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Scramjet Fuels Autoignition Study

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A series of shock-tube experiments was conducted to measure and compare the ignition-delay times of several fuel candidates for scramjet propulsion and to evaluate the importance of fuel cracking on the autoignition of endothermic-fuel/product mixtures. Ignition delays of ethylene, heptane, and JP-10 were measured in dilute mixtures behind reflected shock waves for temperatures in the range 1100–1500 K, pressures of 3–8 atm, and equivalence ratios of 0.5–1.5. The experimental data were compared to results published for heptane and ethylene, and new ignition-delay correlations were determined from the combined data sets. The resulting expressions were also compared to prior work on methane and hydrogen. In addition, typical endothermic-fuel product mixtures (representing different degrees of cracking of the parent fuel) were simulated and their ignition-delay times measured for equivalence ratios 0.5 and 1.0. The relative ignition-delay times for the different fuels were found to be methane > JP-10 ≅ heptane > reformed endothermic fuel > ethylene > hydrogen. The results support the premise that fuel cracking enhances ignition. However, autoignition of the endothermic reaction product mixture is not driven entirely by the constituent with the shortest ignition delay (i.e., ethylene or hydrogen). Furthermore, small changes in concentrations of the individual component species are not likely to make dramatic changes in the ignition-delay times of the fuel. The empirical data were compared to ignition-delay times predicted using detailed chemical kinetics models and they support the validity of published reaction mechanisms for methane and heptane.

Introduction

IN scramjets rapid spontaneous ignition and reaction of the fuel-air mixture are required to achieve efficient combustion in a practical length. The relatively long ignition-delay times of hydrocarbons relative to hydrogen present a key obstacle to development of storable-fueled scramjets. In addition, autoignition affects heat-release rates, and, if too rapid, it can promote dynamic instabilities or choking.

High-speed propulsion systems are being designed to utilize storable hydrocarbon fuels for cooling and endothermic decomposition of the fuel to increase the available heat sink. Implementation of endothermic reaction technology involves cracking the fuel into a mixture of small hydrocarbons and hydrogen in a heat-exchanger/reactor prior to combustion. This reaction will result in the formation of some species (e.g., ethylene and hydrogen) that are more reactive than the parent hydrocarbon and others (e.g., methane) that are less reactive. Therefore, the design and development of endothermic-fueled combustors require knowledge of the autoignition characteristics of typical cracked product mixtures as well as the component species.

Consequently, shock-tube experiments were performed to measure the ignition-delay times of several candidate scramjet fuels, namely ethylene, heptane, and JP-10, as well as model endothermic-fuel/cracked product mixtures. Testing of ethylene and heptane also allowed validation of the experimental techniques, using the database in the literature, and, together with published data for methane and hydrogen, established a basis for comparisons with the cracked product mixtures.

Autoignition of pure hydrocarbons has been studied by many investigators; however, few of the previous authors have examined the interactive effects peculiar to multicomponent mixtures. Small concentrations of hydrocarbon contaminants in commercial-grade methane have been shown to significantly reduce (i.e., by $\frac{1}{3}$ to $\frac{1}{5}$) the ignition delay.[1] Although it is likely that such interactions are less pronounced for mixtures of higher hydrocarbons, their effect cannot be easily quantified nor can the effect of added hydrogen. Previous analyses of the gaseous products of the thermal and catalytic cracking of heptane and Norpar 12 (a blend of C_{10} to C_{13} n-paraffins with average carbon number 12) have shown that mixtures of paraffinic and olefinic species (with $C < 4$) are formed together with a small amount ($<5\%$ on a molar basis) of hydrogen.[2,3] Therefore, mixtures of methane, ethylene, heptane, and hydrogen were prepared to simulate, with a limited number of the major constituents, unreacted fuel and both the saturated and unsaturated gaseous components of the reformed fuel products. Three gas mixtures, representing different levels of reforming of the parent fuel, were tested. The average molecular weight and C/H ratio of each of the simulants were comparable to that of the typical product mixtures, reflecting the extent of cracking. Measurements of ignition-delay times were made behind reflected shock waves by observing the time delay to the onset of emission from excited hydroxyl radicals. Ignition-delay correlations were determined for each fuel/mixture and compared to literature correlations for the pure hydrocarbons and hydrogen.

Background

The ignition-delay time is defined as the time interval between the creation of a combustible mixture and the onset of a flame. It is a readily measurable quantity that is a function of the initial temperature, pressure, and composition of the reactant mixture. For hydrocarbons it has been found that the ignition-delay time can be correlated in the Arrhenius form:

$$\tau = A\exp(E/RT)[C_xH_y]^a[O_2]^b[Ar]^c$$

where the term E is a parameter equivalent to a global activation energy and A is an empirically determined constant. The terms $[C_xH_y]$, $[O_2]$, and $[Ar]$ are the molar concentrations (mol/cc) of hydrocarbon, oxygen, and argon, respectively, in the combustible mixture. The empirical exponents a and b of these terms express the power dependencies of ignition-delay time on fuel and oxidizer concentrations. The concentrations are determined by

$$[\,]_i = X_iP/RT$$

where X_i is the mole fraction, P is the pressure, T is the temperature of the mixture at the point of ignition, and R is the universal gas constant. Correlation of experimental data for typical hydrocarbon fuels by means of these equations shows that ignition-delay time decreases for both increasing temperature and increasing pressure, with temperature changes providing a much greater effect.

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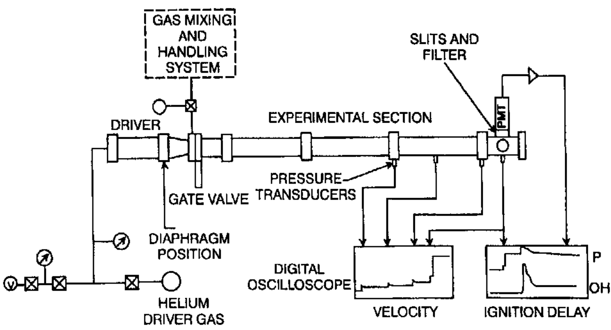

Fig. 1 Shock-tube apparatus.

(Although pressure is not specifically included in the preceding correlating expression for τ, the ignition-delay times are implicitly dependent on pressure through the concentration terms; hence, $\tau \alpha P^{a+b+c}$.)

Test Apparatus and Procedures

Measurements of ignition delay were obtained behind reflected shock waves using a stainless-steel shock tube apparatus shown in Fig. 1. The shock tube has an internal diameter of 3.8 cm, and the driven section is extended to 526 cm so that residence times up to 1.8 ms can be achieved at elevated temperatures and pressures. The driver section is 88 cm long. The test procedure consisted of loading a fuel-oxygen-argon mixture at low pressure in the driven section. The pressure of helium in the driver section was then raised until a prestressed aluminum diaphragm burst, propagating a shock wave down the tube past a series of pressure transducers (rise times of 2 μs). The pressure transducers were located 167, 90.8, 14.6, and 1.7 cm from the end wall. Signals from the transducers were monitored on a high-speed Nicolet storage oscilloscope, with a time resolution of 1 μs per point. From the arrival times of the wave at each of the transducers, shock velocities could be calculated. A small decay in velocity was accounted for by extrapolating velocities to the end wall to calculate the shock strength at the end wall and initial temperatures and pressures behind the reflected shock. The ± 1 μs uncertainty in determination of shock arrival times near the end wall translates into a ± 15 K uncertainty in temperature and $\pm 1.8\%$ uncertainty in total pressure. Shock heating in the incident wave has negligible effects on the initial reactant conditions behind the reflected gas as the residence time is small and the pressures and temperatures of the gases behind the incident wave are much lower than that for the reflected wave. Chemical reactions proceed immediately following the arrival of the reflected wave, leading to the buildup of reactive radicals until rapid radical chain branching or explosive conditions occur. It is this rapid chain branching that leads to increased temperature and pressure, which is denoted as ignition.

Ignition-delay times were monitored in two ways at the measurement station located 1.7 cm from the end wall. After arrival of the reflected wave and an appropriate rise in pressure, ignition was accompanied by another rapid pressure rise. The time delay between the arrival of the reflected wave and the rise in pressure caused by ignition was one measure of the ignition-delay time. A second and usually more sensitive technique for measuring the ignition delay involved monitoring the emission from electronically excited hydroxyl radicals formed during the induction period. The OH emission was monitored using a narrow bandpass filter centered at 307 nms and a 9659QB-EMI photomultiplier (PMT) attached near the end of the shock tube. Slits located next to the sapphire windows and near to the entrance of the PMT tube minimized signals from internal reflections. Overall response time of the optical system (slits, PMT electronics) was about 3–6 μs. (Ignition delays used in this study are >75 μs.) Ignition-delay times were determined by measuring the time from arrival of the reflected shock wave to the initial rapid rise of OH emission. Typically, the time to the rapid increase in signal could be determined within ± 5 μs and was generally within 20% of the delay time obtained from the pressure trace. At the lower temperature range of this study, this rapid rise was sometimes preceded by a slow increase in the OH emission, starting about 10–30% ahead of the rapid increase in the emission signal. OH emission signals and pressure profiles near the end wall were recorded on a LeCroy digital storage oscilloscope controlled from a personal computer.

Test mixtures of fuel, oxygen, and argon were premixed to obtain the desired compositions using a stainless-steel mixing rack, and they were stored in stainless-steel cylinders and/or quartz bulbs prior to usage. Gases were blended, using partial-pressure mixing techniques, and allowed to thoroughly mix overnight prior to testing. All components were obtained at high purity (i.e., greater than 99.95%). Estimated uncertainties in the final mixture compositions using the partial-pressure mixing technique are about 3% of the stated values.

Pure Fuels

Methane

Methane autoignition data obtained by more than 25 previous investigators have been reviewed and correlated by Spadaccini and Colket.[1] The correlation, derived from more than 500 methane-oxygen ignition-delay measurements over the temperature range 1250–2500 K, is presented in Fig. 2 along with selected data acquired in the previous study using the same apparatus and methods described here. Five mixture ratios were studied over a temperature range from 1350 to 2000 K and pressures from 3 to 15 atm. The ignition-delay correlation indicates a strong inverse dependence on the oxygen concentration and a relatively weak direct dependence on the methane concentration. As shown in the figure, the data obtained in Ref. 1 are in close agreement with the empirical expression derived from the literature survey, thereby validating the present experimental techniques and establishing a basis for comparison with the candidate scramjet fuels and surrogate endothermic-fuel/product mixtures.

Recently, a detailed chemical kinetics reaction mechanism for methane (called GRI-Mech) has been developed by Frenklach et al.[4] They demonstrate that their computed ignition-delay times agree with the experimental data set of Ref. 1 and others, to within a factor of two.

Ethylene

There have been several studies of ethylene ignition in shock tubes[5–9]; however, few of the authors have compared their results with those of other investigators. When comparisons are made, large differences are apparent. Different exponents have been used to describe the power dependencies of the reactant concentrations on delay time, and the overall activation energies vary significantly. Only one study[6] has attempted to carefully determine the overall reaction orders. Perhaps the most unifying feature of the earlier works is the agreement that the dependence of ignition on oxygen concentration

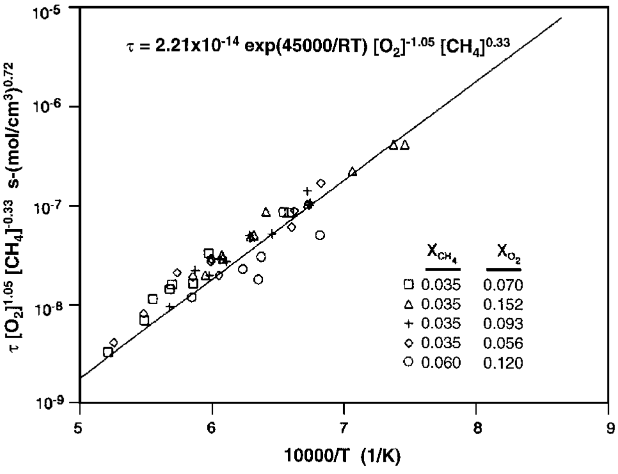

Fig. 2 Methane autoignition.[1]

is strong (i.e., $b < -1$), and the dependence on fuel concentration is weak (i.e., $0.3 < a < 0$). In contrast, reported values for the overall power dependency on argon diluent (or total pressure) range from +0.4 to −1.0. Unlike the methane system, there has been no effort to resolve these seemingly disparate results. Numerical comparisons of induction times are difficult because the reporting of experimental data has generally been incomplete. Therefore, because of large uncertainties inherent in extrapolating the different ignition-delay expressions, a reexamination of the existing data was undertaken, and additional experiments were performed to extend the range of the data sets and improve the correlating equation.

Three ethylene/oxygen/argon mixtures with equivalence ratios of 0.5, 0.75, and 1.0 (molar percentages of 0.7/4.2/95.1, 0.7/2.8/96.5, and 0.7/2.1/97.2, respectively) were tested at reaction pressures of 5–8 atm and temperatures ranging from about 1125 to 1410 K. The data are listed in the Appendix. Because there are very few existing data at similar pressures, the delay times were compared to the correlating expressions found in the literature. This comparison demonstrated the wide variation in the predictions of the previous investigators and verified the inadequacy of the existing empirical correlations. Therefore, the published data were combined with the newly acquired test results in an attempt to provide a better characterization of the overall reaction dependencies.

Direct comparison of results is difficult, as detailed tabulations of ignition-delay data for ethylene are generally not reported. High-temperature ($T > 1000$ K) ignition-delay data were extracted from information provided by Baker and Skinner[6] and from Suzuki et al.[9] and commingled with the present measurements to yield a large database with a sufficiently wide variation in the independent variables to provide a meaningful correlation. Most of the previous investigators have arbitrarily presented their data in a correlated form based on $[O_2]^{-1}$, even though much of their data suggest a greater negative oxygen power dependence. Sensitivity studies by Baker and Skinner[6] indicated oxygen concentration dependencies of −1.47, −1.37, and −0.61, with a reported average value of −1.1. However, the comparison that yielded the lowest exponent was obtained using a very lean mixture (i.e., $\Phi = 0.125$). For mixtures in the range $0.5 < \Phi < 2.0$, typical of the present study, the Baker and Skinner data support a stronger dependency on oxygen.

The overall dependence on the oxygen concentration was evaluated by plotting

$$\log\left\{\tau\big/[C_2H_4]^a[Ar]^c\exp(E/RT)\right\}\ \mathrm{vs}\ \log[O_2]$$

for dilute mixtures with nearly the same ethylene concentration. The values for a, c, and E were initially selected from the existing correlating expressions and later updated in an iterative process. The overall reaction order was established by the slope of the line and determined to be −1.2 (±0.15) for oxygen. Following this procedure, the ethylene and argon concentration dependencies were shown to be very weak and, because of the large relative uncertainties, a and c were equated to zero. These values for the exponents are reasonably consistent with those found in the literature. A least-squares fit of the combined data results in the expression

$$\tau = 2.82 \times 10^{-17}\exp(35{,}000/RT)[O_2]^{-1.2}$$

with an R^2 correlation coefficient of 0.947. The experimental data and the correlation are plotted in Fig. 3 and are shown to be in reasonable agreement.

Some effort was applied to comparing ignition-delay times computed using various ethylene reaction mechanisms found in the literature against these experimental data. The comparisons for this olefinic species were unsatisfactory and significantly inferior to those obtained for the alkanes, methane and heptane, suggesting that additional work is required in modeling ethylene ignition.

Heptane

Ignition delay of heptane in shock tubes has been studied by several investigators.[10–17] However, similar to ethylene, there has been little comparison of results from different investigations, although much of the data are presented along with initial conditions. Only Burcat et al.[14] developed a correlating equation. The expression that best describes their (Technion) data is

$$\tau = 3.2 \times 10^{-12}\exp(35{,}300/RT)[C_7H_{16}]^{0.2}[O_2]^{-1.1}[Ar]^{0.6}$$

where the preexponential has been modified here to convert from mass to molar concentration units.

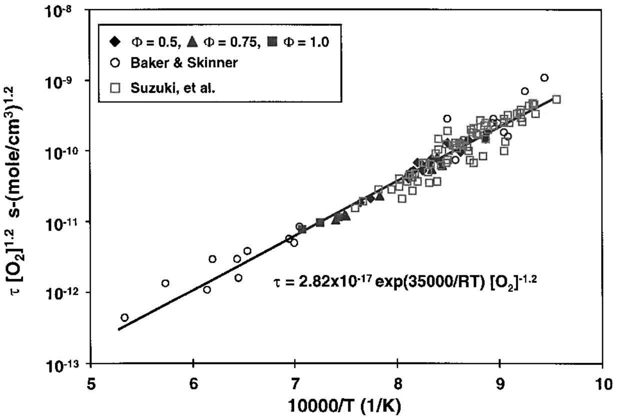

Fig. 3 Ethylene autoignition.

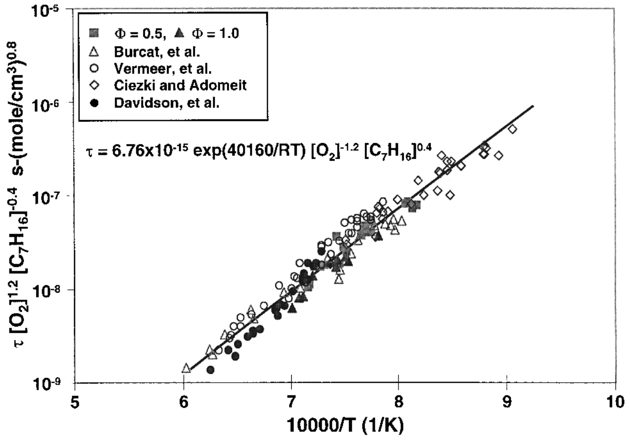

Fig. 4 Heptane autoignition.

Additional ignition-delay experiments were conducted for dilute mixtures of heptane in argon over the range of temperatures 1150–1410 K, pressures of approximately 6–8 atm, and equivalence ratios of 0.5 and 1.0 (corresponding to C_7H_{16}/O_2 mole fractions of 0.0019/0.042 and 0.0019/0.021, respectively). The results are also listed in the Appendix and plotted in Fig. 4, along with reflected-shock ignition measurements obtained from several other studies for $T > 1100$ K. (For $T < 1100$ K Ciezki and Adomeit[16] have observed a nonlinear ignition behavior, characterized by a negative temperature dependence and attributed to a transition in the kinetic mechanism.)

Overall reaction orders for heptane were determined using the data in Fig. 4 and the procedures just described for ethylene. A best fit for temperatures of 1080–1670 K was obtained using a weak power dependency (−0.2) for argon. However, to be consistent with the formulations for the other fuels, the argon dependence was set to zero, and the ignition-delay correlation for heptane was found to be

$$\tau = 6.76 \times 10^{-15}\exp(40{,}160/RT)[C_7H_{16}]^{0.4}[O_2]^{-1.2}$$

with an R^2 correlation coefficient of 0.958.

Ignition-delay times for heptane can now be calculated from detailed chemical kinetic mechanisms with quite good accuracy.[18–20] Delays calculated using the reaction mechanism of Held et al.[18] are compared with the experimental results in Fig. 5. In the predictions the ignition delay was defined as the time to the initial rapid rise in temperature, analogous to the interpretation of the experimental results based on the formation of excited OH radicals. Although

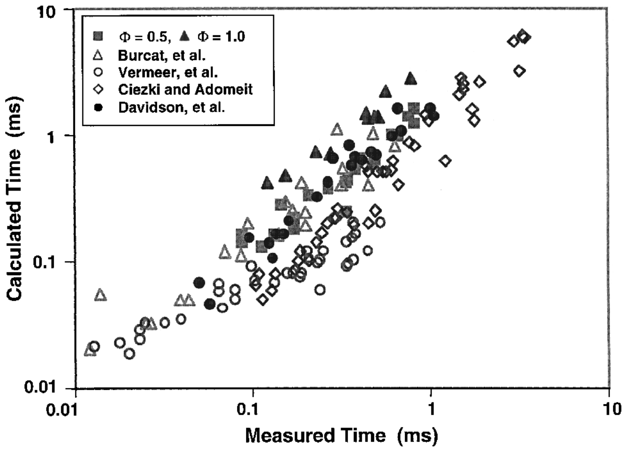

Fig. 5 Comparison of measured and calculated delay times for heptane.

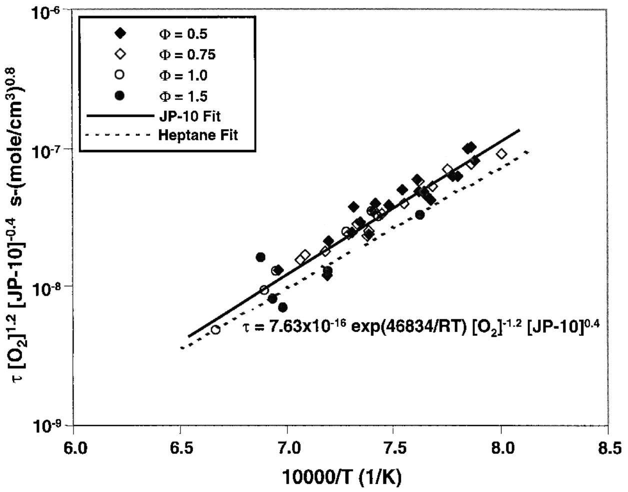

Fig. 6 JP-10 autoignition.

there are some systematic differences for selected data sets, most times are predicted to within a factor of two of the measured value. Some of the differences can be attributed to slight differences in the determination of the ignition-delay times by different authors. Overall, this agreement should be considered quite good considering the wide range in variation of the experimental parameters ($0.5 < \Phi < 2.0$, $1.35 < P < 13.5$ atm, and $1080 < T < 1670$ K).

JP-10

JP-10 is often used in volume-limited scramjet applications because of its high density; however, there is very little ignition-delay information available that is relevant to high-speed propulsion systems. Ignition-delay times for JP-10 have been reported by Ryan et al.[21] for liquid fuel injection into a heated cylindrical bomb that was developed for rating the ignition quality of diesel fuels. Tests were conducted at much higher pressure (~28 atm) and lower temperatures (590–855 K), and the system was subject to boundary-layer and geometry effects (e.g., surface/volume ratio) and uncertainties regarding the discrimination between physical and chemical delay times.

The very low vapor pressure of JP-10 (i.e., 3.1 torr at 25°C) limits the range of experiments that can be performed using an unheated shock tube and premixing system. However, because JP-10 is a single-component fuel (viz., exotetrahydrodicyclopentadiene), gaseous mixtures can be prepared by specifying the appropriate partial pressures. Tests were performed with gaseous mixtures of JP-10 and oxygen in argon, at equivalence ratios of 0.5, 0.75, 1.0, and 1.5 (molar percentages of 0.145/4.2/96.7, 0.218/4.2/95.6, 0.145/2.1/97.8, and 0.218/2.1/97.7, respectively). The data from this series of experiments are also included in the Appendix and plotted in Fig. 6.

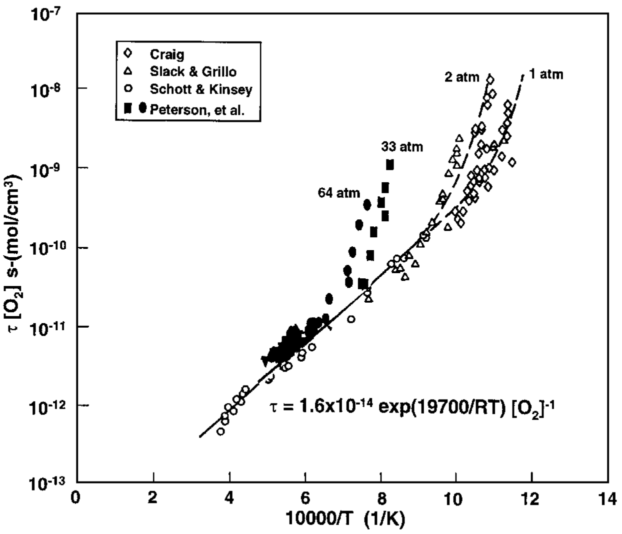

Fig. 7 Hydrogen autoignition.

Because the JP-10 ignition delays seemed to agree reasonably well with the heptane data, they were correlated using the same overall reaction orders developed in the analysis of the heptane data. The best fit yielded the expression

$$\tau = 7.63 \times 10^{-16} \exp(46{,}834/RT)[\text{JP-10}]^{0.4}[O_2]^{-1.2}$$

with an R^2 correlation coefficient of 0.908. For reference the heptane line is shown on this figure as well. The activation energy, 43.14 kcal/mol, is slightly higher than that for the heptane results, but may be a consequence of the use of a limited data set to obtain the correlation. In fact, the heptane correlating expression provides an adequate representation of the JP-10 data.

Hydrogen

There were no hydrogen autoignition experiments conducted in this study. Instead, experimental data showing the effects of initial pressure and temperature on the ignition-delay times of hydrogen-oxygen mixtures were extracted from the literature and presented in Fig. 7. Results reported by several investigators[22–25] for different mixture ratios, temperatures from 850 to 2500 K, and pressures from 1 to 64 atm are shown in the figure and correlated using the parameter $\tau\ [O_2]$. As shown, at high temperatures and relatively low pressures the induction times vary inversely with the oxygen concentration (pressure) and can be correlated by a single line described by the equation

$$\tau = 1.6 \times 10^{-14} \exp(19{,}700/RT)[O_2]^{-1}$$

However, at lower temperatures and relatively high pressures the pressure dependence of the ignition delay becomes nonlinear and shifts from an inverse proportionality (i.e., $\tau\alpha[O_2]^{-1}$) to a nearly direct proportionality. Furthermore, in these regions the induction periods can be very long and are extremely sensitive to small changes in temperature. This unusual pressure dependence is well known and can be explained by the removal of active hydrogen atoms through the formation of the HO_2 radical ($H + O_2 + M = HO_2 + M$), which does not participate in chain propagation. Because this reaction is weakly dependent on temperature, it is kinetically favored at low temperatures where the other chain-carrying reactions are slower. Furthermore, because it is a three-body reaction it becomes more important at higher pressures.

Surrogate Reformed Fuel Mixtures

Tests were conducted to evaluate the importance of fuel cracking on ignition-delay time of endothermic-fuel/product mixtures.

Specifically, ignition delays of typical constituents of a simulated reformed fuel were measured as a function of initial reactant temperatures for different equivalence ratios. A baseline or reference fuel mixture of 30/60/10 relative molar ratios of methane, ethylene, and heptane was specified as a surrogate for the endothermic reaction products. This mixture was selected to simulate, with a limited number of constituents, both the saturated and unsaturated hydrocarbon components of the gaseous product mixture.[2,3] The average molecular weight and C/H ratio of the simulant are comparable to that of a typical product mixture, reflecting a typical extent of cracking. Ignition-delay measurements were made for this surrogate mixture at equivalence ratios of 0.5 and 1.0. The mole fractions of oxygen were set to the same levels (0.042 and 0.021 for $\Phi = 0.5$ and 1.0, respectively) as for the tests of the neat fuels to facilitate comparisons. The ignition-delays measured for the two series of tests with the baseline reformed fuel are shown in Figs. 8 and 9. For comparison, ignition-delays calculated (for the same O_2 mole fractions) using the correlations for methane, heptane, ethylene, and hydrogen are also shown. The data at both lean and stoichiometric conditions indicate that ignition-delay times for ethylene are approximately one-third to one-half those for heptane at initial temperatures near 1300 K. Throughout the temperature range investigated, the ignition delays for the baseline reformed fuel lie between the correlations for ethylene and heptane. This result is reasonable because despite the significant molar quantity of methane it is well established that the other fuel components play a dominant role in defining the overall ignition delay.[1]

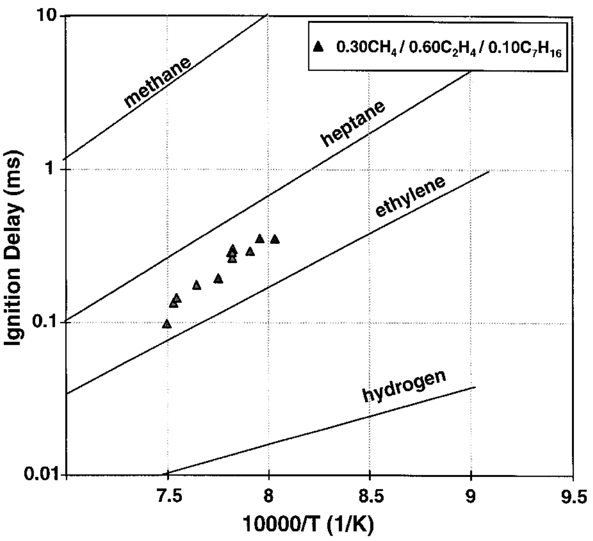

Fig. 8 Ignition delay of surrogate fuel ($\Phi = 0.5$ and $P = 7$ atm).

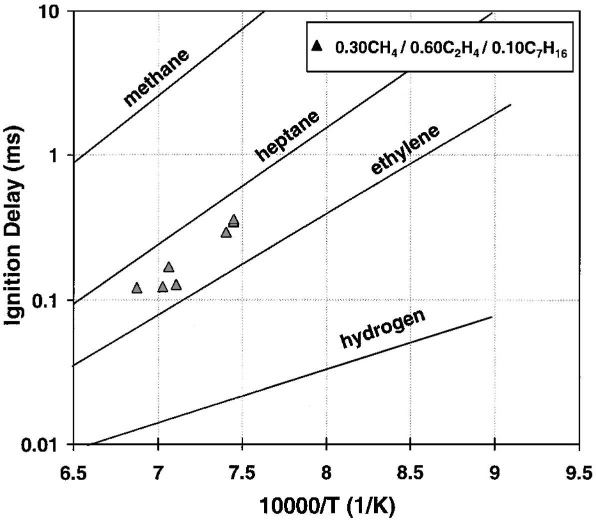

Fig. 9 Ignition delay of surrogate fuel ($\Phi = 1.0$ and $P = 7$ atm).

In the transition from a lean to a stoichiometric condition, the fuel concentration was maintained constant while the oxygen concentration was reduced; as a result, the ignition delays increased at the stoichiometric conditions. This seemingly anomalous result is simply a consequence of the reduced oxygen concentration caused by the experimental procedure. (In a more comprehensive analysis the corresponding data sets would be combined and general correlating equations derived for each fuel in terms of the reactant molar concentrations.)

In addition to the baseline reformed fuel, two other mixtures were selected to simulate different levels of reformation of the parent fuel, including the effect of the presence of hydrogen. The latter mixtures comprised 1) 20/80% baseline-fuel/heptane (low conversion) and 2) 90/10% baseline-fuel/hydrogen (dehydrogenation). As already shown, experiments were performed in an argon atmosphere at two equivalence ratios, 0.5 and 1.0, for each fuel, with the initial molar concentrations of oxygen equal to 0.042 and 0.021 (for the lean and stoichiometric mixtures, respectively).

Figures 10 and 11 depict the ignition-delay times for these two modified fuels at the two equivalence ratios. The correlations of the

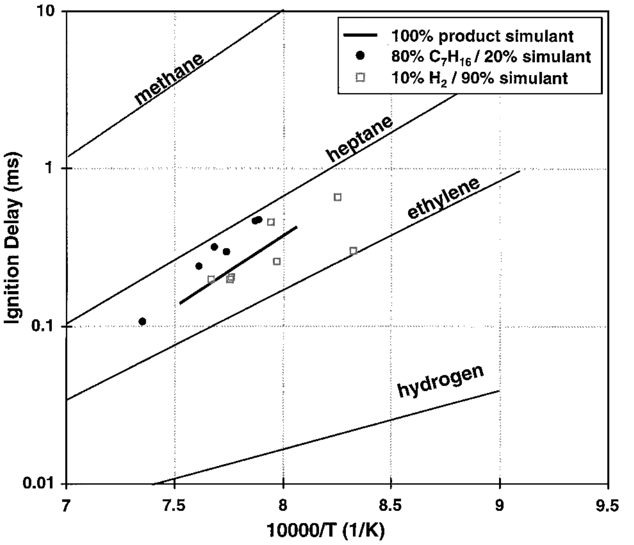

Fig. 10 Effects of partial decomposition and dehydrogenation ($\Phi = 0.5$ and $P = 7$ atm).

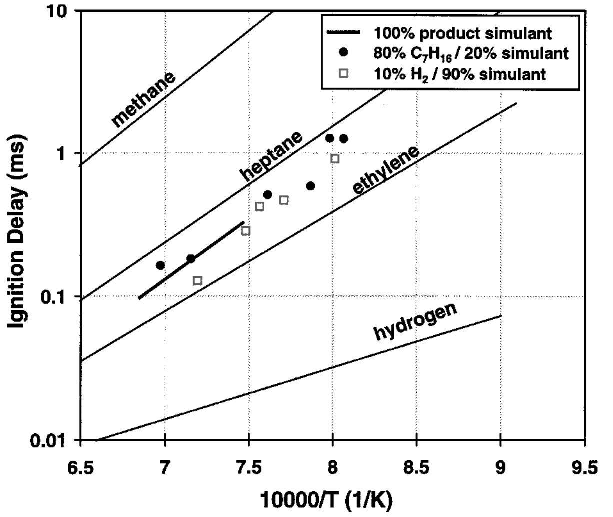

Fig. 11 Effects of partial decomposition and dehydrogenation ($\Phi = 1.0$ and $P = 7$ atm).

pure fuels are included along with least-square-fit representations of the baseline endothermic fuel (from Figs. 6 and 7) for comparison. Virtually all of these ignition-delay times fall between those of ethylene and heptane (at comparable temperatures). Not surprisingly, the mixture with 80% heptane and 20% simulated reaction products has ignition characteristics closer to that of the neat heptane. Despite the extremely short ignition delays for hydrogen inferred from the correlating expressions, the addition of hydrogen to the surrogate fuel shortens the ignition delay only a small amount. Because the effect is not dramatic, additional mixture studies with lower hydrogen concentrations are not warranted, especially because typical cracking of alkane-based fuels produce small quantities (<5%) of hydrogen.

The ignition-delay data for the three surrogate reformed fuel mixtures are also listed in the Appendix. A regression analysis was performed on each of the data sets and an ignition-delay correlation determined for each mixture, based upon the Arrhenius expression $\tau = A\ \exp(E/RT)$. These expressions are not reported here because they are based on a limited data set and are applicable for only a narrow range of conditions. Using these expressions and the correlations just determined for ethylene and heptane, ignition delays for the simulated reaction products were determined and compared to those of heptane at two temperatures and for two equivalence ratios. These relative values are listed in Table 1. For these computed values the mole fractions of oxygen were assumed to be $X_{O_2} = 0.042$, for $\Phi = 0.5$, and $X_{O_2} = 0.021$, for $\Phi = 1.0$.

Table 1 Comparison of ignition delay times (pressure = 7 atm)

	Relative ignition delay times			
	$\Phi = 0.5$		$\Phi = 1.0$	
Fuel	1300 K	1400 K	1300 K	1400 K
Methane	16.8	14.6	15.1	13.1
JP-10	1.33	1.20	1.33	1.20
Heptane	1	1	1	1
80% heptane/20% baseline[a]	0.96	0.72	0.86	0.73
Baseline fuel[a]	0.64	0.60	0.77	0.70
10% H_2/90% baseline[a]	0.58	0.49	0.66	0.51
Ethylene	0.33	0.39	0.33	0.39
Hydrogen	0.04	0.07	0.03	0.06

[a] ($0.3CH_4/0.6C_2H_2/0.1H_2$).

Conclusions

Shock-tube experiments were performed to measure and compare the ignition-delay times of several candidate scramjet fuels, namely ethylene, heptane, JP-10, and three model endothermic-fuel/cracked product mixtures. The newly acquired data for heptane and ethylene were compared to published data. Evaluations of the combined data sets demonstrated the inability of the already reported correlating expressions to reliably predict ignition-delay times over a wide range of conditions. Therefore, new empirical expressions for the ignition delays of ethylene and heptane were determined. Also, data were obtained for the ignition delay of JP-10 (for which few previous measurements have been reported), and an analogous autoignition correlation was determined, based on a limited range of conditions. Furthermore, the effect of thermal and catalytic cracking of alkane fuels on ignition delay was studied by simulating reformed-fuel/product mixtures and measuring ignition-delay times at lean and stoichiometric conditions. The results were compared to the ignition delays of the constituent species—methane, heptane, ethylene, and hydrogen. The autoignition correlations for each of the pure fuels are summarized in Table 2.

Relative ignition-delay times for the different fuels were found to be methane > JP-10 ≅ heptane > reformed fuel > ethylene > hydrogen. The delays for the simulated reformed fuel were about 50–70% that of heptane, the "parent hydrocarbon," supporting arguments that the endothermic reaction products will ignite more readily. Addition of heptane to the simulated reformed fuel increased the ignition delay, whereas addition of hydrogen decreased the ignition delay. However, the ignition delay of the mixture is not driven entirely by that of the constituent with the shortest ignition delay (in this case, ethylene or hydrogen). Based on the studies of the cracked product simulant with heptane and hydrogen added, small changes in concentrations of the individual component species of a (partially) reformed fuel are not likely to make dramatic changes in the ignition-delay times.

Table 2 Ignition delay correlations, ($\tau = A\ \exp(E/RT)\ [O_2]^a\ [\text{fuel}]^b$; $1100\ K \leq T \leq 1500\ K$)

Fuel	A	E	a	b
Methane[1]	2.21×10^{-14}	45,000	−1.05	0.33
Heptane	6.76×10^{-15}	40,160	−1.20	0.40
Ethylene	2.82×10^{-17}	35,000	−1.20	0.00
Hydrogen	1.60×10^{-14}	19,700	−1.00	0.00
JP-10	2.36×10^{-15}	43,855	−1.20	0.40

[ ] concentrations in mol/cc.

Appendix: Autoignition Data

Fuel	T, K	P, atm	τ, s	[fuel], mol/cc	[O_2], mol/cc	10,000/T, 1/K
Ethylene	1210	5.27	3.16E−04	3.72E−07	2.23E−06	8.26
$\phi = 0.5$	1223	5.82	2.90E−04	4.06E−07	2.44E−06	8.18
$X_{C_2H_4} = 0.007$	1127	4.83	9.00E−04	3.65E−07	2.19E−06	8.87
$X_{O_2} = 0.042$	1186	5.45	4.00E−04	3.92E−07	2.35E−06	8.43
	1291	6.46	1.06E−04	4.27E−07	2.56E−06	7.75
	1232	5.82	2.22E−04	4.03E−07	2.42E−06	8.12
	1308	6.62	9.35E−05	4.31E−07	2.59E−06	7.64
	1158	5.22	5.54E−04	3.84E−07	2.31E−06	8.64
	1229	5.96	2.67E−04	4.14E−07	2.48E−06	8.14
	1149	5.73	7.42E−04	4.26E−07	2.55E−06	8.71
	1125	5.62	9.48E−04	4.26E−07	2.56E−06	8.89
	1201	6.72	3.06E−04	4.77E−07	2.86E−06	8.33
	1198	7.01	3.26E−04	5.00E−07	3.00E−06	8.35
	1219	7.62	2.64E−04	5.33E−07	3.20E−06	8.20
	1210	7.89	2.34E−04	5.56E−07	3.34E−06	8.26
	1176	7.05	5.37E−04	5.11E−07	3.07E−06	8.50
$\phi = 0.75$	1350	6.97	8.55E−05	4.41E−07	1.76E−06	7.41
$X_{C_2H_4} = 0.007$	1333	7.07	9.20E−05	4.53E−07	1.81E−06	7.50
$X_{O_2} = 0.028$	1182	5.76	5.24E−04	4.15E−07	1.66E−06	8.46
	1334	7.53	8.90E−05	4.82E−07	1.93E−06	7.50

(Continued)

Appendix: Autoignition Data (continued)

Fuel	T, K	P, atm	τ, s	[fuel], mol/cc	[O_2], mol/cc	10,000/T, 1/K
	1276	6.94	1.73E−04	4.64E−07	1.85E−06	7.83
	1197	6.16	4.42E−04	4.39E−07	1.76E−06	8.35
	1233	6.60	3.45E−04	4.57E−07	1.83E−06	8.11
	1191	6.18	6.36E−04	4.43E−07	1.77E−06	8.40
$\phi = 1.0$	1414	7.09	9.05E−05	4.28E−07	1.28E−06	7.07
$X_{C_2H_4} = 0.007$	1346	6.58	1.36E−04	4.17E−07	1.25E−06	7.43
$X_{O_2} = 0.021$	1380	7.64	1.02E−04	4.72E−07	1.42E−06	7.25
Heptane	1393	7.72	8.85E−05	1.30E−07	2.86E−06	7.18
$\phi = 005$	1299	7.78	3.45E−04	1.40E−07	3.09E−06	7.70
$X_{C_7H_{16}} = 0.00192$	1235	7.04	6.31E−04	1.33E−07	2.94E−06	8.10
$X_{O_2} = 0.0423$	1299	6.38	3.48E−04	1.15E−07	2.53E−06	7.70
	1372	7.53	1.34E−04	1.28E−07	2.83E−06	7.29
	1236	6.08	6.78E−04	1.15E−07	2.54E−06	8.09
	1340	7.35	1.48E−04	1.28E−07	2.83E−06	7.46
	1328	6.63	2.11E−04	1.17E−07	2.57E−06	7.53
	1395	6.94	8.90E−05	1.16E−07	2.57E−06	7.17
	1289	4.88	4.17E−04	8.86E−08	1.95E−06	7.76
	1383	5.53	1.76E−04	9.36E−08	2.06E−06	7.23
	1403	6.09	1.14E−04	1.02E−07	2.24E−06	7.13
	1334	5.50	2.72E−04	9.64E−08	2.12E−06	7.49
	1304	5.13	3.84E−04	9.21E−08	2.03E−06	7.67
	1229	4.62	7.73E−04	8.80E−08	1.94E−06	8.14
	1344	5.87	3.42E−04	1.02E−07	2.25E−06	7.44
	1238	4.83	8.32E−04	9.13E−08	2.01E−06	8.08
	1223	4.36	8.44E−04	8.33E−08	1.84E−06	8.18
	1297	4.85	5.04E−04	8.75E−08	1.93E−06	7.71
	1367	5.63	1.76E−04	9.64E−08	2.12E−06	7.32
	1290	5.44	4.93E−04	9.86E−08	2.17E−06	7.75
$\phi = 1.0$	1427	7.22	1.23E−04	1.18E−07	1.30E−06	7.01
$X_{C_7H_{16}} = 0.00192$	1332	6.45	4.42E−04	1.13E−07	1.24E−06	7.51
$X_{O_2} = 0.0211$	1413	7.08	1.55E−04	1.17E−07	1.29E−06	7.08
	1387	6.93	2.76E−04	1.17E−07	1.28E−06	7.21
	1280	5.77	7.97E−04	1.05E−07	1.16E−06	7.81
	1345	5.83	4.56E−04	1.01E−07	1.11E−06	7.44
	1406	4.51	2.31E−04	7.51E−08	8.26E−07	7.11
	1326	4.16	5.68E−04	7.33E−08	8.07E−07	7.54
	1356	4.46	5.19E−04	7.69E−08	8.45E−07	7.37
	1348	4.10	5.00E−04	7.12E−08	7.83E−07	7.42
JP-10	1353	6.98	1.81E−04	9.11E−08	2.64E−06	7.39
$\phi = 0.5$	1285	6.76	4.65E−04	9.30E−08	2.69E−06	7.78
$X_{\text{JP-10}} = 0.00145$	1312	7.06	3.59E−04	9.51E−08	2.75E−06	7.62
$X_{O_2} = 0.042$	1325	7.03	3.68E−04	9.38E−08	2.72E−06	7.55
	1336	7.01	2.84E−04	9.27E−08	2.68E−06	7.48
	1274	6.42	7.59E−04	8.90E−08	2.58E−06	7.85
	1268	6.22	6.40E−04	8.67E−08	2.51E−06	7.88
	1312	6.40	4.68E−04	8.62E−08	2.50E−06	7.62
	1282	6.28	4.96E−04	8.66E−08	2.51E−06	7.80
	1391	4.52	1.31E−04	5.74E−08	1.66E−06	7.19
	1360	6.80	2.24E−04	8.83E−08	2.56E−06	7.35
	1348	6.83	3.06E−04	8.96E−08	2.59E−06	7.42
	1271	6.16	8.09E−04	8.57E−08	2.48E−06	7.87
	1302	6.45	3.28E−04	8.75E−08	2.53E−06	7.68
	1366	7.14	2.81E−04	9.24E−08	2.68E−06	7.32
	1306	3.91	5.28E−04	5.29E−08	1.53E−06	7.66
	1436	4.59	1.43E−04	5.65E−08	1.64E−06	6.97
	1389	4.40	2.34E−04	5.60E−08	1.62E−06	7.20
	1350	4.22	3.96E−04	5.52E−08	1.60E−06	7.41
	1368	4.37	2.71E−04	5.65E−08	1.64E−06	7.31
$\phi = 0.75$	1356	7.09	2.00E−04	1.39E−07	2.68E−06	7.38
$X_{\text{JP-10}} = 0.00218$	1301	6.36	4.93E−04	1.30E−07	2.51E−06	7.68
$X_{O_2} = 0.042$	1248	6.07	8.40E−04	1.29E−07	2.49E−06	8.01
	1270	6.40	6.90E−04	1.33E−07	2.58E−06	7.87
	1363	7.21	2.43E−04	1.40E−07	2.71E−06	7.34
	1371	7.65	1.96E−04	1.48E−07	2.86E−06	7.29
	1354	7.53	2.12E−04	1.47E−07	2.85E−06	7.39
	1288	6.53	6.31E−04	1.34E−07	2.60E−06	7.76
	1312	6.61	5.24E−04	1.34E−07	2.58E−06	7.62
	1342	7.15	2.87E−04	1.41E−07	2.73E−06	7.45
	1307	6.39	4.43E−04	1.30E−07	2.51E−06	7.65
	1411	4.24	2.28E−04	7.96E−08	1.54E−06	7.09
	1393	4.08	2.46E−04	7.77E−08	1.50E−06	7.18
	1415	4.36	2.06E−04	8.17E−08	1.58E−06	7.07

(Continued)

Appendix: Autoignition Data (continued)

Fuel	T, K	P, atm	τ, s	[fuel], mol/cc	[O_2], mol/cc	10,000/T, 1/K
	1348	4.01	4.59E−04	7.88E−08	1.52E−06	7.42
	1324	3.93	5.46E−04	7.88E−08	1.52E−06	7.55
$\phi = 1.0$	1449	6.77	1.74E−04	8.26E−08	1.20E−06	6.90
$X_{C_2H_4} = 0.00145$	1439	6.88	2.31E−04	8.45E−08	1.22E−06	6.95
$X_{O_2} = 0.021$	1344	6.23	6.03E−04	8.19E−08	1.19E−06	7.44
	1351	5.83	6.99E−04	7.62E−08	1.10E−06	7.40
	1372	6.26	4.75E−04	8.05E−08	1.17E−06	7.29
	1499	3.16	1.71E−04	3.72E−08	5.39E−06	6.67
$\phi = 1.5$	1440	4.33	2.53E−04	7.96E−08	7.72E−07	6.94
$X_{\text{JP-10}} = 0.00218$	1432	4.48	2.12E−04	8.29E−08	8.04E−07	6.99
$X_{O_2} = 0.0211$	1388	4.25	3.90E−04	8.11E−08	7.86E−07	7.20
	1310	3.62	1.10E−04	7.33E−08	7.11E−07	7.63
	1454	4.34	5.03E−04	7.92E−08	7.68E−07	6.88
Simulant[a]	1308	6.41	1.77E−04	3.59E−07	2.54E−06	7.64
$\phi = 0.5$	1245	6.07	3.51E−04	3.57E−07	2.53E−06	8.03
	1334	7.19	9.80E−05	3.95E−07	2.80E−06	7.50
	1328	6.47	1.36E−04	3.57E−07	2.53E−06	7.53
	1279	6.01	2.64E−04	3.44E−07	2.44E−06	7.82
	1257	6.04	3.53E−04	3.52E−07	2.49E−06	7.96
	1278	6.34	3.01E−04	3.63E−07	2.58E−06	7.82
	1280	6.45	2.85E−04	3.69E−07	2.62E−06	7.81
	1279	6.50	2.86E−04	3.73E−07	2.64E−06	7.82
	1290	6.79	1.95E−04	3.85E−07	2.73E−06	7.75
	1265	6.64	2.92E−04	3.85E−07	2.73E−06	7.91
	1326	7.46	1.45E−04	4.12E−07	2.92E−06	7.54
$\phi = 1.0$	1416	6.70	1.68E−04	3.48E−07	1.21E−06	7.06
	1351	6.17	2.91E−04	3.36E−07	1.17E−06	7.40
	1455	7.24	1.22E−04	3.66E−07	1.28E−06	6.87
	1407	6.92	1.28E−04	3.62E−07	1.26E−06	7.11
	1343	6.26	3.58E−04	3.43E−07	1.20E−06	7.45
	1343	6.55	3.44E−04	3.59E−07	1.25E−06	7.45
	1423	7.20	1.23E−04	3.72E−07	1.30E−06	7.03
0.8 Heptane/0.2 Simulant	1271	6.32	4.62E−04	1.35E−07	2.56E−06	7.87
$\phi = 0.5$	1361	7.67	1.08E−04	1.53E−07	2.90E−06	7.35
	1315	6.33	2.37E−04	1.30E−07	2.48E−06	7.61
	1269	6.00	4.75E−04	1.28E−07	2.43E−06	7.88
	1302	6.42	3.14E−04	1.33E−07	2.53E−06	7.68
	1293	6.45	2.97E−04	1.35E−07	2.56E−06	7.74
$\phi = 1.0$	1434	7.40	1.64E−04	1.42E−07	1.33E−06	6.97
	1398	7.14	1.82E−04	1.41E−07	1.31E−06	7.15
	1314	6.66	5.14E−04	1.39E−07	1.30E−06	7.61
	1253	6.37	1.27E−03	1.40E−07	1.31E−06	7.98
	1240	6.07	1.26E−03	1.35E−07	1.26E−06	8.06
	1271	5.31	5.90E−04	1.15E−07	1.07E−06	7.87
0.1 Hydrogen/0.9 Simulant	1259	5.92	4.61E−04	3.68E−07	2.40E−06	7.94
$\phi = 0.5$	1290	6.87	1.97E−04	4.17E−07	2.72E−06	7.75
	1212	6.26	6.57E−04	4.04E−07	2.64E−06	8.25
	1212	6.36	6.59E−04	4.11E−07	2.68E−06	8.25
	1255	7.08	2.58E−04	4.42E−07	2.89E−06	7.97
	1289	7.64	2.04E−04	4.64E−07	3.03E−06	7.76
	1305	7.41	1.97E−04	4.45E−07	2.90E−06	7.67
	1201	6.36	3.03E−04	4.15E−07	2.71E−06	8.32
$\phi = 1.0$	1298	6.09	4.72E−04	3.77E−07	1.20E−06	7.71
	1337	6.54	2.87E−04	3.92E−07	1.25E−06	7.48
	1391	7.32	1.28E−04	4.23E−07	1.34E−06	7.19
	1322	6.65	4.26E−04	4.04E−07	1.28E−06	7.56
	1248	6.13	9.17E−04	3.94E−07	1.25E−06	8.01

[a] $0.3CH_4/0.6C_2H_4/0.1H_2$.

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