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MINIMUM IGNITION ENERGY MEASUREMENTS USING LASER INDUCED SPARK INITIATION*

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Abstract

Measurements of low energy ignition of combustable mixtures is reported using ns and ps laser induced breakdown. Ignition studies are presented for homogeneous H_2/air, hexane/air and unsymmetrical dimethyl hydrazine/air mixtures. The extent of flame inhibition in H_2/air was investigated as a function of CO_2 concentration. Our electrodeless spark ignition results are compared with earlier work using electric discharge ignition. A simple model for flame initiation is advanced based on the temporal and energy density characteristics of the source energy.

I. INTRODUCTION

The chemistry of the ignition process in combustable mixtures is not well understood and yet is of vital importance to understanding the mechanism of propellant detonation and combustion initiation. The vapors of hydrocarbon and hydrazine based fuels present extreme combustion and explosion hazards. Detonation or deflagration of fuel/air mixture may be initiated by energy sources such as electric sparks or discharges. Data on minimum ignition energies for flame propagation, therefore, are required for the design of ignition systems and especially for the establishment of safety standards for instrumentation such as those encountered during ground based support operations for launch vehicles. We are engaged in studies to probe the dynamics of flame propagation from incipient formation to stages in the evolution of the flame front that give rise to deflagration, detonation, or extinction. It is expected that a detailed understanding of the time-dependent kinetics and energy-transfer mechanisms at the flame front (i.e. the preheat and reaction zone interface) will prove vital in learning how to enhance or inhibit flame propagation.

The use of laser induced breakdown to initiate the spherical propagation of the flame front was investigated as an alternative to the use of electrode discharge[1] which is considered to be too intrusive for these studies. The effects of heterogeneous catalysis, ablation of material, and interference with the expanding flame front are particular concerns in using electric discharge to study properties of ignition. The use of laser induced breakdown to initiate spark ignition

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provides a well-defined source of energy localized in free space. The properties of laser induced breakdown (or optical discharge) have been studied intensely[2,3]. Several groups reported studies involving laser induced spark ignition[4-8], however, in only one case was an attempt made to systematically control the energy of the laser spark[4] to measure ignition energies. A number of other studies have investigated photochemical ignition[9-12], however, this process involves resonant multiphoton dissociation to generate a reactive species, as opposed to nonresonant laser induced breakdown which is considered to serve as a thermal ignition source. The extent to which laser induced ignition is a thermal process is a critical concern. Consequently, we shall identify and model the problem of flame initiation and extinction to emphasize the temporal properties of the ignition energy source[13].

II. EXPERIMENTAL

A schematic of the experimental apparatus is presented in Fig. 1. The full details of the components and operation of the experiment are presented elsewhere[13]. The reaction chamber consists of a 4 in conflat cube that has been teflon coated to eliminate metal surface interactions. Ignitions are quenched when the pressure wave punctures an Al foil mounted on one wall and leading to an evacuated buffer chamber. Two lenses serve as the entrance and exit windows for the laser pulse; the remaining lens and window, which are orthogonal to the laser axis, serve for detection of scattered light and spark and/or flame emission, respectively.

The laser induced ignition is achieved by focussing the output of the second or third harmonic of a Nd:YAG laser (Quantel QY471) operating either as a Q-switched ns laser or a pulsed mode-locked ps laser. Spark energy measurements are made by splitting off about 10 % of the incident laser pulse and comparing its energy relative to the pulse transmitted through the reaction chamber after spark formation. The two energy levels are calibrated in the absence of breakdown by evacuating or reducing the pressure of the reaction chamber. The attenuation of the transmitted light, in the case of breakdown, is attributed to absorption of energy by the

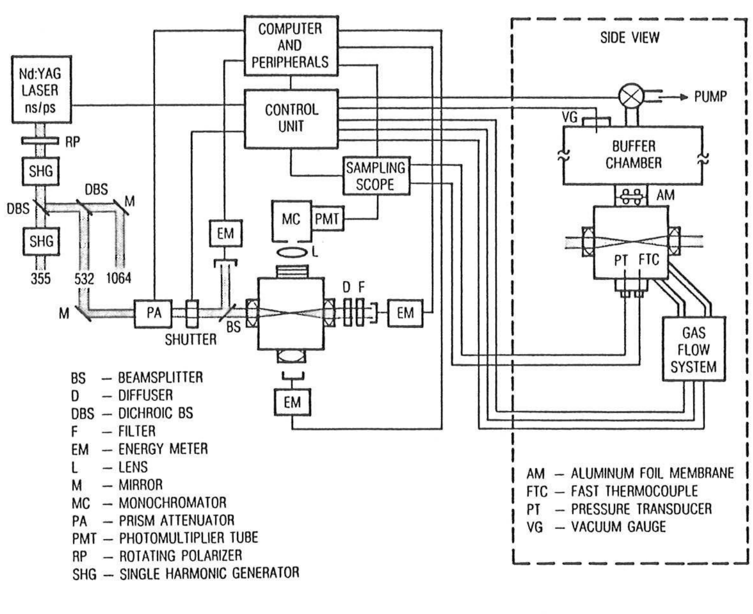

Fig. 1. Schematic of experimental apparatus viewed from the top and from the side (insert) along with associated excitation and detection components.

spark. The transmitted and reference pulse energies are measured using calibrated pyroelectric energy meters[13]. Spark energies are controlled by attenuating the laser output using either a rotatable polarizer or a wedge prism beam attenuator.

The laser induced ignition studies made use of a gas handling system that delivers a precise and homogenous combustion mixture prior to the introduction of a single laser pulse to initiate the combustion. We have automated this operation by building a digital control unit and computer interface that controls the necessary sequence of events[13]. Specific proportions of up to four gases are controlled using mass flow controllers and are allowed to circulate through the reaction chamber for a time sufficient to reach equilibrium (about 1 min). A shutter is then triggered to allow a single laser pulse to enter the chamber to create the spark. The transmitted and reference energy meter readings are digitized by an A/D card in an IBM PC and the spark energy computed and displayed in real-time. Ignition events are detected by monitoring the pressure increase in the buffer chamber due to the rupturing of the Al foil membrane. The occurence of ignition is also evident by detecting OH luminescence or pressure reaching the chamber walls.

III. Minimum Ignition Energy Measurements

Measurements of laser induced spark ignition energies were made using ns and ps duration laser pulses. The shorter ps pulses were essential for measuring very low energy ignition levels, such as for H_2/air mixtures near stoichiometry. The higher peak powers and lower total pulse energies compared to ns pulses extended the practical low energy range for spark formation from 0.5 mJ to 20 μJ. The measured minimum ignition energy results for H_2/air mixtures are plotted in Fig. 2 using 532 nm ps pulses and 355 nm ns pulses as the ignition source. The average of the highest energy non-ignition and lowest energy ignition results for each fuel ratio are represented. (The calculated curves are discussed in Sec. IV). The results of Lewis and von Elbe[14] using electric discharge are included in Fig. 2 and indicate a discrepancy between the two

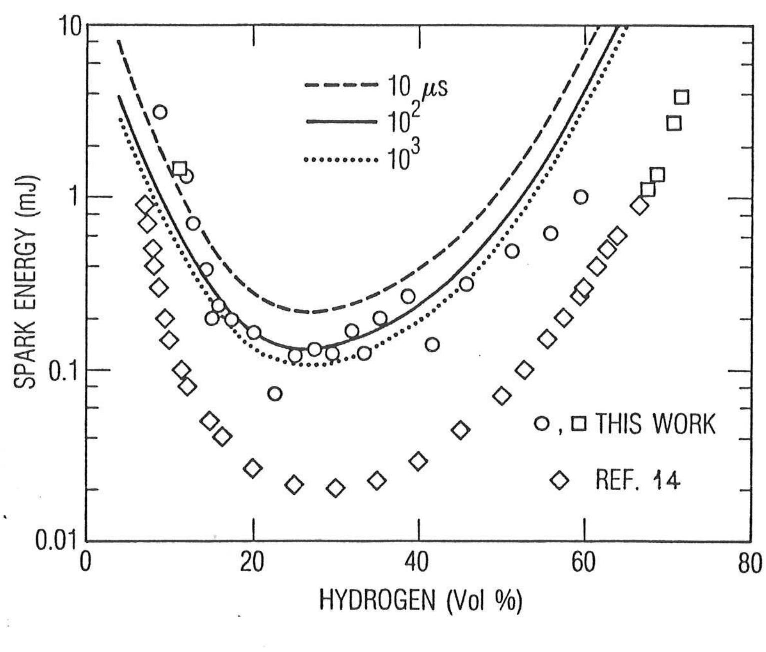

Fig. 2. Minimum ignition energy measurements for H_2/air mixtures using 355 nm nanosecond (□) and 532 nm picosecond (○) laser induced sparks. Electric discharge results of Lewis and Von Elbe[14] are indicated by (◇). Curves represent calculated minimum ignition energies assuming a homogeneous hot gas model for H_2/air at 1 atm and 300 K and various induction times.

sets of results that decreases toward the upper ignition limit. We consider the source of these differences in Sec. IV. The minimum in the energy curve occurs to the lean side stoichiometry (0.11 mJ at 23% H_2 or an equivalence ratio of $\phi = 0.8$). This behavior is characteristic of light, highly diffusive fuels (e.g. H_2) which tend to replenish burned fuel at the spherical flame front during the critical early stages of the minimal flame[14,15].

The effect of CO_2 dilution on the H_2/air ignition process by laser induced spark ignition was investigated. The results for 20% and 40% CO_2 content are compared to the undiluted H_2/air results in Fig. 3. A pronounced inerting effect is observed for increasing CO_2 composition. The mixture becomes completely inert to sparks of less than 10 mJ (and possibly much higher energy) for all H_2/air ratios at 55% CO_2 dilution. Ignition energies for hexane and unsymmetrical dimethyl hydrazine (UDMH) in air were measured using 355 nm ns laser induced sparks; the results for the latter fuel mixture are presented in Fig. 4. Our initial flow system, did not permit us to verify the actual concentrations in the reaction cell due to possible condensation of these fuels. The UDMH concentrations were, therefore, independently measured using a calibrated IR absorption cell that monitored the C-H methyl bond stretch. The UDMH results in Fig. 4, corrected for condensation effects on concentration, indicate an ignition threshold energy of 0.44 mJ at the minimum of the curve. We are not aware of any previous ignition energy measurements of UDMH. Ignition energies for hexane/air have been previously measured by Lewis and von Elbe using electric discharge initiation[14]. Although the location of the minima is in close agreement to the present laser induced spark results ($\phi \sim 1.6$), the ignition energy thresholds are greater by about a factor of four compared to electric discharge ignition.

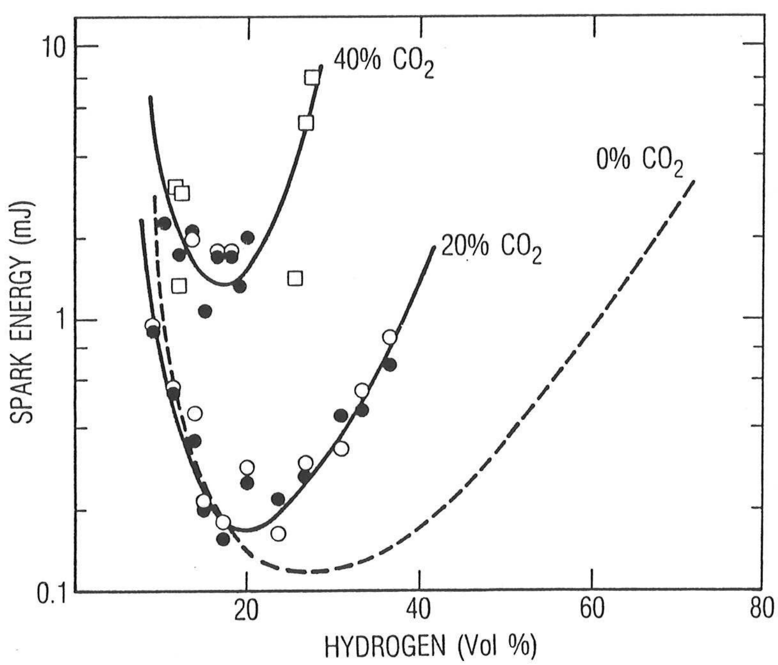

Fig. 3. Minimum ignition energy measurements for H_2/air/CO_2 mixtures showing the effect CO_2 dilution. The laser induced spark ignition source was either a 355 nm ns (■,□) or a 532 nm ps (•,○) pulse. Solid symbols represent highest energy non-ignitions and open symbols represent lowest energy ignitions. The curve through the data is drawn for visualization. The dotted line represents the data of Fig. 2 for no CO_2 dilution.

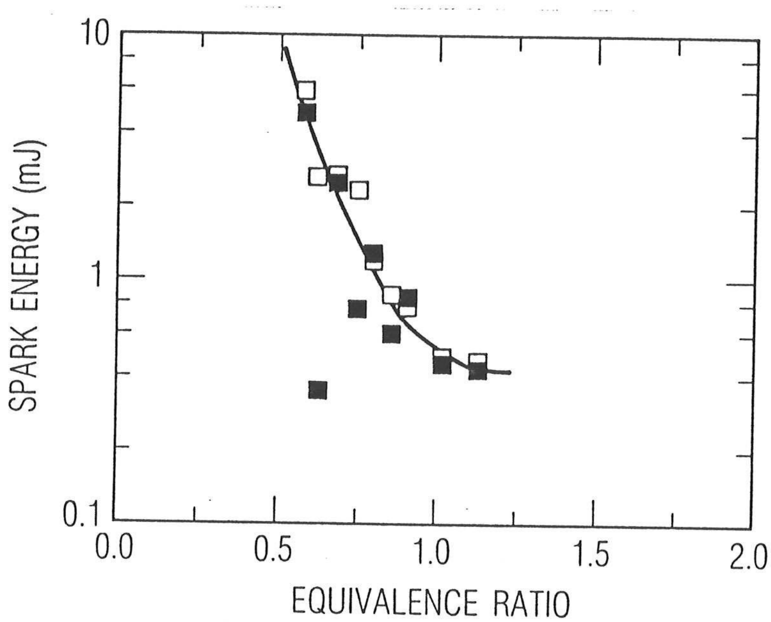

Fig. 4. Minimum ignition energy measurements for UDMH/air, using 355 nm ns laser induced spark ignition. The reaction cell concentrations were verified using an independent calibrated IR cell.

IV. MODELS FOR LASER SPARK IGNITION

The initiation of a flame requires localizing a sufficient amount of energy to heat a minimum flame volume to some threshold temperature. However, since an induction time τ is associated with ignition[16], processes that contribute to energy dissipation play a critical role in the initiation and extinction of an incipient flame. Consequently, one can identify an optimum power density for flame ignition. The threshold condition for flame initiation is defined as the temperature at which the heat of combustion offsets heat that is lost by cooling to the surrounding cold gas or by flame stretch resulting from the increasing volume and hence surface area of the flame front. In the absence of these loss mechanisms, the threshold temperature can be associated with the autoignition point. For H_2/air under ambient conditions this occurs at about 800 K with an induction time on the order of 1 s.[17] For minimum energy ignitions, the dissipation of heat over the relevant dimensions of the flame kernel restricts the usable time duration for localizing heat. Hence, a higher temperature must be reached in a shorter amount of time in order to initiate combustion. In Fig. 5, we have represented the dependence of τ on temperature as a function of the fuel mixture ratio for H_2/air. The induction time contours were derived from calculations and parametrized equations of Oran *et al.*[18].

A. Homogeneous Hot Gas Model

We begin with a very simple model for source heating which assumes that the energy is deposited homogeneously in a spherical volume[14]. The volume temperature as a function of energy E is given by

$$T = T_o + E\left[\frac{4\pi}{3}r^3 c_p \rho_o\right]^{-1}. \tag{1}$$

where T_o is the initial temperature, and c_p and ρ_o are the heat capacity and density, respectively, of the ambient gas mixture. Ideally, ρ_o should be allowed to vary with temperature. A minimum ignition energy may be derived by identifying an ignition temperature and a minimum flame kernel radius. The latter quantity may be related to measured quenching distances[14], d_q. The value of d_q is proportional to the preheat zone thickness and hence becomes greater away from stoichiometry as well as for increasing pressure and turbulence[14,15]. The ignition temperature T_{ig}, which is associated with an induction time (Fig. 5), assumes a relevant time scale for dissipation. Without adopting a specific model for dissipation at this time, we can derive an approximate expression for ignition energies by requiring that the chemical induction time τ be less than the characteristic decay time for dissipation. Rearranging Eq. (1) then gives

$$E_{ig}(\tau) = \frac{\pi}{6}d_q^2 c_p \rho_o \left(T_{ig}(\tau) - T_o\right). \tag{2}$$

where all terms except T_o vary with the fuel mixture ratio. A more accurate expressions should average $E_{ig}(t)$ over time according to a model for dissipation over the relevant geometry of the flame kernel. However, for our purposes, the simple relation given by Eq.(2) will suffice.

The calculated ignition energies as a function of fuel mixture ratio are compared to the experimental data for H_2/air in Fig. 2. The calculated curves are not a very sensitive function

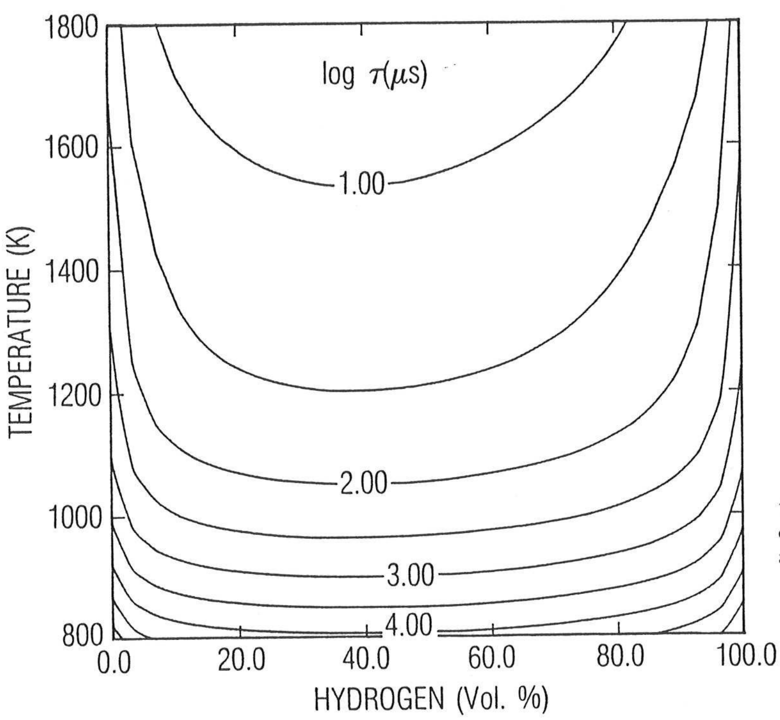

Fig. 5. Calculated dependence of the chemical induction time for H_2/air combustion as a function of temperature and H_2 volume percent at 1.0 atmosphere.

of induction time over the range considered. This is because the large activation energy for the combustion kinetics causes the reaction rate to be steeply dependent on temperature. Consequently small changes in temperature, and hence energy, have large effects on the induction time as evidenced in Fig. 2. The excellent agreement between the calculated and observed laser induced spark ignition energies by this simple model must be considered somewhat fortuitous in view of the rather different results obtained by electric discharge. Further refinements to the working model for flame initiation and their relevance to the two sets of experimental data are discussed shortly.

B. Blast Wave Model

The other extreme to the homogeneous hot gas model is the instantaneous point source deposition of energy. This treatment is somewhat representative of laser induced sparks which require high power thresholds to induce breakdown ($\sim 10^{13}$ W/cm^2)[2]. Short pulse durations are used to minimize spark energy. The instantaneously high pressures created by the tightly focussed laser spark can be modeled as a Taylor blast wave process[19]. The relevant time dependent equations of state for the spherical shock have been expressed before[6,13,19]. Here we present the expressions for velocity and position of the blast wave front;

$$v = \frac{2}{5}(E/\rho_o)^{1/2} r^{-3/2}. \tag{3}$$

$$r = (E/\rho_o)^{1/5} t^{2/5}. \tag{4}$$

where E is the spark energy and ρ_o is the gas density.

If one ignores the initial shock of the blast wave, then the heat generated by the expansion after the blast wave has decayed to near ambient conditions should be available for ignition. If the blast wave completely relaxes on a time-scale that is short compared to the induction time for combustion, then one might expect the heated gas to efficiently ignite the mixture in a manner similar to the hot gas model (Fig. 2). However, two effects argue against this being the case; (i) the blast wave energy is typically dissipated over dimensions greater than the minimum flame volume, and (ii) the blast front is still moving with significant velocity over times that are comparable to combustion. These points are supported by the blast wave velocity calculations represented in Fig. 6. According to Fig. 6a, the blast wave, for relevant spark energies, continues to expand outside of the minimum flame volume, thereby removing energy from this critical kernel. The ignition model assumes that a threshold energy density must be reached inside of the minimum flame kernel. Consequently, the proportion of energy lost due to the expansion of the blast wave must be compensated by adding more source energy. The time-scale for the expansion also approaches the induction time and hence can cause a turbulent disturbance that can extinguish a fragile minimal flame. According to Fig. 6b, the blast wave is calculated to be supersonic only over very short times (~ 1.4 μs for a 1 mJ spark), however substantial velocity remains for much longer times ($\sim 10^4$ cm/s at 10 μs and 1 mJ). Although, the

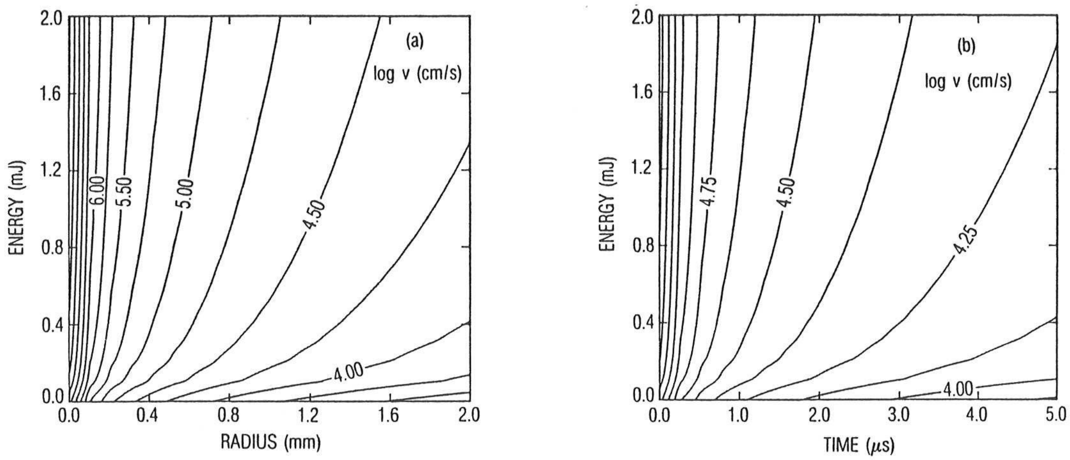

Fig. 6. Calculated blast wave velocity contours as a function of; (a) energy and radius, an (b) energy and time. (H_2/air, 1 atm, 300 K).

validity of the simple blast wave model is qualitative for subsonic conditions, the possibility for turbulent disturbance[1,20] at these low energies cannot be ignored. Furthermore, recompression effects from the collapsing blast wave may contribute disturbances over even longer and more important time-scales.

C. Release of Combustion Energy

Evidence has been presented suggesting that blast wave disturbances in the ignition process by laser induced sparks might explain the higher ignition energies measured relative to earlier electric discharge results[14] (Fig. 2). However, the present laser spark measurements for H_2/air conform nicely with calculated minimum ignition energies using the ideal hot gas model. Furthermore, earlier workers have had trouble explaining the lower than expected ignition energies measured by electric discharge. Explanations have included catalytic surface enhancement at the electrode surface to a contribution to the total energy due to the heat of combustion. In another publication we examined the latter possibility by calculating the available reaction enthalpy in a minimal flame assuming complete combustion within the flame core[13]. The available combustion energy was computed using the enthalpy associated with the net reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g)$ ($\Delta H =$ -241.83 kJ/mol) and the molar content of reactants in a mimimum flame kernel as a function of fuel ratio. Mimimum ignition energies were calculated by subtracting the maximum chemical energy available from the total energy required to reach ignition. A number of simplications acted to overestimate the importance of the heat of combustion[13]. Nonetheless, the calculated ignition energies were still greater than the measured values by electric discharge over much of the range of fuel ratios.

The inability to explain the low electric discharge energy thresholds may be attributable to a variety of effects. For instance, agreement can be obtained if we reduce the assumed minimum flame volume in proportion to the discrepancy. However, the appropriate volumes are based on measured quenching distances, which are considered in the literature to be very reliable

(~ ±10%)[15]. Another possibility is that small turbulences by low energy electric discharge can promote burning velocities, thereby reducing the necessary ignition energy[1]. (For greater turbulence, the pre-heat zone thickness increases, ultimately raising the necessary ignition energy). Finally, it may be argued that catalytic effects involving the electrode surfaces may contribute to the ignition efficiency. Naturally, a combination of these and other effects may be implicated.

V. SUMMARY AND CONCLUSIONS

The method of laser induced spark ignition has been demonstrated to be a viable technique for measuring ignition energies. The minimum ignition energy curve as a function of H_2/air ratio is approximately parallel to electric discharge results, although larger by about a factor of five at stoichiometry. (The discrepancy decreases for higher H_2/air ratios). A similar trend was observed for hexane/air; no available electric discharge data for unsymmetrical dimethyl hydrazine is available for comparison. Several characteristic properties that distinguish laser induced sparks from electric discharge initiation were identified. Calculations based on blast wave propagation indicate that the high energy density and short duration of laser induced sparks is less efficient for flame initiation than electric discharge.

Simple models for calculating the thermodynamic minimum ignition energy requirements are in good agreement with the laser induced sparks results for H_2/air, but are incapable of accounting for the low electric discharge energy thresholds. Agreement can be reached if we reduce the assumed minimum flame volume in proportion to the discrepancy, although reliable meaurements of quenching distance exist to refute this possibility. Other possible explanations for the low electric discharge energy thresholds include; (i) small turbulences which promote burning velocities, thereby reducing the necessary ignition energy[1], and (ii) catalytic effects involving the electrode surfaces that may contribute to the ignition efficiency.

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