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Report Title

Exploratory Study to Determine the Ignition Properties and Combustion Chemistry of Explosives Using Shock Tube Methods

ABSTRACT

We investigated the potential of a new experimental method for combustion studies of solid nano-particle energetic materials. This new method is based on the recent development in our laboratory of an aerosol shock tube and its combined use with laser extinction (for characterization of particle size and loading) and absorption diagnostics (for characterization of vapor species). We accomplished three main objectives in this study: 1) we demonstrated the ability to load significant amounts of solid materials into our aerosol carrier and deliver this aerosol into our shock tube; 2) we demonstrated laser-based diagnostic measurements of several key aspects of the ignition process of solid/liquid fuel systems; and 3) we characterized the effect of the addition of aluminum nano-particles on n-dodecane ignition under conditions previously not studied.

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David Jackson	0.25
Daniel Haylett	0.10
FTE Equivalent:	0.35
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<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Ronald Hanson	0.02	Yes
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Names of Personnel receiving masters degrees

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Names of personnel receiving PhDs

<u>NAME</u>

Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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David Davidson	0.10	No
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**Final Technical Report
Short Term Innovative Research Program
ARO Grant (STIR) W911NF-07-1-0123**

**Exploratory Study to Determine the Ignition Properties
and Combustion Chemistry of Explosives
Using Shock Tube Methods**

Prepared for:

**DEPARTMENT OF THE ARMY
Dr. Ralph Anthenien Jr., Program Manager**

For the period April 1, 2007-December 31, 2007

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January 31, 2008

**HIGH TEMPERATURE GASDYNAMICS LABORATORY
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STIR: Exploratory Study to Determine the Ignition Properties and Combustion Chemistry of Explosives Using Shock Tube Methods

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Abstract

We investigated the potential of a new experimental method for combustion studies of solid nano-particle energetic materials. This new method is based on the recent development in our laboratory of an aerosol shock tube and its combined use with laser extinction (for characterization of particle size and loading) and absorption diagnostics (for characterization of vapor species). We accomplished three main objectives in this study: 1) we demonstrated the ability to load significant amounts of solid materials into our aerosol carrier and deliver this aerosol into our shock tube; 2) we demonstrated laser-based diagnostic measurements of several key aspects of the ignition process of solid/liquid fuel systems; and 3) we characterized the effect of the addition of aluminum nano-particles on n-dodecane ignition under conditions previously not studied.

These results provide the DoD with a demonstration of a new method to investigate solid/liquid fuel or explosive mixtures, in particular the influence of nano-particles on combustion processes. We believe that this technique can be used for the study of nano-particle additives to liquid fuels or to non-reactive carrier liquids, as well as for gel-like materials that can be converted into aerosol using ultrasonic spray nozzle technology. Our approach permits the application of an array of advanced state-of-the-art laser diagnostic systems, developed originally for gas-phase chemistry studies, to research problems of solid fuels. This present exploratory research program has successfully demonstrated that these shock tube methods can be used to obtain critically needed information about rapidly thermalized explosives. We thus anticipate that our aerosol shock tube will prove to be an important tool in future DoD research on advanced propellants, including gelled and nano-propellants.

Project Description

Introduction

A major problem in understanding the mechanisms controlling the explosions of energetic materials is that there is currently no optimal way of probing the details of the first decomposition steps of the transition from solid to gaseous phase in these systems, particularly under extreme conditions. An accurate assessment of the nascent species entering the gas phase during this transition would provide important kinetic targets for constraining and refining the particle combustion models [1]. These types of transient species measurements have proven to be very difficult, though some progress along these lines has been made using STMBMS methods (simultaneous thermogravimetric modulated beam mass spectrometry) by Rich Behrens and co-workers at Sandia National Laboratories in the 1990's [2]. In those experiments the authors identified major decomposition pathways for some explosive materials when the solids were heated slowly. However, other methods which probe the dynamics of the interface between the solid and the gaseous phase are needed, particularly those that can operate under the extreme conditions of temperature and pressure and the rapid time frames found during actual explosions.

An Innovative Solution: Aerosol Shock Tube

We believe that these phenomena can be studied using shock tube methods combined with laser diagnostic methods. We proposed to explore the use of a recently-developed aerosol shock tube and an existing array of laser extinction and absorption diagnostics for studies of solid/liquid materials, in particular nano-particles/fuel mixtures, and the transition from solid to gaseous phase in explosives. This new shock tube facility at Stanford uses aerosols to handle liquid and, now potentially, solid fuels [3]. A schematic representation of the operation of this aerosol shock tube is shown in Fig. 1.

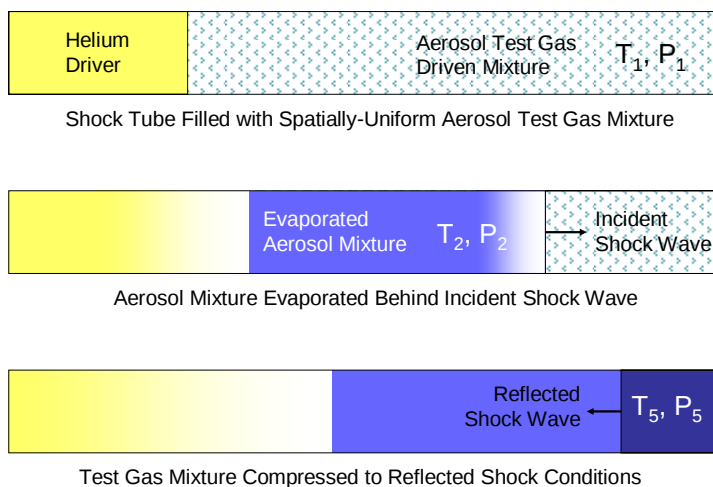


Fig. 1. Schematic of aerosol shock tube technique.

The aerosol shock works by allowing the introduction of nebulizer-generated mist into a shock tube in a spatially-uniformly manner. Any fluid or fluid/particle suspension that can be converted into a mist by a nebulizer can be used as a reactant. (This reactant fills the shock tube at the initial temperature and pressure, i.e. T_1 , and P_1 . A shock wave is generated in the shock tube by rupturing a diaphragm in the driver section with high-pressure helium gas and this incident shock wave propagates down the shock tube. Droplets formed by the nebulizer completely evaporate behind the incident shock wave at the elevated conditions (T_2 , P_2) and the evaporated fluid (vapor) rapidly diffuses to form a uniform distribution. The reflected shock wave (from the endwall) then passes back through the test mixture, compressing and heating it to the targeted temperature and pressure conditions for combustion (T_5 , P_5). Optical access to the viewing section permits the probing of the heated test gas mixture with laser diagnostics and allows the measurement of species concentration time histories for species, such as OH, CH₃, benzyl, NO₂, H₂O, and others, during the complete ignition process.

Research Goals

What is of direct and immediate interest to the study of solid explosives chemistry is the application of the aerosol shock tube technique to study the effect of nano-particles on fuel mixtures. Only limited quantitative chemical kinetic data are available on the influence of nano-particles on kerosene-type fuels; most previous studies have been concerned with larger aluminum particles (micron to millimeter size).

Bazyn et al. [4] investigated the burning of nano-aluminum particles in shock tubes in CO₂/N₂ and O₂/N₂. They characterized the burning time as a function of temperature and pressure and found that nano-aluminum reacted at lower temperatures than 10 μ m particles under similar conditions. At 8 atm and at temperatures lower than 1400 K, 80 nm aluminum particles exhibited light emission characteristic of burning for over 500 μ s.

Mueller et al. [5] investigated aluminum/RP-1 slurries with 60% by weight aluminum by feeding the slurry into a nonpremixed methane flame. They observed rigid slurry shells to form whose composition was a function of diameter.

Wong and Turns [6] investigated aluminum/JP-10 slurry droplets of diameter 500 to 110 microns (with 4 micron Al particles) which were suspended on micro-fibers. The slurry droplets were large enough that their ignition model included several steps including burnoff of the JP10, agglomeration/heating of the remaining aluminum, and finally ignition of the aluminum particle. Ignition times were of the order of 0.4 seconds 600 micron slurry droplets in CO/10% O₂/N₂ flames at 1800 K.

Beloni et al. [7] investigated decane-based slurries with metallic additives. They used a lifted laminar flame slurry burner and studied Al, Al_{0.7} Li_{0.3} and 2B+Ti powders. The Al particles were 1-5 microns in diameter. They observed that the aluminum particles did not burn in the flames.

In this study we have investigated the influence of aluminum nano-particles on the ignition delay times of a single component kerosene/jet fuel surrogate n-dodecane. This

was accomplished in three steps. 1) We demonstrated the ability to load significant amounts of solid materials into our aerosol carrier and deliver this aerosol into our shock tube; 2) we demonstrated laser-based diagnostic measurements of several key aspects of the ignition process of solid/liquid fuel systems; and 3) we characterized the effect of the addition of aluminum nano-particles on n-dodecane ignition delay times.

One of the key accomplishments of the present study was to demonstrate that we can suspend very finely ground solid energetic material particles (in these experiments aluminum nano-particles) in a solvent that acts as a carrier for these particles. This solvent could either be non-reactive (e.g. water) or part of the fuel chemistry (in these experiments n-dodecane). In either case, this liquid would carry the particles from the nebulizer into the shock tube, and then evaporate completely behind the incident shock. What would be left would be the nano-particles of energetic materials in a gas-phase carrier (e.g. air and water vapor or air and gaseous fuel as in the current experiments), uniformly-distributed spatially and shock-heated to temperatures and pressures where we could study the chemistry. Using this method enables experiments that directly investigate the early decomposition chemistry of these materials and detection of the initial gas phase decomposition products.

Experimental Description

The current experiments were performed in the aerosol shock tube facility at Stanford University. The description of this work is in three sections: the operation of the spray nozzle, the laser diagnostic scheme, and the ignition time measurements.

Aerosol Generation

We found that the addition of solid nano-particles to the liquid aerosol solvent carrier significantly reduced the aerosol output of our existing disk nebulizers. To maintain higher aerosol loading levels, the disk nebulizers were replaced with a Sono-Tek Ultrasonic spray nozzle. A photograph of the operating nozzle is shown in Fig. 2. This device can nebulize suspensions with up to 40 wt.% nano-particles. This nozzle operates at 120 kHz and produces aerosol with number mean diameter of approximately 18 microns. A representative size distribution is shown in Fig. 3.

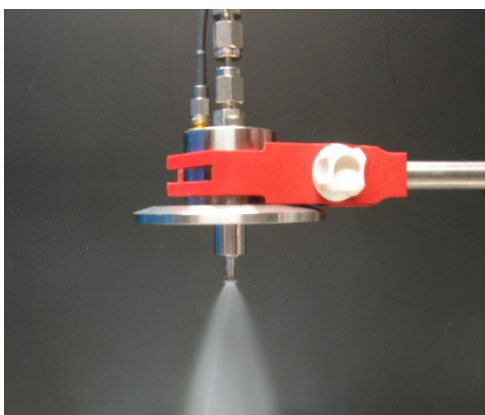


Figure 2. Sonotek ultrasonic spray nozzle in operation.

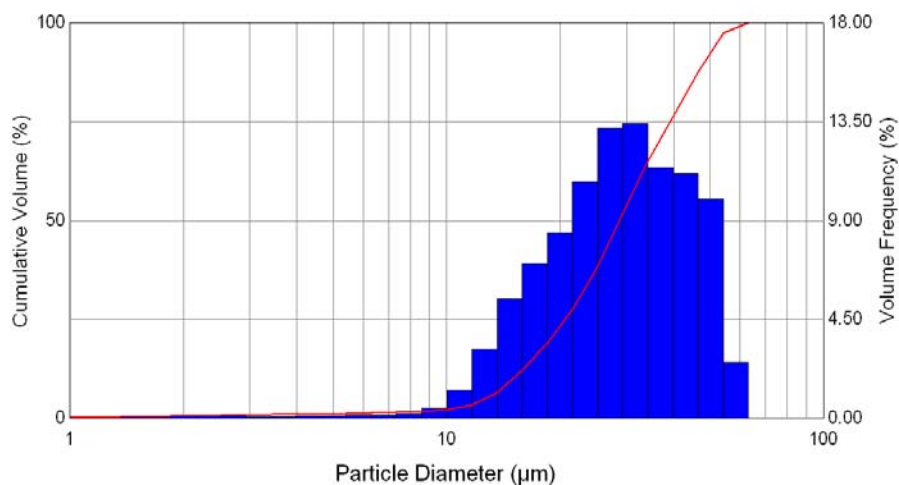


Figure 3. Volume size distribution plot for a n-dodecane aerosol produced using the 120 kHz Sonotek spray nozzle at a mass flow rate of 200 ml/hr and a power of 1.0 watt.

The Sonotek ultrasonic spray nozzle was installed in the loading chamber located immediately adjacent to the test section of our aerosol shock tube facility in place of the disk nebulizer assembly. See Figs 4a and 4b.

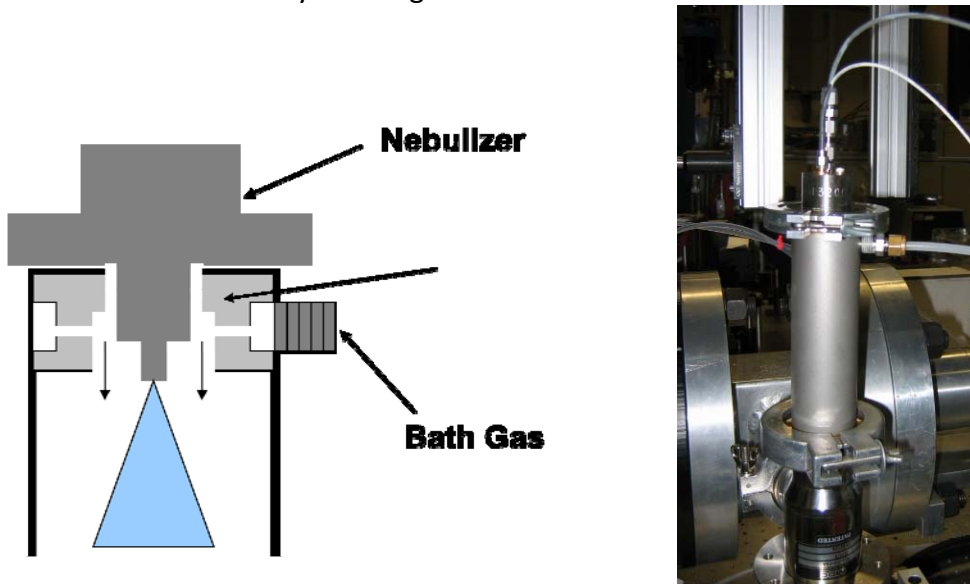


Figure 4a (left). Schematic of spray jet installation with co-axial bath (carrier) gas.

Figure 4b (right). Photo of spray jet installed on aerosol shock tube.

The larger aerosol droplets (larger number mean diameter) produced using the spray jet (than with the disk nebulizers) experience faster drop-out rates due to gravity. We characterized these drop-out rates using laser extinction measurements (described in the next section.) A representative *in situ* life time measurement is shown in Fig. 5. Based on these measurements, we anticipated that successful shock wave experiments would require very short (less than 10 seconds) delays between filling and breaking the

diaphragm. We thus modified our experimental protocol to enable this type of operation.

In the future we plan to upgrade this ultrasonic nozzle. Discussions with the manufacturer of the Sonotek nozzle indicate that a higher frequency model (180 kHz) which will have a number mean droplet diameter of 10 microns, may soon become available. The use of this nozzle would improve the aerosol loading levels, as well as reduce the amount of settling and dropout.

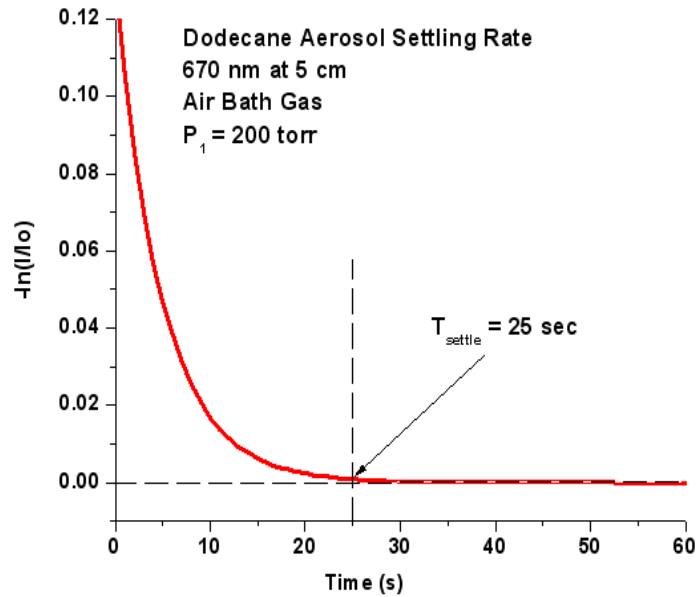


Figure 5. Dodecane aerosol settling rate. Mie scattering was measured using 670 nm diode laser extinction at pre-shock filling conditions similar to those of typical shock wave experiments.

Laser Diagnostics Measurements

Figure 6 shows the laser diagnostic systems used in the shock wave experiments. Three laser systems are used. Two diode lasers at 660 and 670 nm (referred to as the non-resonant laser systems) are used to measure droplet evaporation and particle loading. One HeNe gas laser at 3.39 microns (referred to as the resonant laser system) is used to measure hydrocarbon (n-dodecane in the current experiments) absorption. The 3.39 micron absorption measurement is also used to measure fuel loading after droplet evaporation behind the incident shock waves. Details of the use of these laser systems to probe shock wave experiments can be found in Ref. [3].

Baseline Ignition Measurements with Neat n-Dodecane

Representative data traces from baseline ignition measurements with neat n-dodecane using the new jet nebulizer are shown in Fig. 7. The 660 nm extinction measurement location is 2 cm from the shock tube endwall; the 670 nm and the 3.39 micron measurement location is 5 cm from the endwall.

First, examining the pressure trace in Fig. 7, we see that there is a step in pressure at $2250\ \mu\text{s}$ which corresponds to the arrival of the incident shock wave at the location of the Kistler PZT sensor 2 cm from the end wall. The next set in pressure at $\sim 2340\ \mu\text{s}$ corresponds to the arrival of the reflected shock wave returning from the end wall. Near $3000\ \mu\text{s}$, the pressure begins to rise and at about $3220\ \mu\text{s}$, ignition occurs causing the pressure transducer to begin to ring.

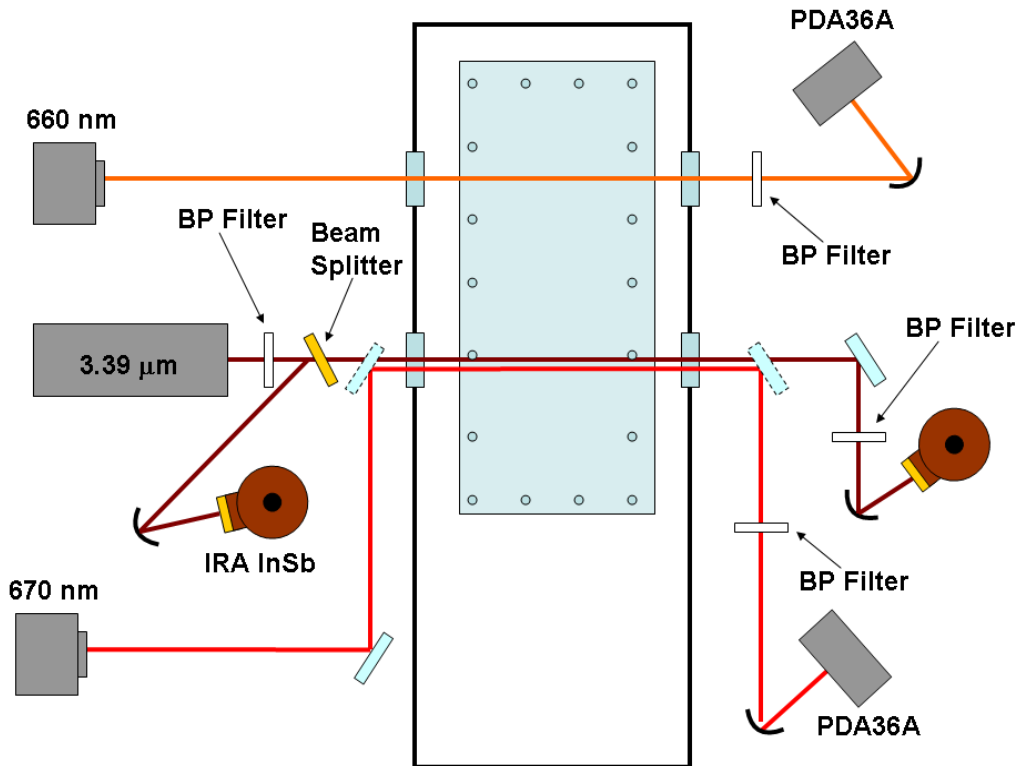


Figure 6. Schematic of laser diagnostic setup for aerosol shock tube.

Next, examining the non-resonant 670 nm diode laser extinction signal and the 3.39 micron laser signals which are both located 5 cm from the shock tube end wall, we see that when the incident shock wave arrives at this location the pre-shock extinction (670 nm) and pre-shock extinction and absorption (3.39 micron) signals (from the pre-shock n-dodecane aerosol-vapor/ O_2 /argon mixture) jump as a result of the compression and heating by the incident shock wave. The 3.39 micron signal rapidly achieves a plateau level indicative of complete evaporation of the n-dodecane, while the 670 nm signal decays to zero confirming the complete absence of droplets. At $2480\ \mu\text{s}$, the reflected shock wave passes the 5 cm location and further compressing the n-dodecane vapor as indicated by the step in the 3.39 micron absorption signal; this shock also momentarily disrupts the 670 nm diode laser beam owing to beam-steering. Near $3220\ \mu\text{s}$, the 3.39 micron signal goes to zero as the fuel (n-dodecane) is consumed at ignition. Coincident

with the ignition is a rise in CH* emission which is an indicator of the rapid radical production that occurs during ignition.

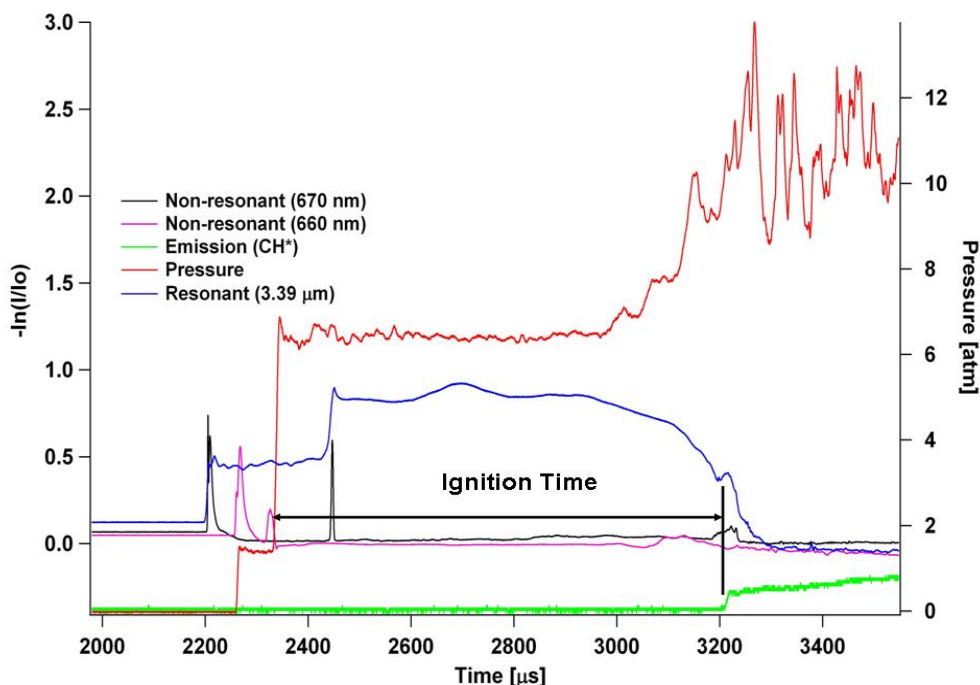


Figure 7. Representative data traces for n-dodecane ignition. Pre-shock conditions: $T_1 = 295$ K, $P_1 = 201$ torr; incident shock speed: $V_s = 757.93$ m/s, fuel loading $X_{\text{fuel}} = 0.0021$ in 21% O_2 in argon; reflected shock conditions: $T_5 = 1187$ K, $P_5 = 7.1$ atm, ignition time = 793 μs .

Effect of Nano-Aluminum on n-Dodecane Ignition

Figure 8 shows similar data traces for a shock tube ignition experiment with 5% or 20% by weight nano-aluminum particles added to the n-dodecane aerosol. Several significant differences are seen between this set of measurements and the neat n-dodecane measurements. The aluminum nano-particles were supplied by Sigma-Aldrich Chemicals: Aluminum nanopowder, 99.5%, part #653608. These aluminum particles have an average diameter of 100 nm and a thin Al_2O_3 coating with a core of pure aluminum.

Pressure: The pressure trace (blue) in Fig. 8 shows a much larger step and much more sudden rise in pressure at ignition. (The pressure signal actually goes off scale.) This is coincident with a shorter ignition time, even when normalizing (using P^{-1} and ϕ^{-1}) for the difference in fuel concentration and pressure of the two examples. We have found no previous direct measurement of the influence of aluminum nano-particles on the ignition times of kerosene-type fuels.

Non-Resonant Lasers: Both non-resonant (to hydrocarbon species) laser signals (660 and 670 nm) show continued constant extinction behind the incident shock wave after the

complete evaporation of the liquid aerosol carrier, confirming the presence (and allowing measurement) of the nano-propellant loading. This can be seen in the 670 nm signal (black) from 2180 to 2350 μs and in the 660 nm signal (pink) from 2180 to 2250 μs . For both these two measurements there is also a significant step in extinction after the arrival of the reflected shock wave at 2350 μs for the 670 nm signal and at 2250 μs for the 660 nm signal, consistent with the increase in density across this wave.

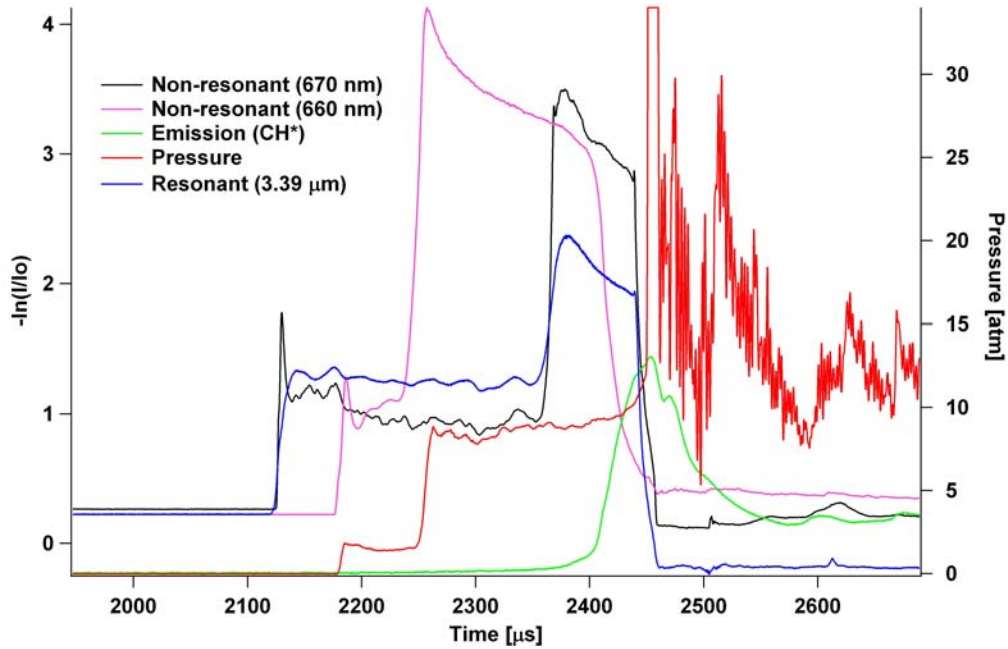


Figure 8. Representative ignition experiment using n-dodecane with 20% nano-aluminum by weight. Initial conditions: $T_1 = 296 \text{ K}$, $P_1 = 223.4 \text{ torr}$; incident shock speed $V_s = 781 \text{ m/s}$, fuel concentration $X_{\text{fuel}} = 0.00550021$ in 21% O_2 in argon; reflected shock wave conditions: $T_5 = 1197 \text{ K}$, $P_5 = 9.53 \text{ atm}$, ignition time = 193 μs .

The extinction in the 660 nm signal decays after the passage of the reflected shock wave until just before ignition when it rapidly decays. Similar behavior is seen in the 670 nm signal at the 5 cm location, except that the blast wave from the ignition that occurs upstream (at the 2 cm location and closer to the endwall) rapidly sweeps by the 5 cm location and causes the rapid decrease in the 670 nm almost immediately after the ignition event at the 2 cm location. After the ignition event, both of the 660 and 670 nm signals continue to show absorption/extinction. This absorption/extinction is consistent with absorption features of gaseous aluminum oxides near these wavelengths or possibly with the appearance of aluminum oxide particles.

3.39 μm Laser: After the passage of the incident shock wave, the 3.39 μm laser experiences both extinction from the aerosol droplets and bare aluminum nanoparticles, and absorption from the n-dodecane vapor. A calculation of the expected Mie scattering of 100 nm nano-particles at 3.39 microns indicates that only about 1%

extinction will result from the nano-particles after the aerosol has evaporated and thus the measured absorption after evaporation is effectively due entirely to fuel vapor.

The 3.39 micron laser signal (blue) shows a more rapid decay behind the reflected shock wave than is seen in the neat n-dodecane experiment, possibly owing to the involvement of the aluminum nano-particles with the n-dodecane oxidation chemistry. After ignition, there is no apparent absorption, consistent with a complete consumption of hydrocarbon species and not absorption by aluminum oxides.

Emission: This rapid decay in the 660 nm signal at the 2 cm location is coincident with the strong rise seen in the 431 nm emission signal (green). This emission extends through the ignition event with a FWHM of approximately 80 μ s. No emission peak is seen in the experiment with no aluminum nano-particles.

Ignition Delay Time Measurements

Figure 9 shows a summary of the ignition delay time measurements of neat n-dodecane and n-dodecane with aluminum nano-particles. In this figure previous measurements in our laboratory of n-dodecane ignition delay times are shown as “standard disk nebulizer C12H26” [3]. Measurements of neat n-dodecane using the new jet nebulizer are shown as “Sonotek jet nebulizer C12H26.” Measurements with 5% or 20% added aluminum nano-particles (by weight) are also identified.

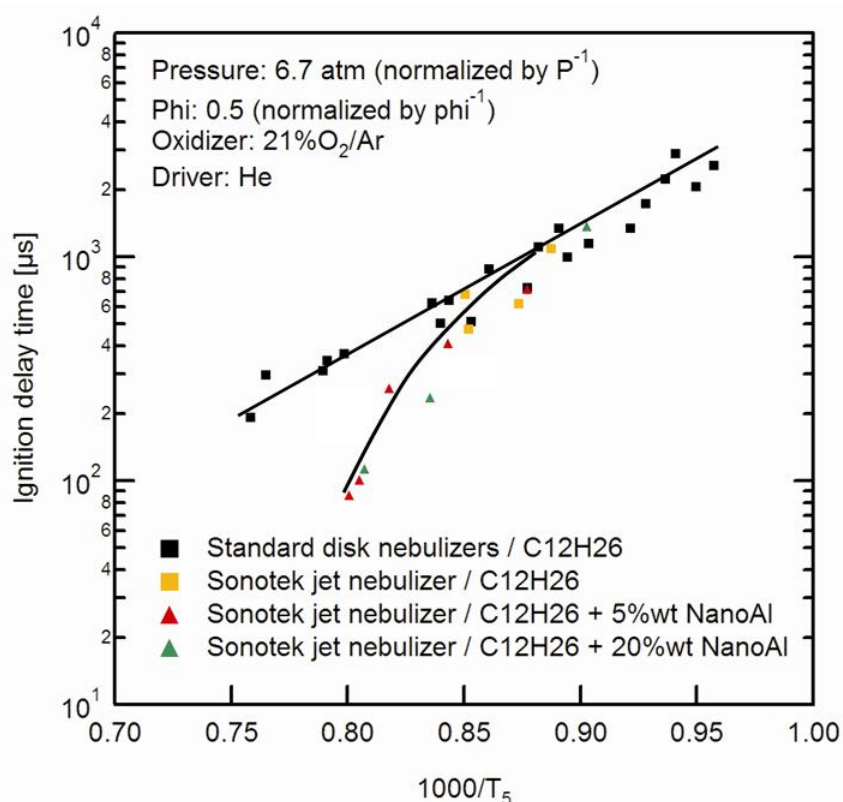


Figure 9. Ignition delay time measurements of n-dodecane and n-dodecane/NanoAl.

At temperatures below 1175 K, there appears to be no significant difference in the ignition times of n-dodecane and n-dodecane/nanoAl mixtures. Nano aluminum shortens the ignition times at temperatures above 1175 K. This is particularly evident for the three data points near 1250 K where the ignition times are significantly shorter than the ignition delay times of the neat n-dodecane experiments at the same temperatures.

Discussion of Results and Conclusions

The present experiments extends significantly the range of combustion conditions for which mixtures of aluminum and kerosene-like fuels have been studied. Several observations can be made in comparison with previous work.

Bazyn et al. observed slow burning in pure aluminum nano-particles (burning times of greater than 500 μs at temperatures below 1400 K). Based on the same criteria of burning times used by Bazyn et al. (emission measurements) we find burning times of less than 100 μs near 1200 K in our n-dodecane/nano-aluminum ignition experiments.

Wong and Turns observed long ignition times (of order 0.1 to 1 second) for large slurry droplets (of order 1000 microns). The slurries investigated in the present study have initial droplet diameters of order 10-20 microns with 100 nm aluminum nanoparticles. Our laser absorption and extinction measurements indicate that these droplets fully evaporate in times of order 100 μs behind incident shock waves and when heated to ~ 1200 K, ignited in 100 μs .

The combustion regime studied in the current experiments is different than that previously studied. Mueller et al., Beloni et al., and Wong and Turns studied larger droplets in flame geometries where the ignition process is a combination of evaporation, agglomeration, particle heating and particle flame kinetics. This ignition process in the current study, we believe, is that of a “dry” aluminum nano-particle in a high-temperature gas-phase bath of n-dodecane/21% oxygen/balance argon, similar to that of Bazyn et al. but in an hydrocarbon fuel environment.

Using the aerosol shock tube method, the chemical kinetics of nano-particles in reactive fuel mixtures can be investigated without interference from other physical-chemical processes. This is done by separately evaporating the aerosol droplets and then heating them to ignition temperatures. This avoids the overlap of evaporation phenomena and particle agglomeration processes that can occur with larger droplets. Several examples of these experiments are described in the next section.

Potential Applications of the Aerosol Shock Tube Method

The main thrust of this initial effort was to establish feasibility of using the aerosol shock tube to study solid energetic materials. With this demonstrated, there are several immediate and obvious problems currently of interest to the energetic materials community that we believe merit investigation.

- 1) RDX decomposition pathways and rates. Large uncertainties exist in the decomposition chemistry of RDX [8]. Measurements of NO₂ concentration time-histories (using laser absorption at 472 nm) could provide needed accurate quantitative measurements of the decomposition of RDX and related compounds.
- 2) Rapid testing of mixtures of energetic materials and reactive solvents. It has long been known that the decomposition rate of energetic materials can be influenced by the addition of various agents. A comparison of the magnitudes of the effect on decomposition rate of an energetic material by various solvents, both reactive and non-reactive, can be made in a straightforward manner using the aerosol loading method. Information from these studies may guide the development of new energetic materials.
- 3) Relationship of ignition delay time to material properties. Ignition delay time measurements may provide a simple indicator of energetic material properties [9]. An initial survey of the ignition delay times of several established energetic materials would allow this relationship to be studied.
- 4) Extension of the method to investigate gel propellant components. While we have not yet developed a method to convert fully gelled propellant mixtures into aerosols for shock tube loading, it should be immediately possible to study the combustion properties of gel propellant components dissolved in solvents or slurries.

Current Publications Base on This Study

D. E. Jackson, D. F. Davidson, R. K. Hanson, *"Application of an Aerosol Shock Tube for the Study of Nano-Energetic Material Decomposition Processes,"* abstract submitted for Fundamental Combustion Processes Session of 44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 2007.

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