

Report Title

DEVELOPMENT OF AN AEROSOL LOADING TECHNIQUE FOR IGNITION TIME MEASUREMENTS IN SHOCK TUBES

ABSTRACT

We have developed a new aerosol loading technique to be used in shock tube measurements of combustion kinetics, in particular ignition times, of low-vapor pressure fuels. This technique provides a uniform spatial distribution of aerosol in the shock tube, which ensures well-behaved shock-induced flows and a narrow micron-sized aerosol size distribution that rapidly evaporates, thereby providing the capability to produce high-concentration vapor mixtures derived from a wide variety of fluids including low-vapor-pressure practical fuels and fuel surrogates. At present we utilize the incident shock wave to vaporize the fuel droplets, and the reflected shock wave to induce chemical reaction. We report here the first aerosol shock tube ignition delay time measurements of n-dodecane/O₂/argon mixtures. These measurements are found to be consistent with those made in our heated shock tube facility.

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S. S. Vasu, D. F. Davidson, R. K. Hanson, "Shock Tube Measurements of Jet Fuel Ignition Delay Times," in press Combustion and Flame, January 2007.

D. F. Davidson, M. A. Oehlschlaeger, R. K. Hanson, "Methyl Concentration Time Histories during iso-Octane and n-Heptane Oxidation," Proceedings of the Combustion Institute 31, 321-328, 2007.

T. C. Hanson, D. F. Davidson, R. K. Hanson, "Shock Induced Behavior in Micron-Sized Water Aerosols," Physics of Fluids 19, (DOI:10.1063/1.2736082) 2007.

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S. S. Vasu, D. F. Davidson, R. K. Hanson, “Jet Fuel Ignition Delay Times: Shock Tube Investigations at High Pressures,” 21st ICDERS Meeting, Poitiers France, July 2007.

S. S. Vasu, N. N. Parikh, D. F. Davidson, R. K. Hanson, “Methylcyclohexane Oxidation: Shock Tube Experiments and Modeling,” 5th U.S. Combustion Meeting, Paper D17, San Diego CA, March 2007.

S. S. Vasu, D. F. Davidson, R. K. Hanson, “Shock Tube Ignition Delay Times and Modeling of Jet Fuel Mixtures,” Paper AIAA-2006-4402, 42nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Cincinnati OH, July 2006.

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Number of Inventions:

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Megan MacDonald	0.10
FTE Equivalent:	0.60
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Names of Post Doctorates

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FTE Equivalent:	
Total Number:	1

Names of Faculty Supported

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FTE Equivalent:	0.01	
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Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
n/a	
FTE Equivalent:	
Total Number:	1

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**Development of an Aerosol Loading Technique for
Ignition Time Measurements in Shock Tubes**

Prepared for:

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DEVELOPMENT OF AN AEROSOL LOADING TECHNIQUE FOR IGNITION TIME MEASUREMENTS IN SHOCK TUBES

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SUMMARY

We have developed a new aerosol loading technique to be used in shock tube measurements of combustion kinetics, in particular ignition times, of low-vapor pressure fuels. This technique provides a uniform spatial distribution of aerosol in the shock tube, which ensures well-behaved shock-induced flows and a narrow micron-sized aerosol size distribution that rapidly evaporates, thereby providing the capability to produce high-concentration vapor mixtures derived from a wide variety of fluids including low-vapor-pressure practical fuels and fuel surrogates. At present we utilize the incident shock wave to vaporize the fuel droplets, and the reflected shock wave to induce chemical reaction. We report here the first aerosol shock tube ignition delay time measurements of n-dodecane/O₂/argon mixtures. These measurements are found to be consistent with those made in our heated shock tube facility.

STATEMENT OF THE PROBLEM STUDIED

There is a need for a research facility that will enable the study of aerosols in both the liquid phase and solid phase in a gaseous medium with the same flexibility that a shock tube facility can provide for gas phase studies. Shock tubes can provide well-defined temperatures and pressures that cover broad regimes of engineering and scientific interest (temperatures of 500-5000 K and higher, pressures from sub-atmospheric to 500 atm and higher), with near-instantaneous heating of spatially uniform mixtures and stationary flow behind reflected shock waves. The ability to generate these conditions has enabled shock tubes to be used for chemical studies such as ignition delay time and elementary reaction rate determinations. Current interest in the chemistry and high temperature behavior of low-vapor-pressure liquid fuels (such as jet and diesel fuel), solid phase energetic materials (such as RDX and other explosives and propellants) and biological materials has motivated our laboratory to seek a method that would enable application of shock tube techniques to these different materials.

Shock tubes have been used to study aerosols in the past.¹ The previous experimental studies in the area of combustion have concentrated on measurements of the shock interaction, evaporation and ignition of single fuel droplets^{2,3,4} or the ignition properties of diesel-injector-generated sprays.⁵ The single fuel droplet experiments provide images of shock waves interacting with millimeter size droplets and thus yield only a macroscopic description of droplet ignition behind shock waves. The diesel injector spray studies provide information about the relative ignition properties of different fuels, but analysis of the data is complicated because the chemistry of ignition of these sprays is strongly convoluted with the evaporation processes of the droplets. As a consequence of the large size of the single droplets and the strongly varying spatial distribution and highly non-uniform size distribution of the diesel injector spray aerosols, details of the shock-spray interaction and the chemistry of these experiments are not easily quantified.

What is required is a shock tube method: to generate a spatially uniform aerosol so that the conditions which the aerosol experiences behind the shock wave are uniform along the line of sight; to generate a narrow aerosol size distribution that also has a small diameter ($D_{v50} = 1\text{-}10$ microns) that will permit a simpler interpretation of the evaporation effects; and is applicable to a wide variety of fluids, particularly those with low-vapor-pressures, that will permit chemical kinetics studies of fuels of current interest.

We have built a new aerosol shock tube that fits these requirements. In brief, we have modified a standard shock tube design to allow spatially-uniform filling with an aerosol mixture. The aerosol is generated using a nebulizer and has a small mean droplet diameter and a very narrow size distribution. The aerosol diameter is chosen to be small enough that it rapidly evaporates, and generally does not react, at the elevated temperatures and pressures behind the incident shock wave. This produces a purely-vapor-phase mixture that can react at still more elevated temperatures and pressures behind the reflected shock wave.

Using this aerosol shock tube, the vapor-phase ignition delay times of low-vapor-pressure fuels and fuel surrogates, such as JP-7 and n-dodecane, can be measured at high fuel loading concentrations. Previous to this, high fuel loading ignition time measurements (stoichiometric in air for example) required a heated shock tube and mixing facility, typically to 120 C or higher. This was necessary, as the room temperature vapor pressure of these substances is significantly below 1 torr, and high fuel concentration mixtures required substantially higher vessel temperatures. One concern with the heated shock tube method is that the mixture is heated to the intermediate temperature for a long time (minutes to hours) during experimental setup, and this mixture of fuel and oxidizer may begin to react before the actual experiment. Using the aerosol shock tube, this intermediate heating (behind the incident shock wave) is limited to a few hundreds of microseconds.

SUMMARY OF THE MOST IMPORTANT RESULTS

We present a description of the aerosol shock tube, some of the theory of its operation, and representative ignition delay time data taken using this facility for a low-vapor pressure surrogate fuel: n-dodecane. This work required the development and application of both a shock code to predict the conditions behind the shock wave after evaporation, and a laser absorption method to determine the fuel loading; both of these techniques are also described.

Aerosol Shock tube

The aerosol shock tube method has been developed based on preliminary work in our laboratory.^{6,7} A schematic of the aerosol shock tube is shown in Fig. 1, and its operation is highlighted in Fig. 2.

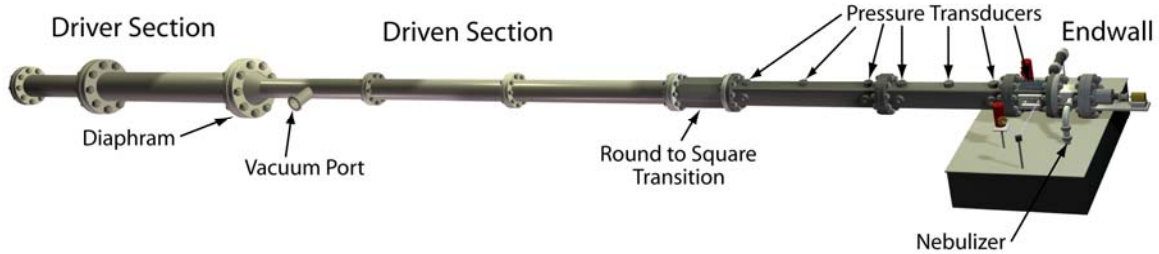


Fig. 1. Schematic of aerosol shock tube. Overall length 18 m.

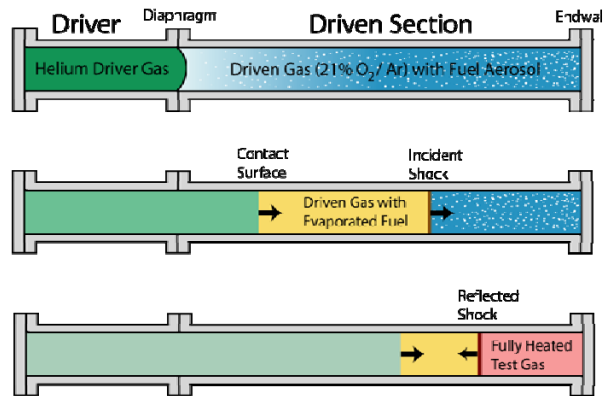


Fig. 2. Schematic of operation.

The shock tube is of standard design with a modified endwall section to permit filling with an aerosol mixture. The shock tube has a 3 m driver section with a 15 cm internal diameter and a 9.6 m driven section with a 10 cm diameter, which transitions to a 2 meter long square end section 10 cm in width. Polycarbonate diaphragms which isolate the driven section are burst by pressurizing the driver with helium. All sections of the facility are pumped using two-stage mechanical pumps. Incident shock speeds are

measured using seven fast-response, small-area pressure transducers (PCB 132A32) evenly spaced along the last quarter of the shock tube, and end section pressure is measured using a Kistler 603B1 PZT pressure transducer at 2 cm from the endwall.

A uniform aerosol mixture is created by entraining an aerosol created by an ultrasonic nebulizer (Ocean Mist, 20 mm disk size) in the carrier gas. The typical fuel aerosol created by this nebulizer has a lognormal distribution with a count mean diameter of approximately $2.9\ \mu\text{m}$ (VMD 5.05) and a lognormal width of approximately $1.5\ \mu\text{m}$, measured with a Malvern RTS particle sizer. A typical size distribution is shown in Figure 3. The size distribution was also measured using a four and five wavelength Mie-scattering diagnostic as described by Hanson et al.⁷ The shape and size distribution of the droplets is not heavily affected by the type of fuel.⁶ Droplet loading is typically 5-15 ppm by volume. The nebulizer is located approximately 100 cm from the end wall. The transit time (~ 0.1 seconds) for the aerosol to travel this distance, allows for heavier droplets/particles to settle out of the flow.

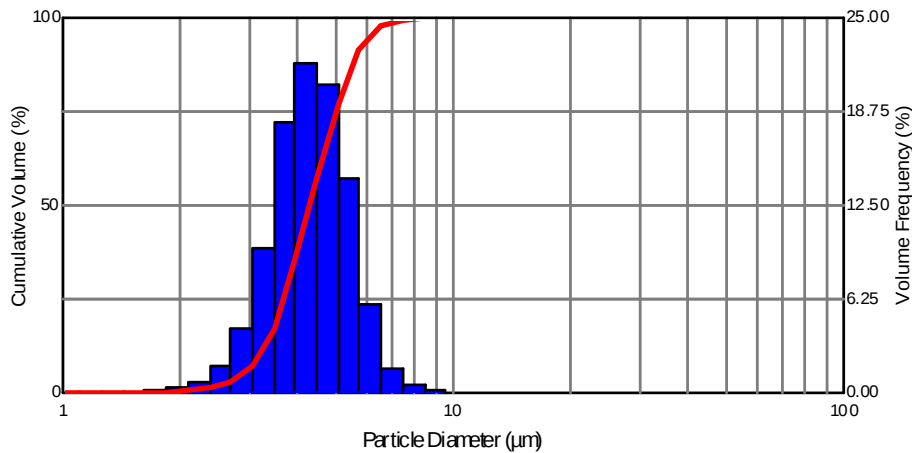


Fig. 3. Representative nebulizer-generated aerosol size distribution for water.

In carrying out an ignition time test, the shock tube is first fully evacuated, and then the driven section is filled with an oxidizer-inert gaseous mixture to the desired initial pressure. For the present ignition study a 21% oxygen-79% argon mixture was used. Poppet valves in the endwall are then opened as well as a valve near the diaphragm connected to a vacuum pump, and a steady-state flow of aerosol/carrier gas mixture is feed into the shock tube while keeping the pressure in the driven section of the tube constant. The narrow flow passage past the poppet valves serves to accelerate the flow and generate turbulence near the endwall, facilitating creation of a spatially uniform distribution of particles. This filling approximates a plug flow of aerosol mixture which displaces the dry carrier gas mixture. The amount of fuel in the reactant mixture can be varied by adjustments in the aerosol carrier gas flow rate. The flow of fuel droplet-laden oxidizer-inert mixture is allowed to flow for about 50-60 seconds until uniform conditions are established in the shock tube. All valves are then closed and the driver section is filled until the diaphragm bursts. Optical access to the test gas volume is made through opposing windows at several locations in the end section.

Laser and Optical Diagnostics

Measurements in the test volume before and during the shock wave experiments are made using several IR laser systems and a visible emission scheme. A Mie scattering measurement to determine the lifetime of the aerosol droplets is made using a tunable IR laser diode (NEL model 0301155-NLK1U5E1AA) at a non-resonant (i.e. non-absorbing) wavelength (1625 nm). A gas-phase concentration measurement of the fuel vapor is made using a low-noise IR He-Ne laser (Jodon HN-10G-IR) resonant with the C-H stretch vibration mode (3.39 μm). The ignition time is measured using CH* emission (431 nm) with a photomultiplier/filter (10 nm bandpass) combination;⁸ similar ignition times are recovered from the PZT pressure transducer in the end section. Hydrocarbon species time-histories and temperature have also been measured simultaneously using a new multi-wavelength method developed in our laboratory.⁹

The non-resonant laser provides a time-history of droplet extinction at the observation location 2 cm from the end wall. Based on Mie theory the extinction of an aerosol can be represented by Equation 1.

$$-\ln\left(\frac{I}{I_0}\right)_v = C_{\text{Mie}}\sigma NL \quad (1)$$

In this equation, I is the transmitted light intensity, I_0 is the incident light intensity, the quantity $-\ln(I/I_0)$ is the extinction, C_{Mie} is a coefficient that depends on the complex refractive index of the droplets, σ is an effective scattering cross section, N is the number density of particles in the laser path, and L is the path length. The Mie coefficient and the cross-section both depend on the size distribution function of the poly-disperse aerosol. However, in our case what is important is the fact that the extinction is proportional to the particle cross section. While the droplet distribution and the refractive index may not be accurately known, if the laser extinction goes to zero, no liquid droplets remain in the laser path.

The resonant laser beam is attenuated by both scattering and absorption when droplets exist in the flow. Interpretation of the measurement during this period is complex, however, once the non-resonant laser sensor indicates complete evaporation, the resonant wavelength measures pure gas-phase absorption only. This measurement can then be interpreted using the Beer-Lambert relation shown in Equation 2,

$$\alpha_v \equiv -\ln\left(\frac{I}{I_0}\right)_v = \sigma_v N_i L \quad (2)$$

where α_v is the spectral absorbance, N_i is the number density of absorbing molecules in the laser path and σ_v the spectral cross section. We have measured the spectral cross section for various fuels over a range of temperatures in a heated cell with known amounts of fuel.¹⁰ See Fig. 4 for representative data for n-dodecane. Using the cross-sections for a given fuel and the measured absorbance, the number density of fuel molecules can be easily determined.

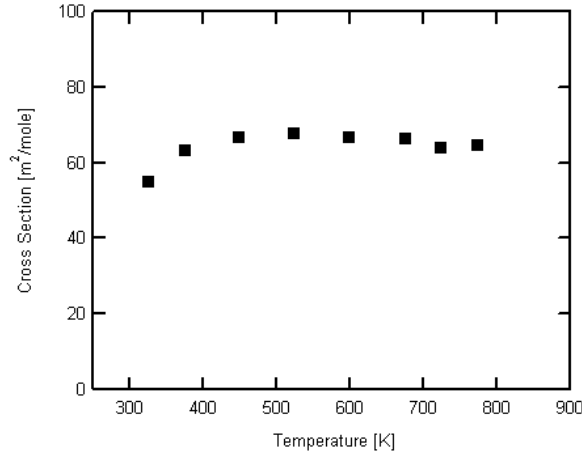


Fig. 4. Spectral absorption cross-section data at $\lambda = 3.39224 \mu\text{m}$ for n-dodecane.

Theory of Operation

After the shock wave passes a droplet in the aerosol, the carrier gas around the droplet accelerates almost instantly and increases in pressure and temperature; consequentially, the droplet encounters a strong convective influence that will stimulate the transfer of momentum, energy, and mass. The acceleration and/or breakup of these small droplets is relatively fast; the transfer of energy and mass which leads to evaporation is slower, but still relatively quick because of the hot and strongly under-saturated nature of the region 2 environment. Diffusion of the aerosol vapor will occur simultaneously with the evaporation process. The process is shown schematically in Figure 5 on an x-t diagram. It is of note that the gas mixture that is ultimately probed at the measurement location was originally located well upstream of the measurement location, was swept downstream behind the incident shock wave, and came to rest behind the reflected shock wave.

Measurements made at locations very close to the endwall probe gas mixtures that have very short residence times behind the incident shock wave and will likely only fully evaporate and diffuse behind the reflected shock wave. If the evaporation and diffusion times behind the reflected shock are short relative to the chemical process being studied, this may not be a significant disadvantage. However, in the work to be reported here the evaporation is observed to be complete at the measurement location, prior to arrival of the reflected shock wave. The interaction of a shock wave and an aerosol has been studied by numerous researchers.^{11,12,13} In the following section, we describe some theoretical and experimental aspects of the operation of the aerosol shock tube.

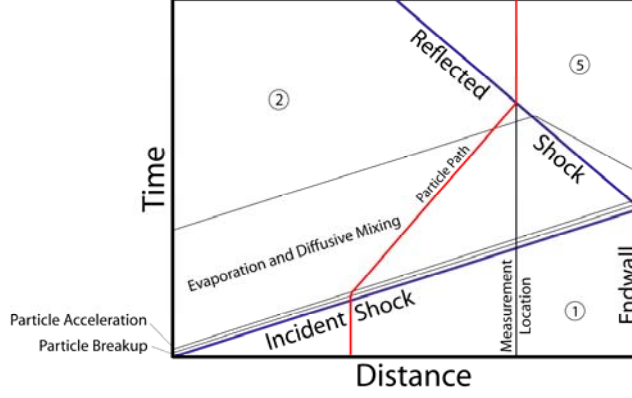


Fig. 5. Schematic x-t diagram for aerosol shock tube driven section.

Shock Wave Calculations

To determine the conditions behind the incident and reflected shock waves, the shock jump relations are used. The shock relations employed for an evaporating two-phase flow are of the same form as those given by Guha¹⁴ and are shown in the first four equations of (3). To solve these equations in a pure gas-phase shock wave experiment, the initial pre-shock (region 1) conditions of temperature T_1 , pressure P_1 and gas composition X_{1i} and the incident shock speed V_s are required. In the current two-phase experiments, the initial fuel concentration is not precisely known, but the evaporated aerosol concentration and the carrier gas composition behind the incident shock wave (region 2) are known. The information about the evaporated aerosol concentration is implicit in the last equation for $X_{2,f}$ that includes the known absorption cross-section of the fuel and the total absorption observed when the aerosol is fully evaporated. The absorbance is measured in region 2 just before the arrival of the reflected shock.

$$\begin{aligned}
 \rho_1 u_1 &= \rho_2 u_2 \\
 P_1 + \rho_1 u_1^2 &= P_2 + \rho_2 u_2^2 \\
 h_1 + \frac{1}{2} u_1^2 &= h_2 + \frac{1}{2} u_2^2 \\
 P &= \rho R T \\
 X_{2,f} &= -\ln \left(\frac{I}{I_o} \right) \left(\frac{\hat{R}}{\sigma_v L} \right) \left(\frac{T_2}{P_2} \right)
 \end{aligned} \tag{3}$$

In the above equations the numbered subscripts indicate the region, and it is assumed that region 2 is defined such that the aerosol mixture has reached equilibrium and is fully evaporated. Other variables are: ρ , the total density of the fluid; u , the velocity in a shock-fixed coordinate system; P , the pressure; h , the specific enthalpy of the fluid which includes the enthalpy of the liquid phase if present. These equations can be solved numerically to converge to a unique solution that satisfies continuity, the Beer-Lambert absorption relation, the ideal gas law, and the conservation of momentum and energy; we use an in-house code named AEROFROSH. Specific heats are calculated using the Sandia database,¹⁵ and for larger hydrocarbons are taken from Burcat.¹⁶ The result of

these calculations yields the region 2 composition, pressure, and temperature. These results can then be used to calculate the region 5 temperature and pressure without the complication of having a liquid phase. The results of this calculation show good agreement with the end section pressure measurements; see Fig. 6.

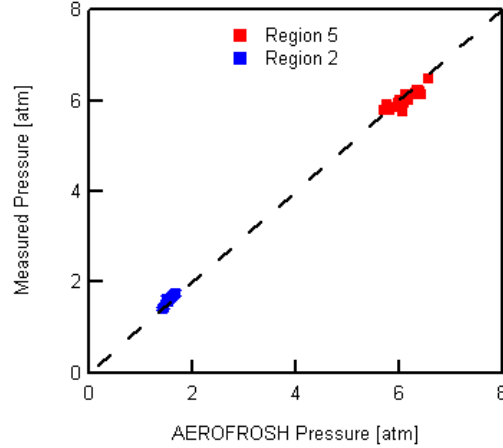


Fig. 6. Comparison of measured and AEROFROSH calculated pressures P_2 and P_5 for n-dodecane/21% O_2 /argon mixtures, $\Phi=0.5$ originally containing ~ 10 ppmv of n-dodecane aerosol.

Evaporation and Diffusion

The above calculation is predicated on the assumption of complete evaporation of the aerosol in region 2. In Fig. 7 the entire time history of the aerosol mixture is shown. Laser extinction and absorption by the region 1 aerosol mixture can be seen at times before $t=0$. The next step change in the laser extinction and absorption is a result of the compression of the flow by the incident shock wave. Over the next approximately 80 μs laboratory time (200 μs particle time) the droplets are quickly accelerated ($< 10 \mu s$) and evaporate. When evaporation is complete, the non-resonant laser signal (1625 nm) goes to zero and the 3.39 μm absorption signal, which was comprised of both Mie extinction and resonant absorption, achieves a plateau value (at 70-80 μs) representative of the fuel vapor concentration. This plateau value is used to determine the fuel concentration in region 2 and 5. The next step change in the absorption signal and pressure trace is a result of the passage of the reflected shock wave at about 100 μs . After this step, the 3.39 μm absorption gradually disappears as the fuel is consumed, until, at approximately 1200 μs laboratory time ($\tau_{ign} = 1100 \mu s$ particle time), ignition occurs, and the pressure and CH^* emission rise dramatically. At intermediate laboratory times of about 650-750 μs (550-650 μs particle time) there is clear evidence in the pressure trace of pre-ignition energy release. A small change in the behavior of the resonant absorption trace is also observed at this time.

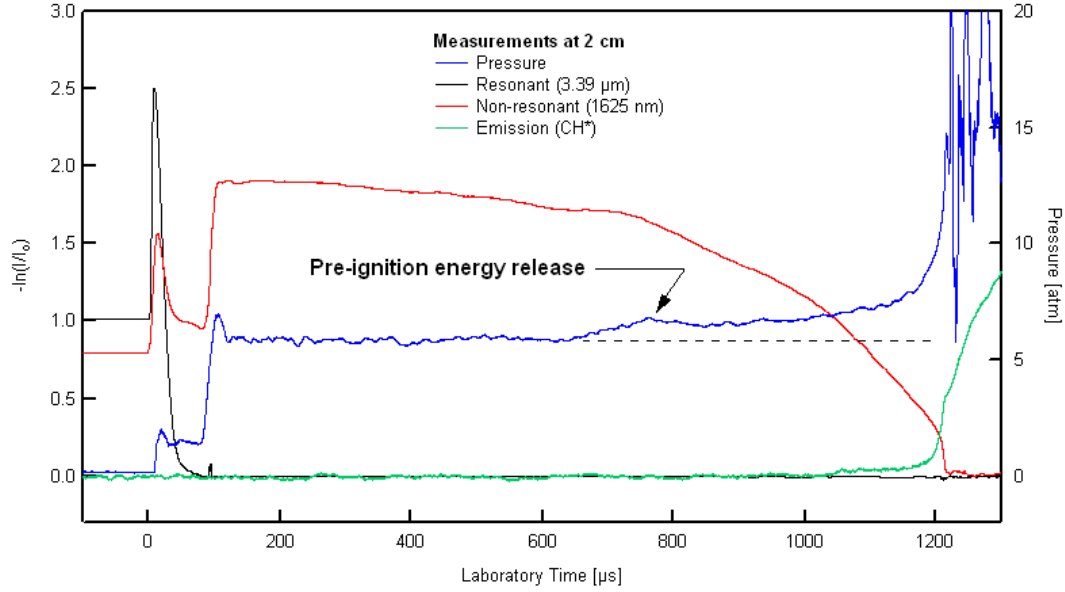


Fig. 7. Representative n-dodecane/21% O₂/argon ignition time experiment. Initial conditions: $T_1 = 294$, $P_1 = 0.189$, $V_s = 771$ m/s, $C_v = 10.0$ ppmv, $X_{\text{fuel}} = 0.0063$, $T_2 = 695$ K, $P_2 = 1.46$ atm, $T_5 = 1162$ K, $P_5 = 5.88$ atm, ignition time = 1124 μ s (particle time).

Example evaporation times of the aerosol (see Fig. 3 for size distribution) as a function of temperature are shown in Fig. 8. Note that the times plotted are in particle time, the time the particle experiences in the region behind the incident shock, not the laboratory time at the observation location. These times vary from approximately 250 to 150 microseconds, for T_2 values of 650 to 780 K. These conditions correspond to T_5 values in the fuel/O₂/Ar mixture of approximately 1050 to 1350 K. As expected the evaporation time is a relatively strong function of T_2 .

We do not have a way to measure directly the time it takes the fuel vapor to diffuse into the carrier gas and achieve uniformity (e.g., < 5% fuel concentration variation in the test gas volume). We have performed calculations based on average aerosol droplet spacing and size, and representative diffusion constants to estimate this diffusion rate.^{17,18} Representative diffusion relaxation times (time to <5% fuel concentration non-uniformity) are shown in Fig. 9. The majority of the aerosol droplets have diameters less than 5 μ m, and are thus expected to have diffusion relaxation times of order 10 μ s. This is a short enough time to consider the gas-phase vapor in region 2 to be of uniform distribution. The relaxation of any remaining non-uniformities is accelerated by the higher temperatures of region 5.

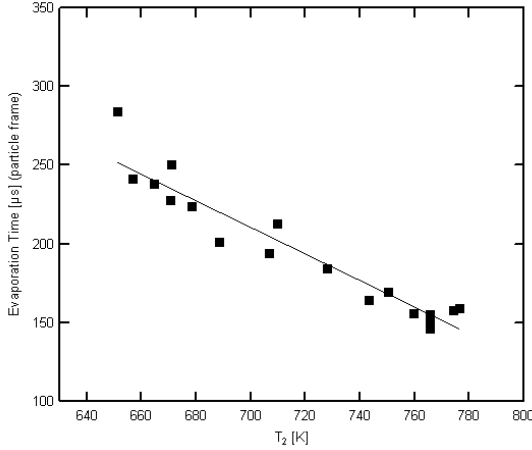


Fig. 8. n-Dodecane evaporation times in 21% O_2 /argon as a function of temperature. Average conditions: $C_v = 10$ ppmv, $X_{fuel} = 0.006$, $P_2 = 1.6$ atm, V_S (650 K) = 740 m/s, V_S (780 K) = 820 m/s.

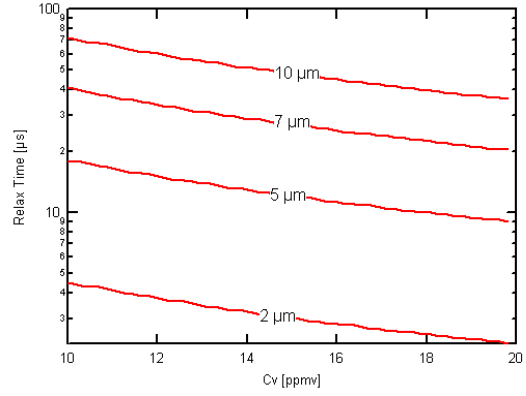


Fig. 9. Representative diffusion relaxation times of n-dodecane in 21% O_2 /argon: Typical incident shock wave conditions: $T_2 = 700$ K, $P_2 = 1.5$ atm.

A separate issue is that of spatial uniformity of the initial aerosol distribution throughout the end section of the shock tube. This has been examined using transparent walls and end section, but also can be investigated by examining the uniformity of the vapor-phase absorption in region 2 at some distance from the end wall. Fig. 10 shows similar measurements to that of Fig. 7, but at a location 5 cm from the end wall. Of note is that the $3.39 \mu m$ absorption signal is constant to within approximately $\pm 7\%$ over 150 μs of laboratory time. This corresponds to a uniform initial spatial distribution of the aerosol extending approximately 42 cm up the shock tube from the endwall (see Fig. 1). Beyond that distance, we do begin to see evidence of a laminar separation of the dry carrier gas and the aerosol mixture. In practice we can adjust the location of the measurement location to ensure operation with sufficiently uniform spatial distributions. However, it should be noted that a perfectly uniform mixture is not required; all this is really necessary is that we know the fuel concentration that applies along the streamline of fuel monitored at the observation window.

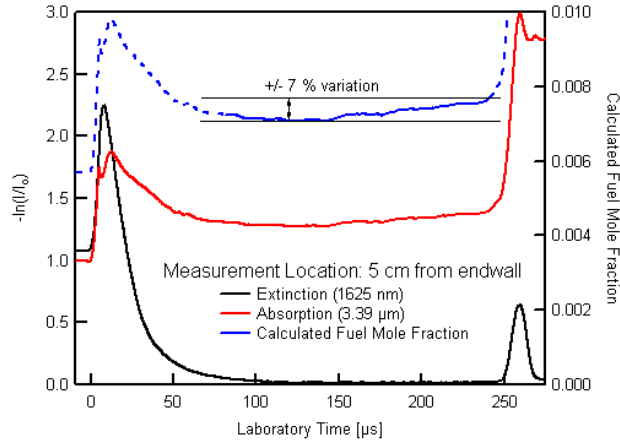


Fig. 10. Representative 3.39 μm absorption measurement at 5 cm from end wall for n-dodecane/21% O_2 /argon mixture. Initial conditions: $T_1 = 298 \text{ K}$, $P_1 = 0.245 \text{ atm}$, $V_s = 736.5 \text{ m/s}$, $C_v = 17 \text{ ppmv}$, $X_{\text{fuel}} = 0.0080$, $T_2 = 641 \text{ K}$, $P_2 = 1.75 \text{ atm}$, $T_5 = 1058 \text{ K}$, $P_5 = 7.26$, ignition time = 2150 μs .

Example Application: n-Dodecane Ignition Delay Times

Using the aerosol shock tube method described here, a preliminary study was conducted of ignition delay times for n-dodecane/21% O_2 /argon mixtures. The conditions of these experiments are: temperatures from 1050-1350 K, pressures near 7 atm, and equivalence ratios of approximately 0.5. To reconcile the data to a common set of conditions, $P = 6.7 \text{ atm}$ and $\phi = 0.5$, a pressure scaling of $P^{-1.0}$ and an equivalence ratio scaling of $\phi^{1.0}$ was applied. See Horning 2002 for details.¹⁹ These initial n-dodecane ignition times are shown in Figure 11.

We are unaware of any other high concentration ignition delay time data for n-dodecane other than from our own laboratory.²⁰ Conventional n-dodecane/Air ignition time measurements were performed in a comparison study conducted in a heated high-pressure shock tube in our laboratory. The temperature of the mixing tank was 125°C and the shock tube was 100°C. At these temperatures, there was no evidence of significant fuel decomposition in the mixing tank or shock tube before the experiment for holding times of 2.5 to 8 hours. A comparison of those high-pressure ($P = 18\text{-}31 \text{ atm}$, $T_5 = 943\text{-}1177 \text{ K}$) data with the 6.7 atm data of the present study shows the expected variation in pressure ($\tau \sim P^{-1}$) and a similar temperature dependence.

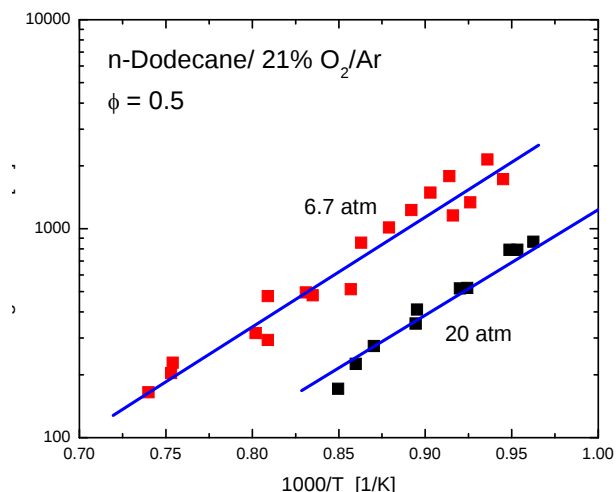


Fig. 11. n-Dodecane/21% O₂/argon ignition delay times. Aerosol reflected shock conditions: 6.7 atm, $\phi = 0.5$; high pressure shock tube conditions¹⁹: 20 atm, $\phi = 0.5$.

Conclusion

This work details the initial application of a new method for the measurement of the ignition times of liquid fuels. This method greatly extends the range of fuels that can be tested using shock tube methods without the complexity and uncertainties associated with heating the initial mixture. The fuel loading is measured using a 3.39 μm laser absorption diagnostic. The shock jump equations are solved in an iterative numerical scheme using the information obtained from the absorption measurement as well as the shock speed. Using these techniques new data on gas phase ignition times of n-dodecane have been obtained. A comparison of ignition delay time data acquired with the aerosol method and the heated shock tube method was made for n-dodecane, with good agreement.

The aerosol shock tube method is applicable to studies of jet and diesel fuel (JP-8 and DF-2 for example) as well as low-vapor-pressure surrogate fuel components including n-dodecane, n-hexadecane and surrogate mixtures currently being considered for jet fuel. We also have plans to use this method to investigate the effects of shock waves on biological materials in solution, as well as the chemistry of nano-particles of energetic materials delivered in liquids.

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