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Ignition behavior and surrogate modeling of JP-8 and of camelina and tallow hydrotreated renewable jet fuels at low temperatures

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ABSTRACT

The autoignition characteristics of the conventional jet fuel, JP-8, and the alternative jet fuels, camelina and tallow hydrotreated renewable jet (HRJ) fuels, are investigated using a rapid compression machine and the direct test chamber charge preparation approach. Ignition delay measurements are made at low compressed temperatures ($625 \text{ K} \leq T_c \leq 730 \text{ K}$), compressed pressures of $p_c = 5, 10, \text{ and } 20 \text{ bar}$, and equivalence ratios of $\phi = 0.25, 0.5 \text{ and } 1.0$ in air. The HRJ fuels ignite more readily than JP-8 for all tested conditions, consistent with derived cetane number data in the literature. The camelina and tallow HRJ fuels exhibit similar autoignition characteristics, but the two fuels can be distinguished under stoichiometric conditions. Kinetic modeling is conducted with a 2-component surrogate (10% *n*-dodecane/90% 2-methylundecane) and a single component surrogate (2-methylnonane) to evaluate the potential to predict ignition behavior of the HRJ fuels. Modeling results indicate that the surrogate fuels can only provide useful predictions at a limited set of conditions ($p_c = 5 \text{ bar}$ and $\phi = 1.0$), and that the agreement of the model and experimental data improves with decreasing compressed pressure. Under most conditions, the 2-component surrogate provides better prediction of ignition behavior, but the single component surrogate is superior at low pressures near the negative temperature coefficient region.

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1. Introduction

A strong interest exists within the United States military and the civilian aviation field to replace conventional, petroleum-based jet fuels with alternative kerosene-type fuels that can be produced using biomass, coal, or natural gas [1,2]. The U.S. Department of Defense has adopted initiatives to support this interest in order to reduce reliance of foreign energy sources, to mitigate supply disruption risks, and to develop economically-attractive fuel sources in the face of rising petroleum prices.

Significant progress toward the development of “drop-in” replacement fuels has been made by the U.S. Air Force using Fischer–Tropsch (F–T) synthetic jet fuels. S-8, the synthetic F–T alternative to conventional JP-8, has been approved for use in 50/50 blends with JP-8 in virtually all USAF aircraft [3]. Tests to certify 50/50 blends of hydrotreated renewable jet (HRJ) fuel with JP-8 are ongoing [4], which will provide a renewable fuel stream for powering USAF aircraft in the future. The certification process may be aided by simulations that predict combustion behavior such as autoignition response, flame speed, and extinction limits; however,

only limited data has been reported in the literature that could support and validate these types of models for biosynthetic and synthetic jet fuels [5–9]. Recent work by Hui et al. [6] has compared the reactivity of the conventional jet fuel, Jet-A, with several synthetic jet fuels, including camelina-derived HRJ and tallow-derived HRJ, both of which are investigated in this work. Hui et al. [6] observed enhanced reactivity of the HRJ fuels relative to Jet-A in the form of higher derived cetane numbers and shorter ignition delay times for the HRJ fuels. Additionally, Wang and Oehlschlaeger [9] have reported valuable autoignition delay measurements for several F–T fuels and for Jet-A. The data of Wang and Oehlschlaeger [9] demonstrate shorter ignition delay times for the S-8 relative to Jet-A, and specifically at temperatures lower than 1000 K. Shorter ignition delay times for S-8 relative to JP-8 have also been noted in the rapid compression machine study by Kumar and Sung [8]. Kumar and Sung conducted tests in the low-to-intermediate temperature range (615–933 K), where S-8 ignited faster than JP-8 for all test conditions. The same behavior has been identified by Gokulakrishnan et al. [5] in their comparison of JP-8 and S-8 ignition delay times in an atmospheric pressure flow reactor, where the enhanced reactivity of S-8 relative to JP-8 is attributed to the lack of aromatics in the S-8 fuel. Additional work, by Kahandawala et al. [7], investigated the influence of chemical composition differences between S-8 and JP-8 and their influence on ignition delay

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times and soot precursor formation. For the high temperature (1100–1600 K), lean ($\phi = 0.5$) test region considered, the ignition delay measurements for S-8 and JP-8 were very similar. These findings concur with those of Wang and Oehlschlaeger [9], where S-8 and JP-8 could only be distinguished at test temperatures less than 1000 K.

The purpose of this paper is to investigate the ignition characteristics of HRJ fuels relative to conventional military-grade jet fuel (JP-8), and to evaluate the potential for predicting the ignition behavior of the biosynthetic HRJ fuels with either a 2-component surrogate or single-component surrogate. The results of this work provide fundamental data concerning the chemical ignition behavior of alternative HRJ fuels relative to JP-8, and will provide insight into how the ignition characteristics of synthetic fuels are influenced by changes in hydrocarbon species distribution.

2. Experimental methods

2.1. Heated rapid compression machine

Ignition delay measurements were made using a pneumatically-driven, hydraulically-stopped rapid compression machine (RCM) that appears in Fig. 1. The RCM uses a piston to rapidly compress (25–30 ms) a homogeneous mixture of fuel, oxidizer, and diluent gases to elevated temperatures and pressures. At the end of compression, the reactive mixture is held at constant volume until the fuel autoignites. Pressure is monitored during the test using a piezoelectric pressure transducer (Kistler 6125C, uncoated), and the resulting data are used to calculate the time required for autoignition upon achievement of a given test condition (i.e., ignition delay). The RCM uses a creviced piston to promote temperature homogeneity in the core gases during compression. The creviced piston is based on the numerically-optimized design of Mittal and Sung [10]. The RCM is preheated so that all fuel components are vaporized prior to commencing the compression stroke. The initial temperature of the RCM test chamber is maintained by a control system composed of six wall-embedded thermocouples and six band heaters wrapped in insulation. Temperature measurements along the interior wall of the test chamber confirmed that a uniform temperature profile is maintained, with all measurements falling within 1.3% of the temperature setpoint. Additional characterization data regarding the RCM and heating system can be found in prior publications [11,12].

2.2. Direct test chamber charge preparation approach

Creation of a reactive charge in the RCM requires preheating to volatilize all of the jet fuel components. A unique approach has been used in this study to prepare these premixtures, in which fuel is injected directly into the RCM test chamber rather than being prepared in a separate mixing vessel before being transferred to

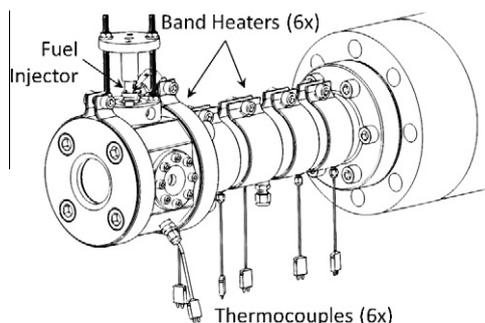


Fig. 1. Schematic of the RCM test chamber, illustrating position of the fuel injector, band heaters, and wall-embedded thermocouples.

the RCM. Preparation of the charge directly in the RCM has distinct advantages when testing non-volatile fuels, and for convenience, the method is referred to here as the direct test chamber (DTC) charge preparation approach. In the conventional approach, fuel is added to an independent vessel with oxidizer and diluent gases, which are subsequently heated and stirred for a period of hours. This premixture must be made with sufficient mass to be used for multiple RCM tests, and the initial pressure may approach 2.5–3.0 bar. The fuel pressure in the mixing vessel is correspondingly higher at these mixture conditions than may be required in the RCM combustion chamber where the total initial test pressure is much lower (0.5–2.0 bar). Preparation of the reactive charge directly in the RCM test chamber minimizes the fuel partial pressure; hence, the initial temperature requirement for a given equivalence ratio. Lower initial test temperatures are useful for minimizing fuel pyrolysis concerns and extending the range of testable equivalence ratios.

The creation of a premixture directly in the RCM requires the ability to accurately load small quantities of fuel into the combustion chamber. Tests in this study utilized fuel masses between 10 and 100 mg. These fuel quantities are dispensed into the RCM by a gasoline direct injector mounted on the top of the test chamber, as depicted in Fig. 1. The injector is water-cooled to promote consistent performance as the RCM is heated to temperatures in excess of 100 °C. A hydraulic accumulator maintained at 3 MPa is used to pressurize the fuel line, and the injector is operated by a National Instruments LabView virtual instrument that interfaces with a custom injector-driver box. Each combination of hydraulic accumulator, fuel injector and jet fuel are carefully calibrated to ensure the correct quantity of fuel is injected into the test chamber. Details of the calibration procedure are documented in a prior characterization study [13]. To compensate for any shot-to-shot variation in fuel mass, fuel is loaded by using several short injection pulses (typically 10–30).

2.3. Test fuels

Ignition delay times were measured in this study for the conventional military jet fuel, JP-8, and for the two hydrotreated renewable jet fuels (HRJ), camelina HRJ (CHRJ) and tallow HRJ (THRJ). The fuel samples have been furnished by the Air Force Research Laboratory at Wright Patterson Air Force Base, and carry the standard identifiers of POSF-6169 (JP-8), POSF-6152 (CHRJ), and POSF-6308 (THRJ). A total ion chromatogram (TIC) for each of these fuels appears in Fig. 2. The JP-8 TIC is characterized by large peaks for each of the normal hydrocarbons between C₈ (*n*-octane) and C₁₆ (*n*-hexadecane). The other peaks correspond to *iso*-paraffins, cycloparaffins, and aromatics (15.7 vol.%). The TICs for the HRJ fuels are distinctly different, and the data show evidence of the high ratio of branched to normal paraffinic content that is characteristic of HRJ fuels [4,14]. In fact, these HRJ fuels are expected to consist almost entirely of branched and normal paraffins with aromatics and olefins together comprising less than 1% of the fuel blend. The TIC data have been analyzed to estimate that the camelina HRJ and tallow HRJ fuels both have a branched to normal paraffin mass ratio of approximately 90:10 [14]. Although not apparent in the TIC data, cycloparaffins do constitute a small amount of the CHRJ (10 vol.%) and THRJ (2 vol.%) fuels [4]. For testing and analysis purposes, the fuel average molecular formulae are estimated using the methods of Rao et al. [15] as C_{11.89}H_{23.06}, C_{11.51}H_{24.96}, and C_{12.59}H_{27.10} for JP-8, camelina HRJ, and tallow HRJ, respectively.

2.4. Data analysis and experimental uncertainty

Pressure history data recorded during the tests are used to calculate ignition delays with a commonly accepted definition [10].

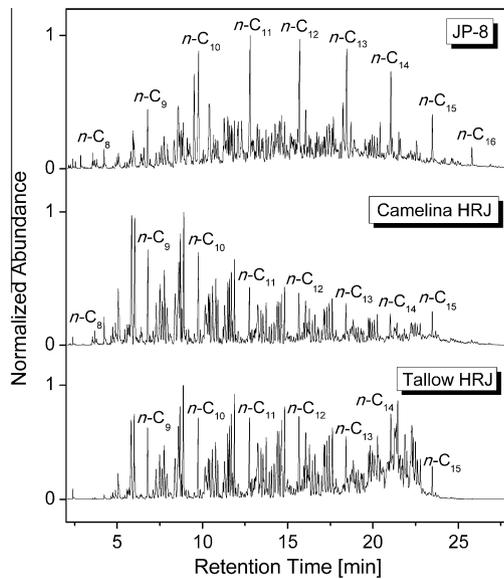


Fig. 2. Total ion chromatograms for JP-8, camelina HRJ, and tallow HRJ fuels.

Sample pressure data appear in Fig. 3 and are used to illustrate the ignition delay periods described as follows. Time $t = 0$ corresponds to the end of compression or top dead center (TDC) when the time derivative of the pressure (dp/dt) becomes negative. The first stage of ignition, which is not present in all tests, is identified some period of time (τ_1) later as a local maximum in dp/dt . The main hot ignition event occurs a time, τ , after TDC and is referred to in this paper as the overall or total ignition delay. The difference between these two ignition delays is referred to as τ_2 , or the second stage ignition delay. The data in this paper are focused on reporting total ignition delays, and as such, the term ignition delay refers to τ .

Compressed gas temperatures, T_c , are calculated at TDC and used as the reference temperature for comparing ignition delay experiments. The compressed temperatures are calculated using the relationship, $\int_{T_0}^{T_c} \frac{\gamma}{\gamma-1} \frac{dT}{T} = \ln \frac{p_c}{p_0}$, where T is temperature, γ is the specific heat ratio (C_p/C_v), p is pressure, and the subscripts 0 and c correspond to initial and compressed conditions, respectively. This relationship, for the adiabatic compression of ideal gases, is expected to represent the core gas temperature because heat losses are restricted to the boundary layer near the wall when a creviced piston is used [10]. Calculations for T_c rely on heat capacity data for

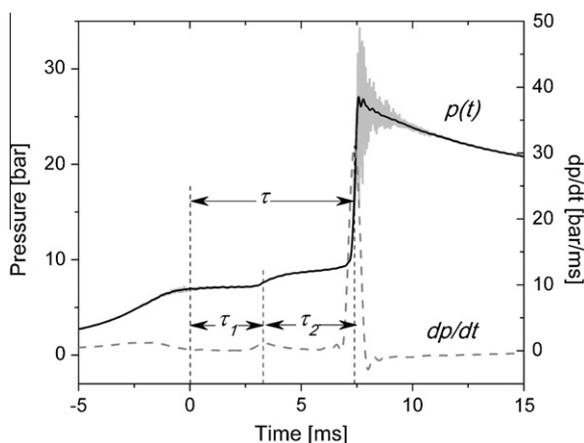


Fig. 3. Sample JP-8 ignition pressure history data and pressure derivative data (dp/dt) illustrating the filtering operation and the ignition delay definitions for τ_1 , τ_2 and τ . Test conditions: $\phi = 1.0$, $p_0 = 0.68$ bar, $T_0 = 125$ °C.

all gas phase components in the charge, but it is impractical to quantify all the species in the complex hydrocarbon blends tested in this study. Furthermore, thermophysical property data are unavailable for many of these species. This issue is addressed for the JP-8 tests by using a surrogate¹ proposed by Violi et al. [16] to represent the fuel during T_c calculations. For the HRJ fuels, which are greater than 99% paraffinic, we can calculate T_c using the thermophysical properties of any single paraffin. This is true because mixtures have been made by injecting a known fuel mass, and subsequently calculating fuel mole fractions from the molecular weight estimations that are based upon the proposed average molecular formulae. Although each paraffin has a unique constant-pressure heat capacity (C_p), weighting the values by their respective fuel mole fractions (X_f) makes the differences in $X_f \cdot C_p$ negligible. For all of the compressed temperature calculations, we have used the thermophysical property data of *n*-dodecane [17]. The use of a single paraffin to represent the synthetic fuel when calculating compressed temperatures has been evaluated in a prior work [13], where calculations showed that any single normal paraffin with between 8 and 16 carbon atoms always yielded a compressed temperature within 4 K of the calculated compressed temperature obtained using a more complicated hydrocarbon blend intended to mimic the component distribution in a synthetic fuel.

Three tests have been conducted for each condition, and the standard deviations of the measurements are represented by error bars when presenting results in this paper. Total ignition delay measurements were repeatable to within $\pm 5\%$ and first stage ignition delay measurements were repeatable to within $\pm 8\%$. The main uncertainty in the results is the calculated compressed temperature, which relies on uncertainties in initial temperature (± 3 K), initial pressure ($\pm 0.08\%$), initial volume (± 0.004 L), compressed pressure (± 0.3 bar), injected fuel mass ($\pm 3\%$), and thermophysical property data ($\pm 0.5\%$). These inputs have been used to calculate the uncertainty in the compressed temperature as $\pm 1.25\%$ (8–9 K), which is represented by error bars in subsequently presented data. Uncertainty in the timing of TDC is not considered significant for these tests, and has not been included. Sufficient heat release prior to the end of compression could obscure application of our ignition delay definition, but effective volume testing where all of the oxygen is replaced with nitrogen indicates that this is not a significant source of uncertainty because the non-reactive pressure tests closely match the reactive pressure data up to the point of TDC.

2.5. Experimental test conditions

Ignition delay measurements have been made in the RCM for JP-8, CHRJ and THRJ fuels at compressed temperatures of $625 \text{ K} \leq T_c \leq 730 \text{ K}$, compressed pressures of $p_c = 5, 10$ and 20 bar, and at equivalence ratios of $\phi = 0.25, 0.5$ and 1.0 . All reactive charges have been prepared in synthetic dry air, 21% O_2 and 79% N_2 . The compressed temperatures and pressures are attained through a combination of changes in compression ratio and by changing the initial temperature and pressure of the charge. Initial temperatures between 110 °C and 125 °C were selected to ensure complete fuel vaporization, which has been confirmed using gas chromatography/mass spectrometry (GC/MS) analysis as discussed in prior work [13]. The prior characterization [13] work also documents the uniformity of the test chamber initial temperatures, and provides data demonstrating the accuracy of the expected fuel loading and time required for charge homogenization in the test chamber. The upper limit of tested compressed temperatures

¹ JP-8 surrogate composition: 73.5% *n*-dodecane, 5.5% *iso*-octane, 10% methylcyclohexane, 10% toluene, 1% benzene.

was selected to avoid first stage ignition activity during the compression stroke. Such an occurrence prohibits use of the ignition delay definition, and prevents accurate assignment of a compressed temperature.

3. Kinetic modeling for HRJ fuel surrogate

Kinetic modeling has been used to evaluate the potential of using a simple 2-component surrogate fuel or single-component surrogate fuel to predict the ignition behavior of the biosynthetic HRJ fuels. The major species in the HRJ fuels are *n*-paraffins and *iso*-paraffins, and analysis of the TIC in Fig. 2 yielded a composition estimate for both the CHRJ and THRJ fuels of 10% *n*-paraffins and 90% *iso*-paraffins when cycloparaffins are neglected. This estimation is consistent with data in the literature [4], and has been chosen as basis for setting the 2-component surrogate fuel composition. Considering the average molecular formulae presented in Section 2.3 and the TIC data for the fuels, we propose using a surrogate fuel blend of two C₁₂ hydrocarbons: 10% *n*-dodecane and 90% 2-methylundecane. A second, single-component surrogate (2-methylnonane), was chosen after having reviewed the modeling results from the 2-component surrogate fuel. The selection of 2-methylnonane was made to address deficiencies that the 2-component surrogate exhibited in predicting ignition delay times approaching the negative temperature coefficient region at low pressures. The results of the simulations using each of these surrogates will be reviewed in Sections 4.2 and 4.3.

The proposed surrogates have been used with the kinetic model of Sarathy et al. [18] for modeling the oxidation of 2-methylalkanes. The kinetic mechanism consists of 7171 chemical species and 31,669 reactions and includes refined chemistry for C₈–C₁₆ *n*-alkanes [19]. We have selected this mechanism because to our knowledge, no other mechanism exists which can accommodate high molecular weight *iso*-paraffins. However, we note that validation studies published with the mechanism considered fuels of only modest molecular weight: 2-methylhexane, 2-methylheptane, and *n*-octane. The authors suggest that validation using these fuels is representative of the class of 2-methylalkanes, and that the results can be considered valid for larger 2-methylalkanes where the same reaction rate rules have been applied [18].

The kinetic simulations have been conducted in CHEMKIN Pro using the closed homogeneous batch reactor model. Heat loss from the RCM has been considered in these models by including a volume addition term in the effective volume profiles that constrain volume during the CHEMKIN simulations. In this approach, the time-dependent effective volume is determined empirically as a CHEMKIN input so that the calculated pressure during a non-reactive simulation (adiabatic compression and expansion) matches that of the non-reactive experimental pressure data (non-adiabatic compression and expansion). The non-reactive pressure data used to calculate the effective volume profiles are obtained by compressing an inert mixture of nitrogen and fuel. These mixtures mimic the reactive tests, except all of the oxygen has been displaced by nitrogen. A thorough discussion of this approach, including the equations needed to determine the effective volume profile from the pressure data appear in Mittal [20] and Mittal and Sung [10]. Readers may obtain the effective volume profiles for modeling purposes by emailing the corresponding author.

4. Results and discussion

The raw pressure history data recorded in this work has been used to calculate ignition delay data which is reported and discussed in this section. Sample pressure history data is included as Supplemental electronic data with the publication, and they are available for a subset of tests that covers all the tested pressures, equivalence ratios and fuels.

4.1. Comparison of conventional and biosynthetic paraffinic kerosene fuels

Ignition delay measurements for JP-8, CHRJ and THRJ fuels recorded in this work are compared in Fig. 4a with Jet-A ignition delay measurements reported by Dooley et al. [21] and with S-8 ignition delay measurements reported by Wang and Oehlschlaeger [9]. All measurements from this study that appear in Fig. 4a were taken for $\phi = 1.0$ and a compressed pressure of 20 bar. The shock tube measurements reported by Dooley et al. [21] were made at $\phi = 1.0$ and pressures between 14.5 and 25.2 bar, and the shock tube measurements reported by Wang and Oehlschlaeger were made at

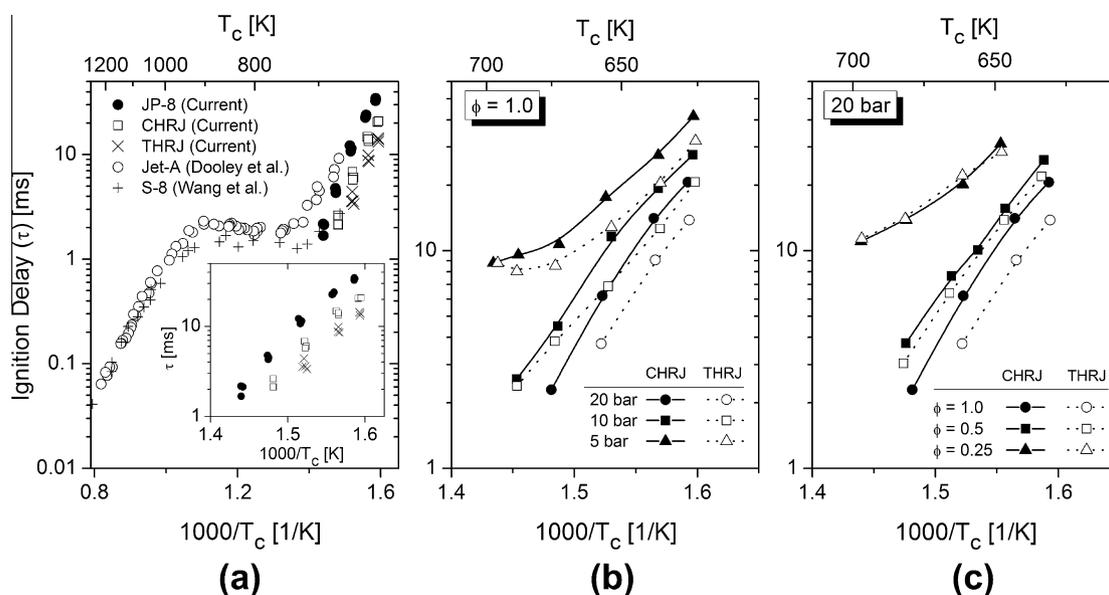


Fig. 4. (a) Comparison of conventional, synthetic, and biosynthetic kerosene fuels. Data for JP-8, CHRJ, and THRJ fuels are based on the current work, the Jet-A data are adapted from the work of Dooley et al. [21], and the S-8 data are adapted from the work of Wang et al. [9]. Measurements correspond to $p = 20$ bar and $\phi = 1.0$. The inset figure provides more resolution for the JP-8, CHRJ and THRJ fuels data. (b) Ignition delays for CHRJ and THRJ fuels at $\phi = 1.0$ and $p_c = 5, 10, \text{ and } 20$ bar. (c) Ignition delays for CHRJ and THRJ fuels at $p_c = 20$ bar and $\phi = 0.25, 0.5, \text{ and } 1.0$.

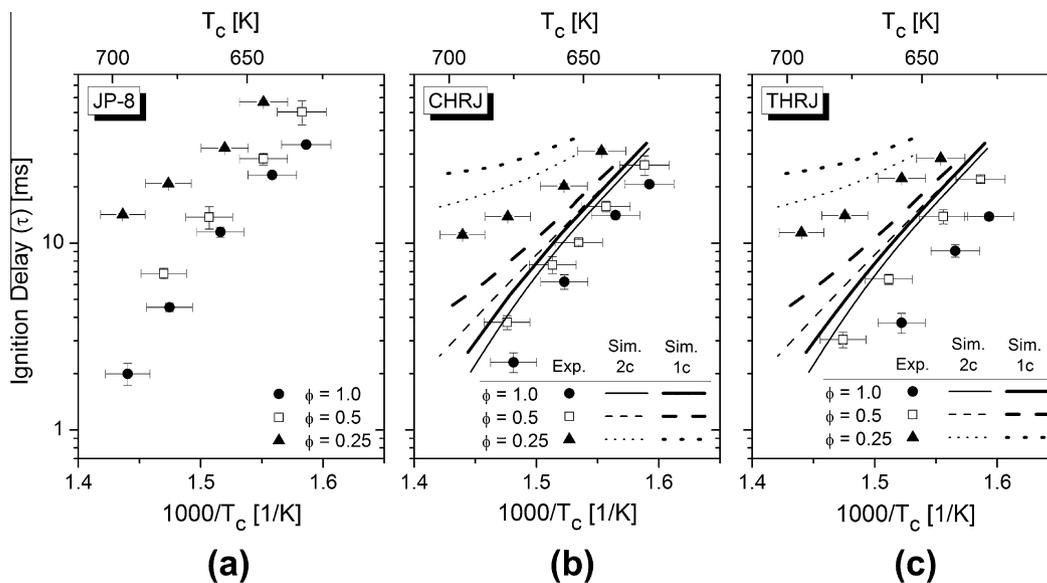


Fig. 5. Ignition delay measurements for (a) JP-8, (b) CHRJ, and (c) THRJ fuels at $p_c = 20$ bar and $\phi = 0.25, 0.5$ and 1.0 . The same set of kinetic simulation results appear in (b) and (c) for $\phi = 0.25, 0.5$ and 1.0 , using the proposed single component (Sim. 1c) and 2-component (Sim. 2c) surrogates.

$\phi = 1.0$ and pressures between 18.7 and 24.0 bar. These data have been scaled to 20 bar using $\tau \sim 1/p$ to facilitate the comparison. Ignition delays for the conventional petroleum-based jet fuels JP-8 and Jet-A are generally consistent, which is not unexpected because the compositions of the two fuels are quite similar [22]. The agreement between the two datasets improves as the compressed temperature decreases. For shorter ignition delays, specifically those less than 10 ms, the measurements in the RCM become increasingly affected by preignition reactions that may occur during the late stages of the compression stroke. The shock tube data are not influenced by this type of physical process, and we attribute the qualitative deviation in the two datasets to the influence of compression. This hypothesis is meant to address only the qualitative nature of the ignition delay trend and not the absolute measurements. We are comparing two different fuels and we should not expect perfect congruency between the datasets. The influence of the preignition reactions during compression may cause the reported ignition delays to be marginally shorter (likely on the order of 1 ms) than tests with near-instantaneous compression. However, we do note that kinetic modeling results reported subsequently would be similarly affected by compression because the same ignition delay definition is applied to the experimental results and modeling results, and because the compression stroke and heat loss processes are fully modeled. Therefore, the influence of compression should only be considered by the reader when comparing RCM results with data from a shock tube, and its consideration should not have any significant effect on the agreement between experimental and modeling results. S-8 has been chosen for comparison because it resembles the composition of the HRJ fuels, with greater than 80% of the blend being branched paraffins, and normal paraffins largely comprising the balance of the mixture [9]. Given the resemblance in composition between S-8 and the HRJ fuels, the similarity in ignition delays between the fuels is expected. The trend of enhanced reactivity of the synthetic fuel, relative to the conventional fuel is seen in the measurements from this work, as well as the S-8 data when compared to the Jet-A measurements.

The JP-8, CHRJ and THRJ fuels data in Fig. 4a are repeated in the inset figure for improved visibility. Error bars have been omitted from these data for clarity. For a given test condition, the JP-8 clearly exhibits a longer ignition delay than either of the HRJ fuels. On average, the JP-8 ignition delays are two times and three times longer than those of the CHRJ and THRJ fuels, respectively. These

differences are outside the uncertainty range for the measurements. The enhanced reactivity of the HRJ fuels relative to JP-8 can be attributed primarily to the lack of aromatics in the HRJ fuels. Conventional jet fuel may contain up to 25% aromatics, and the blend of JP-8 tested in this study contained 15.7% aromatics by volume. The difference in reactivity between an HRJ fuel and conventional jet fuel (Jet-A) has also been described by Hui et al. [6], in which several synthetic jet fuels were tested in a RCM. Hui et al. observed shorter first stage and total ignition delays for the CHRJ and THRJ fuels compared to Jet-A. Our findings are also consistent with derived cetane number (DCN) data reported in the literature. JP-8 DCNs of 45.2–46.7 have been reported previously [23], while a DCN of 53.9 has been obtained for CHRJ fuel using ASTM D6890 [24]. The DCN provides a measure of fuel ignition quality, and a higher number corresponds to a shorter ignition delay time. The DCN of the CHRJ fuel is notably higher than the DCN described for JP-8 (45.2–46.7), and it is similar to the DCN of S-8 (58.7), an F-T synthetic jet fuel that has been tested in the literature [25]. To our knowledge, no DCN data have been reported for THRJ fuel, although a DCN of 49.82 has been reported for a 50/50 blend of JP-8/THRJ fuel [26]. The same report noted a DCN of 49.22 for a 50/50 blend of JP-8/CHRJ fuel, which may seem to suggest a modest difference between the fuels. However, the 0.6 point difference between the DCNs cannot be considered significant because it is within the uncertainty range of a DCN measurement [24]. Comparisons of unique data points for these two HRJ fuels in Fig. 4a are within the uncertainty range of the measurements, but the overall trend suggests that the ignition delays for the fuels are distinct.

Additional comparisons of the HRJ fuels appear in Fig. 4b and c. The error bars have been omitted from these data for clarity, and the authors note that the data for the two fuels at any given condition are within the uncertainty range of one another. However, trends within the datasets suggest the ignition characteristics of the two fuels are distinct under certain conditions. Considering Fig. 4b, where all measurements have been made at $\phi = 1.0$, the THRJ fuel ignition delays are generally shorter than for the CHRJ fuel, especially with decreasing compressed temperature. The variation between the datasets does not appear to be influenced by the compressed pressure. In Fig. 4c, where all data have been recorded with a compressed pressure of 20 bar, a different pattern appears, in which the ignition characteristics increase in resemblance as the charge is made more fuel-lean. Taken together,

Fig. 4b and c indicate that the hydrocarbon distribution of the two HRJ fuels influences ignition characteristics only for stoichiometric conditions, and not for fuel-lean mixtures.

Although the data indicates that THRJ fuel is more reactive than CHRJ fuel, this is not supported by the work of Hui et al. [6], which measured shorter total ignition delay times for CHRJ fuel than for THRJ fuel. Hui et al. [6] attributes the enhanced reactivity of CHRJ fuel to its greater content of *n*-paraffins (10.2 wt.%) relative to THRJ fuel (8.8 wt.%). Although it is true that additional *n*-paraffin content will impart enhanced reactivity to the fuel blend, it is difficult to be conclusive about this finding with only limited experimental data. The authors state this because the THRJ fuel also has less cycloparaffinic content [4] at 2 vol.% relative to the CHRJ fuel where cycloparaffins comprise 10 vol.%, and a larger fraction of the THRJ fuel is shifted toward higher hydrocarbons than for the CHRJ fuel. This shift is evident in the TIC data in Fig. 2 and in the average molecular formulae reported for the fuels in Section 2.3 (CHRJ: $C_{11.51}H_{24.96}$, and THRJ: $C_{12.59}H_{27.10}$). Both of these characteristics would tend to diminish reactivity of the CHRJ fuel relative to the THRJ fuel, and the authors believe these characteristics tend to support the data presented here, which suggest THRJ fuel exhibits shorter total ignition delays than CHRJ fuel.

4.2. Influence of equivalence ratio on ignition delay time measurements and surrogate predictions

Figure 5 reports ignition delay measurements for JP-8, CHRJ and THRJ fuels at a compressed pressure of 20 bar, and equivalence ratios of 1.0, 0.5 and 0.25. The total ignition delays for all of the fuels exhibit an inverse dependence on the equivalence ratio; and qualitatively, the $\phi = 1.0$ and the $\phi = 0.5$ tests exhibit more similarity than the $\phi = 0.5$ and the $\phi = 0.25$ tests for each fuel. The $\phi = 0.25$ test cases for all of the fuels provide evidence of the onset of negative temperature coefficient (NTC) behavior, a region which is characterized by a loss of reactivity with increasing temperature. No evidence of NTC behavior can be observed in the $\phi = 1.0$ and the $\phi = 0.5$ tests, although it may be expected to emerge at higher compressed temperatures.

For the CHRJ and THRJ fuels, the qualitative behavior of ignition delays with changing temperature is well-represented by the simulations using both the 2-component (10/90 *n*-dodecane/

2-methylundecane) and single component surrogate (2-methylnonane), however, the absolute magnitudes of the predicted ignition delays do not match measured values for either of the surrogates. It is worth noting that some of the predictions are within the estimated uncertainty of the compressed temperatures, but the mechanism and surrogates predict ignition delays that are longer than the measurements for all test cases. For all of the simulated cases, the 2-component surrogate exhibited shorter ignition delay times than the single-component surrogate, although the disparity between the surrogates for the $\phi = 1.0$ and $\phi = 0.5$ cases is typically only 1–2 ms across the entire range of simulated temperatures. The disparity between the predictions for the $\phi = 0.25$ cases is more significant with the 2-methylnonane ignition delay predictions typically 50% longer than the 10/90 *n*-dodecane/2-methylundecane predictions. The shorter ignition delay times predicted by the 2-component surrogate results in better agreement with the data for all test cases, and it is a better choice for simulating the HRJ fuels at 20 bar conditions and all stoichiometries. The overprediction noted for the mechanism of Sarathy et al. relative to the experimental data has been reported in the publication describing the mechanism [18], with respect to 2-methylhexane ignition delay measurements obtained with an RCM and published by Silke et al. [27]. However, the authors make this remark cautiously because the results reported here are for simplified surrogates that can, at best, approximate global behavior. The predictive accuracy of the model cannot be directly evaluated with the surrogate data reported here, although empirical feedback can be obtained. Typically, we may suggest improvement of the predictions by modifying the surrogate composition to include more reactive species (i.e., normal hydrocarbons), although the compositional changes that improve the predictions would not be reflective of the actual blend composition. A more realistic representation of the fuel may include di-alkylated paraffins (e.g., 2,5-dimethyldecane) or cycloparaffins, but these species will have a tendency to increase the ignition delay predictions, thus deteriorating the agreement with the data. Furthermore, we may not expect dramatic improvements in the predictions because at temperatures below the NTC region (~ 750 K), demethylation at the penultimate carbon does little to enhance reactivity, especially for alkane chain lengths greater than 7 carbons [28]. This analysis suggests that the model generally overpredicts the ignition delay, and that the mechanism may benefit from reassessment of the rate constants.

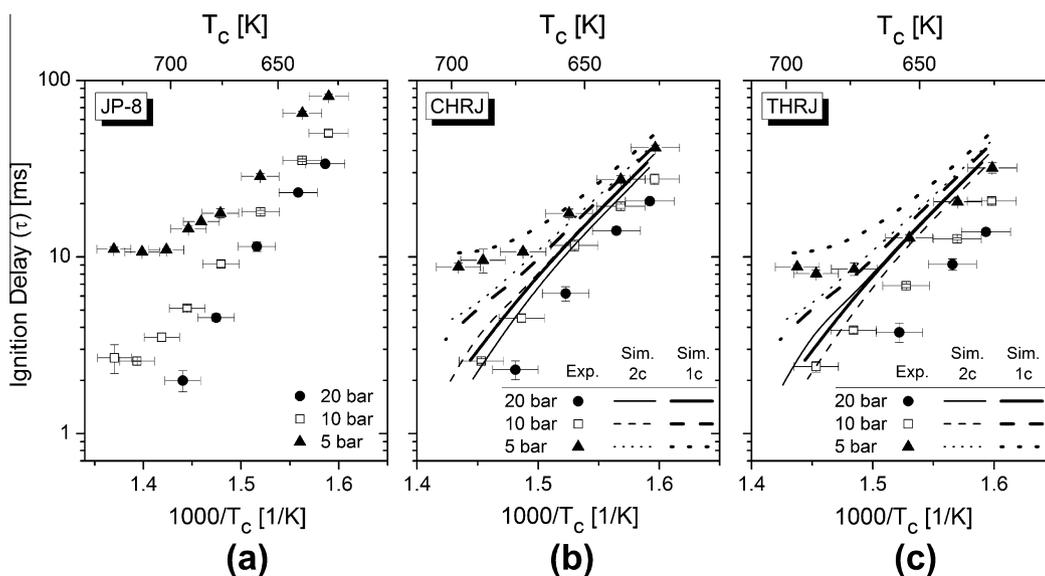


Fig. 6. Ignition delay measurements for (a) JP-8, (b) CHRJ, and (c) THRJ fuels at $\phi = 1.0$ and $p_c = 5, 10,$ and 20 bar. The same set of kinetic simulation results appear in (b) and (c) for $p_c = 5, 10,$ and 20 bar, using the proposed single component (Sim. 1c) and 2-component (Sim. 2c) surrogates.

Table 1
Ignition delay (τ) correlation parameters for JP-8, CHRJ and THRJ.

	A	m	n	T_a
JP-8	8.111E-11	-0.68	-0.75	13,739
CHRJ	5.250E-11	-0.60	-0.76	13,441
THRJ	2.136E-10	-0.67	-1.02	12,442

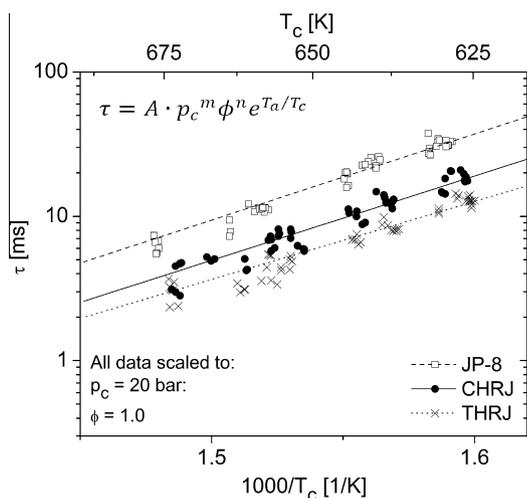


Fig. 7. Global ignition delay correlations for JP-8, CHRJ and THRJ fuels.

4.3. Influence of compressed pressure on ignition delay time measurements and surrogate predictions

Total ignition delays for JP-8, CHRJ and THRJ fuels are shown in Fig. 6 at compressed pressures of 5 bar, 10 bar, and 20 bar. All measurements were taken under stoichiometric conditions in air. The ignition delays for all fuels exhibit an inverse dependence on compressed pressure, and the 5 bar tests clearly demonstrate NTC behavior with increasing compressed temperature. NTC behavior for the JP-8 tests becomes visible near $T_c = 700$ K, while the transition temperature is slightly lower for the HRJ fuels at 680 K. Approaching the NTC region from low temperatures, the datasets for each of the compressed pressures begin to diverge for all the fuels. The distinction between the datasets arises because of the competition between decomposition (i.e., chain-terminating) of the alkyl hydroperoxy radical (QOOH) and an oxygen addition reaction (QOOH + O₂) with ensuing chain-branching. The competition between these pathways is highly pressure-dependent [28], and as the QOOH decomposition pathways are activated in the NTC region, the strong pressure dependence emerges.

The model predictions using the Sarathy et al. mechanism [18] with the 10/90 *n*-dodecane/2-methylundecane surrogate and the 2-methylnonane surrogate are included in Fig. 6b–c. The model results for the 2-component surrogate reflect the functional dependence on pressure, including prediction of the pronounced NTC region for the 5 bar CHRJ and THRJ fuels test results. Considering the aggregate results, the mechanism predictions capture the pressure dependence with more accuracy than the equivalence ratio dependence, as presented in Section 4.2. The best agreement with the 2-component surrogate is observed for the 5 bar test cases, with the CHRJ fuel ignition delay measurements providing a closer match than those of the THRJ fuel. For $T_c < 675$ K, the mechanism predicts ignition delays that are an average of 8% shorter than the CHRJ fuel measurements, and an average of 4% longer than the THRJ fuel measurements. Entering the NTC region, the predictions diverge for both HRJ fuels to become 40% shorter than the

experimental measurements. The increased sensitivity to pressure in the NTC region is reason to consider lower molecular weight surrogate components such as the C₁₀ hydrocarbons, *n*-decane or 2-methylnonane. Replacement of the C₁₂ hydrocarbons in the surrogate with C₁₀ hydrocarbons will tend to increase the ignition delay in the NTC region, while having minimal influence at lower temperatures where the agreement is already satisfactory. For this reason, we have chosen 2-methylnonane as an additional surrogate fuel for simulation, with the results of the simulations also appearing in Fig. 6b and c. The results of the simulations demonstrate that for compressed temperatures of less than 675 K, there are only modest differences in the predictions between the single component and 2-component surrogate fuels. However, entering the NTC region at $p_c = 5$ bar, a marked improvement is seen in the agreement with the data for the single component surrogate relative to the 2-component surrogate. The agreement in this region is better with the CHRJ fuel than the THRJ fuel, and future work will fine tune the surrogate compositions to provide unique matches for each of the HRJ fuels, as well as seek to improve the agreement with the lean ignition delay data presented in Section 4.2.

4.4. Global regression: ignition delay correlations

Global correlations describing the total ignition delay time have been derived for each of the fuels, using the expression $\tau = A \cdot p_c^m \phi^n e^{T_a/T_c}$, where A , m , n and T_a are optimization parameters. The correlation only considers low-temperature data ($T_c \leq 675$ K) where the total ignition delay exhibits a monotonic dependence on inverse temperature. For temperatures in excess of this point, NTC behavior becomes evident, and the correlation fails to adequately represent the ignition delay time dependence on pressure and equivalence ratio. The correlation calculates the total ignition delay in ms and requires inputs of the compressed pressure (bar), equivalence ratio (non-dimensional), and compressed temperature (Kelvin). The optimized regression parameters for this correlation appear in Table 1, and the accuracies of this correlation for each fuel are reviewed in Fig. 7, where the data and correlation are scaled to $p_c = 20$ bar and $\phi = 1.0$ using the correlation parameters. The data clearly capture the distinct difference between the JP-8 and HRJ fuels test data, and a more subtle difference exists between the two HRJ fuels.

5. Conclusion

In this study, the autoignition characteristics of JP-8, CHRJ and THRJ fuels have been investigated at low compressed temperatures, low-to-moderate compressed pressures, and at fuel-lean and stoichiometric conditions. The ignition behavior of the HRJ fuels is distinct from the JP-8 at all conditions, with the HRJ fuels exhibiting a more rapid onset of ignition than the JP-8 at a given test condition. The ignition delay measurements of the two HRJ fuels can be distinguished under stoichiometric conditions, although these measurements are generally within the uncertainty range of one another. For fuel-lean mixtures, the ignition delays for the HRJ fuels cannot be distinguished. The data indicate that minor changes in hydrocarbon species distribution have little-to-no effect on synthetic fuel autoignition properties under lean conditions, which may be of importance as the military considers advanced lean-burn technologies and a single fuel for the battlefield.

Kinetic modeling results using a 2-component surrogate (10% *n*-dodecane/90% 2-methylundecane) and a single-component surrogate demonstrate that the functional dependence on compressed pressure and equivalence ratio can be represented by the mechanism, but that quantitative agreement is lacking for most test conditions. Good agreement between the data and the simulations

using both the 2-component and single-component surrogates can be achieved for the 5 bar, stoichiometric tests at compressed temperatures below the NTC region. The agreement between the data and the predictions is strongly improved in the NTC region at low pressures by using the single-component surrogate rather than the 2-component surrogate.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.combustflame.2012.10.008>.

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