# Ignition Characteristics of Alternative JP-8 and Surrogate Fuels under Vitiated Conditions

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Atmospheric pressure flow reactor experiments were performed to investigate the ignition characteristics of Fischer-Tropsch and hydrotreated renewable JP-8 fuels under vitiated conditions in order to compare these properties to conventional JP-8. Ignition experiments were conducted with reactor temperatures between 832 K and 917 K with standard air as well as vitiated air with 17%  $O_2$  and  $NO_x$  levels varied between 0 and 755 ppmv. Experiments were also performed with jet fuel surrogate components such as n-dodecane and iso-octane to investigate the ignition behavior of normal- and iso-paraffins, respectively. Experimental measurements show that the presence of  $NO_x$  in the oxidizer stream reduces the ignition delay time of jet fuels and surrogates significantly. Furthermore, the effect of  $NO_x$  on iso-octane ignition delay time is more pronounced than for n-dodecane. Surrogate kinetic modeling results are also compared with the experimental data regarding the effect of  $NO_x$ . Overall, the modeling results agree with trends observed for the effect of  $NO_x$  on ignition delay time. However, the ignition delay time predictions for Sasol-IPK are much longer than the experimental data. This is due to the fact that the representation of iso-paraffinic components in Sasol-IPK is not correctly represented by iso-octane alone.

#### **Nomenclature**

Φ or Phi - fuel-air equivalence ratio: (fuel/air)/(fuel/air)<sub>stoich</sub>

ρ - mass density [kg/m³]
 DCN - derived cetane number
 TSI - threshold sooting index

H/C Ratio - hydrogen to carbon molar ratio
MW - molecular weight [g/mol]
FT - Fischer-Tropsch fuels

HRJ - hydrotreated renewable jet fuels

PMT - photomultiplier tube IDT - ignition delay time

# I. Introduction

V itiated air refers to a high-preheat oxidizer stream with recycled combustion products used in various devices to reduce emissions [1,2], improve flame stability [3], improve combustion efficiency [4,5], or to achieve highenthalpy hypersonic flight conditions at ground level [6]. The presence of combustion products in the inlet oxidizer stream has been found to influence the combustion chemistry of hydrocarbon fuels. In particular, the presence of NO<sub>x</sub> has an effect on induction chemistry [7,8,9], and CO<sub>2</sub> and H<sub>2</sub>O affect the flame propagation [7,10]. A previous study applying a three-level fractional factorial design of experiments by the authors [8] demonstrated that the presence of NO<sub>x</sub> in the vitiated air has significant influence on the ignition delay time of JP-8. A seven-variable, three-level Box-Behnken design of experiments was performed to investigate the effect of vitiation on JP-8 ignition between 950 K and 1125 K [8]. The experimental variables were temperature, equivalence ratio, and vitiated air

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composition (i.e.,  $O_2$ ,  $H_2O$ , CO,  $CO_2$ , and  $NO_x$ ). The summary of the experimental results in Figure 1 shows that  $NO_x$  and  $O_2$  each play a significant role on the ignition of JP-8 at these conditions in addition to temperature. The positive and negative values for  $NO_x$  and  $O_2$ , respectively, indicate that increasing  $NO_x$  reduces the ignition delay time while reduced  $O_2$  in the oxidizer increases it.

Previous flow reactor ignition delay time measurements [8,9] showed that a small amount of  $NO_x$  (50-900ppm) can significantly reduce the ignition delay time of JP-8 under atmospheric and sub-atmospheric pressure conditions. The primary objective of the current work is to investigate the effect of  $NO_x$  on alternative JP-8 fuels produced from natural gas via the Fischer-Tropsch (FT) process and from fatty oils via hydrotreatment techniques (forming renewable jet (HRJ) fuels). Experiments were also performed with typical surrogate components of jet fuels: n-dodecane and iso-octane.

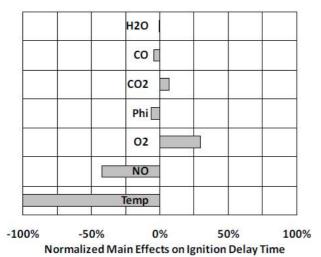


Figure 1. Main effects of experimental variables on ignition delay time of JP-8. Effects are normalized based on the effect of temperature. (adopted from Fuller et al. [8]).

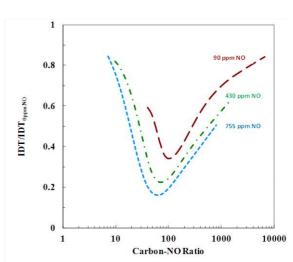


Figure 2. Normalized ignition delay time versus carbon–NO molar ratio for stoichiometric propane/ $O_2/NO/N_2$  mixture at 875 K and 1 atm (adopted from Gokulakrishnan et al. [7]).

Several experimental studies of the effect of  $NO_x$  on natural gas fuel components have been reported in the literature, and a detailed review of this can be found elsewhere [7]. Most of the experimental conditions used in the previous works were performed using heavily diluted fuel/oxidizer mixtures, and hence, the carbon to NO ratio in these studies were less than is found in typical combustion devices. The experimental and modeling study of Gokulakrishnan et al. [7] showed that the carbon to NO ratio plays a significant role in determining the reaction pathways of propane ignition. Figure 2 shows modeling results [7] demonstrating the influence of carbon to NO ratio on the reduction in propane ignition delay time at 875 K and 1 atm. The effect of NO to promote ignition increases as the carbon to NO molar ratio is increased until it reaches a turn-over point. The effect of NO in reducing the ignition delay time diminishes as the carbon to NO molar ratio is further increased beyond the turn-over point as shown in Figure 2.

The experimental and modeling results [7] found that the chemical kinetics effect of  $NO_x$  to promote fuel oxidation stems from the interaction between  $NO_x$  and less reactive radical species such as  $HO_2$ ,  $CH_3$  and  $CH_3O_2$ . In the low- and intermediate-temperature oxidation regimes, a chain-terminating reaction (R1) is favored over a chain-branching reaction (R2). However, when NO is present, the relatively less reactive hydroperoxy radical (HO<sub>2</sub>) is converted to OH radical via reaction (R3). The  $NO_2$  generated in reaction (R3) converts  $CH_3$  into  $CH_3O$  and NO via (R4), while relatively less reactive  $CH_3O_2$  is converted to more reactive  $CH_3O$  radicals via (R5).

$$H + O_2 + M = HO_2 + M$$
 (R1)  
 $H + O_2 = OH + O$  (R2)  
 $HO_2 + NO = NO_2 + OH$  (R3)

$$CH_3 + NO_2 = CH_3O + NO (R4)$$

$$CH_3O_2 + NO = CH_3O + NO_2$$
 (R5)

It was shown [7] that H-atom abstraction from the fuel molecule by NO<sub>2</sub> also plays a critical role in promoting hydrocarbon fuel oxidation under high carbon to NO ratios (i.e., right-hand side branch of the curves in Figure 2) via reactions (R6) and (R7).

$$C_x H_y + NO_2 = C_x H_{y-1} + HNO_2$$
 (R6)  
 $C_x H_y + NO_2 = C_x H_{y-1} + HONO$  (R7)

$$C_x H_v + NO_2 = C_x H_{v-1} + HONO$$
 (R7)

HNO<sub>2</sub> species formed in reaction (R6) will quickly be converted to HONO via reaction (R8), while HONO will decompose into NO and OH via (R9).

$$HNO_2 + M = HONO + M$$
 (R8)

$$HONO (+ M) = NO + OH (+ M)$$
(R9)

Reactions (R3) to (R9) form a chemical catalytic cycle to promote the oxidation of hydrocarbon fuels at low- and intermediate temperatures.

#### II. **Experiments**

In the current work an atmospheric pressure flow reactor facility is used to measure the ignition delay time of JP-8 and its alternatives at various conditions. A premixing section, shown in Figure 3, consists of a swirler to achieve near-perfect mixing of fuel and oxidizer streams at the inlet of the flow reactor. The downstream portion of the premixing section is a gradually expanding duct that connects to the test section, a long ceramic alumina tube with an internal diameter of 5 cm. The test section is heated and insulated to maintain a uniform reactor temperature up to 1200 K using with three independently controlled electric zone heaters. The total mass flow rate of the oxidizer stream was maintained at ~2.0 g/s for each test condition in this study, and the fuel flow was varied depending on the desired equivalence ratio. The oxidizer stream is pre-heated prior to mixing with the fuel stream in order to maintain the same inlet temperature of the fuel/oxidizer mixture as in the test section. The liquid fuel is prevaporized under a nitrogen environment at 650 K before mixing with the oxidizer stream. The fuel stream is radially injected into the oxidizer stream prior to passing through a swirled, annular mixing section as shown in Figure 3. The well-mixed fuel and oxidizer streams enter the diffuser section and then the test section.

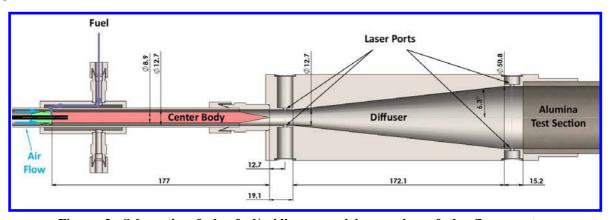


Figure 3. Schematic of the fuel/oxidizer premixing section of the flow reactor apparatus. Dimensions are in millimeters

A laser absorption technique to monitor the fuel injection system was installed at the inlet of the diffuser section to monitor the time of injection of the fuel into the flow reactor. An infrared beam at 3.39 µm supplied by a HeNe laser is directed across a diameter of the flow channel through quartz optical ports in the diffuser (see Figure 3). A photodiode measures the intensity of the transmitted beam. When the laser beam passes through a medium that contains a hydrocarbon fuel, the signal is attenuated due to the absorption of the laser by the C-H bonds in the fuel. This attenuation denotes the presence of fuel entering the diffuser and is used to determine the actual start time for timing the autoignition of the fuel/oxidizer mixture. The start time used to measure the ignition delay time of the mixture is the time at which the laser signal attenuates to 50% of the difference between the maximum and minimum measured signals during fuel injection. The time of ignition is measured by the detection of the chemiluminescence signal of OH\* emission that occurs during ignition. A photomultiplier tube (PMT) is located at the downstream end of the flow reactor with direct line of sight along the axis of the test section through a quartz window. The PMT is equipped with a 310 nm narrow band pass filter (± 5 nm) to observe OH\* chemiluminescence

emission. The ignition delay time values reported in this work are designated as the difference between the time recorded to mark 50% attenuation in the pre-diffuser laser signal (which denotes the fuel/air mixture entrance into the diffuser) and the time of PMT excitation due to the chemiluminescent radical emission of OH\*. A detailed description of the flow reactor set-up can be found elsewhere [7,9,11].

The primary objective of the current work is to investigate the effect of vitiation on alterative JP-8 fuels relative to conventional JP-8. The chemical composition of typical vitiated air consists of combustion products such as  $CO_2$ ,  $H_2O$ , CO and  $NO_x$  under reduced  $O_2$  levels. Previous work by the authors [8,9] showed that  $NO_x$  and  $O_2$  had significant impact on the induction chemistry of JP-8 compared to other vitiated species such as  $CO_2$  and  $H_2O$ . Therefore, in the current work, experiments were performed by varying NO and  $O_2$  concentrations in the oxidizer stream along with temperature and equivalence ratio to study the effect of vitiation on the autoignition of alternative JP-8 fuels relative to conventional JP-8. Four different alternative JP-8 fuels and one conventional JP-8 were chosen for the experiments. The alternative fuels include two Fischer-Tropsch fuels (i.e., Shell-SPK and Sasol-IPK) produced from natural gas and two hydro treated renewable jet fuels (i.e., HRJ-Camelina and HRJ-Tallow) produced from biodiesel. The chemical and physical properties of these fuels are listed in Table I. Figure 4 shows the chemical class compositions, namely, normal-paraffins, iso-paraffins, cyclo-paraffins and aromatics, which comprise these fuels. It can be noted that the Shell-SPK, HRJ-Camelina and HRJ-Tallow mainly consist of normal- and iso-paraffins (> 95%) with nearly identical DCN values, while the Sasol-IPK consists almost entirely of iso-paraffins (> 95%) which leads to the lowest DCN.

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Jet Fuel Type	Air Force POSF #	Density <sup>a</sup> [kg/m <sup>3</sup> ]	DCN <sup>b</sup>	TSI <sup>b</sup>	H/C Ratio <sup>b</sup>	MW <sup>b</sup> [g/mol]	Molecular Formula <sup>b</sup>
JP-8	6169	785	47.3	19.28	2.02	153.9	$C_{11.0}H_{22.1}$
Sasol IPK	7629	739	31.3	17.28	2.20	149.2	$C_{10.5}H_{23.0}$
Shell SPK	5729	730	58.4	9.11	2.24	136.7	$C_{09.6}H_{21.4}$
HRJ Camelina	7720	752	58.9	11.99	2.20	165.0	$C_{11.6}H_{25.5}$
HRJ Tallow	6308	748	58.1	11.58	2.18	161.0	C <sub>11.3</sub> H <sub>24.7</sub>

Table I: Properties of the fuels used in the current work

a – Edwards [12]; b – Won et al.[13]

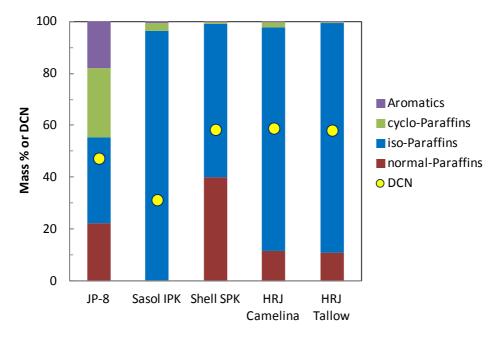


Figure 4. Chemical class composition (in mass %) [12] of the jet fuels listed in Table I along with DCN (circles) [13].

Figure 5 compares the distribution of normal- and iso-paraffin species present in the alternative fuels with that of the conventional JP-8. The carbon number distribution in Figure 5 indicates that FT fuels have narrower distribution, while HRJ fuels have a broader range compared to JP-8. For example, more than 90% of the constituents in the FT fuels account for isomers between  $C_9$  and  $C_{13}$ , whereas more than 90% of the HRJ fuels is made up of iso- and normal-paraffins between  $C_8$  and  $C_{17}$ . The variability in the carbon number distribution is reflected in the molecular weights. FT and HRJ fuels have lower and higher molecular weights, respectively, than JP-8 as shown in Table I.

Ignition delay time experiments were performed under vitiated conditions for each fuel listed in Table I. Extensive experiments were also performed to study the effect of vitiation on n-dodecane and iso-octane, which are two of the primary surrogate components to model the alternative fuels. The reactor temperature was maintained at 832 K, 875 K or 917 K, while the fuel/oxidizer equivalence ratio was varied between 0.5 and 1.5. The  $O_2$  level in the oxidizer stream was set to 14, 17 or 20 mol %, while the  $NO_x$  concentration was varied between 0 and 755 pmmy.

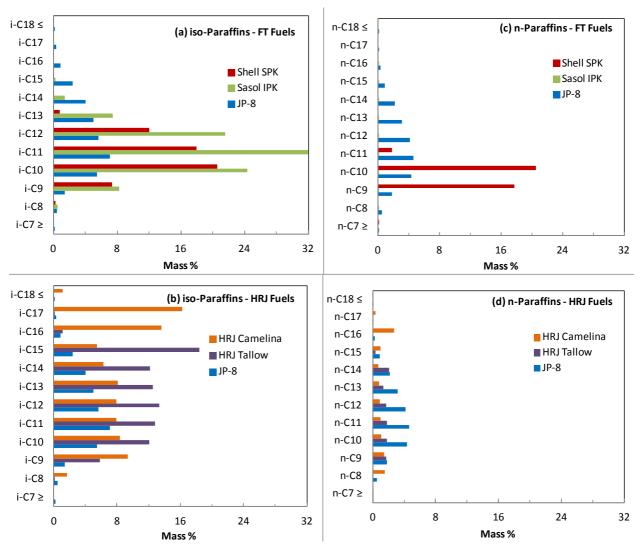


Figure 5. iso- and normal-Paraffin species composition of the alternative fuels listed in Table I are compared with JP-8 [12].

## **III.** Chemical Kinetics Modeling

A five-component surrogate kinetic mechanism for jet fuel combustion is used to model the ignition characteristics of JP-8 and its alternative fuels. The current detailed reaction mechanism is based on an improved version of the surrogate kinetic model previously reported by authors that primarily consists of n-decane (n- $C_{10}H_{22}$ ), n-propylcyclohexane ( $C_9H_{18}$ ), and n-propylbenzene ( $C_9H_{12}$ ) to represent paraffins, naphthenes and aromatics, respectively [14]. In the current model, additional surrogate components, namely, n-dodecane (n- $C_{12}H_{26}$ ) and iso-octane (i- $C_8H_{18}$ ) are included to better represent the normal- and iso-paraffin components, respectively, that are present in typical jet fuels, including the alternative fuels shown in Figure 5. Moreover, the current surrogate kinetic mechanism also consists of a detailed nitrogen sub-mechanism that can predict the effect of  $NO_x$  (typically present in vitiated air) on ignition at low- and intermediate-temperatures as well as emissions from high-temperature flames. This surrogate kinetic mechanism was validated for a wide range of conditions using the experimental data obtained in the current work as well as various literature data for individual surrogate components. A detailed model description and validation of  $NO_x$  emissions from high-temperature combustion and the role of  $NO_x$  on vitiated combustion at low- and intermediate-temperatures can be found elsewhere [7,15,16].

The reaction sub-mechanism for the iso-octane used in the current model is a reduced version of the detailed kinetic mechanism of Curran et al. [17], and the model validation was reported elsewhere [18]. A detailed kinetic mechanism for n-dodecane is developed in the current work using a similar approach used for n-decane in the previous work [14,19]. Most of rate parameters for the low-temperature chemistry were estimated using the values recommended by Curran et al. [17] and Miyoshi [20] via the group additivity method [21,22]. The model has been validated for various experimental data from the literature.

The vitiated kinetics sub-mechanism, especially the interaction between  $NO_x$  and the smaller hydrocarbon species (<C<sub>4</sub>), were adopted from Refs. [7,23]. Previous experimental and modeling work [7] on the effect of  $NO_x$  on propane showed that the H-atom abstraction of fuel molecules by  $NO_2$  via (R6) and (R7) plays a critical role in vitiated combustion. A reaction subset for H-atom abstraction by  $NO_2$  from n-decane, n-dodecane, iso-octane, n-propylcyclohexane and n-propylbenzene has been included in the current vitiated kinetic sub-model. The reaction rate parameters were estimated by the group additivity method using the theoretical rates recommended by Chan et al. [24], and optimized for the current experimental conditions.

Figure 6 shows the present surrogate kinetic model predictions for ignition delay times of n-dodecane and Jet-A compared with the shock tube experimental measurements of Vasu et al. [25,26]. The present kinetic model agrees fairly well with the experimental data including the NTC behavior. The ignition delay time shown in Figure 6 for Jet-A was computed using a surrogate mixture composition of 35.9 mol% n-dodecane, 33.6 mol% iso-octane and 30.5 mol% n-propylbenzene.

Table II shows the surrogate compositions used in the current work for various jet fuels listed in Table I. There are various approaches to formulate the surrogate mixture composition [27,28,29,30]. In the current work, the method proposed by Dooley et al. [28] is adapted for the surrogate mixture formulation in which the DCN, H/C ratio and TSI of the actual fuel (listed in Table I) are matched with the model fuel mixture listed.

Surrogate	JP-8	Sasol IPK	Shell SPK	HRJ Camel.	HRJ Tallow
n-decane	0.0	0.0	74.6	0.0	0.0
n-dodecane	38.2	16.0	4.5	61.1	59.5
iso-octane	37.2	64.7	12.2	29.2	31.5
propyl- benzene	24.6	19.3	8.7	9.6	9.0
H/C	2.00	2.05	2.13	2.12	2.12
DCN	48.1	31.8	58.2	60.0	59.0
TSI	18.3	15.7	9.1	11.4	11.0
MW (g/mol)	137.1	124.3	138.2	149.1	148.1

Table II: Surrogate mixture composition (in mole %) and properties

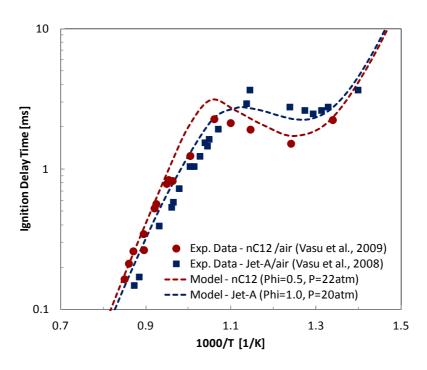


Figure 6. Shock tube ignition delay time measurements of Vasu et al. [25,26] for n-dodecane and Jet-A compared with current surrogate kinetic model.

#### IV. Results and Discussion

Figure 7 compares the measured ignition delay time of stoichiometric fuel/air mixtures for FT and HRJ fuels with that of JP-8 obtained in the current work in the absence of NO<sub>x</sub>. The overall activation energies based on the ignition delay time in Figure 7 are listed in Table III. The experimental data show that Shell-SPK has very similar ignition delay time as the JP-8 with almost the same activation energy. However, Sasol-IPK has very different ignition delay time profile compared to JP-8 and Shell-SPK with the largest overall activation energy among the fuel studied. For example, Sasol-IPK has lower ignition delay time than JP-8 at 917 K, while the opposite trend is seen at 832 K. Moreover, both HRJ fuels have longer ignition delay time than JP-8 across the temperature range investigated. It is noteworthy that Sasol-IPK has a lower DCN than JP-8, while both HRJ fuels have higher DCN than JP-8 (see Figure 4). DCN is a measure of the ignition quality of fuels based on the ASTM 6890 method [31], in which ignition delay time of liquid fuels are measured using ignition quality test (IQT) meter at diesel engine conditions (i.e., 22 atm and 833 K [28]).

Table III: Overall activation energy from the experimental data shown in Figure 7

Jet Fuel	kcal/mol
JP-8	30.90
Sasol IPK	40.40
Shell SPK	30.78
HRJ Camelina	31.49
HRJ Tallow	33.11

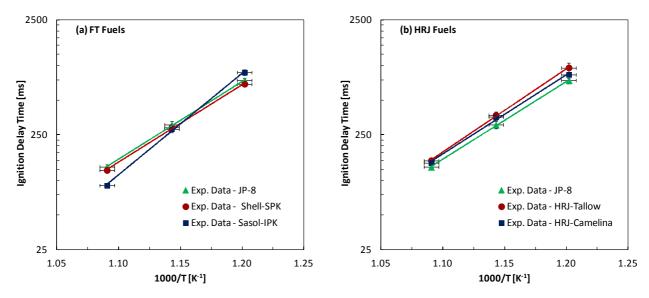


Figure 7: Ignition delay times of alternative jet fuels compared with JP-8 fuel. Symbols – experimental data, lines – least square fit.

Figure 8 shows the effect of  $NO_x$  on the ignition delay time experimental data for stoichiometric n-dodecane/oxidizer mixtures at various nominal reactor temperatures (i.e., 832 K, 875 K and 917 K) and various  $O_2$  levels in the oxidizer stream (14 mol %, 17 mol % and 20 mol %). Similar experiments were also performed for stoichiometric iso-octane/oxidizer mixtures with  $NO_x$  addition as shown in Figure 9. As expected, iso-octane has a longer ignition delay time than n-dodecane at similar conditions. Experimental data shows that addition of  $NO_x$  reduces the ignition delay time significantly for both n-dodecane and iso-octane. For example, 430 ppm  $NO_x$  reduced the ignition delay time of n-dodecane by ~65 % at 875 K and 20 mol %  $O_2$ , whereas the reduction is ~75 % for iso-octane at similar conditions. It can also be noted that the reduction in ignition delay time is more pronounced at lower  $O_2$  levels as shown in Figure 8(b) and Figure 9(b).

Figure 8 and Figure 9 also compare the experimental data with the chemical kinetic modeling results for n-dodecane and iso-octane, respectively. Overall, the current model predicts the effect of  $NO_x$  on n-dodecane reasonably well. However, the model needs further improvement to accurately predict the effect of  $O_2$  on ignition delay time. The modeling results for iso-octane in Figure 9 predict the trends for the effect of  $NO_x$  on ignition delay time. The model consistently predicts longer ignition delay time than the experimental values.

Experiments were performed to study the effect of  $NO_x$  on jet fuel ignition delay time at 875 K with 17 mol % and 20 mol %  $O_2$ . Figure 10 shows the experimental data of JP-8, Shell-SPK, Sasol-IPK and HRJ-Tallow for stoichiometric fuel/oxidizer mixtures as a function of  $NO_x$ . The experimental data show that Sasol-IPK has shorter ignition delay time compared to other jet fuels at 875 K, despite the fact that Sasol-IPK has the lowest DCN among the jet fuels tested (see Figure 4). However, the trends for the effect of  $NO_x$  on jet fuel ignition delay time are very similar to n-dodecane. For example, 430 ppm  $NO_x$  addition reduced the ignition delay time by ~65% on average at 875 K and 20 mol %  $O_2$ . Figure 10 also compares the experimental data with the jet fuel surrogate kinetic model predictions. The ignition delay times for JP-8, Shell-SPK, Sasol-IPK and HRJ-Tallow were computed using the surrogate mixture composition provided in Table II.

Overall, the model predicts the effect of NO<sub>x</sub> on ignition delay time reasonably well except for Sasol-IPK. The surrogate mixture composition of Sasol-IPK consists of 64.7 mol% iso-octane, 19.3 mol % n-propylbenzene and 16 mol% n-dodecane that matches DCN of the actual fuel shown in Table I. However, the chemical class composition break-down shown in Figure 4 indicates that Sasol-IPK is made-up of more than 95 % iso-paraffins. Alternatively, a surrogate mixture with 82 mol % iso-octane and 18 mol % n-dodecane would produce an estimated DCN of 31, and a H/C ratio of 2.23. Figure 11 shows the ignition delay time of 82 % iso-octane/18 % n-dodecane surrogate mixture as a function of NO<sub>x</sub> addition at 875 K. It can be noted the ignition delay time of this surrogate mixture is much longer than Sasol-IPK at 0 ppm NO, although the estimated DCN and H/C is similar to the Sasol-IPK. The experimental data in Figure 11 show that the ignition delay time of Sasol-IPK is closer to n-dodecane than iso-octane. Therefore, representation of iso-paraffinic components in Sasol-IPK is not correctly characterized by iso-octane alone, and work is in progress to identify alternate iso-paraffinic model fuels.

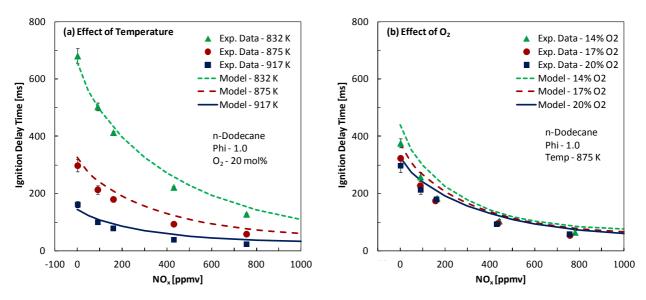


Figure 8: n-Dodecane ignition delay time: (a) effect of temperature; (b) effect of  $O_2$ . Symbols – experimental data; lines – modeling results.

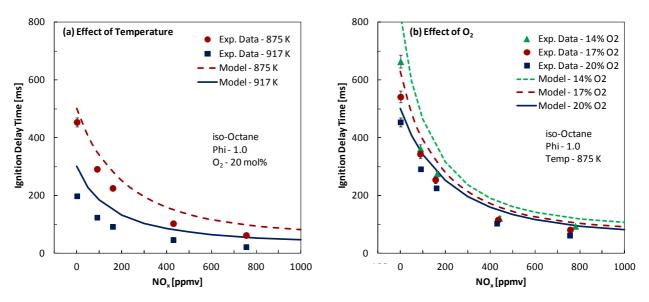


Figure 9. iso-Octane ignition delay time: (a) effect of temperature; (b) effect of  $O_2$ . Symbols – experimental data; lines – modeling results.

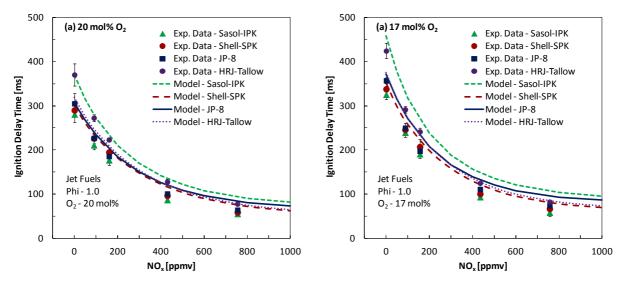


Figure 10. Ignition delay time for JP-8, FT and HRJ fuels: (a) 20 mol% O<sub>2</sub>; (b) 17 mol% O<sub>2</sub>. Symbols – experimental data; lines – modeling results.

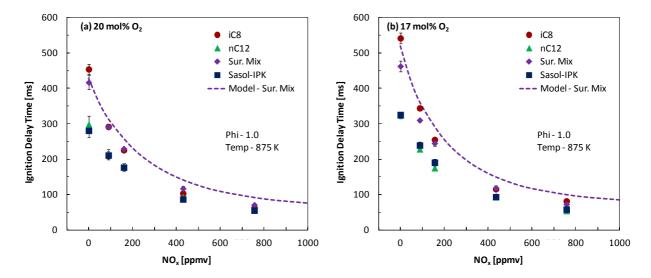


Figure 11. Ignition delay time for 82 mol% iso-octane and 18 mol% n-dodecane (denoted by Sur. Mix) compared with Sasol-IPK, n-dodecane and iso-octane: (a) 20 mol%  $O_2$ ; (b) 17 mol%  $O_2$ . Symbols – experimental data; lines – modeling results for 82 mol% iso-octane and 18 mol% n-dodecane.

Figure 12 shows the normalized sensitivity coefficients of the important reactions that are responsible for the promotion of ignition of jet fuels with  $NO_x$  addition. The sensitivity coefficients were computed for stoichiometric fuel/air mixtures of n-dodecane and iso-octane with and without 500 ppm NO at 875 K and 1 atm. A sensitivity analysis was also performed for a mixture of 67 mol% no-dodecane/33 mol% iso-octane with 500 ppm NO at these conditions. The three most sensitive reactions for the oxidation of fuel molecules in the absence of NO are:

$$C_xH_y + HO_2 = C_xH_{y-1} + H_2O_2$$
 (R10)  
 $H_2O_2 (+M) = OH + OH (+M)$  (R11)  
 $HO_2 + HO_2 = H_2O_2 + O_2$  (R12)

These reactions indicate that oxidation occurs under intermediate temperature regimes where the  $HO_2$  radical formed in reaction (R1) reacts with the fuel molecules to produce an alkyl radical ( $C_xH_{v-1}$ ) and  $H_2O_2$  via (R10). In

addition,  $H_2O_2$  is also formed via a bimolecular recombination reaction (R12).  $H_2O_2$  then undergoes unimolecular decomposition to produce OH radicals via reaction (R11).

When 500 ppm NO is added, reaction (R4) becomes the single most sensitive reaction with respect to all three fuels shown in Figure 12. When NO is present, the relatively less reactive  $HO_2$  radical formed in reaction (R1) is converted to OH via (R3). In the process, NO is converted to  $NO_2$ , which in turns reacts with  $CH_3$  to form  $CH_3O$  while converting  $NO_2$  back to NO in reaction (R4). In addition,  $NO_2$  generated in reaction (R3) reacts with fuel molecules to form alkyl radicals and HONO via reaction (R7). Then, HONO undergoes unimolecular decomposition to produce OH radicals and NO via reaction (R9). In addition, HONO is also generated by the decomposition of  $HNO_2$  formed in reaction (R6).

The comparison of the experimental data in Figure 8 and Figure 9 shows that the effect of  $NO_x$  in reducing the ignition delay time is more pronounced for iso-octane as compared to n-dodecane. This is due the fact that highly-branched paraffinic molecules, such as iso-octane, have a higher number of  $CH_3$  groups compared to normal-paraffins. Therefore, iso-octane generates a higher concentration of  $CH_3$  intermediates, which in turn helps to increase the sensitized oxidation of  $NO_x$  via reaction (R4).

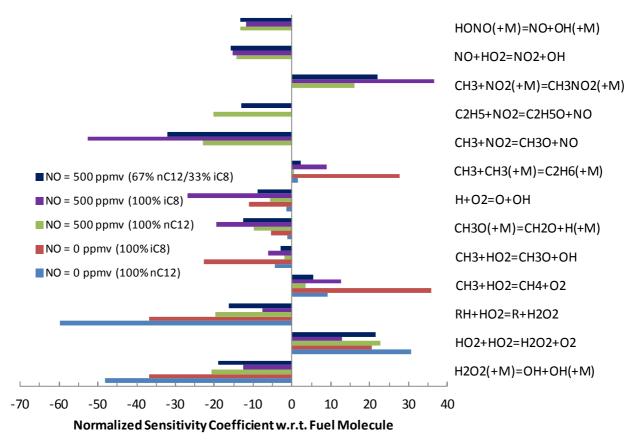


Figure 12. Normalized sensitivity coefficients for stoichiometric fuel/air mixtures of neat n-dodecane (nC<sub>12</sub>), neat iso-octane (iC<sub>8</sub>) and 67 mol% nC<sub>12</sub>/33 mol% iC<sub>8</sub> at 875 K and 1 atm with and without NO.

#### V. Conclusions

Atmospheric pressure flow reactor experiments were performed to investigate the ignition characteristics of FT and HRJ alternative jet fuels in comparison to conventional JP-8 between 832 K and 917 K. Experiments were conducted with standard air as well as vitiated air composed of 17 mol %  $O_2$  and  $NO_x$  between 0 and 755 ppmv. Experiments were also performed with jet fuel surrogate components such as n-dodecane and iso-octane to investigate the ignition behavior of normal- and iso-paraffins, respectively. Ignition delay time measurements show that the ignition behavior of Shell-SPK is very similar to that of JP-8, while HRJ-Tallow and HRJ-Camelina have

longer ignition delay times than JP-8. However, Sasol-IPK showed varying ignition behavior relative to JP-8 depending on the temperature with the highest overall activation energy. The presence of  $NO_x$  in the oxidizer stream reduced the ignition delay time of the jet fuels significantly. A similar behavior was also observed for surrogate jet fuels as well. However, the effect of  $NO_x$  on iso-octane ignition delay time was more pronounced than n-dodecane. Surrogate kinetic modeling results were also compared with the experimental data for the effect of  $NO_x$ . Overall, the modeling results agree with trends observed for the effect of  $NO_x$  on ignition delay time. However, the ignition delay time predictions for Sasol-IPK are much longer than the experimental data. This is due to the fact that the representation of iso-paraffinic components in Sasol-IPK is not correctly represented by iso-octane alone. Work is in progress to investigate additional surrogate components that can better represent iso-paraffinic jet fuels.

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#### References

- [1] A. Amato, J. M. Seitzman, and T. C. Lieuwen, "Emissions from Oxyfueled or High-Exhaust Gas Recirculation Turbines," in *Gas Turbine Emissions*. New York, NY: Cambridge University Press, 2013.
- [2] B A Fleck, A Sobiesiak, and H A Becker, "Experimental and Numerical Investigation of the Novel Low NOx CGRI Burner," *Combustion Science and Technology*, vol. 161, p. 89–112, 2000.
- [3] J. Kalb and T. Sattelmayer, "Lean Blowout Limit and NO x Production of a Premixed Sub-ppm NO x Burner with Periodic Flue Gas Recirculation," *Journal of Engineering for Gas Turbines and Power*, vol. 128, no. 2, p. 247 –54, 2004.
- [4] K. Al-Qurashi, A. D. Lueking, and A. L. Boehman, "The deconvolution of the thermal, dilution, and chemical effects of exhaust gas recirculation (EGR) on the reactivity of engine and flame soot," *Combustion and Flame*, vol. 158, p. 1696–1704, 2011.
- [5] A. M. ElKady, A. T. Evulet, A. Brand, T. P. Ursin, and A. Lynghjem, "Application of Exhaust Gas Recirculation in a DLN F-class Combustion System for Postcombustion Carbon Capture," *Journal of Engineering for Gas Turbines and Power*, vol. 131, no. 3, p. 034505, 2009.
- [6] C. P. Goyne, J. C. McDaniel, R. H. Krauss, and W. B. Whitehurst, "Test Gas Vitiation Effects in a Dual-Mode Scramjet Combustor," *Journal of Propulsion and Power*, vol. 23, pp. 559-565, 2007.
- [7] P. Gokulakrishnan et al., "Experiments and modeling of propane combustion with vitiation," *Combustion and Flame*, vol. 161, p. 2038–2053, 2014.
- [8] C. C. Fuller, P. Gokulakrishnan, M. S. Klassen, R. J. Roby, and B. V. Kiel, "Investigation of the Effects of Vitiated Conditions on the Autoignition of JP-8," *45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, vol. AIAA 2009-4295, August 2009.
- [9] C. C. Fuller, P. Gokulakrishnan, M. S. Klassen, R. J. Roby, and B. V. Kiel, "Investigation of the Effect of Nitric Oxide on the Autoignition of JP-8 at Low Pressure Vitiated Conditions," in 49th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Orlando, FL, 2011.
- [10] C. Fuller et al., "Effects of Vitiation and Pressure on Laminar Flame Speeds of n-Decane," in *AIAA 50th Aerospace Science Meeting*, Nashville, TN, 2012, pp. AIAA 2012-0167.
- [11] P. Gokulakrishnan, G. Gaines, M. S. Klassen, and R.J. Roby, "Autoignition of Aviation Fuels: Experimental and Modeling Study," in *AIAA/ASME/SAE/ASEE 43rd Joint Propulsion Conference*, vol. AIAA 2007-5701., Cincinnati, OH, 2007.
- [12] T. Edwards, UDRI-AFRL GCxGC Analysis of Jet Fuels, 2014, Peronal Communication.
- [13] S. H. Won, P. S. Veloo, J. Santner, Y. Ju, and F. L. Dryer, "Comparative Evaluation of Global Combustion

- Properties of Alternative Jet Fuels," in 51st AIAA Aerospace Science Meeting, Dallas, TX, 2013, pp. AIAA 2013-0156.
- [14] P. Gokulakrishnan, G. Gaines, J. Currano, M. S. Klassen, and R. Roby, "Experimental and Kinetic Modeling of Kerosene-Type Fuels at Gas Turbine Operating Conditions," *Journal of Engineering for Gas Turbines and Power*, vol. 129, pp. 655-663, 2007.
- [15] P. Gokulakrishnan, C. C. Fuller, R. G. Joklik, and M. S. Klassen, "Chemical Kinetic Modeling of Ignition and Emissions from Natural Gas and LNG Fueled Gas Turbines," in *Proceedings of ASME Turbo Expo 2012*, Copenhagen, Denmark, 2012, pp. GT2012-69902.
- [16] P. Gokulakrishnan and M. S. Klassen, "NOx and CO Formation and Control," in *Gas Turbine Emissions*, T. Lieuwen and V. Yang, Eds. New York, NY: Cambridge University, 2013, pp. 175-208.
- [17] H J Curran, P Gaffuri, W J Pitz, and C K Westbrook, "Curran, H. J., Gaffuri, P., Pitz, W. J. and Westbrook, C. K., "A Comprehensive Modeling Study of iso-Octane Oxidation", Combust. Flame, Vol.129, 2002, pp. 253–280.".
- [18] P. Gokulakrishnan, M. S. Klassen, and R. J. Roby, "Ignition Characteristics of A Fischer-Tropsch Synthetic Jet Fuel," in *ASME Turbo Expo 2008: Power for Land, Sea and Air*, Berlin, Germany, 2008, pp. GT2008-51211.
- [19] P. Gokulakrishnan, M. S. Klassen, and R. J. Roby, "Development of Detailed Kinetic Mechanism to Study Low Temperature Ignition Phenomenon of Kerosene," in *ASME Turbo Expo 2005*, Reno-Tahoe, NV, 2005, pp. GT2005-68268.
- [20] A. Miyoshi, "Systematic Computational Study on the Unimolecular Reactions of Alkylperoxy (RO2), Hydroperoxyalkyl (QOOH), and Hydroperoxyalkylperoxy (O2QOOH) Radicals," *Journal of Physical Chemistry A*, vol. 115, p. 3301–3325, 2011.
- [21] S W Benson, Thermochemical Kinetics. New York: John Wiley & Sons, 1976.
- [22] E R Ritter and J W Bozzelli, "THERM: Thermodynamic Property Estimation for Gas Phase Radicals and Molecules," *International Journal of Chemical Kinetics*, vol. 23, pp. 767-778, 1991.
- [23] T. Mendiara and P. Glarborg, "Ammonia chemistry in Oxy-Fuel Combustion of Methane," *Combustion and Flame*, vol. 156, pp. 1937-1949, 2009.
- [24] W. Chan, S. M. Heck, and H. O. Pritchard, "Reaction of Nitrogen Dioxide with Hydrocarbons and its InÑuence on Spontaneous Ignition. A Computational Study," *Physical Chemistry and Chemical Physics*, vol. 3, pp. 56-62, 2001.
- [25] S Vasu, D F Davidson, and R K Hanson, "Jet Fuel Ignition Delay Times: Shock Tube Experiments Over Wide Conditions and Surrogate Model Predictions," *Combustion and Flame*, vol. 152, p. 125–143, 2008.
- [26] S. S. Vasu, D. F. Davidson, Z. Hong, V. Vasudevan, and R. K. Hanson, "n-Dodecane oxidation at high-pressures Measurements of ignition delay times and OH concentration time-histories," *Proceedings of the Combustion Institute*, vol. 32, p. 173–180, 2009.
- [27] A Violi et al., "Experimental Formulation and Kinetic Model for JP-8 Surrogate Mixtures," *Combustion Science and Technology*, vol. 174, pp. 399-417, 2002.
- [28] S. Dooley et al., "A Jet Fuel Surrogate Formulated by Real Fuel Properties," *Combustion and Flame*, vol. 157, pp. 2333-2339, 2010.
- [29] A. Shrestha, Z. Zheng, T. Badawy, N. Henein, and P. Schihl, "Development of JP-8 Surrogates and their Validation using Ignition Quality Tester," *SAE International Journal of Fuels and Lubricants*, vol. 7, pp. 337-351, 2014.
- [30] D. Kim, J. Martz, and A. Violi, "A surrogate for emulating the physical and chemical properties of conventional jet fuel," *Combustion and Flame*, vol. 161, p. 1489–1498, 2014.
- [31] "ASTM D 6890," ASTM International, West Conshohocken, PA, 2007.
- [32] D. Goodwin. Cantera. [Online]. www.cantera.org