hydrocarbon compositions to represent the real gasolines. Surrogates included binary mixtures of *n*-heptane and *iso*-octane, as well as more complex multi-component mixtures. The oxidation characteristics of FACE gasolines and their surrogates were experimentally examined in JSR-1 and numerically simulated under the following conditions: pressure 1 bar, temperature 500-1050K, residence time 1.0 and 2.0 s, and two equivalence ratios ($\phi=0.5$ and 1.0). In the high temperature region, all real fuels and surrogates showed similar

oxidation behavior, but in the low temperature region, a fuel's octane number and composition had a significant effect on its JSR oxidation characteristics. Low octane number fuels displayed more low temperature reactivity, while fuels with similar octane number but a larger number of n-alkane components were more reactive. A gasoline surrogate kinetic model was examined with FACE gasoline experiments either measured in JSR-2, or taken from previous work under the following conditions: pressure 10 bar, temperature 530-1200K, residence time 0.7s, and three equivalence ratios ($\phi=0.5$, 1.0 and 2.0). Comparison between FACE gasoline experimental results with surrogate model predictions showed good agreement, demonstrating considerable potential for surrogate fuel kinetic modeling in engine simulations.

Keywords: gasoline surrogate, jet stirred reactor, kinetic model, FACE gasoline fuel, oxidation chemistry.

1. Introduction

Gasoline combustion engines are essential to civilization[1]; 20% of the world's total energy use is utilized for transportation[2]. 95% of the transportation energy source is from refined petroleum, while 40% of transportation energy is used for light-duty passenger cars, driven by spark ignition internal combustion engines[3]. Whereas vehicle electrification is of growing importance, vehicles powered by high-efficiency and low-emission gasoline engines coupled with electric motors will remain important in the future [4, 5].

In powering passenger cars, gasoline engines generate pollutants, e.g. NO_x, CO, soot and unburnt hydrocarbons[6]. Restrictive regulations on engine exhausts have been made and applied in recent decades[7]. Several strategies, such as alternative bio-fuels[8], improving gasoline refining[9] and advanced engine design[10] have been made in an effort to reduce emissions and improve energy efficiency. Designing gasoline fuels which perform well across all engine running conditions is a promising path to controlling emissions and achieving higher energy efficiency[11]. To realize this goal, and to develop numerical models for fuel/engine design, it is essential to understand gasoline oxidation chemistry.

Real gasoline fuels have thousands of hydrocarbon components, making numerical simulations problematic; consisting of several hydrocarbon molecules, surrogates are used to represent real fuels as a viable approach[1, 12]. Proposed surrogates must have key physical and chemical properties similar to real fuels, e.g. H/C (hydrogen to carbon) ratio, density, average molecular weight, RON (research octane number) and MON (motor octane number)[1]. In addition, good surrogates should also predict gas-phase combustion properties, such as ignition

delay time[13-15], laminar flame speed[16], species distributions in flames[17, 18] and jet-stirred reactor (JSR) oxidations[19, 20].

Considerable work has been done on studying oxidation of gasoline surrogates and real gasoline fuels[1]. Ignition delay times have been measured for binary primary reference fuels (PRF) [21-26], ternary primary reference fuels (TPRF) [31, 32], and multi-component surrogates [34-36], while flame speeds have been measured for PRFs [27-30] and TPRFs [33]. Recently, FACE (Fuels for Advanced Combustion Engines) gasolines have attracted scientific attention[1]. FACE gasolines were designed based on statistical methods and target values established by the Coordinating Research Council Advanced Vehicle, Fuel and Lubricant Committee Working Group[37]. Investigations on FACE gasolines have been performed on two alkane-rich, medium octane number, low sensitivity FACE fuels, FACE A and C, with measurements of ignition delay time[15, 38], species profiles in premixed flames[17] and JSR oxidation[20]; two high octane number, high sensitivity FACE fuels, FACE F and G, with measurements of ignition delay time [14] and JSR oxidation[19]; and two low octane number, low sensitivity FACE fuels, FACE I and J, with measurements of ignition delay time[39]. All six FACE fuels--regardless of their different octane number and hydrocarbon compositions--exhibited similar reactivity in the high temperature region[39]. In the low temperature region, however, different gasolines and their surrogates were observed to have different behavior[20]. Comparisons with the experimental results also found that current gasoline kinetic models[12] over predicted low temperature oxidation reactions[14, 15, 19, 20].

In this work, nine gasoline surrogates are selected to represent the FACE gasolines by varying various target properties[40]. Three of these are binary n-heptane/*iso*-octane mixtures with different octane numbers, while the remaining six are multi-component mixtures with five to eight

hydrocarbons. The oxidation of FACE gasolines and their surrogates is investigated in JSR facilities. The effects of fuel octane number and hydrocarbon composition on oxidation behavior are investigated systematically, and species measurements are used to validate a gasoline surrogate chemical kinetic model. Additionally, JSR oxidation data on five real FACE gasolines, taken either from previous work [19, 20] (FACE A, C and F), or measured experimentally in this work (FACE I and J), are utilized to examine whether surrogate fuel kinetic modeling accurately represents real fuel behavior. Numerical simulations are conducted to help explain and investigate surrogate oxidation chemistry. The objectives of this work are to provide a comprehensive set of gasoline surrogate and real gasoline fuel oxidation data, elucidate the effects of fuel octane number and hydrocarbon composition on oxidation chemistry, and examine surrogate kinetic model predictions against real gasoline and surrogate mixture oxidation data.

2. Experimental and computational methods

2.1 Gasoline properties descriptions and surrogate formations

The FACE gasolines utilized in this work were purchased from Chevron Phillips Chemical Company LP. As stated by Cannella *et al.*[37], FACE gasolines were formulated by the Coordinating Research Council (CRC) to meet target values determined by the CRC Advanced, Fuel, and Lubricant (AVFL) Committee's FACE Working Group. The objective of the AVFL Working Group was to develop test fuels that facilitate researchers in evaluating fuel effects in advanced combustion engine systems. The present work on FACE gasolines provides a thorough investigation of FACE gasolines in a simplified reactor configuration, supporting the ultimate goal of developing knowledge of how gasoline fuels behave in engines.

Detailed hydrocarbon analyses (DHA) for five FACE gasolines were performed to help in the development of surrogate mixtures. The analyses were performed at the Research and Development Center in Saudi Aramco, with standard test method ASTM D6733 and D6730. Hydrocarbons were divided into five major groups (PIONA): paraffins (n-alkanes), *iso*-paraffins (*iso*-alkanes), olefins (alkenes), naphthenes (cyclo-alkanes) and aromatics, based on their different carbon sites and carbon chain structures. Information on FACE gasolines was taken from previous literature [14, 15, 38]. Key physical and chemical properties for FACE gasolines are listed in Table 1. Detailed compositions for FACE A, C, F, I and J are in Supplementary Material-1, and their distillation curves are in Supplementary Material-2.

Table 1: Physical and chemical properties of FACE gasolines

Properties	FACE A	FACE C	FACE F	FACE G	FACE I	FACE J
RON	83.5	84.7	94.4	96.8	70.3	71.8
MON	83.6	83.6	88.8	85.8	69.6	68.8
H/C	2.29	2.27	2.13	1.83	2.24	1.91
MW (g/mol)	97.8	97.2	94.8	99.7	95.45	100.2
Density (kg/m ³)	685.3	690.5	707.0	760.0	688.0	741.0
Sensitivity (=RON-MON)	-0.1	1.1	5.6	11.0	0.7	3.0
Average molecular formula	C _{6.74} H _{15.57}	C _{6.74} H _{15.57}	C _{6.71} H _{14.29}	C _{7.21} H _{13.19}	C _{6.71} H _{15.02}	C _{7.20} H _{13.76}

Next, surrogates were formulated for target FACE gasolines. PRFs, which are binary mixtures of n-heptane and *iso*-octane, were first examined since they are the simplest surrogates to represent gasoline. PRF 70, 84 and 91.5 were selected to match the antiknock index (AKI= (RON+MON)/2)

of the different FACE gasolines. Next higher fidelity, multi-component surrogates for each real FACE gasoline were investigated because they can represent better more of the target fuel properties. A surrogate palette was chosen based on the DHA: n-butane and n-heptane to represent n-alkanes, 2-methylbutane, 2-methylhexane and *iso*-octane for *iso*-alkanes, 1-hexene for olefins; cyclo-pentane for cycloalkanes, toluene and 1,2,4-trimethylbenzene for aromatics. The majority of chemicals were purchased from Sigma Aldrich, except 2-methylhexane was purchased from ChemSampCo and n-butane was purchases from Abdullah Hashim Industrial Gases (AHG). Composition of multi-component surrogates were determined using an optimization algorithm of RON, MON, PIONA, H/C ratio, average molecular weight, density and distillation curve[40], following same methodology as in previous work[14, 20], and referred to as FGX-KAUST (X=A,C,F,G,I,J) in this work. Thus, each FACE fuel had two candidates, a PRF surrogate and multicomponent surrogate (FGX-KAUST), with similar AKI but different compositions, in order to reveal octane number and composition effects on gasoline surrogate oxidation chemistry. Surrogate compositions, physical and chemical properties are provided in Table 2.

Table 2: Surrogate properties and compositions in mole fraction (FGA-, FGC-, FGF-, and FGG-KAUST compositions taken from previous work [14, 20]). RON and MON for each molecule is from CloudFlame database[41].

Compound/ RON/MON	FGA- KAUST	FGC- KAUST	FGF- KAUST	FGG- KAUST	FGI- KAUST	FGJ- KAUST	PRF 70	PRF 84	PRF 91.5
n-butane/94/90	0.08	0.18	0.07	0.08	0	0.10	0	0	0
2-methylbutane/92/90	0.12	0.05	0.10	0.09	0.11	0	0	0	0
2-methylhexane/42/46	0.10	0.05	0.07	0.10	0.27	0.23	0	0	0
<i>iso</i> -octane/100/100	0.60	0.55	0.44	0.18	0.34	0.12	0.67	0.82	0.90
1-hexene/77/64	0	0	0.08	0.08	0.06	0	0	0	0

n-heptane/0/0	0.10	0.12	0	0	0.12	0.25	0.33	0.18	0.10
Cyclopentane/100/85	0	0	0.16	0.15	0.06	0	0	0	0
Toluene/118/103	0	0.05	0	0.11	0.04	0	0	0	0
1,2,4-trimethylbenzene/110/101	0	0	0.08	0.21	0	0.30	0	0	0
RON	84	84	93.6	96.8	70.7	70.6	70	84	91.5
MON	84	84	88.9	85.8	68.4	66.5	70	84	91.5
AKI	84	84	91.3	91.3	69.6	68.6	70	84	91.5
H/C	2.29	2.28	2.12	1.85	2.21	1.95	2.26	2.26	2.25
MW (g/mol)	101.5	98.4	96.2	94.3	98.9	103.2	109.7	112.0	112.9
Density (kg/m ³)	694	696	707	742	683	730	688	689	690

2.2 Experimental setup of jet stirred reactor

JSR-1 experiments were performed at KAUST, Saudi Arabia. A detailed description follows. Fused silica was used to make a spherical reactor (volume 76 cm³) to prevent wall reactions. Four opposing nozzles (ID 0.3 mm) were used as the inlets of the reactor to achieve perfect mixing by creating jet flow stirring. The mixing performance has been checked experimentally in previous work[42]. Gasoline surrogates were vaporized at 450K and then diluted with nitrogen, which also functioned as a carrier gas to introduce fuel vapor into the spherical reactor through the inner capillary inlet. Diluted oxygen was introduced into the reactor through an outer quartz channel, so that oxygen and fuel would not meet until admission into the spherical reactor. A K-type thermocouple, inside the reactor, monitored reaction temperature. Temperature profiles were measured with a pure nitrogen flow and showed good uniformity (gradient <3K/cm) inside the reactor. Controlled by MKS mass flow controllers, the gas flow rates were adjusted with the reactor temperature to achieve fixed residence time inside the reactor. The gases were extracted through the tip of a quartz microprobe. Further gas reactions of the extracted gases were frozen by a

pressure-drop in the sonic-throat gas sampling. Then the sample gas was analyzed online using two GCs (Agilent Refinery Gas Analysis (RGA) and 7890B). The Agilent RGA system, for quantifying O₂, CO₂, CO, CH₄, C₂H₄, *etc.* is a gas chromatograph configured with three parallel channels that can analyze different species simultaneously. After sample injection, analytes are divided into three columns, one is connected to a flame ionization detector (FID) and the other two to thermal conductivity detector (TCD). Light hydrocarbons from C1 to C6 are detected on the FID channel, while permanent gases are detected by a TCD. The second TCD is used for H₂ detection only with N₂ as reference gas. Two 10-port valves are utilized filling the sample loops and back-flushing heavier components in-lines. Three 6-port valves are used to distribute the sample to the various columns. The Agilent 7890B system was equipped with a DB-1 column to analyze 2-methylbutane, 2-methylhexane, *iso*-octane, n-heptane, 1-hexene, cyclopentane, toluene, 1,2,4-trimethylbenzene.

Once obtaining signals for each peak on the GC, two calculation methods were employed to convert signals to mole fractions. The first one is an internal calibration. Fuel molecules in surrogate mixtures (of known composition) were assumed to be non-reactive at 500 K, and the detected signals were assumed to be the input mole fraction. Detected signals at other temperatures were compared with the signals at 500K to determine their concentration. For other species, cold calibration gas with known composition was used to achieve GC detector response factors. Species signals at each temperature were then converted to mole fractions by comparing to the signals of calibration gas using the response factors. The second method employed is based on FID effective carbon number. For each species except CO, CO₂, O₂ and H₂, the FID effective carbon numbers can be found in our database, and utilized to convert absolute signal to species mole fraction. We compared the results of these two methods, and found them to be close. The uncertainty is mainly

from GC sampling instability, which was minimized by averaging three repeated measurements at each temperature point.

JSR-1 conditions were as follows: fuel concentration at 0.5% and 0.25%, pressure 1 bar, residence time 1s and 2s, various temperatures from 500K to 1050K and equivalence ratios of 0.5, 1.0, within 10% of uncertainty. Blank runs were performed before experiments to ensure no residual fuel in the system. Experiments were performed in triplicate and the average values are reported. Measurement repeatability was observed to be within 10%, and uncertainty of temperature measurement was determined as 25 K.

Surrogate samples were blended among different hydrocarbon compositions in liquid phase (purity no less than 97.0%), while n-butane (purity 99.5%) was introduced in gas phase and mixed in the vaporizer. The fuel concentration was kept low to eliminate excessive heat release and temperature rise during oxidation. The experimental setup scheme is presented in Scheme 1. This new experimental setup JSR-1 was validated by comparing n-heptane oxidation measurements from literature[43]. The results for JSR-1 are presented in Figure S1 in the Supplementary Material-3, and indicate that the KAUST setup is in agreement with similar setups available elsewhere, within 10% of uncertainty.

Scheme 1. Schematic of the JSR-1 setup at King Abdullah University of Science and Technology (KAUST).

JSR-2 experiments were performed in Centre National de la Recherche Scientifique (CNRS), Orleans, France. The experimental setup was similar to JSR-1; its descriptions can be found in previous work[20, 44]. JSR-2 was operated at pressure nearer to those in an engine. The conditions were fuel concentration of 1000 ppm, pressure 10 ± 0.1 bar, residence time 0.7 ± 0.05 s, temperatures from 530K to 1250K and equivalence ratios of 0.5, 1.0 and 2.0. Species mole fractions determined in experiments showed good repeatability within experimental errors of 10% and good carbon balance was also achieved. A summary on the experimental conditions of two JSRs is presented in Table 3.

Table 3. Experimental apparatus and conditions of two JSRs with nitrogen as diluent. Experimental uncertainty is estimated as 10%. (FACE A, C and F experiments in JSR-2 were performed in previous work [19, 20])

Apparatus	Target fuels	Fuel concentration	Temperature (K)	Residence time (s)	Pressure (bar)	ϕ
JSR-1	PRF 70,84,91.5 FGX-KAUST (X=A,C,F,G,I,J)	5000 ppm	500-750	2	1 bar	0.5, 1.0
JSR-1	PRF 70,84,91.5 FGX-KAUST (X=A,C,F,G,I,J)	2500 ppm	750-1050	1	1 bar	1.0
JSR-2	Real FACE A,C,F,I and J gasoline fuels	1000 ppm	530-1200	0.7	10 bar	0.5, 1.0, 2.0

2.3 Numerical gasoline surrogate kinetic modeling

The gasoline surrogate kinetic model adopted in this work is a recently updated model[45]; the base model was developed by Mehl *et al.*[12], and recently updated[45]. Sub-models of C₀-C₄ hydrocarbons[46], *iso*-pentane[47], 2-methylhexane[48, 49], n-heptane[43], *iso*-octane[50], 1-hexene[12], cyclopentane [51], toluene[12] and 1,2,4-trimethylbenzene reactions[14, 52] have been validated and updated, covering the entire surrogate palette. The *iso*-octane model utilized in the gasoline surrogate model here is a modified version showing similar level of agreement that of Atef *et al.*[50]. Scheme S1 in Supplementary Material-3 displays structures for all species notations presented in the followed discussions.

CHEMKIN-PRO software[53] and a perfect-stirred reactor code were applied in all numerical simulations, with a transient solver at end time of 50s for converged solutions. Input of each

surrogate for the JSR-2 was modified to meet the carbon balance with real gasoline fuels. For example, the average molecule formula of FACE I is $C_{6.71}H_{15.02}$, while PRF 70 is $C_{7.67}H_{17.35}$ and FGI-KAUST is $C_{6.94}H_{15.32}$. To meet the carbon balance of FACE I, instead of 1000 ppm, the input of PRF 70 and FGI-KAUST was modified to 874.4 ppm and 966.9 ppm, respectively. The input of FGJ-KAUST (average molecule formula $C_{7.46}H_{14.54}$) was changed to 965.1 ppm to meet FACE J carbon balance. No modifications on simulations were applied on JSR-1 surrogate simulations.

3. Gasoline surrogate oxidation

The oxidation of nine surrogate fuels is shown in Figs 1-3. Figures 1 and 2 show the low temperature (500-750K) behavior and Figure 3 shows the intermediate temperature behavior (750-1050K). Fuel profiles were determined with experimental and numerical summation of all the surrogate components. Symbols represent experimental results and lines represent simulations.

Figures 1a and 2a compare measured and computed fuel profiles for three PRF fuels for equivalence ratios of 0.5 and 1.0, with the aim of revealing the effect of octane number on fuel oxidation chemistry. At both equivalence ratios, fuel reactivity decreased with increasing octane number. The model matches these trends, albeit agreement is better at equivalence ratio of 0.5 than at 1.0. Fuel consumption is generally initiated in the simulations about 30 to 40 K lower in temperature than in the experiments. This suggests that some improvements can be made in the initial reactivity of the model at low temperatures. Model analysis is performed later to point out responsible key reactions in low temperature oxidation.

Figures 1b-d, 2b-d and 3b-d compare PRF and two multi-component surrogates with similar octane numbers but different compositions; this enables us to understand the compositional effects on oxidation chemistry. Other species profiles, e.g. O_2 , CO , CO_2 , C_2H_4 , C_3H_6 and butene isomers

are presented in the Supplementary Material-4 (low temperature) and Supplementary Material-5 (high temperature).

Two stages of oxidation were found experimentally and predicted numerically. Hydrocarbons first reacted with oxygen when the temperature was 500-600K, and then reactivity was reduced between 600-750K (Fig. 1 and Fig. 2); finally, oxidation increased between 800-1050K (Fig. 3). This phenomenon is called negative temperature coefficient behavior[54, 55]. The explanation for this phenomenon is that low temperature oxidation and high temperature oxidation have two different reaction mechanisms, which are both thermodynamically and/or kinetically limited in the intermediate temperature. For low octane number surrogates (e.g. FGI-KAUST and FGJ-KAUST), some reactivity was observed between 700 and 750K in Figure 2c. For high octane number surrogates (e.g., FGF-KAUST and FGG-KAUST), no reactivity was found between temperatures of 500-800K and at an equivalence ratio of 1.0.

Figure 1: Low temperature oxidation (500-750K) fuel profiles for nine selected surrogates. Experimental data from JSR-1 and numerical simulation ($\phi=0.5$).

Figure 2: Low temperature oxidation (500-750K) fuel profiles for nine selected surrogates. Experimental data from JSR-1 and numerical simulation ($\phi=1.0$).

Figure 3: High temperature oxidation (750-1050K) fuel profiles for nine selected surrogates. Experimental data from JSR-1 and numerical simulation ($\phi=1.0$).

3.1 Low temperature oxidation

Low temperature oxidation is important for governing the anti-knock quality of fuels in spark ignition internal combustion engines[56] and ignition delay in compression ignition . Therefore, it is necessary to investigate low temperature oxidation chemistry.

A comprehensive detailed low temperature oxidation (500-750K) scheme has been given by Battin-Leclerc *et al.* [57]. A brief description of alkane low temperature oxidation reaction

pathways is presented here. When the temperature is between 550-650K, hydrogen abstraction from large alkane molecules (RH) forms large alkyl radicals ($R\cdot$), which then react with oxygen to form an alkyl peroxide radicals ($ROO\cdot$). Intramolecular hydrogen migration occurs next through a five- to eight-membered transition state rings, producing another carbon centered radical ($\cdot QOOH$). A second O_2 addition proceeds resulting to form an $\cdot OOQOOH$ radical. Theoretically, more oxygen addition reactions could occur[58], but the most favorable reaction pathway for $\cdot OOQOOH$ is intramolecular hydrogen migration to $HOOQ'OOH$, and then decomposition to form keto-hydroperoxide ($HOOQ'=O$) and release of OH. This is the most important reaction in low temperature oxidation, since it can release OH radicals and keto-hydroperoxides, which further decompose and produce more OH radicals. This reaction is a key chain branching step promoting low temperature oxidation. When temperature increases (e.g., 650-750K), the large oxygenated radical intermediates (e.g., $ROO\cdot$ and $\cdot QOOH$) can overcome energy barriers for dissociation, molecular elimination reactions forming alkenes and less reactive HO_2 radicals, and cyclization reactions forming cyclic ethers and OH radicals. These pathways produce less reactive products than the aforementioned chain branching pathway. Thus, in intermediate temperature region (e.g., 650-750K), the concentration of important radicals (i.e., OH) is reduced and the overall rate of fuel consumption is slowed.

Compared to n-alkanes, some hydrocarbons, such as *iso*-octane[50], cyclopentane[51] and toluene[59] have weak low temperature reactivity because their structures do not facilitate rapid peroxy radical isomerization reactions that lead to chain branching keto-hydroperoxides. Gasoline surrogates and real gasoline fuels are mixtures of both reactive components (e.g. n-alkanes) and non-reactive components (e.g. highly-branched alkanes, cyclopentanes, alkenes and aromatics). In the next sub-sections, experimental and numerical investigations are discussed on PRF surrogates

with different octane numbers and multicomponent surrogates with different hydrocarbon compositions, in order to reveal the effects of octane number and composition on low temperature oxidation behavior. These comparisons also evaluate model predictions for the PRF surrogates and the multi-component surrogates against experimental measurements of the same mixtures.

3.1.1 Effect of surrogate octane number

Experimental and numerical investigations of three selected PRFs are presented in Figs. 1a and 2a under two equivalence ratios ($\phi=0.5$ and 1.0). It is clearly shown that all three PRFs exhibit low temperature oxidation behavior under selected conditions. Of the three PRFs, PRF 70 exhibits the highest reactivity, followed by PRF 84 and PRF 91.5. Numerical simulations show similar reactivity, however the simulated start of reactivity was 30 to 40 K before the measured start reactivity (recall the temperature uncertainty is 25 K).

The three PRFs have identical hydrocarbon components--n-heptane and *iso*-octane--albeit with different concentrations. As illustrated in previous literature[50, 60], n-heptane (RON=MON=0) exhibits low temperature oxidation behavior while *iso*-octane (RON=MON=100) does not. The observed oxidation trends in the JSR experiments are reasonable because low octane number PRFs with more n-heptane are more reactive than high octane number PRFs with high concentration of *iso*-octane [23, 61, 62]. In PRF oxidation, n-heptane oxidation happens first, producing OH radicals and keto-hydroperoxides. Keto-hydroperoxides further decompose to produce additional OH radicals. Highly reactive OH radicals can abstract hydrogen from non-reactive *iso*-octane, thereby initiating its low temperature oxidation reactions. Recent engine experiments showed similar behavior of different PRF compositions on two-stage heat release characteristics[63]. Similar results of oxidation of one reactive component activating the oxidation of another less reactive component have been observed in n-heptane/ethanol[64] and

toluene/dimethyl ether[65] mixtures. With increased n-heptane, the overall octane number decreases and more OH can be produced through n-heptane oxidation reactions. Thus, lower octane number PRFs exhibit greater low temperature reactivity. To conclude, PRFs with lower octane numbers are more reactive under low temperature oxidation conditions. A further deduction is that other multi-component surrogates and real gasoline fuels with lower octane number can be expected to exhibit greater low temperature oxidation. Further evidence to support this postulation is presented in the following sections.

3.1.2 Effect of surrogate composition

Experimental and numerical investigations on nine selected surrogates are presented in Figs. 1b-d and 2b-d under two selected equivalence ratios ($\phi=0.5$ and 1.0). Fuel profiles of three surrogates with similar octane numbers are included in the same graphs for comparison. CO, CO₂ and O₂ profiles are included in Figure S2-S7 in Supplementary Material-3. Each group of three surrogates with similar AKI have different compositions in order to reveal compositional effect on low temperature oxidation.

In each surrogate fuel group, PRFs were experimentally observed to be the most reactive. Amongst multi-component surrogates with similar octane number, surrogates with more low-octane number (e.g., n-alkanes) components exhibited higher reactivity (e.g., FGA-KAUST was more reactive than FGC-KAUST). Another finding is that the aromatic-rich surrogate for FGJ-KAUST has closer reactivity to PRF than the alkane-rich surrogate for FGI-KAUST. This can be explained by the same theory that FGJ-KAUST has more low-octane number components, e.g. n-heptane, than FGI-KAUST. Despite the large amount of aromatics in FGJ-KAUST, more n-alkanes in its composition makes it more reactive in the low temperature region. Some multi-component surrogates (FGF-KAUST and FGG-KAUST) showed little low temperature reactivity.

This can be expected since there is no *n*-heptane in FGF-KAUST and FGG-KAUST, which is needed to initiate low temperature reactivity. However, numerical simulations failed to reproduce this behavior, indicating current kinetic model requires further investigation. CO, CO₂ and O₂ profiles provided further support for these observations and conclusions. In summary, when comparing surrogate fuel mixtures of similar octane number, those with more low-octane number components are expected to have higher reactivity in low temperature oxidation under the conditions explored in JSR-1. Future work should focus on performing similar experiments at higher pressures and a broader range of residence times and equivalence ratios to further corroborate our findings.

3.1.3 Sensitivity and rate of production analysis

Model analysis was performed in this section to reveal key reactions that could promote or inhibit fuel reactivity. Target surrogates were chosen as PRF 70, FGI-KAUST and FGJ-KAUST due to their strong low temperature reactivity. Analysis was performed at 620K, corresponding to the temperature with the strongest low temperature oxidation reactions. Rate of production analysis was conducted first to reveal main fuel consumption reaction pathways. Detailed results are presented in Supplementary Material-6. Scheme S1 in Supplementary Material-3 presents nomenclatures for species discussed in the following text. Top ten OH consumption and production reaction pathways are presented in Figure 4. Primary OH consumption reactions are H-atom abstraction reactions by OH radical, as proved in various hydrocarbon oxidation chemistry studies[43]. Hydrogen abstraction reactions of *iso*-octane and 1,2,4-trimethylbenzene have large participations among OH consumption channels, which consists with proposed low temperature reaction scheme. OH radical produced by *n*-heptane low temperature reactions can further abstract hydrogen from *iso*-octane and 1,2,4-trimethylbenzene and initiate their low temperature reactions.

Figure 4: Top ten OH consumption and production reactions on three selected gasoline surrogates (PRF 70, FGI-KAUST and FGJ-KAUST) simulations at 620K under two conditions, $\phi=0.5$ and $\phi=1.0$.

Sensitivity analysis was performed to reveal the most influential reactions in low temperature oxidation. OH was selected as the reactivity indicator because it is considered to be the most important radical in low temperature oxidation. The analysis was performed using Chemkin sensitivity analysis tools in the PSR reactor model[53]. The chosen temperature was 620K and results are shown in Fig. 5. Nomenclatures for species mentioned in sensitivity analysis are provided in Scheme S1 in Supplementary Material-3. A negative value means that the reactions

inhibited low temperature oxidation, while positive value indicates that the reactions promoted low temperature reactivity. *n*-Heptane reactions are marked in red and appear in *italics*, *iso*-octane reactions are blue and bold, and 1,2,4-trimethylbenzene reactions are olive green and underlined. The top promoting reactions were found to be H-atom abstraction from low-octane number component, e.g. *n*-heptane and 2-methylhexane, while the most inhibiting reactions were high octane number component hydrogen abstraction reactions, e.g. *iso*-octane and 1,2,4-trimethylbenzene. Small molecule reactions had only minor participation among the top ten sensitive reactions. These results indicate that low temperature oxidation chemistry is largely dependent on fuel molecule reaction pathways. Fuels with a greater content of low-octane number component will exhibit greater low temperature reactivity because reactive molecules are needed to initiate the oxidation of the remaining components.

Figure 5: Normalized sensitivity coefficient of top ten OH reactions on three selected gasoline surrogates (PRF 70, FGI-KAUST and FGJ-KAUST) simulations at 620K under two conditions, $\phi=0.5$ and $\phi=1.0$.

3.2 High temperature oxidation

High temperature oxidation of gasoline fuels affects engine stability and energy efficiency, as the major energy release in combustion occurs through high temperature oxidation chemistry. Furthermore, pollutants such as alkenes, oxygenates and soot can be produced via high temperature oxidation[1]. To understand and control these pollutants, high temperature chemistry is investigated.

Next the intermediate to high temperature (750 – 1050K) oxidation of the surrogate fuels is discussed. Experimental and numerical investigation results for the nine selected surrogates are presented in Fig. 3, while CO, CO₂ and O₂ profiles are provided in Figure S8-S10 in Supplementary Material-3. Figure 3a shows that all three PRFs have similar fuel profiles and reactivity to within experimental uncertainty, indicating the negligible effect of octane number on the oxidation chemistry in this temperature region. Figure 3b compares two alkane-rich multi-component surrogates, FGA-KAUST and FGC-KAUST. Despite composition differences, similar reactivity is again found in their fuel reactivity profiles, showing that *n*-alkane and *iso*-alkane distribution has little effect on high temperature oxidation in the JSR. Figure 3c compares two multi-component surrogates, cyclopentane-rich FGF-KAUST and toluene-rich FGG-KAUST. Experimentally and numerically, aromatic-rich FGG-KAUST showed lower reactivity than alkane-rich FGF-KAUST. This behavior is consistent with the lower reactivity of toluene compared to cyclopentane. Meanwhile, two multi-component surrogates, alkane-rich FGI-KAUST and aromatic-rich FGJ-KAUST are also compared in Figure 3d. Aromatic-rich FGJ-KAUST showed similar high temperature reactivity with alkane-rich FGI-KAUST. FGJ-KAUST has similar amount of aromatics with FGG-KAUST, but without toluene in its composition. This indicates that 1,2,4-trimethylbenzene has similar reactivity compared to alkanes in the high

temperature region. Similar observations and conclusions can be supported by CO, CO₂ and O₂ profiles. It can be concluded that octane number and composition has little effect on high temperature oxidation behavior of fuels, except for the toluene-rich surrogate due to the low reactivity of toluene.

4. Real gasoline fuel oxidation

In the final segment of this paper, experimental results are presented on the oxidation of real FACE gasolines (A, C, F, I and J) and compared to simulation of these gasolines using the surrogate fuels previously discussed. Experimental results on FACE fuels A, C, and F were available from previous work[19, 20].

Experiments on FACE I and J experiments were conducted following the same methodology. The selected FACE fuels covered a wide range of fuel properties and compositions from low octane number (FACE I and J, $(RON+MON)/2=70$), medium octane number (FACE A and C, $(RON+MON)/2=84$) to high octane number (FACE F, $(RON+MON)/2=91.5$), as well as alkane-rich gasoline fuels (FACE A, C and I), naphthene-rich gasoline fuels (FACE F) and aromatic-rich gasoline fuels (FACE J).

4.1 Species identification

In FACE I and J oxidation, over 50 species were identified and quantified experimentally in a JSR-2 at 10 atm. Major products were H₂O, CO, CO₂ and H₂. Oxygenates, e.g. aldehydes (formaldehyde and acetaldehyde), alcohol (methanol), ketones (acetone and 2-butanone), and ketene were observed and quantified. Other important intermediates in oxidation are linear and branched alkenes, such as ethylene, propene, isobutene, 1-butene, cis- and trans-2-butene, 1-pentene, cis- and trans-2-pentene and 1,3-butadiene. Detailed experimental data of all species are

included in the Supplementary Material-7. Detailed experimental data of FACE A, C and F can be found in previous literature[19, 20].

Species with maximum concentration over 10 ppm were identified as important intermediates and compared with gasoline surrogate kinetic model simulations. Comparisons between real fuel experiments with surrogate simulations were conducted using temperature versus mole fraction profiles. In the following sections, first the fuel profiles are discussed and then the intermediate species profiles.

4.2 Fuel profiles

Five FACE fuel profiles and their corresponding surrogate simulation results are shown in Fig. 6. Fuel profiles are achieved by summing up all fuel components detected experimentally, and the fuel molecules in corresponding surrogates for simulations. Again, to exclude the difference of input due to carbon balance, simulated fuel profiles are normalized to 1000 ppm and compared with experimental data. Real gasoline experimental data are shown as scattered points, while surrogate simulation results are presented as lines. Different scattered shapes, line styles and colors distinguish the fuel oxidation results, experimentally and numerically.

Two stages of oxidation regimes, one at low temperatures (500-700K) and another at intermediate to high temperatures (700-1200K), were again observed experimentally and predicted numerically, consistent with surrogate oxidation results in the previous section. Some discrepancies between experiments and simulations were observed (e.g. FACE F fuel profiles were over-predicted in low temperature region). However, most of the surrogate simulation results accurately reproduced fuel profiles and oxidation behaviors, proving that a gasoline surrogate kinetic models can successfully mimic real gasoline fuel behavior within a wide range of

experimental conditions and for a variety of gasoline fuels. These experimental validations show that the gasoline surrogate kinetic model is a successful, comprehensive, viable and powerful approach for simulating gasoline engines operating under different conditions and grade gasoline fuels.

Figure 6: Fuel profiles of five FACE gasoline oxidations and their proposed surrogate simulations under three equivalence ratios ($\phi=0.5$, 1.0 and 2.0 ; 10 atm).

4.3 Species profiles

To further examine gasoline surrogate kinetic model, species profiles from FACE gasoline oxidation were provided as additional evidence. Major and key intermediate species profiles of FACE I and J oxidations were measured by JSR-2, while experimental data for species profiles of FACE A, C and F are taken from literatures [19, 20]. Major and key intermediate species profiles are presented in Figure 7 and 8 under lean condition, and compared with two surrogate model simulations. Results under stoichiometry and rich conditions are included in Figure S11-14 in Supplementary Material-3. All simulated species mole fraction data using updated model in this work are included in the Supplementary Material-8. As previously mentioned, species with maximum concentration over 10 ppm were considered important and were therefore chosen for further analysis. Eight species were selected to represent different organic compounds in gasoline oxidation. H_2O , CO , CO_2 , H_2 are major products of oxidation; CH_4 for small alkanes, CH_2O for aldehydes, C_2H_4 and C_3H_6 for alkenes. Detailed experimental data of species profiles in FACE I and J oxidations are included in the Supplementary Material-7. Detailed species profiles of FACE A, C and F are presented and examined in the available literature[19, 20].

For all five FACE gasolines, the differences between experimental data and corresponding surrogate simulations for major products and important intermediates, such as H_2O , CO , CO_2 , H_2 , and CH_2O , are within the limits of acceptable experimental error ($\sim\pm 10\%$) over the entire temperature region. Small hydrocarbons such as CH_4 , C_2H_4 , and C_3H_6 are predicted within uncertainty of a factor of two. It is also found that simple binary PRF surrogate can well predict selected species profiles as well as multi-component surrogates in both low and high temperature regions. By these comparisons, it can be concluded that surrogate kinetic modeling can successfully predict real gasoline fuel behaviors. Future work should perform surrogate mixture

experiments in JSR-2 under same condition as FACE gasolines to further validate the surrogate kinetic model.

Figure 7: Major species profiles of FACE gasolines by JSR-2, with corresponding surrogate simulations, under fuel-lean conditions ($\phi=0.5$, 10 atm).

Figure 8: Key intermediate species profiles of FACE gasolines by JSR-2, with corresponding surrogate simulations, under fuel-lean conditions ($\phi=0.5$, 10 atm).

5. Conclusions

In this work, nine gasoline surrogates and five real FACE gasoline fuels were examined experimentally and numerically under JSR conditions. These gasoline surrogates included three

PRFs and six multicomponent surrogates to match the target FACE fuels. The PRF fuels were chosen to elucidate the effect of fuel octane number on reactivity in the JSR; the multicomponent surrogates were chosen to match the target fuels with higher fidelity than a PRF, and also to reveal compositional effects on JSR oxidation. It was found, both experimentally and numerically, that lower octane number fuel mixtures were more reactive. When comparing fuel mixtures of similar octane number, those containing more low-octane number components were found to be more reactive in the low temperature region. The importance of n-alkanes in driving the low temperature reactivity oxidation of surrogate mixtures was highlighted. Discrepancies between experiments and simulations require further investigation of the surrogate kinetic model.

In high temperature region, the influence of octane number and composition on surrogate oxidation was reduced. All surrogates showed similar reactivity, despite their different octane numbers and hydrocarbon compositions, except for toluene-rich surrogate which showed decreased high temperature reactivity. Numerical simulations accurately reproduced alkane-rich and aromatic-rich surrogates, indicating that different types of hydrocarbons share similar high temperature oxidation chemistry.

To examine the surrogate kinetic model, oxidation of five real FACE gasolines was performed in this work or obtained from data in the available literature. These five FACE gasolines included a variety of gasoline fuels with a wide octane number range and compositional differences. Surrogate simulations successfully reproduced real gasoline oxidation behavior, demonstrating that gasoline surrogate kinetic models to be a comprehensive and viable approach to simulating gasoline oxidation in real gasoline engine operation and design. Species profiles provided further confirmation of this conclusion. Future work should perform FACE gasoline and surrogate mixture experiments at a broader range of JSR conditions (e.g., higher pressures, various equivalence ratios

and residence times, etc.), as well as investigate real fuels and surrogates in other facilities (flow reactors, shock tubes, rapid compression machines, laminar flames, etc.).

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