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Many combustion applications are presently limited by constraints such as flammability, flame propagation, ignition and stability imposed by the combustion process itself. Consequently much attention is being given to techniques which can augment combustion by extending these limits. One such promising technique is Radiative Augmented Combustion. It is based on the fact that radiation of selected wavelengths is capable of photodissociating stable molecules, combustion intermediates and other inhibiting species into reactive radicals. Subsequent increases in concentrations of these radicals can modify the overall kinetics and produce radiative ignition and combustion enhancements. The potential of this technique was previously demonstrated under static conditions.

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22a. NAME OF RESPONSIBLE INDIVIDUAL

Julian M Tishkoff

22b. TELEPHONE (Include Area Code)

(202) 767-4935

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FOREWORD

This is the Final Report on research on Radiative Augmented Combustion conducted at M. L. ENERGIA, Inc. It was a three year research contract funded by the Air Force Office of Scientific Research under Contract Nos. F49620-83-C-0133 and F49620-85-C-0145, with Dr. Julian M. Tishkoff as the Program Manager. This research succeeded and continued the work performed under a previous Contract No. F49620-81-C-0028 at Exxon Research and Engineering Co., Linden, New Jersey.

The research accomplishments over the first and the second year of the program were reported in the First Annual Technical Report (Ref. 1), and the Second Annual Technical Report (Ref. 2), respectively. The Final Report summarizes only research progress that was accomplished subsequent to that already reported. Thus, in order to have a complete status of the research it is suggested to read the first two annual reports prior to this one.

The entire research program was performed at ENERGIA, Inc., Princeton, New Jersey, with Dr. Moshe Lavid as the Principal Investigator.

ABSTRACT

Many combustion applications are presently limited by constraints such as flammability, flame propagation, ignition and stability imposed by the combustion process itself. Consequently much attention is being given to techniques which can augment combustion by extending these limits. One such promising technique is Radiative Augmented Combustion. It is based on the fact that radiation of selected wavelengths is capable of photodissociating stable molecules, combustion intermediates and other inhibiting species into reactive radicals. Subsequent increases in concentrations of these radicals can modify the overall kinetics and produce radiative ignition and combustion enhancements. The potential of this technique was previously demonstrated under static conditions.

This program emphasizes research on the interaction between vacuum ultraviolet/ultraviolet (VUV/UV) radiation and combustion under flow conditions. This short wavelength radiation is capable of effectively photodissociating molecular oxygen and hydroperoxyl radicals. The main objective is to demonstrate proof of concept by radiatively igniting combustible mixtures at conditions where thermal ignition is unreliable. Additional objectives are to increase flame speed and to provide non-intrusive (optical) flameholding. Another important goal is to improve the fundamental understanding of the role of photochemical reactions within the whole kinetic scheme, and ultimately to identify the most effective photodissociative paths. Consequently, the program has been divided into two main subjects: ignition and enhancement. Each subject consists of an experimental effort supplemented by an analytical effort.

The most significant accomplishments of this research are:

- a. Obtaining successful radiative ignitions at very high flow velocities, up to 250 m/s.
- b. Investigating the effects of equivalence ratio and Damkohler number on radiative ignition.
- c. Concluding that xenon short-arc lamps have sufficient VUV output to achieve ignition even under supersonic conditions.
- d. Developing a method to detect combustion enhancement in terms of increases in flame speed by measuring the apex angle of jet flames.
- e. Developing radiative ignition model for static (no-flow) conditions.

- f. Revising the HCT model to be capable of simulating photodissociation of both molecular oxygen and hydroperoxyl radicals.
- g. Investigating the effects of equivalence ratio, pressure and photochemical rate constants on flame speed to determine combustion enhancement.
- h. Investigating the effect of photodissociation on ignition delay time using the CHEMKIN code.
- i. Extending the original radiative concept of photodissociating molecular oxygen (VUV-single photon) to photodissociation of inhibitors (HO₂ and aldehydes) and to infrared multiphoton dissociation (IRMPD).
- j. Identifying other potential applications of the radiative concept such as laser ignition, augmentation of supersonic combustion, IRMPD of natural gas and even utilization of concentrated solar energy.

These accomplishments have supported the concept of radiative augmented combustion. Furthermore, this research has improved the understanding of the complex interactions of photochemical reactions within the overall kinetic scheme and has identified the most effective photodissociative paths, advancing the concept towards practical applications. This improved fundamental understanding will, in turn, assist in determining the feasibility of the concept based on the availability of newly developed light sources and their compatibility with the harsh combustion environment.

STATEMENT OF WORK

1. Facility/Equipment

- a. Provide a combustion test facility capable of conducting radiative ignition and enhancement experiments under flow conditions.
- b. Select and employ the most appropriate VUV/UV sources from currently available devices.

2. Experimental Work

a. Design and conduct radiative ignition tests under flow conditions; investigate effects of equivalence ratio, pressure and velocity (mostly laminar) on radiative ignition; measure radiative ignition energies under flow conditions; and compare them with conventional spark ignition data.

b. Conduct radiative enhancement experiments under flow conditions, measuring enhancement in terms of changes in the fundamental burning velocity and developing highly sensitive measurement techniques to sense changes in the burning velocity.

c. Attempt to detect and to quantify enhancement also in terms of extending the envelope of flashback and blow-off limits; investigate enhancement over a wide range of equivalence ratio, pressure, velocity, and optical path conditions; and compare the results of this work with results obtained under static (no-flow) conditions.

3. Analytical Work

a. Revise and refine the current model of radiative ignition under flow conditions to include fundamental chemical kinetics, spatial dependence of spectral absorption coefficients, and boundary layer velocity profiles.

b. Modify and revise the HCT model to: simulate radiative enhancement under static and flow conditions; calculate flame propagation properties; and compare with experimental data obtained in Statements 2.b. and 2.c.

c. Use the model to explore the interaction between spectral absorptance and subsequent photo and chemical kinetics and transport phenomena in reacting flow systems to optimize system performance.

d. Perform calculations to find the optimum conditions for deposition of radiative energy in the reaction zone and to determine the radical production that results from this radiation, including the effects of wavelength-dependent optical properties, such as absorption coefficients, transmittance, and temperature sensitive reaction rates.

4. Evaluation

a. Determine the feasibility of utilizing the radiative technique particularly as it may be applied in practical combustion hardware.

STATUS OF RESEARCH

The status of the research is summarized below following the Statement of Work.

1. FACILITY AND EQUIPMENT

a. Combustion Facility

A combustion test facility capable of conducting radiative ignition and combustion enhancement experiments under flow conditions was designed, constructed and tested. It included:

- i. A radiative ignition apparatus capable of providing various combustible mixtures at pre-determined equivalence ratios and at velocities up to 250 m/s. (See description in Ref's 2 and 16);
- ii. A "pancake" burner for conducting radiative combustion enhancement experiments. It is basically a conical jet flame exiting from a small orifice (2 mm) in the thin top plate of a plenum chamber. The optical path from window to flame front is in the range of 2-4 millimeters maximizing radiant flux at the vicinity of the flame. (See description in Ref. 1);
- iii. A cylindrical combustion chamber providing the capability of studying the interaction of radiative flux (short-arc xenon lamps and excimer-lasers - see below) with various fuel-air mixtures at room temperature and at atmospheric and sub-atmospheric pressures (Ref's 3 and 13);
- iv. A supersonic combustor equipped with a Mach 2 nozzle and VUV/UV light sources for hydrogen-air ignition tests at a stagnation temperature of 1000 K and equivalence ratios of 0.4 to 1.0 (Ref 2).

b. VUV/UV Sources

Current best capabilities identified for photochemical experiments are various VUV/UV sources. These sources include three plasma short arc lamps and two excimer lasers. All the three lamps were acquired and tested. They are designated according to the names of their manufacturers: ILC, EIMAC and ORC.

The ILC is a xenon point source operating in a pulsed mode with a 2.5 cm diameter sapphire window. It provides radiation in the 140-400 nm spectral region. These ILC sources demonstrated the capability of igniting fuel-air mixtures at static and high speed conditions via dissociation of oxygen molecules (1,2,6,12,16,23,24).

The EIMAC is a second xenon point source used in combination with a lower grade sapphire window and an elliptical reflector (sealed in the arc chamber). It provides a focused source of radiation in the 160-600 nm spectral region. This source can be operated in the continuous mode at power levels up to 50 J. These EIMAC sources are capable of achieving radiative ignitions as well as combustion enhancement (23,24).

The ORC is a continuous mercury-xenon source with quartz optics. It provides up to 1 kW of energy and operates in the 200-700 nm spectral region. Optics provides for either a parallel (8 cm diameter) or focused beam of light. Because of its quartz window the short VUV wavelengths are not transmitted and thus the ORC source was found to be inadequate for radiative tests.

New excimer lasers in the VUV/UV region are currently available: Lumonics TE-860/861 and Lambda Physik 200/201. The relatively longer wavelengths 351, 308, 249 and 222 nm are emitted by Xenon fluoride, Xenon chloride, Krypton fluoride and Krypton chloride, respectively. The more energetic shorter wavelengths, 157 and 193 nm are emitted by Fluorine and Argon fluoride. These various distinct wavelengths offer a unique opportunity to examine the importance of the role of spectral selectivity in the proposed concept. The Lumonics equipment was employed for the conduction of the radiative ignition tests under static conditions (3,13).

2. EXPERIMENTAL WORK

a. Radiative Ignition

This work is based on the fact that a single photon (SP) absorbed by an oxygen molecule in the wavelength region below 245 nm is capable of photodissociating it into two reactive oxygen atoms. Molecular oxygen absorbs most strongly in the vacuum ultraviolet (VUV) region of 130-175 nm, where one of the oxygen atoms produced is in an electronically excited state (25). The photodissociative generation of oxygen atoms which, in turn, produces other reactive radicals such as OH and H, via chain-branching increases the concentration of free radicals. Subsequent reactions of these radicals with other species release heat. Consequently, the temperature of the mixture rises leading to ignition.

The VUV/UV photons needed for this research were generated by two main sources: xenon short arc lamps and excimer lasers (see 1.b. above). A summary of the experimental results is given below for each of these two photon sources.

i. Xenon Lamps

Currently the best xenon lamp for photochemical studies in the VUV/UV region is the ILC lamp. It is a plasma short arc lamp fabricated to our tailored specifications. The ILC is a point source operating in a pulsed mode (pulsed width $10E-4$ s) with a 2.5 cm diameter sapphire window (about the size of a conventional spark plug). It provides radiation in the 140-400 nm spectral region at power levels up to 50 J, however the output efficiency in the UV region is only 6-10%. Employing these lamps, successful photochemical ignitions under static (non flow) conditions with various combustible mixtures were previously reported (18-24). Here, we focus only on hydrogen/oxygen mixtures under flow conditions.

Controlled ignition experiments were conducted (6, 16). Hydrogen and air flow rates were set to give the desired equivalence ratio and flow velocity within the test section. The lamp power supply was set to give the required number of joules per pulse, and the pulse rate was set at 3.2

pulses per second. If no ignition was obtained, the pulse energy was set at a higher value and the experiment was repeated. When ignition was obtained, the experiment was repeated at gradually reduced pulse energies (the least energy increment was 1/2 joule) until ignition was no longer obtained. The least energy at which ignition was obtained during this decreasing energy progression was taken as the minimum ignition energy. Minimum ignition energies were plotted vs. Damkohler number for several equivalence ratios (12,15,16). Damkohler number is defined as the ratio of convective time to chemical reaction time. For this work it was taken as the ratio of the time for a flow element to pass over the aperture of the lamp window (0.75 cm) to the radiative pulse width. Examining these results, it is revealed that minimum ignition energy is least for 0.5 equivalence ratio and increases for either fuel-leaner (0.3), or fuel-rich mixtures (0.7 and higher equivalence ratios for which it is about the same). This experimental finding that fuel-lean mixtures are more favorable for photochemical ignition, is an important corroboration to the above reported results obtained with excimer lasers under static conditions. The experimental results also indicate that minimum ignition energy is relatively independent of Damkohler number for numbers greater than one, but it is a strong inverse function of Damkohler numbers less than one.

These successful photochemical ignitions obtained at velocities up to 250 m/s demonstrate that this idea is feasible for high speed gas streams even at relatively low pulse energies, (we got ignition with as little as three joules), provided the pulse duration is sufficiently short. Flows at still higher velocities may be ignited with low radiative energies if the pulse width is further shortened. This is true because Damkohler number is inversely proportional to the product of pulse width and flow velocity. Thus, raising one while lowering the other to keep their product constant, can maintain constant Damkohler number. By properly controlling pulse width (and thus Damkohler number) this technology may be used to ignite even hypersonic flows.

This idea of using VUV irradiation for supersonic flows, which are known to be very difficult to ignite, was tested at NASA Langley Research Center (2). A test was conducted using a Mach 2 nozzle with the same ILC light sources, used in the previous experiments. The combustible mixture was hydrogen-air at a low stagnation temperature of about 1000 K and at equivalence ratios of 0.4 to 1.0. Strong and intensive kernels indicating partial ignitions were observed on the UV TV monitor, but full ignition was not obtained. However, as the flow became subsonic, yet at very high velocity (250 m/s), full ignition was detected. We concluded that the lack of sustained combustion at supersonic flows was due to inadequate mixing at the vicinity of the lamp, and insufficient light intensity for such high velocity ($Da = 0.1$).

In summary, the successful subsonic ignitions have extended the scope of our experiments by allowing us to reach even higher velocities. Moreover, based on these results we incline to believe that there is no conceptual difference between subsonic and supersonic photochemical ignitions, provided equal quantities of photons are absorbed by the fluid element at the ignition kernel under both conditions.

11. Excimer Lasers

Lasers are excellent research tools to investigate the effect of spectral selectivity on photochemical ignition. Hence, a Lumonic excimer laser (TE861) was used at two distinct wavelengths: 157 nm emitted by fluorine (F₂) and 193 nm emitted by argon fluoride (ArF). The laser operated in a pulsed mode with focused optics through an optical path of argon/helium. The maximum pulse energy of the argon fluoride laser was determined to be 50 mJ, giving a measured fluence of 350 mJ/cm². The corresponding values for the fluorine laser are 6 mJ and 30 mJ/cm². Photons at the above two wavelengths were used to attempt ignitions of premixed H₂/O₂ and H₂/air at several equivalence ratios and pressures (3,13). We found that the shorter wavelength laser (F₂) is capable of achieving photochemical ignitions, while the ArF laser is not. This finding is in good agreement with our numerical calculations. The minimum fluence predicted to ignite by photochemical means a premixed hydrogen-oxygen mixture at an equivalence ratio of 0.6 and at 20 kPa for the wavelengths of the F₂ (157 nm) and ArF (193 nm) lasers were calculated from a radiative ignition model by increasing the value of the fluence until a solution indicating ignition was obtained. The resulting fluences are 36 and 2.7E5 mJ/cm², respectively. This significant difference in fluences (and therefore energies) is primarily due to the spectral selectivity of the absorption coefficient of the oxygen molecule. At 157 nm (F₂), which is in the Schumann-Runge continuum, the absorption coefficient is 167 l/cm whereas at 193 nm (ArF), which is in the S-R bands, it drops to 0.027 l/cm, about four orders of magnitude lower (25). A secondary effect is indicated by comparison of the net absorbed energy (proportional to fluence times absorption coefficient) for these two wavelengths which reveals the F₂ laser is igniting with somewhat lower (83%) energy. Modeling results suggest that this effect is due to the production of O(1D) at the lower wavelengths; that is, when the same calculations are performed using for O(1D) reactions the rate constants for the analogous reactions of the ground state, the difference in absorbed energy requirements disappears. Although the picture is complicated, we suggest that the beneficial effect of O(1D) is due to its great reactivity producing more rapid thermalization, resulting in more efficient utilization of the remaining pool of fast radicals. Experimental results agree very well with these predictions. Although the fluence of the F₂ laser is considerably smaller than that of ArF laser, it successfully achieved ignition, while the ArF failed to photochemically ignite the same gaseous mixtures. It is important to note that experimental and numerical results indicate that fuel-lean mixtures with some excess oxygen are more favorable for VUV photochemical ignitions than other mixtures, with the optimal equivalence ratio in the range 0.6-0.8. The explanation is that increased molecular oxygen results in higher atomic oxygen concentration upon irradiation. However, when the equivalence ratio is further reduced, the rate of chemical heat release is decreased due to the lessened availability of fuel molecules. In contrast, minimum energy for spark ignition is found to occur at an equivalence ratio of about unity (29).

An analytical effort was undertaken to elucidate the fundamental interaction of photon absorption, subsequent dissociation, the chemical kinetics of the reactive mixture, and heat loss to the surroundings. Currently, the chemical kinetics included allow treatment of hydrogen-oxygen mixtures with the possible presence of an inert diluent. Some 90

chemical reactions are included in the model. Rate constants were obtained from the extensive literature on the subject, with emphasis on data in the initiation and early ignition range (300-1200 K). Radiant absorption is reckoned to follow a Beer-Lambert law. The absorbing species, in addition to O₂, include also O₃, H₂O, HO₂, and H₂O₂. Upon absorbing a photon, these species are assumed to dissociate to radicals depending on the energy of the photon. Photodissociation can thus be handled as a unimolecular reaction in which the dissociation rate is obtained as the product of the concentration of the absorbing species and a pseudo-first-order rate constant, which depends on the incident spectral (monochromatic) irradiance, at a given point in the mixture and at a given time. For each species, a rate balance was formed by consideration of all chemical and photochemical reactions in which it participates. To these species balances, a heat balance has been added which accounts for heat liberated or removed by chemical reaction and possible heat loss to surroundings. Solutions of the species and energy conservation equations were given as trajectories in a phase plane. The temperature was plotted versus oxygen atom concentration, with the oxygen acting as a surrogate for all other free radicals. We found that in order to obtain successful photochemical ignition the concentration of atomic oxygen must exceed a threshold value of 10E17 atoms/cc.

iii. Infrared Multiphoton Ignition

The VUV/UV single photon ignition research summarized above stimulated a new idea of infrared multiphoton (IRMP) photodissociation (see also 4.b. below). Although the IRMP work was not a part of this activity, it is relevant to it and deserves some comments.

IRMP ignition of alcohols was demonstrated for the first time. It was achieved by multiphoton excitation of the C-O stretching vibrational manifold. The main advantage of this new technique, in addition to the common radiative advantages (e.g. non-intrusive, selective, manipulative, etc.) is the relative low cost of IR photons. Detailed documentation of this IRMP work can be found in Ref's 8,10,17.

b. Combustion Enhancement

Radiative combustion enhancement experiments were designed to investigate increases in the fundamental burning velocity, extension of the envelope of flashback and blow-off limits, and decreases in ignition delay time.

For determining combustion enhancement in terms of increases in flame speed the pancake burner (see 1.a above) was constructed. Hydrogen and propane flames were tested and Shadowgraph and Schlieren photographs (2) were employed as the diagnostic system for measuring changes in the apex angle of the conical jet flames which, in turn, can determine the burning velocity. The experiments on the pancake burner did not conclusively confirm the idea of radiative combustion enhancement. Everytime the EIMAC VUV source was turned-on, the flame extinguished. Initially it was construed as an encouraging result; the burning rate is increased, thus the conical flame flattens-out until it reaches extinction. However, further tests proved that the flame was inherently unstable, and it quenched due to a thermal effect. This effect was confirmed by filtering-out the VUV

spectrum from the light and still obtaining extinction. Because of exhaustion of funds no further effort was made to modify the pancake burner by suppressing the thermal effect and stabilizing the flame. However, the idea of exploiting changes in the apex angle of conical flames due to changes in the burning velocity was further investigated to prove adequacy and detectability.

A laminar, fuel-rich methane flame was established over a cylindrical tube with a diameter of 9.2 mm, and the apex angle was measured using Schlieren images. The results are given below in Table I. For four different flow rates at equivalence ratio of 1.4 the laminar ($Re \sim 1000$) burning velocity was measured to be in the range of 28 to 31 cm/s. The velocities are higher than the experimental results of 23 cm/s reported by Lewis and von Elbe (29). Nevertheless, the adequacy of the method was established because although the velocity of the pre-mixed gas was more than doubled (from 65.8 to 172.6 cm/s), the burning velocity changed by less than 9% (from 28.32 to 30.84 cm/s). In other words, confirming that the laminar burning velocity is a fundamental property independent of the velocity of combustible gas stream.

TABLE I - Measuring the Burning Velocity of Methane-Air
($\phi = 1.4$) by the Apex Angle Method

Air Flow Rate cc/min	CH ₄ Flow Rate cc/min	Gas Stream Velocity cm/sec	Half-Apex Angle degrees	Burning Velocity cm/sec	Reynolds No.
2286	336	65.8	25.5	28.32	420.4
3430	504	98.7	17	28.86	630.6
4765	700	137.1	13.0	30.84	875.9
6000	882	172.6	10.25	30.71	1078.75

The sensitivity and suitability of this method for detecting radiative combustion enhancement due to in-situ production of radicals was also proven. For the feasibility study rather than using photochemical production of radicals we injected hydrogen peroxide (H₂O₂) similar to the work of Ramohalli, et al. (30). Since the H₂O₂ was in solution in water (30% H₂O₂) it was necessary to preheat the combustible mixture in order to vaporize the water and the H₂O₂. A temperature of 175 C was selected. A methane flame at equivalence ratio of 1.4 was established as before. The burning velocity (at 175 C) was measured using the apex angle method to be 70.8 cm/s. Then pure water was injected (0.7% of flow rate) to establish a new base line, and the velocity decreased to 59.2 cm/s, as expected. Finally, the same amount of hydrogen peroxide in water solution was injected and the burning velocity was increased to 69.65 cm/s. This is an increase of 17% and it provides two significant findings: 1) radical production (H₂O₂ $\rightarrow$ 2OH) in the vicinity of the flame does enhance combustion, 2) the apex angle method is a sensitive and suitable method to measure these enhancing effects due to in-situ production of radicals (thermal and/or photochemical).

3. ANALYTICAL WORK

a. Radiative Ignition

The radiative ignition model elucidating the fundamental interaction of photon absorption, subsequent dissociation, the chemical kinetics of the reactant mixture and heat loss to the surrounding is documented in Ref's 1,3 and 13 for static (no-flow) systems. Good agreement between experimental results from the excimer laser work and analytical predictions is described above (see 2.a.ii) for static conditions. Of special interest are the phase-diagram figures (1) for stoichiometric premixed H₂/O₂ at atmospheric pressure and 300 K. They demonstrate that all major free radicals, O, OH, and H exhibit similar behavior and rapidly equilibrate. Radiative ignition is noticed as a sharp rise in temperature associated with an exponential increase in concentration of these free radicals.

To gain essential insight into the experimental work on radiative ignition under flow conditions, it became necessary to investigate the problem theoretically. Accordingly, a generalized theory of the problem was constructed and then particularized to the experimental configuration (2). In brief, the model considers the photodissociation reaction $O_2 + h\nu \rightarrow 2O$, which is excited by a square pulse of input radiation, and the opposing three body recombination reaction $O + O + M \rightarrow O_2 + M$.

The criterion for ignition is that it occurs when the photochemically produced oxygen atom number density achieves a value of $1E16$ atoms/cc. This value represents 0.06% dissociation, for stoichiometric hydrogen/oxygen at atmospheric pressure and 298 K, (at these conditions the molecular oxygen number density is $8.2E18$ molecules/cc). This is an order of magnitude less than the critical oxygen atom number density that was reported above for static systems. The dependent variable is the criticality ratio, F , which is defined as the ratio of oxygen atom density to the critical oxygen atom density. Thus, when F is equal to or greater than unity, ignition occurs.

Analytical results of this work are presented in Ref's 2, 6 and 16. They exhibit the criticality ratio as a function of axial distance along the stream at the adjacent surface to the lamp window, which extends from 0 to 1.0 (dimensionless) along the abscissa. The results show that for Damkohler numbers greater than unity (velocities less than 75 m/s), the criticality ratio exceeds 30 times the threshold value required for ignition. Furthermore, this value is reached right at the leading edge of the window. When Damkohler number is decreased to 0.1 (750 m/s, supersonic flows), the previously obtained step distribution of the criticality ratio becomes exponential in nature, and the high ratio of 30 is reached only at the trailing edge. For $D = 0.01$ (velocity of 7500 m/s, hypersonic flows) the criticality ratio drops drastically to a value of 6 far at the trailing edge. This means that if the required critical density of atomic oxygen for ignition were an order of magnitude larger than the cited one, (i.e. $1E17$ instead of $1E16$ atoms/cc), the ILC lamp will not be anymore capable of photochemically igniting this hypersonic mixtures. Thus, for Damkohler numbers of 0.01 and lower (velocities over 7500 m/s) photochemical ignitions become questionable with the currently available ILC lamps. A remedy to this difficulty was discussed earlier, suggesting to increase the VUV power by, for example, shortening the pulse width.

It is interesting to note that if the Damkohler number were zero (velocity is infinity), the criticality ratio would everywhere be zero (no ignition), whereas if it were infinity (velocity is zero, i.e. the static case), the ratio would be a step distribution extending along the entire window. The conclusion is that even for very low Damkohler numbers (0.1), the ILC lamp should achieved ignition. This conclusion was corroborated by the experimental results reported above.

b. Combustion Enhancement

i. Flame Speed

The idea of in-situ, photochemical production of free radicals to augment combustion was analytically investigated. Laminar flame speeds (relative to the unburned gas) were calculated using the HCT model (31). The computation was first carried out for a base case without irradiation, i.e., using the reaction mechanism and rate constants for hydrogen chemistry employed by Westbrook and Dryer (32). In order to model the effects of irradiation on the mixture, the key reaction or reactions due to photodissociation were then incorporated into the mechanism. Flame speeds were calculated for cases in which the photodissociation of either molecular oxygen or the hydroperoxyl radical was simulated and then compared to the base case value. The base case of H₂/Air at atmospheric pressure and equivalence ratio of 0.4 gave a calculated flame speed of 47 cm/s (Run 43). In simulating the photodissociation of O₂, it was found necessary to limit this reaction to the flame front to avoid the production of H₂O₂ ahead of the flame. This was done by including the reaction only in those regions in which the temperature was in a specified range ("window"). Significant results are summarized in Table II. Results for Runs 43 through 80 were already reported (2,4,5,11,15), and are summarized below.

We first examine the results of the oxygen photodissociation runs. The first two runs listed (67,69) represent the initial attempt to limit the modeled photodissociation of O₂ with a temperature window of ~375 to 700 K. The flame speed calculated for Run 69 with a photodissociative rate constant of 3000 l/s is 51 cm/s, an increase of 9% over the base case. The oxygen atom profile differs from that of the base case by the presence of a new peak ahead of the flame front stemming from the photodissociation of O₂ in the temperature window. The other peak which follows this induced peak is due to the usual reaction pathways, but has a lower maximum concentration than the corresponding peak of the base case. This lowering of peak values also occurs for H, HO₂, and H₂O₂. These observations hold for Run 67 with the lower rate constant of 300 l/s and the same temperature window, for which the flame speed is only 47 cm/s, equal to that of the base case. The peak in the O profile due to the modeled photodissociation is now smaller than the thermal peak. From these runs it was not possible to distinguish between the effects due to the value of the photodissociative rate constant and those due to the choice of temperature window.

Table II - SUMMARY OF H₂/AIR RUNS

Run Number	Equiv. Ratio	Press. (atm)	Simulated Photo-dissociation	Rate Constant (1/s)	Spatial Extent*	Flame Speed (cm/s)	Increase Over Base Case(%)
43	0.4	1	none	---	----	47	---
67	0.4	1	O2 -->O +O	3E2	W1	47	0
69	0.4	1	O2 -->O +O	3E3	W1	51	9
77	0.4	1	O2 -->O +O	3E2	W2	55	17
78	0.4	1	O2 -->O +O	1.2E3	W2	66	40
72	0.4	1	O2 -->O +O	3E3	W2	76	62

73	0.4	1	HO2-->OH+O	1E4	R	48.5	3
74	0.4	1	HO2-->OH+O	1E5	R	50.5	7
76	0.4	1	HO2-->OH+O	5E5	R	56.5	20
75	0.4	1	HO2-->OH+O	1E6	R	60.5	29

81	0.4	1	O2 -->O +O	2E2	W1	48	2
			HO2-->OH+O	5.5E2	R		
83	0.4	1	O2 -->O +O	2E2	W2	52	11
			HO2-->OH+O	5.5E2	R		
82	0.4	1	O2 -->O +O	3E2	W1	52	11
			HO2-->OH+O	5E5	R		
84	0.4	1	O2 -->O +O	3E2	W2	58	23
			HO2-->OH+O	5E5	R		

86	1.2	1	none	---	---	300	---
88	1.2	1	O2 -->O +O	3E2	W2	300	0
90	1.2	1	HO2-->OH+O	5E5	R	?	?

85	0.4	5	none	---	----	22.5	---
87	0.4	5	O2 -->O +O	3E2	W2	29	29
89	0.4	5	HO2-->OH+O	5E5	R	29	29
91	0.4	5	O2 -->O +O	3E2	W2	34	51
			HO2-->OH+O	5E5	R		

* R - Photodissociation throughout entire reactor

W - Photodissociation confined to reactor region in which temperature is in specified interval: W1; 375-700 K, W2; 375-1300 K

Runs 77, 78, and 72 in order of increasing rate constant were made with a temperature window of 375 to 1300 K with the goal of coalescing the two separate peaks of atomic oxygen into a single peak encompassing the flame front. The calculated species profiles have showed that this goal was achieved. With 3000 l/s as the rate constant, the peak oxygen atom concentration has nearly doubled and the peak has broadened considerably. Through chain-branching, the higher concentration of oxygen atoms has almost doubled the peak of hydrogen atom concentration. The increased concentration of fast radicals has reduced the concentration of HO_2 . The most notable result from Run 72 is the dramatic increase of 62% in calculated flame speed produced by the increased concentration of radicals at the flame front. This result is especially significant when one compares the 76 cm/s obtained to the value of 51 cm/s calculated for Run 69. The only difference between these two runs is the temperature window used. In Run 78, the rate constant was reduced to 1200 l/s, giving a flame speed of 66 cm/s and profiles similar to those of Run 72, but with lower peak values for O, H, and OH. The rate constant was reduced to 300 l/s in Run 77, giving a calculated flame speed of 55 cm/s, still an increase of 17% over the base case.

Runs 73 thru 76 model the photodissociation of HO_2 . No temperature window is required because HO_2 is present only at the flame front. The flame speed calculated in Run 73 with rate constant $1\text{E}4$ l/s is 48.5 cm/s, a small increase over the base case. In Run 74, this constant is increased to $1\text{E}5$ l/s and the flame speed is 50.5 cm/s. When the species profiles are compared to the base case, the differences are that the HO_2 and H_2O_2 peaks are diminished and those of O, H, and OH are slightly increased. These observations apply as well for Runs 76 and 75 with rate constants $5\text{E}5$ and $1\text{E}6$ l/s, respectively. Due to the increased value for the rate constant, the changes in species profiles from those of the base case are more dramatic. The HO_2 and H_2O_2 peaks diminish and the O, H, and OH peaks enlarge as the rate constant is increased. The shoulder on the oxygen atom profile becomes a small peak in Run 76 and a more pronounced peak in Run 75. Most importantly, the greater rate of HO_2 photodissociation has also increased the calculated flame speed to 56.5 cm/s for Run 76 and to 60.5 cm/s for Run 75. The photodissociation of the hydroperoxyl radical evidently results in circumventing the radical terminating pathways leading to HO_2 and H_2O_2 , and results in a significant increase in flame speed. These analytical results reveal that increasing the pool of fast radicals (O, H, OH) via either photodissociation of O_2 or HO_2 results in a substantial increase in flame speed. With the use of the HCT model, we have thus been able to probe the fundamental chemistry of the propagating flame in the presence of photodissociation reactions, and thereby identify the key factors governing photochemical combustion enhancement.

During the last year we investigated additional three effects on flame speed: equivalence ratio, simultaneously combined photodissociation of O_2 and HO_2 and pressure. Relevant runs are 81 through 91 in Table II.

Effect of Combined Photodissociation of O_2 and HO_2

One run (84) was performed to examine the effect of the simultaneously combined photodissociation of O_2 and HO_2 . The photochemical rate constant for O_2 was $3\text{E}2$ l/s, comparable to Run 77, and that for HO_2 was $5\text{E}5$ l/s, as in Run 76. The O profile (not presented) shows a greater resemblance to

that of Run 77 with a somewhat more prominent shoulder. The calculated flame speed of 58 cm/s is somewhat greater than the 55 and 56.5 cm/s obtained for Runs 77 and 76, respectively. Although this run represents a preliminary look at the interaction of the dissociation of O₂ and H₂O₂, no synergistic effect on flame speed is evident at atmospheric pressure.

Photodissociation Effects at Higher Pressure

We discuss here one final series of runs examining the effects of the photodissociation of O₂ and H₂O₂ at higher pressure, 506.5 kPa (5 atm), with other conditions unchanged. Run 85 represents the corresponding base case for these conditions. It is instructive to compare these results with those of Run 43 (base case at atmospheric pressure). At the higher pressure, the peak mole fractions of O, H, and OH have all decreased, to 18, 32 and 55% of the values in Run 43, respectively. Those of H₂O₂ and H₂O have, on the other hand, increased. It is also evident from the calculated profiles that the flame is much narrower at higher pressure, in agreement with the established general trend. The computed flame speed has decreased from 47 cm/s to 22.5 cm/s. Experimental results reported by Strauss and Edse (33) corroborate our computation. They found a decrease of burning velocity with increasing pressure for combustible mixtures whose burning velocity at atmospheric pressure is below approximately 50 cm/s (e.g. our case), and an increase for mixtures whose atmospheric burning velocity is higher than this value. The same occurrence was observed in the theoretical study of methanol-air flames by Westbrook and Dryer (32). We suggest that the effects reported in our study are all related to the increased rate at higher pressure of the three-body recombination reaction $H + O_2 + M \rightarrow HO_2 + M$ which interferes with chain branching by competing for hydrogen atoms and consequently retarding the flame speed to a greater extent than at lower pressure.

Based on the greater role of this recombination at higher pressure, we would expect significant increases in flame speed from photochemical radical deposition and the resulting augmented chain branching. This expectation has been confirmed in runs simulating the photodissociation of O₂ and H₂O₂. Run 87 incorporated the $O_2 \rightarrow O + O$ with rate constant $3E2$ l/s (cf. Run 77 at atmospheric pressure). Again, the modeled photodissociation has produced a significant second peak in the O profile ahead of the flame. This narrow peak is more sharply separated from the conventional peak than in low-pressure runs due to the rapid increase in temperature and rapid decrease in O₂. The computed flame speed of 29 cm/s represents an increase of 29% over the reference value of 22.5 cm/s (cf. Run 85). Thus, as in Run 77, the increased O atom concentration in the induction zone has increased the flame speed, despite a slight decrease in maximum radical concentrations in the immediate post-flame region. The percent increase at the elevated pressure (29%) is larger than at 1 atm (17%).

The photodissociation of H₂O₂ with rate constant $5E5$ l/s was modeled in Run 89. The profiles are similar to those of Run 87 with the exceptions that the secondary O peak is smaller and the peaks of O, H, and OH concentrations have increased slightly over the base case rather than decreased. The net result was a computed flame speed of 29 cm/s, identical to that of Run 87. Lastly, in Run 91, both dissociations O₂ and H₂O₂ were included at 5 atm, giving a flame speed of 34 cm/s which is an increase of

two separate peaks, photo and thermal, into a single broadened peak. Because the oxygen concentration is decreasing rapidly by the point the temperature exceeds 700 K, the difference in total absorbed energy is not great. Comparison of Runs 67 and 77 reveals the same trend in the dependence of flame speed on temperature interval. Deposition too far ahead of the flame depletes radical concentration at the flame front, thereby failing to achieve the full enhancement potential. We conclude that the position of radical deposition is important, with the favored position being from the induction zone to the flame front.

The importance of optimizing this position appears to favor the photodissociation of H_2O_2 in practical combustion systems. Because such systems generally operate fuel-lean, O_2 is present on both sides of the flame, making it difficult to deposit the necessary short wavelength (vuv) energy for its photodissociation at the desired position. In contrast, the H_2O_2 peak is intrinsically in the correct position. In addition, the existence of uv wavelengths (e.g., 200-270 nm) in which H_2O_2 is the primary absorber facilitates the delivery of the photodissociative energy to this location. However, the low H_2O_2 concentration does require more intense irradiation than is available from current continuous light sources in order to achieve rate constants which produce significant enhancement. Advanced multiple-pass optical systems which allow more efficient utilization of the emitted light source energy may alleviate this drawback.

By numerical modeling, we have examined the fundamental chemical and physical processes of the propagating flame in the presence of the photodissociation of O_2 and H_2O_2 and identified the key factors governing photochemical enhancement. Even though there are serious experimental obstacles, we hope that the novel findings reported here with specific physical conditions will provide guidance for the still needed experimental corroboration of photochemical combustion enhancement.

ii. Ignition Delay Time

The CHEMKIN computer code was utilized to investigate the effect of photodissociation of O_2 and H_2O_2 on ignition delay time. We used the kinetic scheme for hydrogen combustion and ran the code at atmospheric pressure, two initial temperatures ($T_0 = 1200 \text{ K}$ and 1500 K), and two equivalence ratios (0.4 and 1.0). Selective results are given in Table III.

The criterion chosen to characterize ignition delay time (IDT) for this system is the time at which maximum H atom concentration occurs with the mixture starting with molecular species $\text{H}_2/\text{O}_2/\text{N}_2$ at time equal to zero. This time was found to coincide quite closely with the time of greatest heat release rate (maximum dT/dt). These times are recorded in Table III for the Base Case (no simulated photodissociation), the dissociation of H_2O_2 to O and OH at the unimolecular rate of $1\text{E}6 \text{ s}^{-1}$, and the dissociation of O_2 to 2O at the rates of 300 s^{-1} and 3000 s^{-1} .

The results presented in Table III are quite internally consistent. In all cases the inclusion of a modeled photodissociation resulted in a decrease in IDT. The decreases predicted for the dissociation of O_2 at a given rate are essentially independent of the equivalence ratio and are somewhat greater for the lower initial temperature than for the higher

value. The inclusion of $\text{HO}_2 \rightarrow \text{O} + \text{OH}$ has a much smaller effect at all conditions (8-9%) than the changes obtained from the dissociation of O_2 (35-68%).

We now examine the reasons for these differences. The peak mole fraction of HO_2 was found to be approximately $6\text{E-}5$. With M representing the molar density of the mixture, the peak rate of radical production from $\text{HO}_2 \rightarrow \text{O} + \text{OH}$ at $k = 1\text{E}6 \text{ s}^{-1}$ would be:

$$(2) (6\text{E-}5 \text{ M}) (1\text{E}6) = 120 \text{ M radicals/vol. sec.}$$

At $\phi = 0.4$, the mole fraction of O_2 is 0.18 giving a radical production rate at $k = 300 \text{ s}^{-1}$ for $\text{O}_2 \rightarrow \text{O} + \text{O}$ of:

$$(2) (0.18 \text{ M}) (300) = 108 \text{ M radicals/vol. sec.}$$

These two peak rates are approximately equal.

The peak rates of production are, however, only part of the reason. Initially only H_2 and O_2 are present. In the Base Case, initiation reactions occur solely by the thermolytic processes $\text{H}_2 + \text{M} \rightarrow 2\text{H} + \text{M}$ and $\text{O}_2 + \text{M} \rightarrow 2\text{O} + \text{M}$. HO_2 is only formed after thermolytic and chain branching reactions have produced a supply of the reactive radicals H , O , and OH . Indeed, the peak HO_2 concentration occurs when initiation is well under way, nearly at the time of maximal heat release. Thus, the simulated HO_2 dissociation is most productive when it is least needed. As a matter of fact, a run in which its dissociation rate was further increased to $1\text{E}10 \text{ s}^{-1}$ gave no significant decrease in IDT. It is interesting that the addition of radicals from HO_2 dissociation at the time of maximal radical production by the usual mechanism is predicted to give the 8-9% decrease observed in Table III.

TABLE III - Calculated Ignition Delay Time for H_2/Air Mixtures

Tabulated values are times (μs) to attain maximum hydrogen atom (H) concentration for initial $\text{H}_2/\text{O}_2/\text{N}_2$ mixtures at 101.3 kPa and indicated equivalence ratio (ϕ) and initial temperature (T_0).

Photodissociation	$\phi = 0.4$ (fuel-lean)		$\phi = 1.0$ (stoichiometric)	
	$T_0 = 1200 \text{ K}$	$T_0 = 1500 \text{ K}$	$T_0 = 1200 \text{ K}$	$T_0 = 1500 \text{ K}$
Base Case	41.3	15.2	38.4	13.8
$\text{HO}_2 \rightarrow \text{O} + \text{OH} (1\text{E}6)$	37.6 (9%)*	13.8 (9%)	35.3 (8%)	12.7 (8%)
$\text{O}_2 \rightarrow \text{O} + \text{O} (300)$	17.5 (58%)	9.4 (38%)	17.3 (55%)	9.0 (35%)
$\text{O}_2 \rightarrow \text{O} + \text{O} (3000)$	13.8 (67%)	8.0 (47%)	12.2 (68%)	7.3 (47%)

*Percentages after times indicate decrease from Base Case value.

In contrast, the simulated photodissociation $O_2 \rightarrow O + O$ proceeds for all times $t > 0$ and is independent of temperature in distinction to the high activation energy of the thermolytic reactions. It is thus not surprising that the decreases in IDT are as great as those found in the Table (35-68%).

Enhancement of combustion initiation in homogeneous mixtures thus stands in contrast to the enhancement of laminar flame speeds. In the latter, HO_2 is always present ahead of the flame (due to the diffusion of H, and $H + O_2 + M \rightarrow HO_2 + M$) in the lower temperature induction zone. In this zone, thermolytic radical production is minimal. Thus, the simulated photodissociation of HO_2 can dramatically increase laminar flame speeds, as discussed above.

In summary, these analytical results have shown that selective photodissociation is capable of substantially reducing ignition delay time, in addition to the previously reported increases in flame speed.

4. EVALUATION AND RECOMMENDATIONS

a. Radiative Augmented Combustion

A comparison between the Statement of Work and the Status of Research reveals that all major objectives were successfully fulfilled.

In addition, the original concept of radiative augmented combustion by VUV photodissociation of molecular oxygen has been extended to include photodissociation of inhibitors (hydroperoxyl in hydrogen flames and aldehydes in hydrocarbon flames). Furthermore, infrared multiphoton absorption has been conceived and successfully tested as a new radiative means. Lastly, in addition to analytical modeling using the HCT code to investigate photochemical combustion enhancement in terms of increases in flame speed, a new code, CHEMKIN was employed. With CHEMKIN, substantial decreases in ignition delay time were shown for hydrogen flames with simulated photodissociation of O_2 .

The major accomplishments of this research are:

- a. Obtaining successful radiative ignitions at very high flow velocities, up to 250 m/s.
- b. Investigating the effects of equivalence ratio and Damkohler number on radiative ignition.
- c. Concluding that xenon short-arc lamps have sufficient VUV output to achieve ignition even under supersonic conditions.
- d. Developing a method to detect combustion enhancement in terms of increases in flame speed by measuring the apex angle of jet flames.
- e. Developing radiative ignition model for static (no-flow) conditions.
- f. Revising the HCT model to be capable of simulating both photodissociation of molecular oxygen and hydroperoxyl radicals,

- g. Investigating the effects of equivalence ratio, pressure and photochemical rate constants on flame speed to determine combustion enhancement.
- h. Investigating the effect of photodissociation on ignition delay time using the CHEMKIN code.
- i. Extending the original radiative concept of photodissociating molecular oxygen (VUV-single photon) to photodissociation of inhibitors (HO₂ and aldehydes) and to infrared multiphoton dissociation (IRMPD).
- j. Identifying other potential applications of the radiative concept such as laser ignition, augmentation of supersonic combustion, IRMPD of natural gas and even utilization of concentrated solar energy.

There are two important tasks that unfortunately were not fully completed due to exhaustion of funds. The first one is more supportive and conclusive experiments to confirm combustion enhancement. It is strongly recommended that this task will be undertaken and completed. The second task is the documentation of three major research findings which appear below as titles in preparation, (References 26, 27, and 28).

b. Spin-Offs

The most gratifying reward of this research is the large number of spin-off ideas and proposals. This research has been the impetus for innovative concepts in infrared multiphoton processes and photochemical ignition and combustion enhancement.

The following is a list of successfully awarded contracts:

- 1. "Infrared Multiphoton Ignition and Enhancement of Combustion", funded by NSF.
- 2. "Infrared Multiphoton Ignition and Combustion Enhancement of Natural Gas", funded by Gas Research Institute.
- 3. "Multiphoton Processes Promoted by Concentrated Solar Energy", funded by DOE.
- 4. "Modifying Combustion Kinetics by Photodissociation of Inhibitors", funded by NSF with a follow-on funding commitment from Eaton Corp.
- 5. "Radiative Ignition and Combustion Enhancement for Navy Aircraft Propulsion Systems", funded by NAVY-NAPC.
- 6. "Photochemical Ignition and Enhancement of Supersonic Combustion", funded by NASA-AMES.
- 7. "Variable Pressure and High Temperature Closed Bomb for Laser Ignition Studies", funded by DOD-BRL.

There are three additional proposals that were stimulated by this contract and that are currently under review. They include: embedded laser and fiber optics system for rocket motor ignition, photochemical flameholding for supersonic combustion, and photochemical means to augment ramjet/scramjet propulsion for the National Aero-Space Plane (NASP).

PUBLICATIONS

This research activity resulted in four publications. Three additional publications are in preparation.

The four publications are:

- 1) Lavid, M., and Stevens, J.G., "Photochemical Ignition of Premixed Hydrogen/Oxidizer Mixtures with Excimer Laser", *Combustion and Flame*, 60, 2 (1985).
- 2) Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of Enhancement of Premixed H₂/Air Flames with Photochemically produced Radicals", *Proceedings of the 1987 ASME/JSME Thermal Engineering Joint Conference*, Vol. 1, pp. 241-248.
- 3) Lavid, M., and Poulos, A.T., "Recent Advances in Photochemical Techniques for Ignition and Combustion Enhancement", *Proceedings of the 24th JANNAF Combustion Meeting*, Monterey, California, October 5-9, 1987, published by CPIA.
- 4) Blair, D.W., and Lavid, M., "Photochemical Ignition of Hydrogen/Air Streams", submitted to the Twenty-Second International Symposium on Combustion, Seattle, Washington, August 14-19, 1988.

The three publications in preparation are:

- 5) Lavid, M., and Tavakoli, J., "Determining Combustion Enhancement in Terms of Increases in the Fundamental Burning Velocity by Measuring Changes in the Apex Angle of Conical Flames", in preparation.
- 6) Lavid, M., and Stevens, J.G., "Photochemical Effects on Ignition Delay Times", in preparation.
- 7) Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of the Effects of Equivalence Ratio, Pressure and Simultaneous Photodissociation of O₂ and H₂O₂ on Combustion Enhancement of Hydrogen Flames", in preparation.

PROFESSIONAL PERSONNEL

- Dr. Moshe Lavid - Principal Investigator - PhD Mechanical Engineering, State University of New York at Stony Brook, 1974.
- Dr. David W. Blair - Senior Staff Member - PhD Mechanical Engineering, Columbia University, 1961.
- Dr. Arthur T. Poulos - Research Staff Member - PhD Physical Chemistry, Northwestern University, 1976.
- Dr. J. G. Stevens - Analytical Consultant - PhD Courant Institute of Mathematic Sciences, New York University, 1972.
- Dr. Charles K. Westbrook - Analytical Consultant - PhD Engineering/Applied Science, University of California at Davis, 1974.

INTERACTIONS

1. Presentations

Most presentations of the research results were given in the Eastern Section of the Combustion Institute over the last five years. They include:

- 1) Lavid, M. and Stevens, J.G., "Photochemical Ignition of Premixed Hydrogen Oxidizer Mixtures with Excimer Laser", Eastern Section of the Combustion Institute, Brown University, Providence, RI, November 8-10, 1983.
- 2) Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of Radiative Enhancement in premixed Hydrogen-Air Flames", Eastern Section of the Combustion Institute, Clearwater Beach, FL, December 3-5, 1984.
- 3) Lavid, M., Stevens, J.G., Westbrook, C.K., "Enhancement of Premixed H₂/Air Flames with Photochemically Produced Radicals: Analytical Modeling", Eastern Section of the Combustion Institute, Philadelphia, PA, November 4-6, 1985.
- 4) Lavid, M., and Blair, D.W., "Experimental and Analytical Results of Radiative Ignition in Premixed Hydrogen-Air Flows", Eastern Section of the Combustion Institute, Philadelphia, PA, November 4-6, 1985.
- 5) Lavid, M., Blair, D.W., and Stevens, J.G., "Photochemical Effect on the Second Explosion Limit of H₂/O₂ System: Experimental and Analytical Results", Eastern Section of the Combustion Institute, Philadelphia, PA, November 4-6, 1985.
- 6) Lavid, M., and Poulos, A.T., "Infrared Multiphoton Ignition of Alcohols", Eastern Section of the Combustion Institute, San-Juan, Puerto Rico, December 15-17, 1986.
- 7) Lavid, M., Stevens, J.G., Tavakoli, J., and Westbrook, C.K., "Combustion Enhancement of Methane/Ethane Mixtures by Photodissociation of Inhibitors", Eastern Section of the Combustion Institute, NBS, Gaithersburg, MD, November 2-6, 1987.
- 8) Poulos, A.T., and Lavid, M., "Diagnosing Infrared Multiphoton Processes During ignition of Alcohols", Eastern Section of the Combustion Institute, NBS, Gaithersburg, MD, November 2-6, 1987.

Other presentations are:

- 9) Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of Enhancement of Premixed H₂/Air Flames with Photochemically Produced Radicals", ASME/JSME Joint Conference, Honolulu, Hawaii, March 22-27, 1987.

- 10) Lavid, M., and Poulos, A.T., "Recent Advances in Photochemical Techniques for Ignition and Combustion Enhancement", 24th JANNAF Combustion Meeting, Monterey, California, October 5-9, 1987.
- 11) 1983 AFOSR Contractors Meeting, Scottsdale, Arizona
- 12) 1984 AFOSR Contractors Meeting, Pittsburgh, Pennsylvania
- 13) 1985 AFOSR Contractors Meeting, Pasadena, California
- 14) 1986 AFOSR Contractors Meeting, Stanford, California
- 15) Battelle Columbus Laboratories, Columbus, Ohio
- 16) Department of Energy, Morgantown Energy Technology Center, Morgantown, West Virginia
- 17) University of Vermont, CEME Department, Burlington, Vermont
- 18) Drexel University, MEM Department, Philadelphia, Pennsylvania
- 19) Technion, Department of Mechanical Engineering, Haifa, Israel
- 20) Technion, Aeronautical Department, Haifa Israel
- 21) Tel Aviv University, Mechanical Engineering Department, Tel Aviv, Israel

2. Interest Expressed by Other Researchers

The interest in the whole subject of combustion enhancement is continually expanding. Ward and Wu (34) proposed microwave radiation as a means of enhancing the flame speed to allow use of lean mixtures in spark-ignition engines. According to their theory, the microwave field principally heats the electrons of the flame, and the hot electrons transfer energy to the reacting species. The resulting increase in the population of higher vibrational states of the reacting species, especially that of oxygen, is said to increase reaction rates in the flame, as suggested by Jagers and von Engel (35). This increase in the reaction rates is expected to be greater than that which results from simple thermal heating of the bulk gases. Ward (36,37) compared theoretically and experimentally cavity quality factors and concluded that the microwave flame-plasma interaction was strong as predicted. Additional work by Ward (38) in a constant-volume combustion bomb suggested that burn time can be reduced by the application of microwaves in conjunction with plasma-jet ignition. Subsequent experiments by Clements and coworkers (39,40) showed that the flame-plasma electrons are heated and that changes in flame speed are on the order of only 5% to 10% when gas breakdown does not occur.

At General Motors Research Laboratory researchers reported an increase of 6% in burning velocity of fuel-lean premixed laminar flames with microwave radiation (41). However, they concluded that the enhancement is not due to a radiative (photochemical) effect but rather due to a thermal effect. The increase in flame speed is explained in terms of

simple microwave heating of the bulk gases in the flame zone, which yields a higher flame temperature.

Interest in our Radiative Augmented Combustion is reflected by the many requests for additional technical information listed below. Special interest was expressed by researchers working on plasma jet ignition and flameholding such as Professor Felix Weinberg at Imperial College, London, Professor Eli Dabora at the University of Connecticut and Dr. G. Burton Northam at NASA Langley, Hampton, Virginia. NASA's interest in our radiative technique resulted in a cooperative experiment in which ENERGIA provides the VUV light sources to be mounted on NASA supersonic combustion facility. The objective was to determine the feasibility of utilizing VUV photodissociation for ignition and flameholding in supersonic flows (scramjets), which are known to be very difficult to ignite. A very limited and preliminary test was already conducted on NASA's Mach 2 combustor. The results and conclusions are given above in section 2.a. Experimental Work. This collaboration is planned to be continued under a new contract from NASA.

Another strong interest in our research was expressed by Dr. Lyle O. Hoppe of the Eaton Corporation. They investigate another approach for achieving enhanced combustion. They preheat the fuel to about 550 C prior to injection. Recent reported results (42) are that reduction in ignition delay time and increase in combustion rate are obtained.

In a related work under a grant from the National Science Foundation, the concept of Radiative Augmented Combustion was successfully demonstrated (7,43). The idea was to promote combustion through photodissociation of reaction-inhibiting species into reactive radicals which participate in chain-branching reactions. This idea was tested in H₂/air system by investigating its capability to extend the second explosion limit. It is well known that this limit is attributed to three body reaction, $H + O_2 + M \rightarrow HO_2 + M$, followed by the removal of HO₂ from the kinetic scheme. This reaction becomes increasingly important at higher pressures where it competes fiercely with the chain-branching reaction, $H + O_2 \rightarrow OH + O$.

This research demonstrated that the photodissociation of the metastable radical HO₂, $HO_2 + h\nu \rightarrow OH + O$, can effectively compete with the terminating reactions. It restores radicals to the pool and mitigates the influence of the three body reaction. The experimental evidence for this was an affirmative extension of the second explosion limit. Increases in the pressure limit as great as 24% percent were obtained.

Other related research activities including infrared multiphoton processes to ignite and enhance combustion, photochemical means to augment supersonic combustion, laser ignition, and modifying combustion kinetics by photochemically produced radicals are currently underway (see 4.b. above).

During the performance of this contract researchers at NASA, Stanford University, TRW, Eaton Corporation, GM, BRL, NRL and JPL expressed interest in our work. A complete list of all interested professionals is given below:

Professor Robert A. Altenkirch, University of Kentucky, Lexington, Kentucky

Dr. Steven L. Baughcum, Los Alamos national laboratory, New Mexico

Mr. Theodore A. Brabbs, NASA Lewis Cleveland, Ohio

Dr. Claudio Bruno, Dipartimento di Energetica, Politecnico di Milano, Italy

Dr. Hartwell F. Calcote, AeroChem Research Lab., Princeton, New Jersey

Mr. Tony Cifone, Naval Air Propulsion, Trenton, New Jersey

Dr. Ronald B. Cohen, The Aerospace Corp., Los Angeles, California

Professor. Eli K. Dabora, University of Connecticut, Storrs, Connecticut

Dr. David Downs, Army Research Development and Engineering Center, Dover, New Jersey

Professor S. Einav, Tel Aviv University, Israel

Dr. Francis E. Fendell, TRW, Redondo Beach, California

Dr. James W. Fleming, Naval Research Lab, Washington, D.C.

Professor Alon Gany, Technion, Haifa, Israel

Dr. Nahum Gat, TRW, Redondo Beach, CA

Dr. I. Gotlieb, Combustion Engineering, Bloomfield, New Jersey

Professor Peter Gray, University of Leeds, England

Dr. Edward G. Groff, GM Research Laboratories, Warren, Michigan

Dr. Alan Hartford, Los Alamos Scientific Lab, New Mexico

Professor Clarke E. Hermance, University of Vermont, Burlington, Vermont

Professor Ronald K. Hanson, Stanford University, Stanford, California

Dr. Lyle O. Hoppie, Eaton Corporation, Southfield, Michigan

Professor H. Krier, University of Illinois at Urbana-Champaign, Illinois

Dr. George A. Lavoie, Ford, Dearborn, Michigan

Dr. Emil A. Lawton, Jet Propulsion Lab, Pasadena, California

Professor W.E. Lear, University of Florida, Gainesville, Florida

Professor K.K. Lehmann, Princeton University, New Jersey

Dr. David Mann, US Army Research Office, Research Triangle Park, North Carolina

Professor Arthur M. Mellor, Drexel University, Philadelphia, Pennsylvania

Professor R.B. Miles, Princeton University, New Jersey

Dr. Andrzej W. Miziolek, US Army Ballistic Research Lab, Aberdeen Proving Ground, Maryland

Dr. G. Burton Northam, NASA, Langley Research Center, Hampton, Virginia

Professor A. K. Oppenheim, University of California, Berkeley, California

Dr. E.S. Oran, Naval Research Lab, Washington, D.C.

Dr. Arie Peretz, RAFAEL, Haifa, Israel

Professor C.L. Proctor, University of Florida, Gainesville, Florida

Professor Herschel Rabitz, Princeton University, Princeton, New Jersey

Dr. Ramohalli, Flow Industries, Inc. Kent, Washington

Dr. Roberto Ruiz, GRI, Chicago, Illinois

Dr. Felix Schuda, ILC Technology, Sunnyvale, California

Professor K. Seshadri, University of California, La Jolla, California

Dr. Tom Sloane, GM Research Laboratories, Warren, Michigan

Dr. Hava Sorek, Ford, Dearborn, Michigan

Professor J.G. Stevens, Montclair State College, New Jersey

Dr. Don Stull, AFWAL, Wright-Patterson AFB, Ohio

Professor Felix Weinberg, Imperial college, London, England

Dr. Charles K. Westbrook, Lawrence Livermore Laboratory, University of California, Livermore, California

Dr. Robert J. Witsonky, Medical Indicators, Inc., Princeton, New Jersey

Dr. L.C. Yang, Jet Propulsion Lab, Pasadena, California

Dr. G. Zizak, Consiglio Naziorale Delle Richerche politecnico, Milano, Italy

Professor Y. Zvirin, Technion, Haifa, Israel

SUMMARY: ASSESSMENT OF RESEARCH RESULTS

This research has demonstrated the capability of the radiative technique to both ignite and enhance combustion processes and to broaden normally encountered stability limits.

The research on radiative ignition and combustion enhancement has provided fundamental information on a unique combustion process. Concepts which represent a new departure and extension of conventional combustion practice can evolve from the experimental and analytical results obtained. Aspects of the radiative ignition and enhancement concept have been demonstrated under both static and flow conditions. Successful pulsed light source ignition experiments at very high flow velocities (up to 250 m/s) reconfirm the radiative augmented concept and demonstrate the technical feasibility of designing an advanced optical-radiative igniter. Potential radiative ignitions with a continuous light source imply the possibility of using the light as an optical radiative flame stabilizer with no pressure loss instead of the conventional intrusive flameholders. Preliminary results of radiative combustion enhancement in terms of higher flame speeds and larger extinction times and distances suggest an opportunity to extend the combustor operating limits. The predicted increase in flame speed is indicative of higher combustion rate which can result in extension of the operating envelope of flash-back and blow-off limits.

The extensive analytical results reported here, in particular, the dramatic increases of up to 62% in flame speed, and decreases of up to 68% in ignition delay time, give us confidence that radiative augmented combustion can become a potentially viable technique for extending current aircraft operating limits associated with combustion phenomena. However, more supportive experimental results are needed before eventual application to gas turbine engine systems can be envisioned both for improved combustor operation and flameholding. Some future areas of potential application are: high altitude combustor reignition following flame-out, drag-free flame stabilization in supersonic combustor, and added flexibility for conventional combustors to use future alternate fuels. To this end, more conclusive combustion enhancement experiments are still needed along with a continued VUV light source development in the direction of improved beam intensity and optics.

REFERENCES

1. Lavid M., "Radiative Augmented Combustion", First Annual Technical Report, M. L. ENERGIA, Inc., AFSOR Contract No. F49620-83-C-0133, August, 1984.
2. Lavid, M., "Radiative Augmented Combustion", Second Annual Technical Report, M. L. ENERGIA, Inc., AFSOR Contract No. F49620-83-C-0133, August, 1985.
3. Lavid, M. and Stevens, J.G., "Photochemical Ignition of Premixed Hydrogen Oxidizer Mixtures with Excimer Laser", Eastern Section of the Combustion Institute, Brown University, Providence, RI, November 8-10, 1983.
4. Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of Radiative Enhancement in premixed Hydrogen-Air Flames", Eastern Section of the Combustion Institute, Clearwater Beach, FL, December 3-5, 1984.
5. Lavid, M., Stevens, J.G., Westbrook, C.K., "Enhancement of Premixed H₂/Air Flames with Photochemically Produced Radicals: Analytical Modeling", Eastern Section of the Combustion Institute, Philadelphia, PA, November 4-6, 1985.
6. Lavid, M., and Blair, D.W., "Experimental and Analytical Results of Radiative Ignition in Premixed Hydrogen-Air Flows", Eastern Section of the Combustion Institute, Philadelphia, PA, November 4-6, 1985.
7. Lavid, M., Blair, D.W., and Stevens, J.G., "Photochemical Effect on the Second Explosion Limit of H₂/O₂ System: Experimental and Analytical Results", Eastern Section of the Combustion Institute, Philadelphia, PA, November 4-6, 1985.
8. Lavid, M., and Poulos, A.T., "Infrared Multiphoton Ignition of Alcohols", Eastern Section of the Combustion Institute, San-Juan, Puerto Rico, December 15-17, 1986.
9. Lavid, M., Stevens, J.G., Tavakoli, J., and Westbrook, C.K., "Combustion Enhancement of Methane/Ethane Mixtures by Photodissociation of Inhibitors", Eastern Section of the Combustion Institute, NBS, Gaithersburg, MD, November 2-6, 1987.
10. Poulos, A.T., and Lavid, M., "Diagnosing Infrared Multiphoton Processes During ignition of Alcohols", Eastern Section of the Combustion Institute, NBS, Gaithersburg, MD, November 2-6, 1987.
11. Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of Enhancement of Premixed H₂/Air Flames with Photochemically Produced Radicals", ASME/JSME Joint Conference, Honolulu, Hawaii, March 22-27, 1987.

12. Lavid, M., and Poulos, A.T., "Recent Advances in Photochemical Techniques for Ignition and Combustion Enhancement", 24th JANNAF Combustion Meeting, Monterey, California, October 5-9, 1987.
13. Lavid, M., and Stevens, J.G., "Photochemical Ignition of Premixed Hydrogen/Oxidizer Mixtures with Excimer Laser", Combustion and Flame, 60, 2 (1985).
14. Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of Enhancement of Premixed H₂/Air Flames with Photochemically produced Radicals", Proceedings of the 1987 ASME/JSME Thermal Engineering Joint Conference, Vol. 1, pp. 241-248.
15. Lavid, M., and Poulos, A.T., "Recent Advances in Photochemical Techniques for Ignition and Combustion Enhancement", Proceedings of the 24th JANNAF Combustion Meeting, Monterey, California, October 5-9, 1987, published by CPIA.
16. Blair, D.W., and Lavid, M., "Photochemical Ignition of Hydrogen/Air Streams", submitted to the Twenty-Second International Symposium on Combustion, Seattle, Washington, August 14-19, 1988.
17. Lavid, M., and Poulos, A.T., "Infrared Multiphoton Ignition of Alcohols", in preparation.
18. Cerkanowicz, A.E., "Photochemical Enhancement of Combustion and Mixing in Supersonic Flows", Interim Scientific Report, Photochem Industries, Inc., AFOSR Contract No. F44620-70-C-0051, March 1972.
19. Cerkanowicz, A.E., "Photochemical Enhancement of Combustion and Mixing in Supersonic Flows", Final Report, AFOSR-TR-74-0153, November, 1973.
20. Cerkanowicz, A.E., and Bartok, W., "Radiation Augmented Combustion", AFOSR TR-78-1508, 1978.
21. Cerkanowicz, A.E., "Radiation Augmented Combustion", AFOSR TR-79-1096, 1979.
22. Cerkanowicz, A.E., and Stevens, J.G., "Case Studies in the Simulation of Novel Combustion Techniques", Proc. of the 1979 Summer Computer Simulation Conference, p. 170, July 1979.
23. Lavid, M., "Radiative Augmented Combustion", Final Technical Report AFOSR-TR-82-0132, July, 1981.
24. Lavid, M., Interim Technical Report, Exxon Research and Engineering Co., AFOSR Contract No. F49620-81-C-0028, May, 1982.
25. Okabe, H., Photochemistry of Small Molecules, Wiley, 1978.
26. Lavid, M., and Tavakoli, J., "Determining Combustion Enhancement in Terms of Increases in the Fundamental Burning Velocity by Measuring Changes in the Apex Angle of Conical Flames", in preparation.

27. Lavid, M., and Stevens, J.G., "Photochemical Effects on Ignition Delay Times", in preparation.
28. Lavid, M., Stevens, J.G., and Westbrook, C.K., "Analytical Modeling of the Effects of Equivalence Ratio, Pressure and Simultaneous Photodissociation of O₂ and H₂O₂ on Combustion Enhancement of Hydrogen Flames", in preparation.
29. Lewis, B., and von Elbe, G., Combustion, Flames and Explosions of Gases, 2nd Edition, Academic Press, 1961, pp. 388-389.
30. Schirmer, A., Green, J., and Ramohalli, K., "Experimental Augmentation of Turbulent Flames Through Free Radicals Delivered In-Situ", Combust. Sci. and Tech., Vol. 53, pp. 411-419, 1987.
31. Lund, C.M., Report No. UCRL-52504, Univ. California, Lawrence Livermore Natl. Lab., 1978.
32. Westbrook, C.K., and Dryer, F.L., Combustion and Flame, 37, 171, 1980.
33. Strauss, W.A., and Edse, R., Seventh Symposium on Combustion, Butterworths, London, 1959, p. 377.
34. Ward, M.A.V., and Wu, T.T., Combust. Flame 32: 57-71 (1978).
35. Jagers, H.C., and von Engel, A., Combust. Flame 16: 275-285 (1971).
36. Ward, M.A.V., J. of Microwave Power 12(3): 187-199 (1977).
37. Ward, M.A.V., J. of Microwave Power 14(3): 241-259 (1979).
38. Ward, M.A.V., J. of Microwave Power 15(3): 193-202 (1980).
39. Clements, R.M., Smith, R.D., and Smy, P.R., Comb. Sci. and Tech. 26: 77-81 (1981).
40. MacLachy, C.S., Clements, R.M., and Smy, P.R., Combust. Flame 45: 161-169 (1982).
41. Groff, E.G. and Krage, M.K., Combustion and Flame 56, 293-306 (1984).
42. Scharnweber, D.H., and Hoppie, L.O., "Hypergolic Combustion in an Internal Combustion Engine", SAE 850089, 1985.
43. Lavid, M., Blair, D.W., and Stevens, J.S., "Modifying Combustion Kinetics by Photodissociation of Inhibitors", Final Report, NSF Grant No. CPE-8460827, 1985.