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PULSED PLASMA JET IGNITERS:
SPECIES MEASUREMENTS IN NITROGEN AND AIR

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ABSTRACT

A molecular beam mass spectrometer was used to obtain quantitative data on the species present in the core regions of nitrogen and air plasma jets. The dilution of the jet as ambient gas is entrained into the turbulent plume was measured by probing an argon jet discharging into a nitrogen atmosphere. The gas from the jet igniter cavity is diluted by more than a factor of ten in the first 4 mm downstream of the orifice, with a further dilution of 40% over the next 8 mm of jet penetration. Comparison of peak mole fractions of reactive species in the jet with the dilution results indicate that the plasma species are not decaying at a rate solely due to dilution. The nitrogen plasma jet was probed for metastable nitrogen (N_2^*) and N atoms as a function of time at various distances along the centerline of the jet. Peak mole fractions of metastable nitrogen and N atoms plotted as a function of probe location demonstrate that N_2^* persists at distances farther downstream than N atoms. Metastable nitrogen concentrations are relatively constant from 4 to 14 mm, indicating that metastable nitrogen is produced in the plume. Nitrogen atoms, oxygen atoms, and nitric oxide were measured in an air plasma. Nitric oxide persists significantly longer than the atoms, and has a peak mole fraction at the point where O and N decrease significantly. The O atom mole fraction of 0.02 is an order of magnitude higher than the N atom concentration, but the radical concentration in the air plasma is lower than that in pure N_2 . No evidence of metastable nitrogen was found in this system. The chemistry with respect to these results is discussed, both in terms of the kinetics of the system and calculated equilibrium concentrations.

INTRODUCTION

The future evolution of internal combustion engines relies on their capability to burn lean mixtures. Since these mixtures are more difficult to ignite, enhancing the ignition process becomes a principal concern (Dale and Oppenheim, 1982). One of the most promising techniques for this purpose are pulsed plasma jet igniters (Oppenheim et al., 1978 ; Topham et al., 1975; Boston et al., 1984; Edwards et al., 1983). Among the attributes of jets are their ability to locate the ignition source at the center of the combustion chamber, away from cold surfaces, to entrain reactant gases, and to distribute radical and other reactive species throughout the combustible mixture.

The aerodynamics of jet penetration and entrainment of ambient charge have been investigated both experimentally and theoretically (Cetegen et al., 1980; Topham et al., 1982; Smy et al., 1982). These studies reveal that it is the highly turbulent nature of the plasma discharge that is the main reason for combustion enhancement, in that it greatly facilitates the distribution of ignition sites and the entrainment of unreacted mixture. Recent evidence (Clements et al., 1984) also suggests that the ability of the plasma jet to ignite mixtures at distances >2 mm downstream of the igniter is due to the existence of small pockets (0.5 mm diameter) of hot reactive gas that emanate at high velocity from the igniter. The presence of such pockets was first detected in continuous discharge plasma jets (Behbahani et al., 1982 & 1983), but the work of Clements et al. (1984) demonstrated that the phenomenon also exists in pulsed plasma jets.

The increased chemical reactivity of plasma jets has long been credited to the presence of radicals in the jet (Clements, 1984; Sloane and Ratcliffe, 1984; Hilliard and Weinberg, 1976; Orrin et al., 1981; Harrison and Weinberg, 1971). Species such as H, N, O, and OH were suspected to be in sufficiently high concentrations to account for a significant decrease in ignition delay and a concomitant increase in burning rate. However, little quantitative species concentration data has been obtained. Behbahani et al. (1982) introduced NO into various regions of the jet and monitored its disappearance using a NO/NO_x chemiluminescence analyzer. It was assumed that NO would react with N atoms to form N₂ and O atoms. Based on this assumption it was determined that N atoms were present at distances as far as 22 mm downstream of a continuous plasma jet igniter. Metastable N₂ was not expected to be formed in any appreciable amount. Clements et al. (1984) also used a chemiluminescence analyzer to measure the NO formed when an N₂ filled plasma cavity was injected into an O₂ atmosphere and vice versa. A matrix of tubes positioned at various distances downstream of the igniter was used as a surface to promote recombination of radicals and quench chemical reactions. They found that NO production remained dependent on the position of the matrix up to 3 cm from the igniter. Calculations based on the NO concentrations measured indicate that the number of atoms produced greatly exceeds the number that would be formed by uniform heating of the gas in the cavity- a result that also supports the hot pocket postulate.

Recent studies have employed molecular beam mass spectrometry (MBMS) to measure stable and radical species in transient systems (Peterson et al., 1984; Lucas et al., 1984; Lucas et al., 1985; Sloane

and Ratcliffe, 1984). Quantitative species data for plasma jet igniters were provided by Lucas et al. (1986) who employed MBMS to measure temperature and N atom profiles in an N_2 plasma issuing from a jet igniter. High temperatures (50,000 K at 2 mm) were measured in a narrow region at the front of the jet. Nitrogen atom concentrations peaked at 2 mm (the shortest measurement distance) from the igniter and were below the detection limit of 100 ppm at locations exceeding 14 mm. The fluctuations in the temperature lends credence to the presence of hot pockets, yet the existence of hot pockets at large distances downstream of the igniter was not confirmed by the N atom data.

In this paper we present quantitative results for species concentrations in air and nitrogen plasma jets, and measure the dilution due to entrainment of ambient species.

EXPERIMENTAL PROCEDURE

The plasma jet igniter and the experimental diagnostic apparatus used in these experiments have been described in detail previously (Lucas et al., 1984, 1986). An arc discharge is formed in the cavity of the igniter which is a quartz lined cylinder, 3 mm long and 3 mm in diameter, inserted in a Macor tube. The cathode, made of high speed tool steel, is at the base of the cavity and the anode, a circular brass plate with a 3 mm orifice, is at the top. The current pulse in the cavity is a slightly overdamped half-wave of an RLC circuit with stored energy of 2.96 J and a duration of approximately 100 microseconds.

The igniter centerline is positioned at various distances in front of the 4 mm high, 120 degree sampling cone of the MBMS. The beam passes through a 60 degree skimmer cone into the second stage where it is modulated by a 50% opened / 50% closed chopper wheel, and is collimated into the third stage where it is ionized, filtered by an Extranuclear Laboratories quadrupole mass spectrometer, and detected by a Channeltron particle multiplier. Sampling timing and data acquisition are controlled by a dedicated DEC Micro PDP-11 computer and CAMAC system described previously (Lucas et al., 1984).

The plume of the plasma jet was probed over a range of separation distances between the igniter orifice and the sampling cone from 2 mm to 19 mm. Normally, twenty-five consecutive igniter firings were recorded and averaged.

In the N_2 case, measurements were made of molecular nitrogen, metastable nitrogen (N_2^*), and nitrogen atoms. The electron energies used to ionize these species were 6.0 eV above the published appearance potentials of Levin and Lias (1982). Since N_2^* ($A^3\Sigma_u^+$) has an energy of 6.3 eV above the ground state of N_2 , the electron energy used for N_2^* was 6.3 eV below the electron energy for N_2 . In the case of the air plasma, measurements included the above nitrogen species along with oxygen species and nitrogen/oxygen compounds. Table I lists the species probed, their respective masses, and the electron energy used for measurement.

The question arises as to whether the decrease in species concentration at larger separation distances is due solely to chemistry or whether it is due to dilution as a result of jet spread and entrainment of gas from the surroundings. An experiment using an igniter with an externally fed plasma cavity was devised to provide an

answer. Argon containing a small (1%) amount of krypton is fed continuously to the plasma cavity through the clearance between the cathode and the insulating wall as previously done by Ridley et al.(1985). As the cavity fills and Ar begins to leak from the orifice into the main reaction chamber (filled with N_2 doped with same concentration of krypton), a 1/8" copper tube oriented perpendicular to the plasma jet axis draws the excess cavity gas away from the region of plasma jet penetration. Less than 0.1 sec before firing the jet, a solenoid valve closes the vacuum line. When the jet fires, the high velocity of the plume (on the order of hundreds of meters per sec) overwhelms any residual effect of the vacuuming process (which has a maximum gas velocity of 3 m/sec at the tube orifice). Thus the concentration of Ar can be measured in the MBMS to determine the degree that jet expansion and/or entrainment is responsible for species concentration changes.

DATA REDUCTION

Molecular beam mass spectrometers have been used with great success to determine species concentrations in steady state phenomena. Reasonably straightforward calibration techniques allow firm concentration values to be assigned to raw mass signals (Bittner, 1981). However, difficulties arise in assigning concentrations to mass signals from transient events. These problems manifest themselves in the form of molecular beam overrun and underrun (Peterson et al., 1984), in addition to the usual problems of random and systematic noise, and signal baseline shifts. To calibrate the signal for the measurement of species concentration it is therefore necessary to carefully account for these effects. Of particular

importance is the availability of a species whose concentration is constant during the course of the reaction and knowledge of relative electron impact ionization cross-sections. This data reduction procedure was outlined briefly by Lucas et al. (1986); it is presented here in full detail.

The strong thermal gradients of the plasma jet create conditions in the molecular beam where hot gas molecules that were sampled at later times actually travel past colder and thus slower moving molecules that were sampled earlier. This overrun phenomenon, graphically depicted by Lucas et al. (1986), results in a larger signal than expected. Consider, for example, a case when a species in the plasma jet is also present in the ambient mixture at essentially the same concentration (i. e. N_2). As the beam chopper opens, the signal rises from its background level to that corresponding to the concentration of the ambient species. It then exceeds that level due to beam overrun as the plasma is sampled. Because the concentration of the sampled species has not increased this signal thus represents a concentration equal to the constant ambient value. This distorted signal serves as a reference against which all species are measured. Species that are not present in the ambient mixture are still affected by the large thermal gradients and, hence, generate signals that are also distorted by beam variations. If their signals are normalized by the reference, direct account of the distortion is taken. Beam underrun, which occurs as the plasma cools and travels at slower velocities resulting in signals that drop below ambient levels, is also corrected by this technique.

Background molecules, electronics, and the particle multiplier contribute to the random noise. By averaging over 25 firings, the random noise was reduced and the salient features exposed. However, information about the shot-to-shot variability that only single firing data can provide is lost. Systematic electrical noise from the discharge of the plasma jet power supply cannot be eliminated by the averaging technique. This noise can be reduced by subtraction from the original data. The systematic noise data is obtained from an average of 25 shots at a mass for which no known species exists in our system.

Certain species experience mass signal interference from other species having the same mass. As an example, the N_2^* signal appears as a superposition on the reference N_2 signal. A small signal due to N_2 is observed even at the lower electron ionization energy used to monitor N_2^* (Table I). The N_2 contribution to this signal is obtained by recording the mass 28 signal at a higher electron ionization energy where the N_2 dominates (>99%) the observed signal. The height of this signal after the chopper opens but before the plasma jet fires is scaled to the height of the original data at the same time in the event. The N_2 signal is then subtracted from the original data. This technique can be applied to any mass where interference is caused by a species present in the ambient mixture.

After these adjustments the signal can be converted to mole fractions by using the fact that the mass signal is proportional to the species concentration and its ionization cross-section. Since cross-section data is readily available in the literature (e.g. Kieffer and Dunn, 1966), and it is possible to choose a reference species whose concentration does not vary during the event, an expression can be derived for determining the mole fraction of most

species.

An example of the above technique is shown in Fig. 1. The top trace is of the mass 28 signal recorded at an electron energy of 21.5 eV, conditions where normal N_2 dominates the signal. The second trace, recorded at higher gain, is the mass 28 signal recorded at 15.2 eV, and shows the presence of some normal nitrogen as well as the signal from metastable nitrogen. The third trace is the metastable nitrogen data corrected for the interfering nitrogen signal and discharge noise. This data is then normalized to the top trace, scaled using relative ionization cross-sections, and presented as quantitative concentration data in the last trace.

RESULTS

The two plasma feed gases used in this study are nitrogen and air. The N_2 jet was probed for N_2 , N_2^* , and N, and the air jet was probed for N_2 , N_2^* , N, O_2 , O, NO, N_2O , NO_2 , and N_2O_2 .

N_2 Plasma

The peak mole fractions for N and N_2^* as a function of cone location are shown in Fig. 2. The plot was obtained from the measurement of mole fraction as a function of time for species at a given probe location, such as the N atom data previously published in the work of Lucas et al. (1986). The N_2 mole fraction does not vary significantly and is therefore not included. As shown in Fig. 2, the peak N atom mole fraction of 0.05 occurs at the closest sampling distance of 2 mm. It drops to less than 0.01 at 6 mm and continues to decrease slowly thereafter until it falls below the detectability

limit of 100 ppm at 14 mm. For all of the species reported here the time of peak concentration increases as the sampling distance increases. The behavior of N_2^* appears significantly different from that of N atoms. The peak N_2^* mole fraction is slightly less than 0.01 and, as with N atoms, occurs at 2 mm. The concentration drops to less than 0.005 at 4 mm, remains reasonably constant until 14 mm, and becomes unmeasurable at 19 mm. As expected, metastable nitrogen exists further from the igniter than N atoms.

Air Plasma

In the air plasma system five species were detected: N_2 , O_2 , N, O, and NO. The mole fractions of O atoms as a function of time and probe location are shown in Fig. 3. The peak mole fractions reached by O, N, and NO at a given probe location are shown in Fig. 4. Oxygen and nitrogen atoms both reached a maximum at 2 mm, O atoms peaking at a mole fraction of 0.02, and N atoms at 0.0025. While N atoms decreased steadily to an undetectable level at 6 mm, O atoms were measured at much larger distances. Its level dropped rapidly to 0.0020 at 6 mm and steadily decreased until it disappeared at 12 mm. The NO mole fraction peaked at a value of 0.0045 at 6 mm, coincident with the fall in N and O concentrations. The NO drops in concentration slower than the O atoms, and becomes unmeasurable at a probe location of 16 mm. Both N_2 and O_2 mole fractions (not shown) remain essentially constant. No other nitrogen/oxygen species, including N_2^* , were observed in measurable amounts.

Dilution Experiments

Results from the dilution experiments described previously are shown in Figs. 5 and 6, with argon in the igniter cavity discharged into a nitrogen filled chamber. The argon concentration was determined at probe locations varying from 4 to 12 mm, the vacuum line preventing measurements at shorter distances.

Argon mole fraction data for three of the probe locations examined is shown in Fig. 5. The concentration of argon peaks at 0.07 at the closest sampling distance of 4 mm, and is followed by a gradual decrease, with easily measured levels remaining as long as 2 milliseconds after the jet firing. As the probe location increases, the peak level decreases and, as expected, appears at later times. Mole fractions exceeding 0.02 are measured even at distances in excess of 12 mm.

The maximum argon mole fraction measured at a given probe location is presented in Fig. 6. The error bars indicate the deviation obtained by evaluating a series of seven different 50 shot averages at the 4 mm location. The line is a least squares fit to the data points.

DISCUSSION

The argon concentrations measured indicate that significant dilution of the gas in the plasma cavity has occurred when the jet has reached the 4 mm probe location, with the peak concentration of 0.07 at that distance implying a dilution by at least a factor of fourteen. This result surprised us in that we expected to observe much higher argon mole fractions close to the igniter surface, followed by a

decrease in argon as ambient gas became entrained in the plume. We thus examined plume growth data to determine if it supports our results.

High speed laser schlieren photographs of the expanding jet were used to estimate the volume of the plume as it grew from its initial gas volume of 25 mm^3 in the igniter cavity. The volume was calculated from the two-dimensional image by assuming spherical symmetry, and raising the measured area of the plume to the $3/2$ power (Cavolowsky et al., 1986). When the jet has penetrated 4 mm into the ambient gas, the plume has a volume of approximately 1000 mm^3 . The plasma jet temperature data of Lucas et al. (1986) indicate that the temperature at the front of the jet at this distance is approximately 3000 K and decays rapidly in the core of the jet to ambient conditions. If a bulk jet temperature of 1500 K is assumed, the plume will attain a volume of approximately 125 mm^3 simply by thermal expansion. This implies that turbulent entrainment is responsible for the remaining plume growth. Given these assumptions the argon mole fraction at 4 mm would be 0.12. Our experimental result, 0.07, thus appears quite reasonable given the uncertainties associated with plume volume measurement and temperature determination.

It should be emphasized that this dilution occurs close to the igniter, and at times short compared to those needed to ignite combustible mixtures. The fact that the plume is more than 90% ambient gas short distances downstream of the igniter may alter ideas on the chemistry of the ignition process. Radical species responsible for ignition are not necessarily produced only in the igniter cavity and spread throughout the gas mixture by the turbulent nature of the plume; sufficient reaction time and pathways exist to view the plume

as a separate chemical system forming reactive species and spreading them throughout the mixture in the combustion chamber.

Comparison of the argon concentration as a function of time with radical species measurements reveals a substantial difference in the rate that the concentrations drop, with the radicals disappearing at a rate faster than can be attributed to dilution alone. This trend is also clearly seen in the plots of peak mole fraction as a function of probe location. The obvious conclusion is that reactions that alter species concentrations occur outside the igniter cavity.

In the N_2 plasma, the rapid decay of N atom concentration indicates a radical recombination reaction of N atoms to N_2^* or N_2 . Metastable nitrogen appears to be formed in two distinct regions of the jet. The large initial mole fraction observed is due to the N_2^* created in the igniter cavity during the arc discharge period or in the hot portions of the jet prior to the 2 mm probe location. These molecules are diluted and quenched, which causes a drop in their concentration until the N atom recombination reaction producing N_2^* significantly contributes to the total metastable nitrogen concentration. The resulting peak mole fraction profile has a maximum at 2 mm, and drops until 6 mm, where it remains constant with perhaps a slight increase near 12 mm. The signal then drops again and is not measurable at 19 mm. The N atom profile, in contrast, exhibits a monotonic decline from its peak value at 2 mm.

In the air plasma the fraction of oxygen atoms is considerably higher than nitrogen atoms at the 2 mm probe location (Fig. 4). This is due in part to the relative ease of breaking the oxygen bond, which has a bond strength of 494 kJ/mole as compared with 942 kJ/mole for

nitrogen. Since the rapid decrease in both O and N atoms has been shown not to be due solely to dilution, it is assumed that reactions involving O, N, and N_2^* occur which form O_2 , N_2 , and NO. Metastable nitrogen was not detected in any significant concentration, implying that it either reacts quickly in the plasma or that it is formed only in small quantities due to the low concentration of N atoms present which are required for its production.

Nitric oxide exhibits similar behavior to that of metastable nitrogen in the N_2 plasma. Its presence at 2 mm suggests that NO is formed in the igniter cavity or in the hot portions of the jet prior to the 2 mm probe location. The later rise at 6 mm presumably is due to downstream radical reactions. The decay at distances greater than 6 mm is a combination of the effects of dilution and NO production and destruction. Possible reactions involving NO are as follows:

Reactions (1) and (2) are the Zeldovich mechanism reactions which produce thermal NO, and have rate constants $k_1 = 7.6 \times 10^{13} \exp(-38,000/T)$ and $k_2 = 6.4 \times 10^9 \exp(-3150/T)$, while (3) is the reverse of (2) and has a rate constant $k_3 = 1.5 \times 10^9 \exp(-19,500/T)$. Reaction (4) is fast and virtually independent of temperature, with a rate constant $k_4 = 1.6 \times 10^{13}$ (all rate constants have units $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$) (Baulch et al., 1973). Due to the high activation

energies associated with reactions (1) and (3), we do not expect them to be important at the lower temperature in the jet at distances greater than 4 mm. Nitrogen atoms are involved in competing reactions (2) and (4), one producing and the other consuming NO. However, at high temperatures the rate of (4) should exceed (2) by several orders of magnitude, even allowing for the higher concentration of O₂. There is a possibility that metastable nitrogen reactions are involved. After forming from the recombination of N atoms, N₂^{*} can react with O and O₂, producing NO, N₂O, and O as reactive products (Thomas and Kaufman, 1985). These reactions are fast at room temperature, but neither the rates nor the product yields have been determined at above ambient temperatures. We can thus only speculate on their importance.

Equilibrium mole fractions were calculated for the air plasma at one atmosphere pressure using the STANJAN code developed by W. C. Reynolds of Stanford University. Results, plotted for the range of temperatures expected in the jet at the probe locations examined, are shown in Fig. 7. Mole fractions of all reactive species at distances as short as 4 mm from the igniter orifice (where the maximum temperature is on the order of 3000 K) are greater than predicted by equilibrium calculations, further evidence that the plume is far from equilibrium. The measurable concentrations of metastable nitrogen at large distances downstream of the igniter in the N₂ plasma also implies a non-equilibrium condition, since metastable nitrogen should not exist at the low temperatures present there. The temporal resolution of our apparatus is not sufficient to observe the existence of individual hot pockets, but our previous temperature measurements and these quantitative species determinations do provide direct evidence of the non-equilibrium nature of the jet.

The observation that a higher concentration of radicals are produced in a nitrogen plasma than an air plasma is not fully understood at this time. A small difference in the electrical characteristics of the plasmas, allowing for more efficient coupling of electrical energy with gas phase species, is possible. Equilibrium calculations indicate that to double the oxygen atom mole fraction from 0.02 to 0.04 requires less than a 10% increase in temperature, from 2750 to 3000 K. Another explanation is that the presence of oxygen greatly alters the chemistry, and radicals produced react faster to produce stable species such as oxygen, nitrogen, and nitric oxide.

It is also important to note that given the high dilution rates seen in the initial stages of jet development species concentrations at least an order of magnitude higher than measured at the 4 mm probe location may be produced in the plasma cavity. Thus the concentration of reactive species distributed through the ambient mixture by the turbulent action of the jet may be much larger than what is measured by MBMS along the center line of the jet, as suggested by Weinberg (1986). We will therefore begin to probe regions off axis of the jet to determine the distribution of species outside the plasma core.

CONCLUSIONS

We have measured the concentrations of species in pulsed plasma jets of nitrogen and air, and the dilution of the jet as ambient gas is entrained into the turbulent plume by probing an argon jet discharging into a nitrogen atmosphere. The gas from the jet igniter cavity is diluted by more than a factor of ten in the first 4 mm

downstream of the orifice, with a further dilution of 40% over the next 8 mm of jet penetration. Comparison of peak mole fractions of reactive species in the jet with the dilution results indicate that the plasma species are not decaying at a rate solely due to dilution. The nitrogen plasma jet was probed for metastable nitrogen (N_2^*) and N atoms at various distances along the centerline of the jet. Peak mole fractions of metastable nitrogen and N atoms plotted as a function of probe location demonstrate that N_2^* persists at distances farther downstream than N atoms. Metastable nitrogen concentrations are relatively constant from 4 to 14 mm, indicating that metastable nitrogen is produced in the plume. Nitrogen atoms, oxygen atoms, and nitric oxide were measured in an air plasma, but no evidence of metastable nitrogen was found in this system. Nitric oxide persists significantly longer than the atoms, and has a peak mole fraction at the point where O and N decrease significantly. The O atom mole fraction of 0.02 is an order of magnitude higher than the N atom concentration, but the radical concentration in the air plasma is lower than that in pure N_2 .

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TABLE I

Electron energies used for nitrogen and oxygen species

<u>Species</u>	<u>Mass</u>	<u>Electron Energy (eV)</u>
N	14	20.5
O	16	20.0
N ₂	28	21.5
N ₂ [*]	28	15.2
NO	30	15.3
O ₂	32	18.1
N ₂ O	44	18.9
NO ₂	46	16.4
N ₂ O ₂	60	75.0

Figure Captions

- Fig. 1. Illustration of the data reduction procedure. a. reference N_2 data. b. original N_2^* data. c. N_2^* data adjusted for N_2 interference d. N_2^* data normalized by the reference data and multiplied by the relative ionization cross-section.
- Fig. 2. Peak mole fractions of N and N_2^* as a function of probe location in a nitrogen plasma.
- Fig. 3. Oxygen atom mole fraction as a function of time in an air plasma at various probe locations.
- Fig. 4. Peak mole fractions of N, O, and NO as a function of probe location in an air plasma.
- Fig. 5. Argon mole fractions as a function of time in the dilution experiments.
- Fig. 6. Peak mole fraction of argon as a function of probe location in the dilution experiments.
- Fig. 7. Equilibrium mole fraction as a function of temperature for N, O, and NO in air at one atmosphere pressure.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

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