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Study of the High-Temperature Autoignition of *n*-Alkane/O_2/Ar Mixtures

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Ignition time measurements of propane, *n*-butane, *n*-heptane, and *n*-decane have been studied behind reflected shock waves over the temperature range of 1300–1700 K and pressure range of 1–6 atm. The test mixture composition varied from approximately 2–20% O_2, and the equivalence ratio ranged from 0.5 to 2.0. To determine more precisely the fuel mole fraction of the test mixture, a new technique has been employed in which a 3.39-μm HeNe laser and multiple-pass setup is utilized to measure the fuel in situ by absorption. Ignition delay times were measured at the shock tube endwall by a CH emission diagnostic (431 nm) that viewed the shock-heated mixture through a window in the endwall. This enabled the ignition time at the unperturbed endwall conditions to be determined accurately, thereby avoiding problems inherent in measuring ignition times from the shock tube sidewall. A parametric study of the experimental data reveals marked similarity of the ignition delay time characteristics among these four *n*-alkanes, and a unique correlation is presented in which the stoichiometric ignition time data for all four *n*-alkanes has been correlated into a single expression with an R^2 value of 0.992:

$$\tau = 9.4\times10^{-12}P^{-0.55}X_{O_2}^{-0.63}C^{-0.50}\exp(46{,}550/RT)$$

where the ignition time is in seconds, pressure in atmospheres, the activation energy in calories per mole, X_{O_2} is the mole fraction of oxygen in the test mixture, and C is the number of carbons atoms in the *n*-alkane. Comparisons to past ignition time studies and detailed kinetic mechanisms further validate the correlations presented here.

Introduction

NUMEROUS ignition time studies have been conducted over a wide range of conditions and for a variety of fuels. One method of reducing the experimental ignition time data involves performing a regression analysis on the experimental data to obtain an expression for the ignition time as a function of key parameters. An advantage of establishing such correlations is that the sensitivity of the ignition time to a given parameter, for example, pressure or temperature, is explicitly revealed, thereby enabling ignition time data to be scaled to different conditions. For example, highly dilute test mixtures, that is, >95% diluent, which are often utilized in shock tube studies, may be scaled to higher, more practical mixture strengths. However, the uncertainty inherent in scaling ignition time data clearly becomes more problematic if the scaling does not follow a simple functional relationship, which may not be explicitly obvious from the regression analysis. Furthermore, a variety of correlation forms have been previously employed, making it difficult to directly compare the results from different studies. Listed hereafter are some example correlation forms found in the literature.

From Ref. 1,

$$\tau = Z[\mathrm{fuel}]^a[O_2]^b[\mathrm{Ar}]^c e^{E/RT}$$

From Ref. 2,

$$\tau = Z[\mathrm{fuel}]^a[O_2]^b\rho^r e^{B/T}$$

From Ref. 3,

$$\tau = [P/\mathrm{RT}]^c e^{A+B/T}$$

From Ref. 4,

$$\tau = Z\phi^k P^n e^{E/RT}$$

where ρ is density in the second equation.

In addition, there is often disagreement among ignition time studies regarding the values of the correlation parameters. For example, in the work of Vermeer et al.[3] the pressure dependence, that is, $\tau \sim P^n$ for *n*-heptane, was found to be $n = -0.86$, whereas a study by Burcat et al.[1] reports a pressure dependence of $n = -0.3$, and reported values for the *n*-heptane ignition time activation energy range from 35.3 kcal/mol (Ref. 1) to 46.4 kcal/mol (Ref. 3). Empirical correlations are also typically derived from measurements of a single fuel, which has led to the development of multiple fuel-specific ignition time correlations. To reduce the amount of experimental work necessary to compare and predict the ignition time behavior of a variety of different fuels, it is clearly advantageous to identify similarities among the ignition time sensitivities for an entire class of fuels.

The initial goal of this work was to obtain ignition time data for *n*-heptane/O_2/Ar mixtures of improved accuracy and reduced scatter in an effort to determine more precisely the ignition time correlation parameters of *n*-heptane over a range of conditions. The empirical correlation parameters are then compared with those predicted by three different detailed kinetic models to determine the feasibility of scaling ignition time data over a wider range of conditions than those studied here. In addition, ignition time measurements of *n*-butane/O_2/Ar mixtures were obtained to compare the ignition time sensitivities of two representative *n*-alkanes. Based on the striking similarity between the sensitivities of these two fuels, additional measurements were obtained for propane and *n*-decane to test the potential of utilizing a single correlation that would accurately express the ignition time behavior of a whole series of *n*-alkanes. To further test and validate the correlations presented here over a wider range of conditions, the current measurements are compared to past studies by scaling the ignition time data sets of each study to a prescribed condition using the ignition time sensitivities presented.

Experimental Method

All ignition times were measured in the reflected shock region of a 15-cm-diam, helium-driven, high-purity shock tube. Four incident

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shock velocity measurements were obtained over a distance extending 1.5 m from the endwall. The endwall incident-shock velocity was calculated from extrapolation of the velocity profile using a second-order polynomial fit. Reflected shock conditions were determined from the endwall incident-shock velocity using the one-dimensional shock relations and the Sandia thermodynamic database, which was amended to include the thermodynamic data for n-heptane and n-decane, as suggested by Burcat and McBride.[5] Uncertainty in the reflected shock temperature is estimated at ±10 K, resulting in about a 10% uncertainty in the measured ignition time. All test gases were of research-grade quality and mixed in a 14-liter stainless-steel tank by an electrically driven stirring rod. Test mixtures drawn from liquid fuels, that is, n-heptane and n-decane, were made by initially evacuating the mixing tank and allowing the vapor pressure of the liquid fuel to flow into the mixing tank from a connecting glass fuel beaker. To minimize the presence of atmospheric air in the fuel beaker, a freeze–pump–thaw procedure was employed.

Ignition time measurements may be subject to a high degree of experimental uncertainty if the composition of the test mixture is not accurately measured. Whereas mixtures composed of compounds that are gases at room temperature can be manometrically measured to a high degree of accuracy, the current study has shown that this method may be subject to a relatively high degree of error when making mixtures that are composed of fuels that are liquid at ambient conditions. The problem arises when, after initially filling the mixing tank with liquid fuel vapor, the subsequent addition of the remaining mixture components, for example, oxygen and argon, causes a compression of the fuel vapor beyond its saturation limit. Although the partial pressure of the fuel vapor should ideally remain constant as additional mixture components are added, this does not occur because the added components do not immediately form a homogeneous mixture with the fuel, and, thus, the pressure of the fuel vapor is temporarily raised above its initial value. Although any condensed fuel will eventually evaporate, additional time must be allowed for the gases to mix to ensure homogeneity of the test mixture. Furthermore, condensation of the fuel will cause errors in the measured mole fractions of the additional mixture components because the total pressure measured in mixing tank will understate the true molar quantity present.

To minimize the degree of fuel vapor condensation, the maximum vapor pressure of the n-heptane and n-decane liquid fuels drawn into the mixing tank was limited to under 50% of their respective room-temperature vapor pressures. Furthermore, subsequent mixture components were added slowly to minimize compression of the fuel vapor, thus enabling a more accurate measurement of the oxygen and argon mole fraction. This procedure was validated by directly measuring the in situ fuel concentration using an infrared (IR) absorption diagnostic that which consisted of a 3.39-μm continuous wave helium–neon (HeNe) laser. The laser output power (approximately 4.5 mW) was measured by a single thermopile detector with a surface diameter of 10 mm and power resolution of 1 μW. The in situ fuel mole fraction X_f of the test mixture was determined from the Lambert–Beer relationship,

$$I/I_0 = e^{-\alpha L P X_f}$$

where I_0 and I are the measured laser intensity before and after filling of the shock tube, respectively; L is the path length traversed by the laser within the shock tube; P is the total fill pressure (P_1) of the mixture in the shock tube; and α is the absorption coefficient per unit length and pressure. The agreement between the manometric and laser absorption fuel measurement was within 5%, which was the approximate uncertainty of the IR absorption measurement.

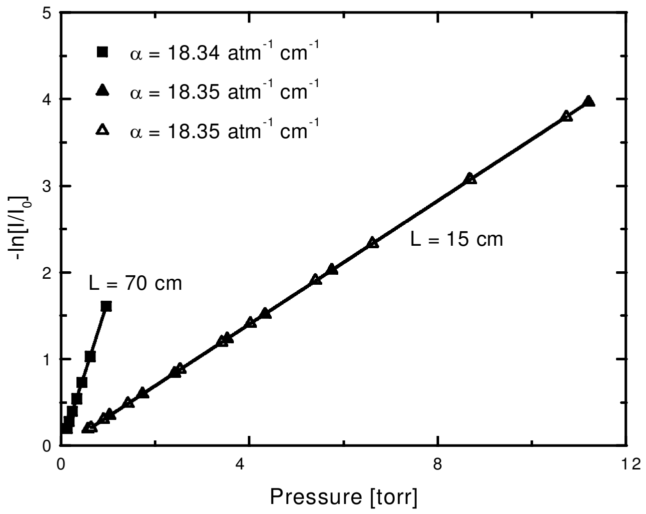

Fig. 1 Measured n-heptane absorption coefficients at 295 K and 3.39 μm.

The absorption coefficient of n-heptane and n-decane was established in a separate set of tests in which attenuation of the IR laser beam was measured as it passed through an absorption cell filled with the pure vapor of the test fuel. The laser beam attenuation was measured over a range of fuel vapor pressures, and the absorption coefficient was calculated from the slope of a best-fit line of the laser beam transmittance (I/I_0) vs vapor pressure. Two absorption cell lengths, 70 and 15 cm, were used to test the repeatability and accuracy of the absorption coefficient measurement (see Fig. 1). The absorption coefficient of n-heptane at 295 K was measured as 18.35 atm^{-1}cm^{-1}, with an uncertainty of less than ±1%. This value is in reasonable agreement with an earlier determination by Jaynes and Beam of 20 atm^{-1}cm^{-1} (Ref. 6). The absorption coefficient of n-decane at 295 K was measured here as 23.0 atm^{-1}cm^{-1}, with an uncertainty of approximately ±1%. This measurement is higher than the value of 10–13 atm^{-1}cm^{-1} previously given by Jaynes and Beam, for which the n-decane absorption measurements were reported to be susceptible to a high degree of uncertainty given the low vapor pressure of the fuel. Furthermore, the room-temperature absorption coefficients of the n-alkanes ($\geq C_2$) at 3.39 μm have been shown to increase with increasing molecular size.[6,7] Thus, the value of 23.0 atm^{-1}cm^{-1} reported here for n-decane is more reasonable than the value of 10–13 atm^{-1}cm^{-1} reported earlier.[6]

In shock tube studies, the ignition time is typically measured in the postreflected shock region and is defined as the time interval between the passing of the reflected shock wave and the onset of ignition. The passing of the reflected shock is simply identified from a pressure trace, whereas the onset of ignition is usually determined from either a pressure signal or detection of an intermediate species, for example, CH or OH. For highly exothermic mixtures, in which ignition leads to an abrupt increase in pressure, the ignition time can be accurately measured from the pressure trace alone. However, for highly dilute mixtures, which are often employed in studying chemical kinetics, the rise in pressure at the point of ignition becomes very gradual and prevents an unequivocal determination of the ignition time. As such, many researchers have employed spectroscopic diagnostics (typically emission or absorption) to measure the presence of select species, such as CH (Refs. 8–10) or OH (Ref. 11) to define more precisely the ignition time. However, these diagnostics are traditionally located along the shock tube sidewall, which may result in measurements errors, as discussed hereafter unless the sidewall measurement is corrected to account for perturbations that result from the energy released during combustion.[12]

After ignition originates at the shock tube endwall, the resulting combustion wave accelerates, and, if the rate of energy release is sufficient, it may eventually transition into a detonation wave. As the combustion wave accelerates, its separation from the reflected shock wave decreases, resulting in a shorter time lag between the two waves as they move away from the endwall. Therefore, when utilizing a sidewall diagnostic, the measured sidewall ignition time will be shorter than the correct ignition time at the unperturbed endwall conditions.[1]

To aid determination of the correct unperturbed endwall ignition time, the current study utilized an endwall diagnostic. Whereas the traditional method for measuring ignition times at the shock tube endwall involves using a pressure transducer set into the shock tube

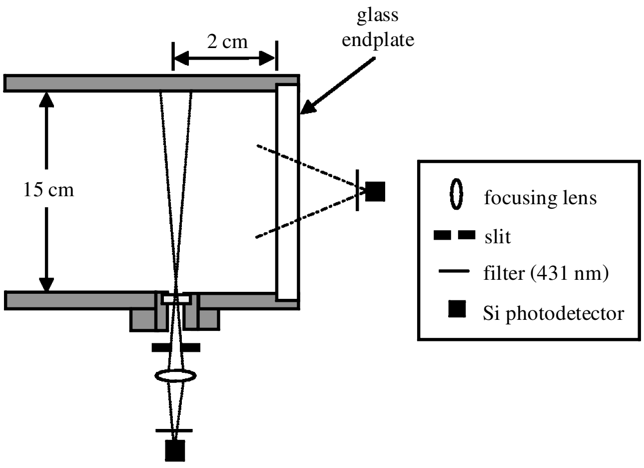

Fig. 2 Schematic of endwall and sidewall CH emission diagnostics.

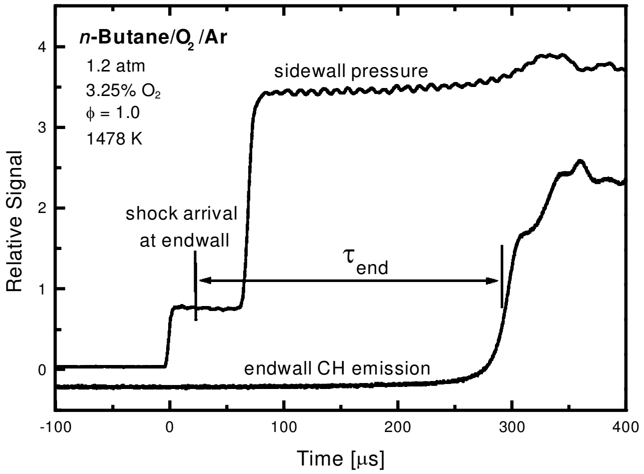

Fig. 3 Representative data trace illustrating endwall ignition time definition.

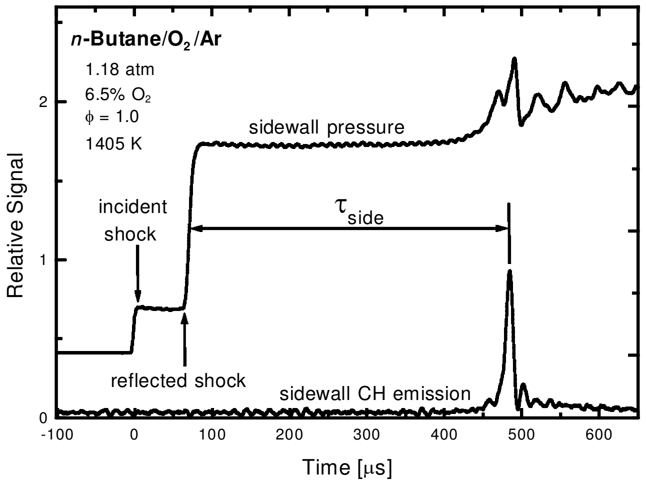

Fig. 4 Representative data trace illustrating sidewall ignition time definition.

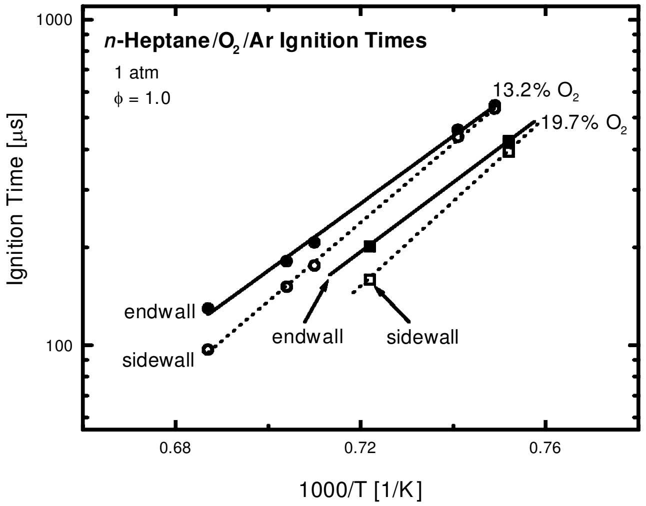

Fig. 5 Comparison of sidewall and endwall ignition time measurements.

endwall,[1] many of the experimental conditions studied herein did not result in an abrupt increase in pressure upon ignition, making it difficult to unequivocally determine the ignition time from the pressure trace alone. Therefore, a new method was employed in which direct measurement of the endwall ignition time was achieved by employing an endwall CH emission diagnostic that viewed the test gas through a window in the endplate (see Fig. 2). The emission of CH was collected using a 431-nm filter with a spectral width of 10 nm and a fast (1.6-μs risetime) silicon photodetector. In comparison to the pressure trace, the endwall CH emission trace shows a more distinct increase on ignition, thereby enabling a more precise measurement of the endwall ignition time. The endwall ignition time is defined as the time interval between the shock arrival at the endwall, which is estimated from the incident shock velocity, and the maximum rate of increase in the CH emission signal (see Fig. 3).

In addition to the endwall ignition time, the sidewall ignition time was also measured to determine the effect of the ignition process on the sidewall measurement. Sidewall measurements were obtained at a distance of 2 cm from the endwall (see Fig. 2). As shown in Fig. 4, the sidewall ignition time was defined as the time interval between the passing of the reflected shock and the peak CH emission signal. A comparison of the sidewall and endwall ignition time measurements (Fig. 5) reveals that, for mixtures with sufficient energy release, the sidewall measurements lead to a much shorter determination of the ignition time relative to the endwall measurement and result in a higher activation energy than that measured at the endwall. Based on the measurements obtained in this study, it is concluded that the endwall–sidewall difference is negligible for mixtures that are highly dilute ($>95\%$ diluent), and/or ignition times that are relatively long (>500 μs). However, these limiting conditions are based on sidewall measurements that were obtained relatively close to the endwall, that is, 2 cm. As the distance between the sidewall measurement location and the endwall is increased, this endwall–sidewall difference in the ignition time will likely increase.

Results and Discussion

In the initial phase of this study, ignition time measurements of *n*-heptane were conducted over a range of temperature, pressure, and mixture composition to determine the sensitivity of the ignition time to a variety of parameters, for example, pressure and stoichiometry. The range of experimental conditions over which each fuel was studied is listed in Table 1. The effect of pressure on the ignition delay *n*-heptane is shown in Fig. 6. Clearly, the ignition time exhibits a systematic decrease with increasing pressure. The same general trend was also observed with respect to mixture strength, which is defined here as the amount of fuel and oxygen relative to the diluent, that is, argon. The ignition time sensitivity to the equivalence ratio was found to increase as the mixture stoichiometry was increased (see Fig. 7). These observed trends in the ignition time with respect to changes in each of the relevant parameters have important implications when developing ignition time correlations. In addition, as discussed later in this section, the empirical relationships found between ignition time and the relevant parameters are also suggested by detailed kinetic modeling, which further validates the correlations presented here.

Table 1 Comparison of current and previous *n*-heptane/O₂/Ar ignition time correlations

Correlation	P, atm	T, K	X_f, %	ϕ	Researcher
$\tau = 6.76 \times 10^{-15}$ [fuel]$^{0.4}$ [O$_2$]$^{-1.2}$ exp(40,160/RT)	4–8	1200–1400	0.2	0.5, 1.0	Colket–Spadaccini[20][a]
$\tau = 3.20 \times 10^{-12}$ [fuel]$^{0.2}$ [O$_2$]$^{-1.1}$ [Ar]$^{0.6}$ exp(35,300/RT)	2–12	1100–1700	0.5–3.0	0.5–2.0	Burcat et al.[1]
$\tau = 5.08 \times 10^{-16}$ [total mixture]$^{-0.86}$ exp(46,350/RT)	1–4	1200–1700	2.5	1.0	Vermeer et al.[3]
$\tau = 4.54 \times 10^{-14}$ [fuel]$^{0.95}$ [O$_2$]$^{-1.58}$ exp(45,000/RT)	1–6	1300–1700	0.2–1.8	0.5–2.0	current study

[a] Correlation is based on the ignition time data from a number of studies.

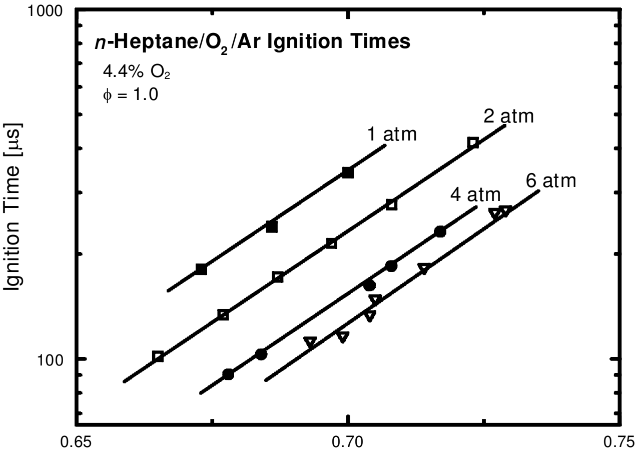

Fig. 6 Effect of pressure on ignition delay of *n*-heptane.

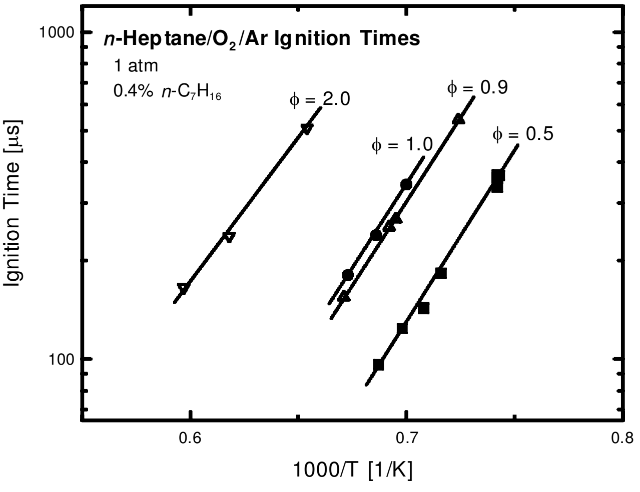

Fig. 7 Effect of stoichiometry on ignition delay of *n*-heptane.

The *n*-heptane ignition time measurements were correlated using the following two correlation forms:

$$\tau = Z_1[\text{fuel}]^a[\text{O}_2]^b e^{E/RT} \tag{1}$$

$$\tau = Z_2 P^n X_{\text{O}_2}^x \phi^k e^{E/RT} \tag{2}$$

where in Eq. (1) the ignition time is expressed in terms of the temperature and the fuel and oxygen concentrations, and, in Eq. (2), the correlation parameters are the total pressure, that is, reflected shock pressure, equivalence ratio, oxygen mole fraction X_{O_2}, and temperature. The parameter Z is simply a constant determined from the regression analysis. Although ignition times are usually correlated in terms of one of more concentration terms, for example, Eqs. (1) and (2) is advantageous in that the ignition time sensitivities of more practical parameters, for example, pressure and equivalence ratio, may be explicitly expressed. A regression analysis of the ignition time data yielded the following correlations for the ignition delay of *n*-heptane:

$$n\text{-heptane}(\phi = 0.5 - 2.0): \tau = 4.54 \times 10^{-14}$$

$$\times [n\text{-heptane}]^{0.95}[\text{O}_2]^{-1.58} \exp(45{,}000/RT) \tag{3}$$

$$\tau = 6.67 \times 10^{-12} P^{-0.61} X_{\text{O}_2}^{-0.68} \phi^{0.96} \exp(44{,}600/RT) \tag{4}$$

where the ignition time is in seconds, concentrations are in moles per cubic centimeter, pressure is in atmospheres, X_{O_2} is the oxygen mole fraction, and the activation energy is in calories per mole. When the results of the two correlation forms are compared, it is apparent that there is consistency between the two correlation forms. Specifically, both correlation forms yield essentially the same activation energy, even though Eq. (1) includes a temperature-dependent term via the fuel and oxygen concentration terms, whereas Eq. (2) assumes a purely exponential temperature dependence. Furthermore, both correlation forms result in essentially the same pressure dependence, which may be inferred from the sum of the concentration sensitivities $(a + b)$ in Eq. (1).

In addition to yielding similar ignition time sensitivities, both correlation forms suffer from the same limitation, they cannot be employed over a wide range of stoichiometries. This limitation is due to the ignition time sensitivity to equivalence ratio increasing significantly as the mixture becomes more fuel rich, and, thus, this ratio cannot be accurately represented by a simple logarithmic relationship. Therefore, to correlate more precisely the experimental data, a regression analysis was performed on only the stoichiometric *n*-heptane ignition time data, resulting in the following correlation:

$$n\text{-heptane}(\phi = 1.0): \tau = 1.86 \times 10^{-12} P^{-0.54} X_{\text{O}_2}^{-0.67} \exp(48{,}100/RT) \tag{5}$$

where the ignition time is in seconds, pressure is in atmospheres, X_{O_2} is the oxygen mole fraction, and the activation energy is in units of calories per mole. The accuracy of this correlation was found to be excellent, having an R^2 value of 0.996.

To further validate the empirical trends presented here and assess the feasibility of extending the preceding correlations over a wider range of conditions, the predictions of three detailed models were compared to the current study. However, rather than simply comparing the models on a quantitative basis, a more rigorous approach was utilized here, in which the ignition time sensitivities predicted by each model are compared to those found experimentally. Thus, both qualitative and quantitative comparisons are made between model and experiment. The three models employed here are those of Held et al.,[13] Lindstedt and Maurice,[14] and Curran et al.[15] The model of Held et al.[13] is a simplified high-temperature reaction mechanism developed specifically for *n*-heptane decomposition and oxidation. It contains 41 species and 266 reactions. The model has been compared to species measurements from a continuous flow reactor and jet-stirred reactor, shock tube ignition time measurements, and premixed, laminar flame speeds. The model of Lindstedt–Maurice[14] is a relatively comprehensive mechanism containing 109 species and 659 reactions, of which 21 species and 201 reactions are specific to the *n*-heptane submechanism. The model has been validated using species measurements from counterflow diffusion flames and jet-stirred reactors and has been validated to premixed, laminar flame speeds. The model of Curran et al.[15] has been built up from smaller to larger hydrocarbons using a compilation of reaction submechanisms. The model includes reaction schemes for both high- and low-temperature modeling and contains over 500 species and more than 2400 reactions. The mechanism was validated using species measurements from a continuous flow reactor and a jet-stirred reactor and ignition time measurements obtained from shock tubes and rapid compression machines.

Whereas the experimental ignition times reported here are determined from the CH emission trace, kinetic models typically do not include electronically excited CH as a species, hence, the modeled CH* concentration was inferred from its production reaction,[16]

$$C_2H + O \rightarrow CH^* + CO$$

and the modeled ignition time was defined as the peak in the $[C_2H][O]$ product. Another possible choice for the ignition time is one based on the OH time history, for which it is most convenient to define the ignition time as the peak in the d[OH]/d*t* trace because the OH trace does not show a distinct peak for the conditions simulated in the current study. Another potential definition for the modeled ignition time is the peak CH concentration because the time histories of excited and ground state are expected to be quite similar. As shown in Fig. 8 for a representative condition, all three of these definitions yield essentially the same value for the ignition time, and, thus, the peak ground-state CH concentration was used to define the modeled ignition time in this study.

Although the numerical value of the ignition time activation energy may vary somewhat depending on the correlation form employed, comparison of the two ignition time correlations presented in Eqs. (3) and (4) show that both forms yield essentially the same value for the ignition time activation energy. Therefore, the modeled activation energies were simply derived from the average slope of log ignition time vs reciprocal temperature. As shown in Fig. 9 for atmospheric pressure and stoichiometric mixtures with 4.4% O_2, the predicted temperature dependence varies significantly among the three models, with the model of Curran et al.[15] most closely predicting the experimental value that is based on the stoichiometric correlation presented in Eq. (5). The predicted activation energy was determined over the range of test conditions and was found to vary only slightly for the Lindstedt–Maurice[14] and Curran et al.[15] models, but varied from 32–60 kcal/mol for the Held et al.[13] model. The relatively wide variation in the ignition time activation energy predicted by the three models is also found in comparing previous *n*-heptane ignition time studies (see Table 1).

The modeled ignition time pressure dependence is calculated from the slope of a log–log plot of the ignition time vs pressure (Fig. 10). The linearity of the plots for all three models over a range of pressures reveals that the models predict the same functional relationship for ignition time pressure dependence as that determined experimentally, that is, $\tau \sim P^n$. In addition, all three models predict a pressure dependence that is very close to the experimental value of -0.54, which was determined from the stoichiometric *n*-heptane data. The pressure sensitivities predicted by the Lindstedt–Maurice[14] and Curran et al.[15] models were found to be essentially constant over the range of test conditions, that is, temperature and mixture composition, whereas that predicted by the Held et al.[13] model was found to vary from -0.5 to -0.85.

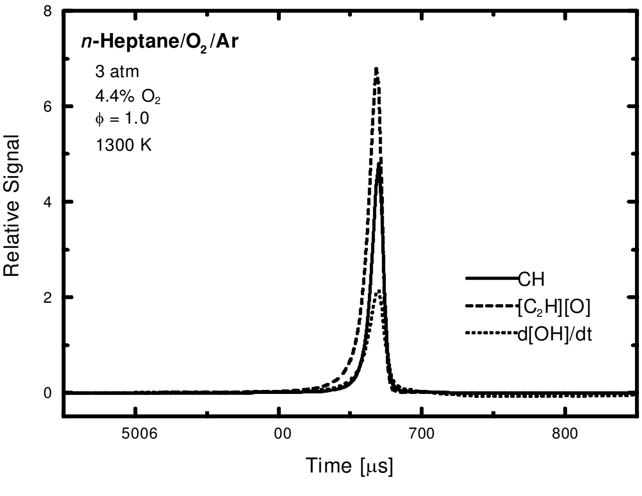

Fig. 8 Comparison of alternative ignition time definitions for detailed models.

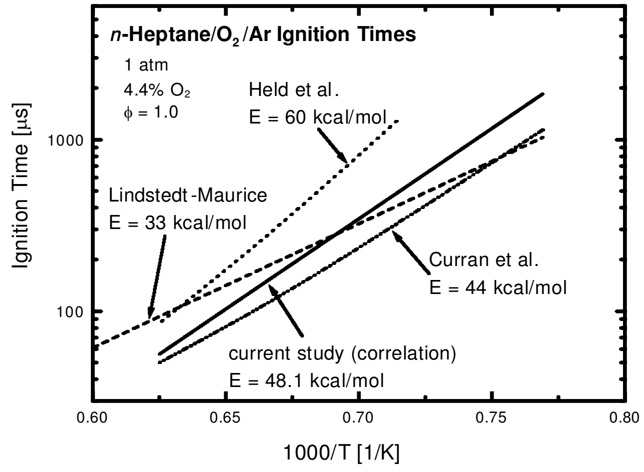

Fig. 9 Comparison of experimental and modeled ignition time temperature dependence.

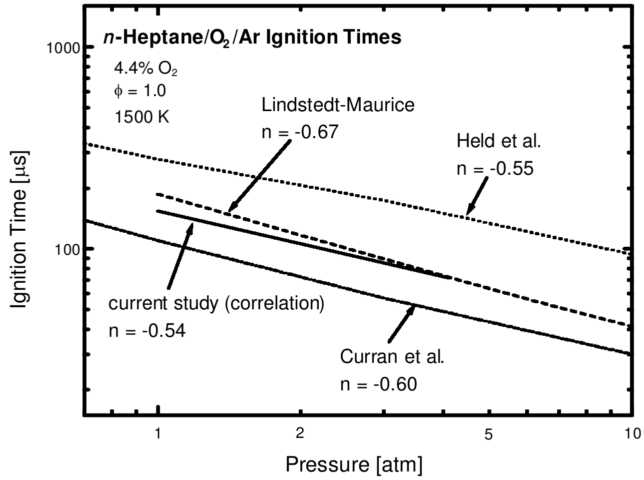

Fig. 10 Comparison of experimental and modeled ignition time pressure dependence ($\tau \sim P^n$).

In addition to the local temperature and pressure, the ignition time is also a function of the test mixture composition. Some previous studies account for this effect by correlating the ignition time in terms of the concentrations of the reacting species.[1,2] However, the results just presented suggest utilizing a correlation form in which the pressure appears explicitly and the temperature dependence is expressed as a single exponential term, thus resulting in a correlation where the ignition time is expressed in terms of the mole fractions of the reacting species as opposed to concentrations.

To assess the effect of mixture composition on the ignition time of *n*-heptane, the equivalence ratio and mixture strength (amount of fuel and oxygen relative to argon) were varied. When the mixture strength sensitivity is determined at constant equivalence ratio, both the Curran et al.[15] and Lindstedt–Maurice[14] models predict a simple logarithmic relationship ($\tau \sim X_{O_2}^x$), which is in agreement with the trend found experimentally (see Fig. 11), whereas the model of Held et al.[13] predicts a nonlogarithmic trend. In addition, the predicted mixture strength sensitivities predicted by the Lindstedt–Maurice[14] and Curran et al.[15] models are reasonably close to the experimental value of -0.67.

The effect of the equivalence ratio on the ignition time of *n*-heptane is shown in Fig. 12. All three models and the experimental data suggest the ignition time equivalence ratio dependence is not

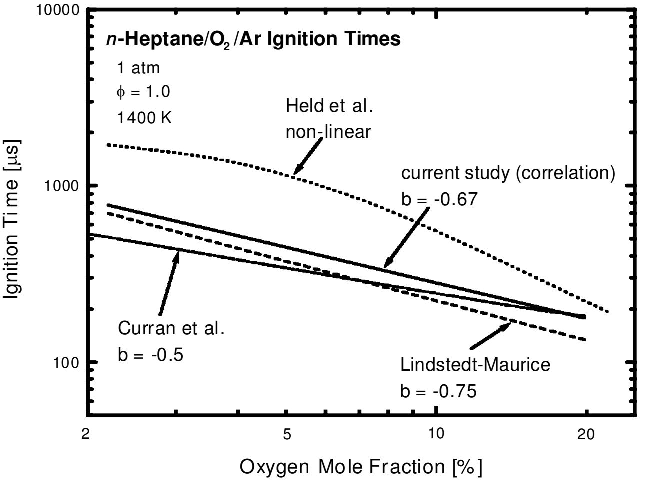

Fig. 11 Comparison of experimental and modeled ignition time oxygen dependence ($\tau \sim X^{x}_{O_2}$) at constant equivalence ratio.

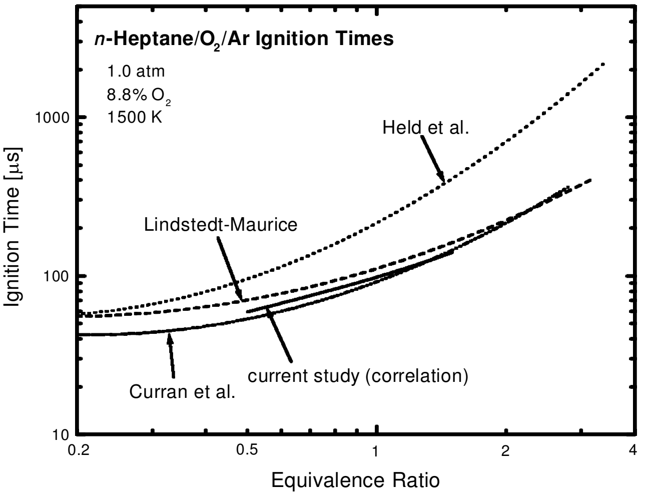

Fig. 12 Comparison of experimental and modeled ignition time equivalence ratio dependency at constant fuel mole fraction.

accurately represented by a simple logarithmic relationship. Therefore, it is concluded that the *n*-heptane ignition time data should not be scaled over a wide range of equivalence ratios when correlating the ignition time as $\tau \sim \phi^k$. In addition, these results suggest that the empirical equivalence ratio sensitivity is dependent on the precise range of equivalence ratios studied. That is, ignition time correlations developed under rich conditions will result in a higher equivalence ratio sensitivity than those based on lean conditions.

To compare the ignition time sensitivities of *n*-heptane to another *n*-alkane, ignition time measurements were obtained for a series of *n*-butane/O$_2$/Ar mixtures over a range of similar conditions. A regression analysis on all the *n*-butane data yielded the following correlations,

$$n\text{-butane}(\phi = 0.5 - 2.0): \tau = 7.63 \times 10^{-14}$$

$$\times [n\text{-butane}]^{0.99}[\mathrm{O_2}]^{-1.61} \exp(42{,}850/RT) \qquad (6)$$

$$\tau = 3.57 \times 10^{-11} P^{-0.64} X_{\mathrm{O_2}}^{-0.62} \phi^{1.00} \exp(41{,}000/RT) \qquad (7)$$

where the ignition time is in seconds, concentrations are in moles per cubic centimeter, reflected shock pressure is in atmospheres, $X_{\mathrm{O_2}}$ is the oxygen mole fraction, and the activation energy is in calories per mole. Again, similar to the *n*-heptane correlations, the two *n*-butane correlations yield about the same pressure and temperature dependence. However, even more striking are the similarities of the ignition time sensitivities for both *n*-butane and *n*-heptane. Both fuels exhibit a fuel and oxygen concentration dependence of nominally 1.0 and −1.6, respectively. Furthermore, both fuels exhibit a pressure and mixture strength $X_{\mathrm{O_2}}$ dependence of roughly −0.65 and a similar activation energy. Note that although both fuels are also shown to exhibit an equivalence ratio dependence near 1.0, this agreement is a result of the similar range of equivalence ratios studied. That is, the ignition delay of *n*-butane exhibited an increasing sensitivity with respect to stoichiometry, similar to that observed for *n*-heptane. To further compare the two fuels, an *n*-butane correlation was determined from only the stoichiometric data,

$$n\text{-butane}(\phi = 1.0): \tau = 5.09 \times 10^{-12} P^{-0.55} X_{\mathrm{O_2}}^{-0.66} \exp(46{,}000/RT) \qquad (8)$$

where the ignition time is in seconds, pressure is in atmospheres, $X_{\mathrm{O_2}}$ is the oxygen mole fraction, and the activation energy is in units of calories per mole. In comparing Eqs. (8) and (5) the ignition time sensitivities are shown to be very similar between the fuels.

To compare quantitatively the ignition time data for *n*-butane and *n*-heptane, all of the stoichiometric data for both fuels were scaled to the conditions of 1 atm and 20% O$_2$ using the respective scaling parameters for each fuel. This mixture strength was selected to provide a comparison at a condition corresponding to a practical fuel–air mixture. Although this condition is arbitrary, a similar comparison at any other pressure of mixture strength yields essentially the same qualitative trend because the scaling parameters for both fuels are very similar.

The similarities observed in the correlations for *n*-butane and *n*-heptane prompted the extension of this study to a higher- and lower-order *n*-alkane, namely, propane and *n*-decane. The relatively high room temperature vapor pressure of propane (approximately 130 psia) enabled its ignition time to be directly measured at stoichiometric, 20% O$_2$ conditions, obviating the need to scale the propane data. However, due to the very low room temperature vapor pressure of *n*-decane (approximately 0.8 torr), the maximum achievable mixture strength at stoichiometric conditions was limited to 3.1% O$_2$, and, thus, this scaling could not be verified up to the 20% O$_2$ condition. Hence, it was necessary to scale the *n*-decane data to the 20% O$_2$ condition, which was achieved by using the average mixture strength scaling ($x = -0.665$) of the stoichiometric *n*-butane and *n*-heptane data.

When the stoichiometric ignition time data of propane, *n*-butane, *n*-heptane, and *n*-decane are compared at the 20% O$_2$ condition, the ignition time is seen to decrease as the carbon content of the fuel increases (see Fig. 13). This relationship may be explained as follows. An increase in equivalence ratio has been shown to increase the ignition time, which may be the result of competition between the fuel and molecular oxygen for H atoms. That is, whereas the reaction between H atoms and molecular oxygen is a highly effective chain-branching reaction, the reaction of H atoms with the fuel is

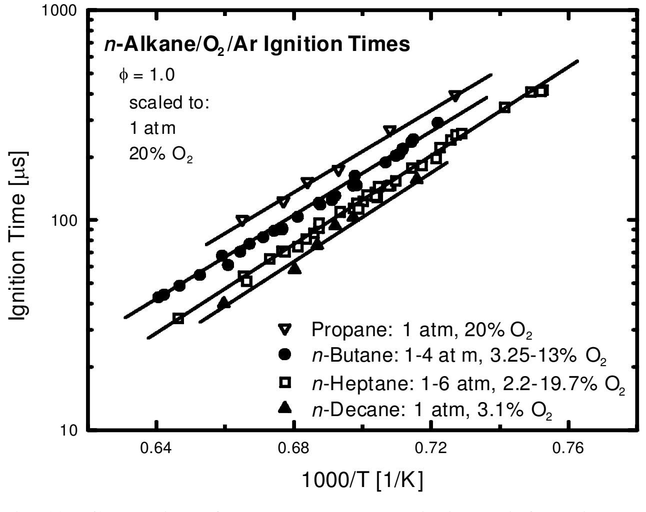

Fig. 13 Comparison of *n*-alkanes scaled to stoichiometric fuel–air conditions.

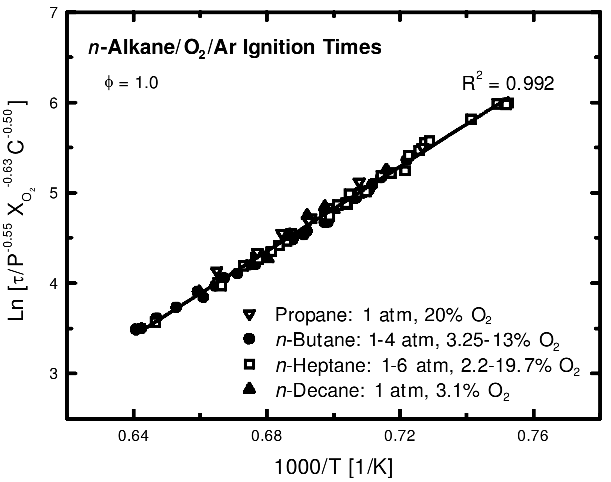

Fig. 14 Correlated stoichiometric *n*-alkane ignition time data.

essentially a termination reaction. Furthermore, as the size of the *n*-alkane increases, the stoichiometric fuel to oxygen ratio decreases from 1:5 for propane to 1:15.5 for *n*-decane. Therefore, the decrease in ignition time with increasing *n*-alkane size may be explained by the higher concentration of oxygen relative to the fuel.

Based on the similarities between the ignition time sensitivities for *n*-butane and *n*-heptane, and the systematic trend in the ignition time with respect to molecular size, an attempt was made to correlate all of the stoichiometric ignition time data for propane, *n*-butane, *n*-heptane, and *n*-decane into a single expression. This required including an additional correlation parameter to account for the effect of the fuel size on the ignition time. The parameter selected was the number of carbon atoms in the molecule, which is represented by the parameter C. A regression analysis on all of the stoichiometric ignition time data for all four fuels yielded the following equation:

$$n\text{-alkane}(\phi = 1.0)\colon \tau = 9.40 \times 10^{-6} P^{-0.55} X_{O_2}^{-0.63} C^{-0.50} \times \exp(46{,}550/RT) \qquad (9)$$

where the ignition time is in microseconds, pressure is in atmospheres, X_{O_2} is the oxygen mole fraction, and the activation energy is in calories per mole. All of the correlated stoichiometric ignition time data are shown in Fig. 14, for which the best-fit line thought the data has an R^2 value of 0.992.

To compare quantitatively the current ignition time measurements to past work and to further test and validate the correlations presented herein, the ignition time sensitivities presented in this study were utilized to scale current and previous ignition time measurements to one specific condition. Because of the inability to represent accurately the ignition time equivalence ratio sensitivity in correlation form, only ignition time measurements obtained at the same equivalence ratio are compared.

The propane ignition time data of the current study were compared to the shock tube measurements previously obtained by Burcat et al.,[17,18] Gray and Westbrook,[9] Brown and Thomas,[10] and Qin et al.[19] In the studies by Burcat et al.,[17,18] ignition times were measured in the reflected shock region, and the ignition time definition was based on the onset of the rapid rise in both pressure and heat-flux measurements, which were obtained at the shock tube endwall. In the study by Gray and Westbrook,[9] ignition time measurements were obtained in the incident shock region, and the ignition time definition was based on the maximum CH emission signal. The measurements by Brown and Thomas[10] were recorded in the reflected shock region, and onset of ignition was based on the initial rapid rise in CH emission, which was recorded by a photomultiplier located at the endwall. In the study by Qin et al.,[19] ignition times were measured in the reflected shock region, and the onset of ignition was defined as the maximum rate of pressure rise as measured at the shock tube endwall.

All ignition time data presented in Fig. 15 were scaled to the average condition of 5 atm and 10% O_2 using the empirical *n*-alkane ignition time sensitivities calculated in this study, $\tau \sim P^{-0.55} X_{O_2}^{-0.63}$. With the exception of some of the lower temperature data by Brown and Thomas,[10] all of the ignition time measurements collapse reasonably well into a single line, thus providing evidence as to the feasibility of scaling ignition time data over a relatively wide range of conditions, that is, pressure and mixture strength, and validating the empirical correlations presented in this study. In the study by Brown and Thomas,[10] the ignition delay was based on the initial rise in CH emission, whereas the maximum rate of increase in CH emission was employed here, which may explain, in part, the shorter delays measured by Brown and Thomas[10] relative to this study.

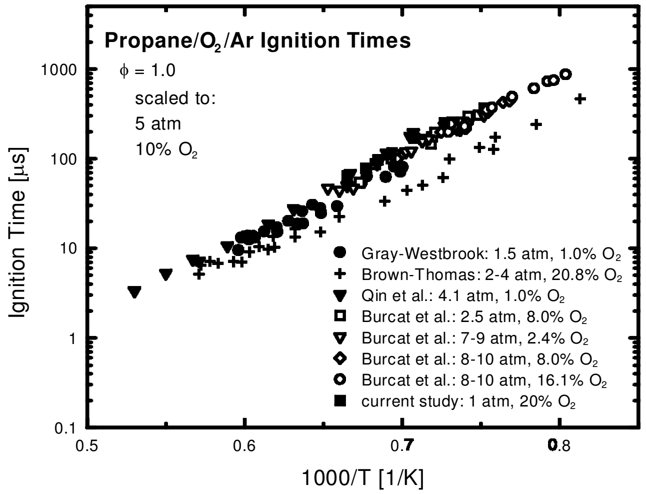

Fig. 15 Comparison of stoichiometric propane ignition time studies (scaled to 5 atm and 10% O_2).

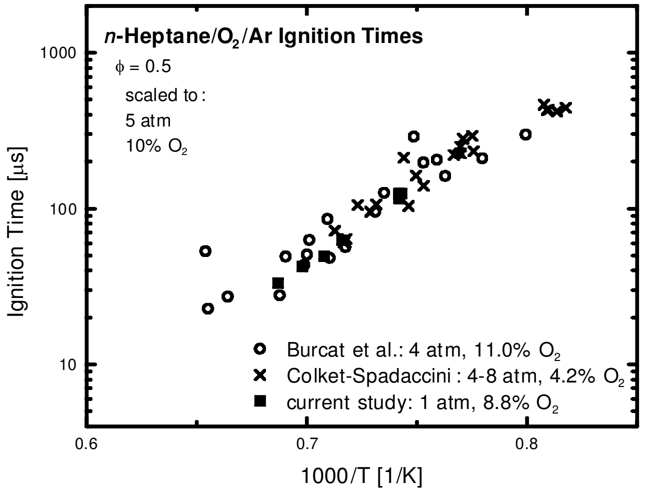

Fig. 16 Comparison of lean *n*-heptane ignition time studies (scaled to 5 atm and 10% O_2).

To test and validate the ignition time sensitivities measured in the current study at conditions other than stoichiometric, a similar scaling method was utilized to compare the lean ($\phi = 0.5$) *n*-heptane ignition time measurements of the current study to those obtained previously by Burcat et al.[1] and Colket and Spadaccini.[20] The results are shown in Fig. 16. Again, the scaled data sets are shown to effectively converge into a single line, thus suggesting that the pressure and mixture strength sensitivities presented herein are applicable under lean conditions as well. A similar comparison at rich ($\phi = 2.0$) conditions is also presented (see Fig. 17) in which the current data are compared to the rich data by Burcat et al.[1] Although three of the data sets collapse accurately into a single line when scaled by *n*-heptane ignition time sensitivities, one of the Burcat et al. data sets clearly does not. When the conditions for the four rich studies presented are compared, the data seem to be well correlated

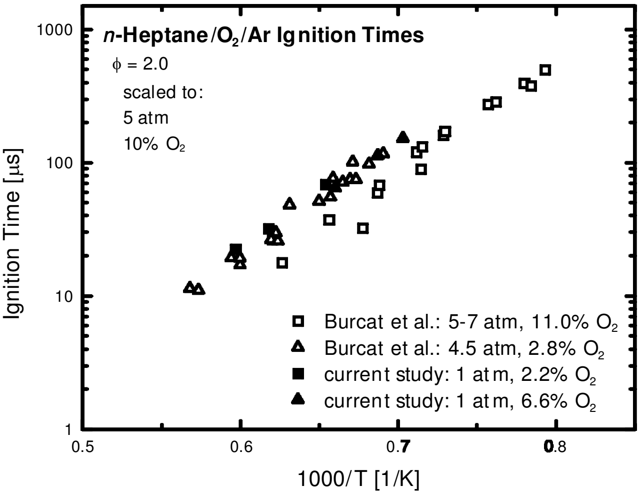

Fig. 17 Comparison of rich *n*-heptane ignition time studies (scaled to 5 atm and 10% O_2).

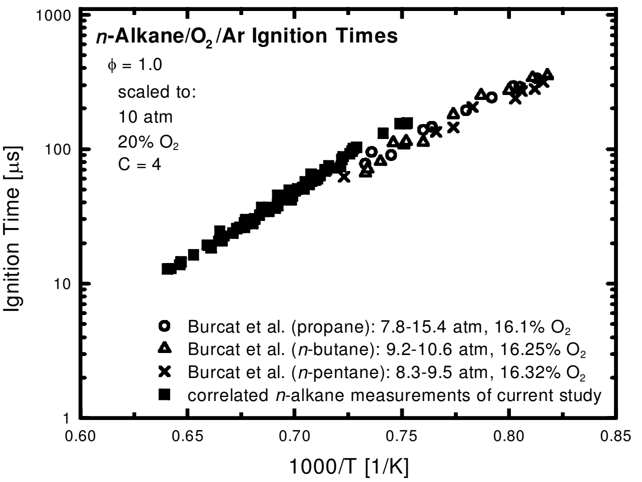

Fig. 18 Comparison of previous and current *n*-alkane ignition time data.

over the pressure range of 1–4.5 atm and mixture strength range 2.2–6.6 % O_2. However, the data set of Burcat et al.[1] that does not correlate well was obtained at a slightly higher pressure (5–7 atm) and higher mixture strength (11.0% O_2) relative to the other data. These findings suggest that the pressure and mixture strength sensitivities presented here may not hold at rich conditions for pressures above 5 atm and/or mixtures strengths above nominally 7.0% O_2. However, the *n*-alkane ignition time sensitivities presented in this study do appear to be valid over the pressure range of 1–15 atm and mixture strength range of 1–20% O_2 under both lean and stoichiometric conditions.

To further validate the *n*-alkane correlation presented in this study, a series of propane, *n*-butane, and *n*-pentane ignition time measurements previously obtained by Burcat et al.[17] were compared to the *n*-alkane data of the current study. When scaled to the same condition and same carbon number, that is, 4, the ignition time measurements by Burcat et al. for propane, *n*-butane, and *n*-pentane are shown (see Fig. 18) to collapse accurately into a single line, providing further validation of the *n*-alkane correlation presented earlier. However, the ignition time measurements of Burcat et al. appear to be approximately 20–30% shorter than those obtained in the current study, and they have an activation energy of about 37 kcal/mol, which is approximately 20% less than that observed with the correlation of the present data. This difference may be due in part to the different ignition time definitions employed. In the Burcat et al. study, the onset of ignition was based on the initial rise in pressure, whereas for the current study, the onset of ignition was defined from the maximum rise in the CH emission trace.

Conclusions

An extensive study of the ignition times of *n*-alkane/O_2/Ar mixtures over a range of parameters is presented. A novel laser absorption technique has been utilized that enables accurate in situ measurement of the fuel fraction, providing a more accurate specification of the test mixture composition. In addition, the unperturbed endwall ignition time was directly measured using an endwall CH emission diagnostic. Two different correlation forms have been presented to correlate the experimental data; however, the correlation form in which the temperature, pressure, oxygen mole fraction, and equivalence ratio are explicitly expressed is thought to be more convenient in assessing ignition time sensitivities.

The experimental data, in conjunction with three detailed kinetic models, have been utilized to gain to a more fundamental understanding of the ignition time sensitivity of *n*-heptane to various parameters. The kinetic models of Lindstedt–Maurice[14] and Curran et al.[15] were found to predict reasonably the present *n*-heptane ignition time measurements; the reduced model of Held et al.[13] was generally found to overpredict the ignition time relative to the current data. All three detailed models closely predict the empirical pressure dependence and the increasing equivalence ratio dependence at higher stoichiometries; however, all three models yield very different temperature dependencies, with the model of Curran et al.[15] most closely predicting the activation energy found in the current study. The models of Lindstedt–Maurice[14] and Curran et al.[15] predict a simple logarithmic oxygen mole fraction scaling, at constant equivalence ratio, in agreement with the experimental data. This trend suggests using a correlation form in which the oxygen mole fraction dependence is explicitly expressed, thereby enabling ignition time data to be directly scaled to more practical fuel–air conditions. To provide a more rigorous test of the detailed kinetic models and guide improvements, we recommend further work involving comparisons of modeled time histories of selected species, determined by sensitivity analysis, to those found experimentally.

A parametric study of the ignition times of *n*-butane and *n*-heptane reveals that the ignition time sensitivities are very similar between the two fuels. Furthermore, the ignition time data for the four *n*-alkanes, propane, *n*-butane, *n*-heptane, and *n*-decane, have been shown to vary inversely with molecular size, and an *n*-alkane correlation has been presented that accurately collapses the stoichiometric ignition time data of all four fuels into a single line, with a resulting R^2 value of 0.992. A comparison of the current study to previous works validates these correlations over a relatively wide range of parameters, thereby enabling ignition time data to be scaled accurately to varying conditions. In addition, detailed modeling further confirms the functional relationships presented here between ignition delay times and the relevant parameters. It is suggested that further work include the direct measurement of selected intermediate species to provide a more detailed assessment of the similarities and differences in the combustion chemistry of the *n*-alkanes.

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