PULSED PLASMA JET IGNITERS: SPECIES MEASUREMENTS IN METHANE COMBUSTION

Cavolowsky, J.A.

1987-08-01

LBL-23515

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

To be presented at the Western States
Section, Combustion Institute Fall Meeting,
Honolulu, HI, November 22–25, 1987

Pulsed Plasma Jet Igniters: Species Measurements in Methane Combustion

J.A. Cavolowsky, P.R. Breber,
A.K. Oppenheim, and D. Lucas

August 1987

**APPLIED SCIENCE
DIVISION**

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

LBL - 23515

PULSED PLASMA JET IGNITERS: SPECIES MEASUREMENTS IN METHANE COMBUSTION

John A. Cavolowsky, Pierre R. Breber, Antoni K. Oppenheim, and Donald Lucas

Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

ABSTRACT

We have determined the mole fractions of the chemical species present in the plume of a pulsed plasma jet igniter during the ignition and subsequent combustion of methane/oxygen/nitrogen and methane/oxygen/argon mixtures. Equivalence ratios of 1.0, 0.6, and 0.4 were used in the jet cavity and in the main combustion chamber to obtain results for both combusting and non-combusting cases.

INTRODUCTION

The ability of pulsed plasma jets to enhance ignition and combustion of mixtures difficult to burn has long been attributed to the presence of radical species in the jet plume. Species such as H, N, O, and OH were suspected to be in sufficiently high concentrations to account for the observed decrease in ignition delay and a concomitant increase in burning rate. However, little quantitative species concentration data has been obtained.

Recent studies have employed molecular beam mass spectrometry (MBMS) to measure stable and radical species in pulsed jets.[1-3] In this paper we continue our study of pulsed plasma jets using MBMS with quantitative data on the concentrations of numerous species during the ignition and combustion of methane/oxygen mixtures diluted with nitrogen and argon.

EXPERIMENT

The pulsed plasma jet igniter and the molecular beam mass spectrometer system have been described previously[3,4]. This same system was used previously to determine the nature of nitrogen and air plasmas, the extent of dilution of the plume by ambient gases, and gas temperatures. The data reduction methods developed in those studies are used presently to obtain quantitative concentrations. Species measured in this study are N_2, N, NO, N_2O, H, H_2, O_2, Ar, CH_4, CO, C_2H_6, CO_2, OH, and H_2O.

The igniter was located in the bottom of a cylindrical constant volume cell with a diameter of 6.3 cm and a height of 3.6 cm, equipped with a piezotron pressure transducer. All measurements were made on the jet centerline at an igniter/sampling cone separation distance of 4 mm and at an initial gas pressure of 400 torr. Equivalence ratios studied were 0.4, 0.6, and 1.0 using argon as the diluent, and 0.6 and 1.0 using nitrogen, with the same gas mixture in the jet cavity and main combustion chamber.

RESULTS

Reactants, products, and intermediate species were measured over a range of equivalence ratios. Argon was used as the diluent gas in place of nitrogen in many experiments to allow measurement of CO, CO_2, and N_2O. The nitrogen diluted mixture would consistently ignite and burn until the equivalence ratio was reduced to 0.6, while it was necessary to lower to 0.4 in the argon diluted case to achieve the same result. Typical pressure traces from several of the mixtures used are presented in Fig. 1. Mole fractions for many of the species measured using nitrogen as the diluent at $\theta = 1.0$ are presented in Fig. 2. These results are the first quantitative species measurements from the plasma jet and ensuing combustion. To separate the species present in the jet plume from those produced by combustion of the bulk of the mixture in the cell, measurements were made at longer times, up to 50 msec. Results for the nitrogen diluted mixture at $\theta = 1.0$ are shown in Fig. 3.

DISCUSSION

Results presented in Fig. 1 indicate that the significant pressure rise occurs after 5 msec for all mixtures that burn. Thus we believe that the concentrations presented in Fig. 2, at times < 2.5 msec, are representative of the species resulting from the plasma cavity gas and the reactions in the plume which subsequently lead to ignition of the bulk mixture. This hypothesis is supported by many of the mass features observed and described below.

While it not possible to separate O from CH_4 in our quadrupole mass spectrometer, we assume that the methane is at a significantly higher concentration than oxygen atoms, and the mass 16 signal is essentially that from CH_4. We previously discovered that the gas from the jet cavity was diluted an order of magnitude by entrainment of ambient gas at distances as short as 4 mm from the igniter orifice[2]. If reactions did not occur outside of the plasma cavity the CH_4 signal would remain constant (to within 10%) because of the entrainment. The results, Fig. 2, show significant changes in the 1.0 to 1.5 msec region, indicating that the CH_4 is rapidly reacting in the jet prior to combustion in the bulk mixture. The CH_4 originates both from the gas in the plasma cavity and the bulk combustion chamber. This is a critical finding since it indicates that the species found early in the plasma jet are not necessarily formed directly in the plasma cavity, and that the mechanism by which ignition occurs using pulsed plasma jets is significantly different from conventional spark ignition.

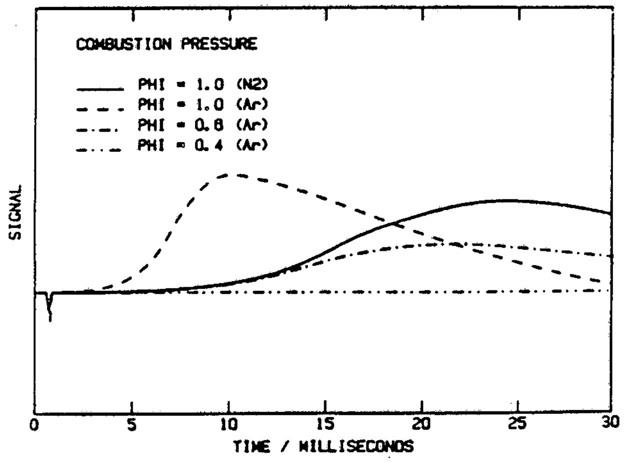

Fig. 1. Pressure transducer signals for mixtures ignited by the plasma jet

The fundamental hydrocarbon oxidation mechanism assumes that H atoms and OH molecules are necessary for the success of plasma jet igniters as enhanced ignition devices. Both of these species are found in significant quantities for all equivalence ratios in the early stages of jet formation. Hydrogen atoms are found to reach a maximum mole fraction of 0.01, with the concentration decreasing as the equivalence ratio is lowered. Hydrogen molecules are measured at comparable levels, but they appear slightly later in time and persist several hundred microseconds longer. Hydroxyl radical also reach a maximum mole fraction of almost 0.01; however, while H and H_2 are short lived, OH reaches a peak concentration at the same time as those species and is detected throughout the plume and main chamber reaction. While the levels of H and OH are indeed sufficient to enhance ignition and combustion, it is not clear that these concentrations are significantly greater than those encountered during conventional combustion.

It should be noted that the methyl radical could not be detected at the concentrations expected in these systems. Cracking of methane in the ionizer tended to mask the CH_3 signal, and increase the minimum detectable level. However,

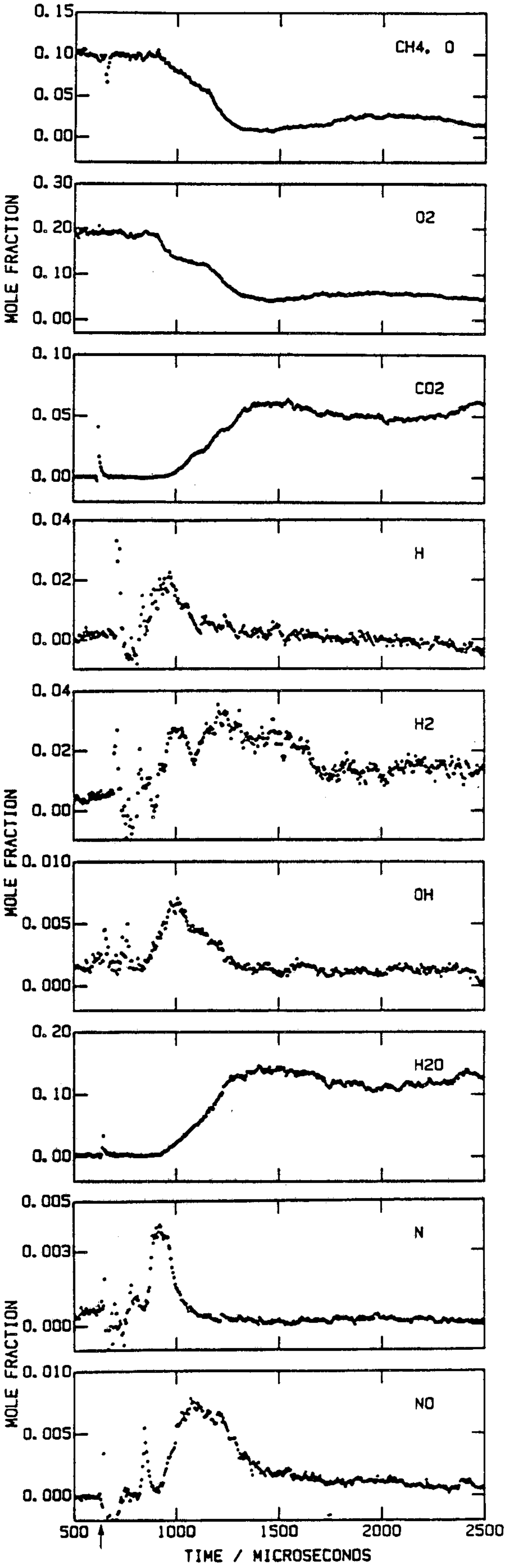

Fig. 2. Mole fractions measured for the combustion of $CH_4/O_2/N_2$ at $\theta = 1.0$ (short time scale). Arrow denotes time of igniter firing.

methyl radicals are expected to be consumed rapidly by reaction with O_2, and by recombination to form ethane. Ethane is measured at levels near 300 ppm, confirming the existence of CH_3. Overlap of the NO signal prevented measurement of ethane in the nitrogen containing systems.

Nitrogen atom and NO levels appear to be similar to those observed in pure air plasmas[2]. However, no measurable quantities of metastable nitrogen were detected in any of the mixtures studied. Stable products of combustion, H_2O and CO_2, reach a maximum several hundred microseconds after the peaks of the combustion intermediates. This timing difference implies that a smaller fraction of the stable products are formed in the plasma cavity than either the intermediates or the incomplete products of combustion such as CO. When combustion does occur in the bulk gas the concentrations of H_2O and CO_2 observed early in the plume remains nearly constant until they increase at the time the bulk mixture ignites and burns, as shown in Fig. 4. When the bulk gas does not burn this later rise is not observed. As expected, the amount of CO_2 and H_2O are greatest for the stoichiometric case, and decrease with decreasing equivalence ratio.

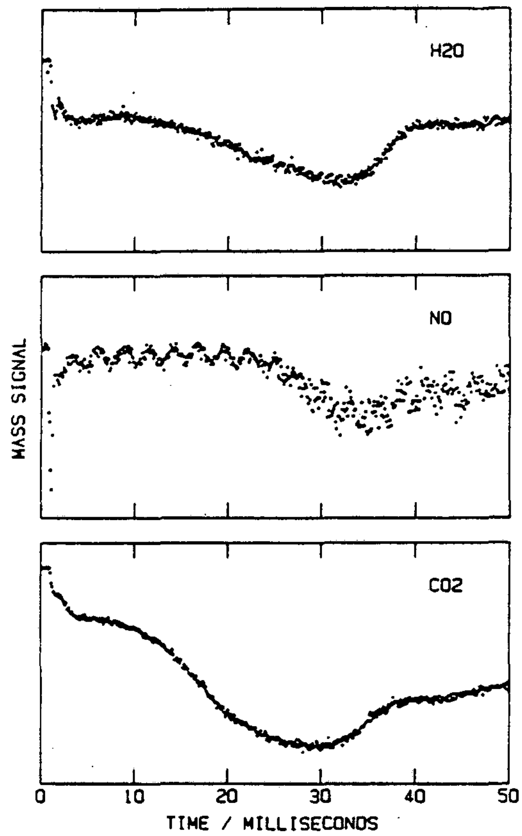

Fig. 3. Mass signals measured for the combustion of $CH_4/O_2/N_2$ at $\theta = 1.0$ (long time scale)

Nitrous oxide is difficult to measure directly due to mass interference from CO_2 and ionization energies that differ by only 1 eV. Concentrations can be estimated from the argon diluent experiments, where no N_2O can be formed. Comparison with the nitrogen diluted cases results in an N_2O concentration in the vicinity of 0.01. These levels are observed only at equivalence ratios for which bulk combustion does not occur, suggesting that the reactions which destroy N_2O are quenched for these conditions. Since no N_2O was detected in the pure air plasma, it is possible that the nitrogen chemistry is significantly affected by the presence of the hydrocarbons.

CONCLUSIONS

We have presented the first quantitative species measurements from the plume of a pulsed plasma jet. It is evident that the species measured in the plume 4 mm from the jet orifice are not produced solely in the plasma cavity discharge, but result from significant entrainment and reaction in the plume. Ignition and combustion in the bulk gas occurs at a much later time. Peak radical concentrations are in the percent range, but there is no evidence that a single species is responsible for the enhanced ignition properties of the plasma jet.

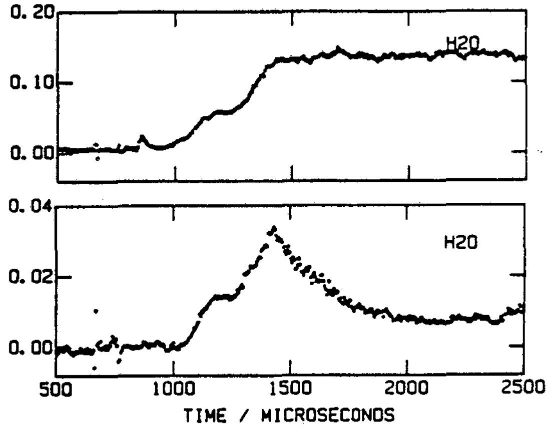

Fig. 4. Water mole fraction for combusting and non-combusting mixtures (argon diluent).

ACKNOWLEDGMENTS

We thank Ken Hom for his efforts. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering, and Geosciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098, and the National Science Foundation under Grant CBT-8502114.

REFERENCES

1. D. Lucas, J. A. Cavolowsky, C. F. Edwards, and A. K. Oppenheim. Combust. Sci. and Tech. 50, 27 (1986).

2. J. A. Cavolowsky, P. R. Breber, A. K. Oppenheim, and D. Lucas. To be published in Combust. Sci. and Tech. (1987).

3. J. A. Cavolowsky Ph.D. Thesis, University of California, Berkeley (1987).

4. Sloane, T. M., and Ratcliffe, J. W. (1984). In The Chemistry of Combustion Processes, ACS Symp. Series, T. M. Sloane, ed., 205.