

A NEW LASER DIAGNOSTIC TECHNIQUE TO EVALUATE CHEMICAL TIME DELAY IN HYPERGOLIC SYSTEMS

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INTRODUCTION

Diagnostic techniques that measure ignition delay times (IDT) of hypergolic reactants are normally classified into a few distinct types. Drop tests are techniques that drop one reactant from a set height into a stationary quantity of the second reactant. Mixing tests are techniques that use a method to enhance mixing of the reactant combinations. Impinging jet techniques are tests that use separate fuel and oxidizer injectors to enhance the mixing rate and simulate engine conditions. Also, a few small scale rocket engines have been equipped to measure ignition delay times.

A typical example of a drop test technique was performed by Broatch⁴. A light beam was focused on a photocell a set distance above the organic fuel, which was located in a crucible. The oxidizer, in a stream of droplets of varying size, broke the light beam as it fell into the fuel. A photocell ended the measurement when it sensed the appearance of a flame. The time between these two events defined the ignition delay for the hypergolic reactant combination. A technique used by Gunn⁶ was defined as a mixing test by Paushkin³ in his review of jet fuels. The only significant difference from Broatch's technique described above was that the quantity of fuel and oxidizer used by Gunn was several times as large. Several milliliters of one reactant was decanted into a similar quantity of the other reactant. The photocell used by Gunn to detect the flame, and the one used in Broatch's technique above, did not indicate the strength of the reaction.

In an effort to reduce the mixing time, a device constructed by Pino⁷ caused the pressurized injection of oxidizer through 4 ports directed into a stationary quantity of fuel. The combined quantity of fuel and oxidizer used was approximately 4 milliliters for one test. The results of Pino's testing show no indication of the oxidizer to fuel ratio. Without this variable accounted for, the minimum ignition delay for a reactant combination will not likely be found. Ladanyi and Miller¹ placed a small glass ampoule containing approximately one milliliter of organic under the surface of several milliliters of acid. The glass ampoule was crushed by a steel rod to enhance mixing. The initial measurement was the moment of ampoule crushing. The final measurement was made by a photocell sensing the appearance of a flame. Kilpatrick and Baker⁵ used a device that forced both fuel and oxidizer together using high pressure gas hydraulics. The reactants were initially located in separate chambers below pistons which forced the propellants together immediately prior to injection into the combustion chamber. The initiation of the timing measurement was through monitoring of piston movement above the fuel and oxidizer. The end of an ignition delay measurement corresponded to an increase of pressure in the test chamber.

Saad and Goldwasser⁸ used impinging fuel and oxidizer jets in their technique. They initiated the ignition delay measurement at the moment the valves for fuel and oxidizer were released. Photocell detection of the flame was again used to end the measurement. The resolution of their oscilloscope was 100 milliseconds/division. As ignition delay values are generally less than 100 milliseconds, the resolution of their technique does not provide the accuracy needed for reactions of this speed. In addition to the drop test technique reported earlier, Broatch⁴ also used the technique of impinging jets. He used high speed photography to capture pictures of the combined jets and flame. The ignition delay was calculated from the length of the combined jets to the fully developed flame front. The benefits of the photography technique were to capture the strength of the flame as Broatch varied oxidizer to fuel ratio and temperature, and the ability to photograph phenomena such as pre-ignition boiling of the liquid phase. Spengler and Bauer⁹ used impinging jets to test the influence of pressure and varying chemical composition on ignition delay measurements. This technique consisted of starting the timing by contacting the fuel and oxidizer, which completed an electrical circuit. The timing measurement was ended by sensing the flame with a photocell located between the two injectors. This technique for impinging jets seemed to be the only true measure of ignition delay among the three discussed.

If the intent of the ignition delay technique is to screen reactant combinations, then the above testers should provide reliable information on relative performance between these combinations. The new laser diagnostic method developed in our laboratories was designed as a research tool to measure relative performance of hypergolic reactant combinations. The technique developed, more than met this expectation. The technique is the first to provide a measure of the chemical

performance of the reactant combinations. This chemical delay time is independent of the mixing technique used.

EXPERIMENTAL

The entire combustion system is designed to study the reaction rates and mechanisms of hypergolic reactants for the ability to propose alternate, enhanced chemistry. The equipment uses a variety of techniques, including visible and near infrared Raman spectroscopic measurements, to meet these objectives. The system, its component make-up, and procedural steps are detailed in recent publications by M. Farmer, L., Mays and J.E. Smith, Jr.^{10,12,13}.

RESULTS AND DISCUSSION

Figure 2 shows the digital storage oscilloscope traces resulting from a typical drop test for unsymmetrical dimethylhydrazine (UDMH) contacted with red fuming nitric acid (RFNA). The reactants for the test were obtained from Aldrich Company. The UDMH had a purity of 98%. The RFNA had a nitric acid concentration of 90-95%, with the balance being nitrogen tetroxide. The results in this figure are for an oxidizer to fuel ratio of 2. In Figure 2, the upper trace (channel 1) shows the output from photodiode #1, which monitors the surface of the oxidizer droplet. The lower trace (channel 2) shows the output from photodiode #2, which monitors flame emission.

Various reference points have been added to this figure to identify key features resulting from this technique. Point A on channel 1 represents the moment of contact between the fuel and oxidizer. A pinhole/diode geometry restricts the view of the photodiode to a region from the oxidizer surface to approximately 200 μm above the surface. Once the lower surface of the fuel droplet contacts the oxidizer, a region of rapid linear decrease follows. To consistently reference the ignition time delay to a definable point, we extrapolate this linear region to the initial reference level. An identical approach is used at point B to neglect the shape of the trailing edge of the droplet and any wake that it creates on entry. Thus, the region from point A to point B represents the droplet of fuel from initial contact to final entry into the oxidizer. When the fuel droplet completely enters the oxidizer, the laser light can again fully reach photodiode #1 as illustrated by the return of the signal to its initial reference level.

The response of photodiode #1 in the region from point B to C is representative of a still liquid to air interface. This is the region in which droplet mixing is taking place between fuel and oxidizer by a combination of convection and diffusion between the two reactants. In Figure 2 region B-C represents the time period when mass transfer limited kinetics are occurring. In other words, the rate of reaction is limited by mass transfer and mixing limitations. All methods reviewed above suffer from mixing limitations at some point in the process. Kilpatrick and Baker⁷, in their study of mixing rates, stated, "If the complete intermixing could be effected in a time very short compared to the (total) ignition delay time, then the measured delay would be the true chemical delay..." Pino made the same observation during attempts to improve mixing with his technique. Following their logic, if the droplet entry and mixing stages, points A-C, could be minimized or eliminated, then region C-D in Figure 2 would represent the true chemical delay.

At point C, the chemical reaction rate increases rapidly, with the reaction producing a gas phase that decreases the signal from photodiode #1. This decrease in signal is due to the density of the vapor phase forming above the liquid surface. This vapor phase was noticed in the work of Ladanyi and Miller¹ using an injector technique with high speed photography. Upon mixing, they noted a thick vapor cloud released by the liquid phase that filled their combustion chamber. Close examination of the photographs was required to locate the appearance of flame within this dense cloud. This vapor phase results from reactive intermediates being released from the liquid phase.

The combination of heat release from the chemical reaction in the liquid phase and the reactivity of the gaseous intermediates causes ignition in the vapor phase, as defined by point D. This analysis is supported in the literature by the work of Saad and Goldwasser⁸, Spengler and Bauer⁹, Twardy², and Habiballah¹⁴. For example, Saad and Goldwasser⁸ found in their work that the liquid phase generated heat 200 times more rapidly than the gas phase at atmospheric pressure. Twardy² found that a minimum droplet diameter was required to generate the heat necessary to cause ignition in the reactive vapor phase.

Durgapal and Venugopal¹⁴ performed an ampoule crushing test similar to Ladanyi and Miller¹ to enhance mixing in the RFNA/UDMH combination. For RFNA that had 92% HNO₃ and 8% N₂O₄, they obtained an ignition delay value of 4.7 milliseconds. This value is much smaller than the IDT value, region A-D in Figure 4, of 16.5 milliseconds. If the time for droplet entry is ignored, then the measure would be of mixing time to ignition, i.e., region B-D in Figure 2, or 9.5 milliseconds. This is not surprising though, as no attempt was made to enhance mixing for

the technique presented in this paper. Therefore, Durgapal and Venugopal¹⁴ should have recorded numbers smaller than those of region B-D. However, it one examines region C-D, then a delay of 1.8 milliseconds is measured. This time is a measure from the moment vaporization begins to increase exponentially to ignition. As all hypergolic systems, upon completion of mixing, produce a vapor phase reaction, this period represents a true measure of chemical performance or the chemical delay time.

The importance of the chemical delay time is seen when one compares hydrazine reacted with RFNA (Figure 3) to UDMH reacted with RFNA (Figure 2). Comparing these figures, we see that the ITD for UDMH/RFNA is only 25% faster than hydrazine/RFNA. When one compares the chemical delay time a 75% increase in the reaction rate is measured. This explains why UDMH/RFNA is preferred over hydrazine/RFNA for propulsion systems.

CONCLUSIONS

A new laser diagnostic technique has been developed to quantitatively measure the chemical performance of hypergolic systems. Past techniques and results show that enhanced mixing can reduce ignition delays in an attempt to approximate the chemical delay time. Regardless of technique, the mixing time associated with hypergolic systems can not be eliminated. This drop test technique shows a region after mixing that characterizes the speed of the reaction alone. The beginning of this region, point C, indicates when free radical generation should be observed to obtain information on the chemical mechanisms involved. This new technique requires smaller quantities of reactants than previous methods making it safer and more cost effective.

ACKNOWLEDGEMENTS

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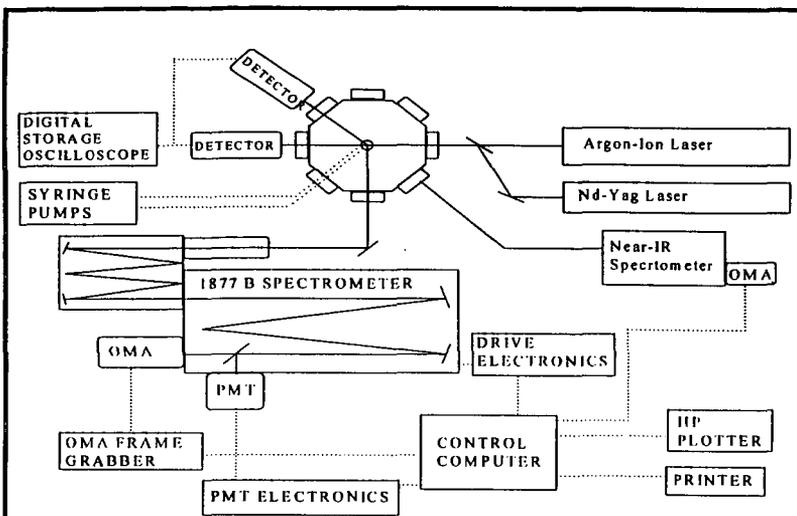


Figure 1. Schematic of the Entire System for Ignition Time Delay and Spectroscopic Analysis

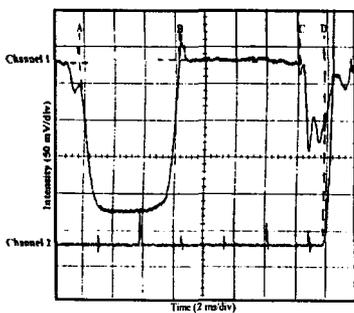


Figure 2. Test Results for UDMH/RFNA

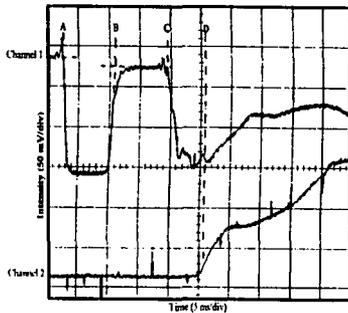


Figure 3. Test Results for Hydrazine/RFNA