LEAN FLAMMABILITY LIMIT AS A FUNDAMENTAL REFRIGERANT PROPERTY

Interim Technical Report - Phase I
1 October 1994 - 31 March 1995

Carole Womeldorf, Michelle King, and William Grosshandler

BUILDING AND FIRE RESEARCH LABORATORY
National Institute of Standards and Technology
Gaithersburg, MD

31 March 1995

DISCLAIMER

NOTICE

ABSTRACT

Due to the ozone-depleting effects of commonly used chlorofluorocarbon refrigerants, safe environmentally-friendly replacements must be found. HFC-32 (CH_2F_2) and other hydrochlorofluorocarbons are potential candidates; however, in contrast with the CFCs, many of these compounds are flammable. Testing the flammability limits of these hydrochlorofluorocarbons using traditional ASTM E-681 methods has produced a range of limits depending upon the vessel and ignition source used. This project demonstrates the feasibility of defining a fundamental flammability limit of HFC-32, that occurs at the limit of a zero strain rate and is independent of ignition source. Using a counterflow twin-flame burner to define extinction points for different strain rates, an extrapolation to zero strain rate is performed. Using this technique, preliminary results on the lean flammability limit of HFC-32 and the critical flammability ratio of HFC-125 (C_2HF_5) in HFC-32 are reported.

SCOPE

This project was initiated to evaluate the suitability of an opposed-flow twin-flame burner for determining flammability limits of refrigerants. Because of their importance as potential replacements of chlorofluorocarbons (CFCs), the lean flammability limit of HFC-32 (CH_2F_2) in air and the critical flammability ratio of HFC-125 (C_2HF_5) and HFC-32 in air were chosen as the two test cases.

From October 1, 1994 through March 31, 1995, a NIST opposed-flow burner was configured and operated to evaluate flammability limits of methane, HFC-32, and mixtures of HFC-32 and HFC-125 in air for different flow conditions. Initial tests with methane in air confirmed the suitability of this burner for evaluation of lean flammability limits. Further tests with HFC-32 and HFC-125 established that the lean flammability limits of refrigerants and refrigerant mixtures could be successfully evaluated with this apparatus. In addition this work has reconfirmed that a fundamental lean flammability limit can be evaluated by extrapolating extinguishment stoichiometries for decreasing strain rate conditions to zero and that this technique can be applied to highly fluorinated compounds. This method, described by Law *et al.* (1986), has been used previously for fuels such as CH_4 and C_3H_8. A fundamental flammability limit is the fuel/air mixture which extinguishes an adiabatic flame when the strain rate (i.e., the normal gradient of velocity) is 0 s^{-1}. Since no method currently exists to measure such a fundamental limit directly, measurements with a counterflow burner provide a quantifiable basis for extrapolating to the zero value.

BACKGROUND

Variations in flammability limits of numerous fuels, including HFC-32, are attributed primarily to differences in flow and test conditions, apparatus differences, and ignition sources. Richard and Shankland (1992) examined a range of conditions for numerous flammable refrigerants using primarily the ASTM E-681 flame limit test apparatus. The

range of results was considerable, depending upon the aforementioned parameters. The lean flammability limit varied from 12.6 to 15.0 % HFC-32 by volume in air, while the rich limit ranged between 28.9 and 33.8 %. This large range for both limits indicates significant variability in the definition of a flammability limit.

A fundamental flammability limit that is independent of the experimental apparatus is an ideal that would permit a greater degree of confidence and a quantitative value for engineering applications and risk analyses. Experimental results from this project and ongoing work elsewhere have established a fundamental flammability limit for methane/air flames using an opposed-flow burner. In addition this project has experimentally evaluated extinction points for HFC-32 in air, with and without added HFC-125, to prove that a fundamental flammability limit can be determined for HFC-32 as evidence that this method will work for low flammability refrigerants and mixtures in general. A description of the burner apparatus, the procedure for evaluating fundamental flammability limits and critical flammability ratios, a review of the equilibrium chemistry involved, and the experimental results, follow.

EXPERIMENTAL APPARATUS AND PROCEDURES

The opposed-flow burner was specifically designed to reduce the influence of burner variations, specifically heat-loss, and to quantify the strain conditions of symmetric, nearly flat flames. Two jets of premixed fuel and air directed at each other form an axisymmetric stagnation layer between them (Figure 1). Figure 2 shows the dimensions of the counterflow burner. Heat loss upstream is negligible because of the continuous motion of the gases into the flame region. Heat loss downstream is minimized because of the symmetry of the twin flames, such that most of what is lost downstream by one flame is gained by the other. The curvature of the flame at the center is minimized due to the flames following the stagnation plane of the impinging gases. The gas mixtures are controlled by the input flows and the flame is shielded from ambient air by a nitrogen coflow. Exhaust gases are swept upwards by an outer uptake system. To avoid preheating of reactant gases, room-temperature water is circulated about the upper jet.

The burner flow control system (Figure 3) allows adjustment of any component of the mixture independently. In addition the premixed flows to the top and bottom burners can be controlled independently so that they balance. Gas flows are measured using

individually calibrated rotameter tubes (FM1050 series, Matheson Instruments[1]). Calibration was performed on site with either a dry test meter (DTM-200A-3, American Meter Company), a digital bubble flow meter (Optiflow 730, Humonics, Inc.), or a 0.600 l manual bubble meter (Hewlett Packard), depending on the range of the flows. An input pressure in the rotometer tubes was held constant at 450 kPa (50 psig). Check valves, flash arrestors, and cutoff valves for the fuels and premixed gases were installed to prevent upstream mixing and to minimize the hazards of working with combustible mixtures.

The air used was dry breathing air with 21.0 ± 0.15 % O_2 by volume. The methane used for the preliminary comparison review was technical grade (97.0 % purity). The HFC-125 used was research grade (99.5 % purity). The HFC-32 used was research grade (99.8 % purity). (The chemicals used in these tests lack the lubricants and other impurities which may affect the flammability of an industrial grade refrigerant.) At this time, procurement of HFC-32 is still difficult because it is not a stock item at the several chemical companies that were contacted. HFC-125 was readily available at this laboratory because it is currently being tested as a fire extinguishing agent by the Building and Fire Research Laboratory of NIST.

Test procedures included several safety measures to prevent exposure to hydrofluoric acid gas, a major byproduct of burning HFCs. The burner is encased in a slightly negatively pressurized box to restrict the outflow of combustion byproducts. An extended, flexible butane lighter inserted through a hole in the side wall provided the ignition source. While HFCs were burning, test personnel wore rubber gloves and a full-face respirator mask with a filter cartridge (Ultravue Demand Face Piece and GMHF-C Cartridge, Mine Safety Appliances Company) designed for absorbing gaseous hydrofluoric acid. This cartridge is significantly larger than those widely used for non-specific acid gases.

FUNDAMENTAL FLAMABILITY LIMIT

A flame near its upper or lower flammability limit extinguishes with less added strain than a flame closer to a stoichiometric mixture. To define the fundamental flammability limits of a gas for certain ambient conditions we need to know the fraction of fuel that burns

---

[1]Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment used are necessarily the best available for the intended use.
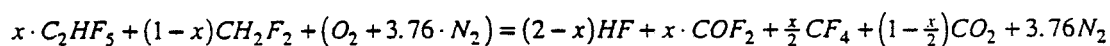
in air with zero strain. Since it is not possible to establish a zero strain rate flame, measurements for low strain rate flames taken at either the upper or lower flammability limits can be extrapolated to zero to define the fundamental limit for either the rich or lean cases, respectively. This method is designed to give an absolute range of flammability, with which important design criteria can be determined for the practical use of a gas or its mixture. The curve shown in Figure 4 (Law *et al.*, 1986) represents the extinction boundary for CH_4 in air for different local strain rates and concentrations of fuel. The points shown are measured extinction points plotted against the locally measured velocity gradient, i.e. the local strain rate. Extrapolations from the lower strain rate values of each end of the curve to a zero strain rate define the fundamental lean and rich flammability limits.

The global strain rate is defined in Figure 5 as the mean incoming jet velocity, V_{in}, divided by half the jet separation, H. This definition neglects any thickness of the stagnation layer, but serves as a convenient reference for effects of different flow velocities. In the experiments discussed below, H remained constant at 15.9 ± 0.1 mm (0.625 in) while the velocity was varied below 200 cm/s (6.6 ft/s). At velocities lower than 15 cm/s (0.5 ft/s), repeatable results could not be obtained because buoyancy effects destabilized the stagnation plane and, as a result, the flame.

EQUILIBRIUM CHEMISTRY

Equilibrium chemistry models the results of reactants, such as HFC-32, HFC-125, and air, in a perfectly adiabatic environment after an infinite amount of time, when the lowest energy state has been reached. In the case of fuels and oxidizers, equilibrium is a useful starting point for examining and explaining the complex chemical kinetics in a premixed flame.

The complete reaction of a stoichiometric mixture of x moles of HFC-125 (C_2HF_5) and ($1-x$) moles of HFC-32 (CH_2F_2) with air can be written as

$$x \cdot C_2HF_5 + (1-x)CH_2F_2 + (O_2 + 3.76 \cdot N_2) = (2-x)HF + x \cdot COF_2 + \tfrac{x}{2}CF_4 + \left(1 - \tfrac{x}{2}\right)CO_2 + 3.76N_2$$

At equilibrium the actual chemical composition includes a large number of additional species. These, and the final temperature, can be calculated from a thermodynamic description of the

system using the NASA equilibrium code (Gordon and McBride, 1994) for any fuel/air equivalence ratio. The equivalence ratio, Φ, is defined as the number of moles of HFC-32 plus HFC-125 in the mixture per mole of air, normalized by the stoichiometric fuel/air molar ratio[2].

Figure 6 shows the calculated equilibrium composition and temperature for a pure HFC-32/air mixture (i.e., $x = 0$) assuming (1) the reactants are initially at room temperature, 25 °C (77 °F), and atmospheric pressure, 101 kPa (14.7 psia), (2) the pressure remains constant, and (3) the combustion process is adiabatic. The peak temperature is about 1930 °C, and it occurs when the mixture is just to the rich side of stoichiometric. HF and CO_2 are the only significant products for lean and stoichiometric combustion. Carbon monoxide increases substantially at the expense of CO_2 when the equivalence ratio becomes greater than one. A small amount of water is present only when Φ is close to unity. Equilibrium predicts solid phase carbon appears when the equivalence ratio is greater than 1.5.

Stoichiometric equilibrium mixtures of pure HFC-125 ($x = 1$) and air produce two additional species in abundance: carbonyl fluoride (COF_2) and tetrafluoromethane (CF_4). The mole fractions and adiabatic equilibrium temperature are plotted in Figure 7. The maximum temperature (1550 °C, 2822 °F) in the HFC-125 reaction is almost 400 °C (750 °F) below that calculated for the HFC-32 reaction. No water vapor is formed from C_2HF_5, and the solid phase carbon begins to appear for much less rich mixtures as compared to CH_2F_2 combustion.

Figure 8 compares the equilibrium adiabatic temperatures calculated for the above compounds to the temperature attained from adiabatic propane (C_3H_8) combustion. The abscissa is the volume fraction of refrigerant in the fuel plus air mixture. The propane temperature exceeds 2000 °C (3600 °F) at a volume fraction of only 4.1 %, which is less than one fourth the molar concentration of CH_2F_2 required to reach its peak temperature.

The impact on the equilibrium state caused by adding small amounts of HFC-125 to HFC-32 is demonstrated by comparing Figure 9a to 9b. When no HFC-125 is present ($x = 0$, Figure 9a) in the CH_2F_2/air mixture, the equilibrium H_2O mole fraction exceeds 10^{-5} out to an equivalence ratio of 1.3, and the hydrogen atom mole fraction reaches a maximum of about 20 ppm. In Figure 9b, 10 % of the HFC-32 has been replaced with HFC-125. This causes the temperature to drop about 160 °C (290 °F), the water to all but disappear, and the peak

---

[2]To convert from equivalence ratio, Φ, to volume percent fuel in air, use one of the following formulas, depending on the fuel: $\%(\text{HFC-32} + \text{HFC-125}) = 100\left(\dfrac{\Phi}{\Phi + 4.76}\right)$ or $\%\text{CH}_4 = 100\left(\dfrac{\Phi}{\Phi + 9.52}\right)$.

mole fraction of H-atoms to drop almost three orders-of-magnitude. The peak in the hydrogen also shifts to richer mixtures and the curve becomes much flatter.

The peak values of temperature, H, and H_2O as a function of a range of volume fraction HFC-125 are shown in Figure 10. While the point of flame extinction, which defines the lower flammability limit, is controlled by non-equilibrium chemical kinetics, equilibrium calculations such as the ones presented here indicate that relatively small amounts of C_2HF_5 act to reduce the temperature and concentration of chemical species that are critical to flame propagation. Additional calculations with a full chemical kinetic mechanism are required to explain how HFC-125 actually inhibits flame propagation, and to predict the amount of the compound necessary to reach the critical flammability ratio.

SIGNIFICANT RESULTS

METHANE FLAMMABILITY MEASUREMENTS

Figure 11 is a plot of the global strain rate at extinction for a premixed lean CH_4/air flame measured in the NIST burner. As discussed above, the global strain rate is the mean incoming flow velocity divided by half the separation of the burners. Work by Law *et al.* (1986) demonstrated that this approximation of the velocity gradient can result in a significant underestimation of the local strain rate for strongly buoyant flames. The difference between global and local strain rates and the purity of the CH_4 tested account for the differences in the NIST results and Law's results, shown in Figures 11 and 12. Note, however that the extrapolation to zero strain results in lower flammability limits which differ by less than 7 %.

HFC-32 FLAMMABILITY MEASUREMENTS

The flammability limits of HFC-32 and air for a range of stoichiometries and strain rates were evaluated. Figure 13 shows the extinction points that were measured in lean and rich HFC-32 flames with no HFC-125. The pale dotted curve is a simple second order fit of the data to demonstrate that the maximum global strain rate obtainable for the HFC-32/air premixed flame is approximately 100 s^{-1}. By using a linear fit for global strain rates less than 40 s^{-1}, an extrapolation to zero strain rate defines the limiting lean equivalence ratio to be 0.65; if the cutoff selected is 80 s^{-1} then the limit is 0.72 (Figure 14). It is for this reason, 0.65 ± 0.03 (12.0 ± 0.6 % by volume), from the lower range of values, represents our current best estimate of the lean flammability limit of HFC-32 in air. The combined standard uncertainty s.own was calculated using Taylor and Kuyatt (1994). It is based primarily on random errors associated with the calibration and measurement of the flows of fuels and air.

The rich flammability limit is not as well determined because of the scarcity of data taken above $\Phi = 1.2$. However, a rough linear fit from the few rich points finds the upper

flammability limit to be around an equivalence ratio of 2.0, or 30 % HFC-32 by volume in air. This falls within the range of published values for upper flammability limits of HFC-32 in air. No uncertainty is quoted here because of the scarcity of data evaluated for this point.

For discussion purposes a table of flammability limits of HFC-32 is presented in Figure 15. The large variability is due primarily to differences in vessel size and type, as well as ignition sources. Smaller but still significant differences are observed between tests performed with similar techniques.

HFC-125/HFC-32 FLAMMABILITY MEASUREMENTS

Plotted in Figure 16 are extinction points for HFC-32 flames with different concentrations of HFC-125 added to replace the fuel in the fuel/air mixture. The equivalence ratio of the HFC-32 and HFC-125 mixture is defined as:

$$\Phi = 4.76 \left(\frac{\dot{X}_{HFC-32} + \dot{X}_{HFC-125}}{\dot{X}_{Air}} \right)$$

where $\dot{X}_i$ is the number of moles per unit time of species i, as it enters the burner. At an equivalence ratio near 1.10, contours of constant HFC-125 fraction reach a maximum. By plotting the maximum strain rate versus percent HFC-125 (Figure 17), one can predict the critical flammability ratio (CFR) by extrapolating to a strain rate of 0 s^{-1}. These peak values for the different fractions of HFC-125 predict the critical flammability ratio at zero strain rate. The intercept value defines the CFR at 18.5 ± 0.8 % HFC-125 by volume in the HFC-32/HFC-125 mixture, with a correlation coefficient of 0.995. This compares very favorably to a value of 18.4 % published by Richard and Shankland (1992) using the ASTM E-681 apparatus.

DISSCUSSION

Many issues arose out of this study of the lean flammability limit with a counterflow burner. In order to evaluate the equivalence ratio accurately, extremely careful flow

calibration must be performed over the wide range of flows, from the high volume air to the minute volume flow of HFC-125. In order to accurately repeat the pressure inside the rotameters the pressure gauges must be placed as close as possible to the tubes. Corrections for daily changes in temperature and barometric pressure were crucial for repeatability and flow calibration. All corrections were incorporated into the data reported for the tests run with methane, HFC-32, and the HFC-32/HFC-125 mixture.

In Phase II an effort will be made to reduce data scatter and uncertainty in our measurements by using mass flow controllers and temperature baths to standardize and simplify flow measurements. Computer control of the flows will facilitate targeted testing of specific variables, such as percent HFC-125 or a specific strain rate. In addition, the redesign and modifications to the burner assembly, e.g. a contraction nozzle and reduced burner diameter, will improve the uniformity of the velocity profile and increase the maximum attainable velocity while decreasing the amount of agent required for testing. This will result in improved flatness of the flame and a wider range of strain rates that can be achieved.

Throughout this report comparisons have been made with results reported in Richard and Shankland (1992) using the ASTM E-681 technique for evaluation of flammability limits. The ASTM E-681 apparatus consists of a spherical glass flask of a specific volume containing a magnetic stirrer for mixing the materials and an ignition source, typically a match, spark, or hot wire. The top of the flask is sealed with a rubber stopper equipped with inlet tubes for air and fuel. The flask is enclosed in an insulated chamber and positioned above a magnetic stirrer drive. For each test, the vessel is evacuated and precise amounts of test gases, measured by partial pressures, are added. Inlet tubes are then closed and the ignition source is triggered. "...the upward and outward propagation of the flame away from the ignition source is noted by visual observation. The concentration of the flammable component is varied between trials until the composition which will just sustain propagation is determined." (ASTM E-681 - 94)

As an experimental method the extrapolation to zero strain rate using the counterflow burner has advantages over the ASTM E-681 apparatus in the areas of safety, efficiency, and accuracy. The ASTM E-681 method requires adequate shielding due to the possibility of rupture of the vessel. In addition, the amount of fuel present is set when the agent is measured and placed in the vessel. Unexpected results can be explosive. In contrast, the fuel input to the counterflow burner can always be adjusted, or simply shut-off, if necessary.

The counterflow burner method is more efficient than the ASTM E-681 method. Tests with the counterflow burner can be performed successively due to the ongoing input of fuels and air and the continuous removal of by-products by the exhaust system. This makes it possible to perform repeatability tests quickly and easily. In the case of the ASTM E-681 however, the vessel must be cleaned between each final trial. For each test performed using the vessel, the precise amount of agent and air must be measured and mixed, and instrument lines must be connected and disconnected. In addition to the set-up time, approximately a half an hour, the ASTM E-681 also requires a series of iterative tests to determine the extinction point. In contrast, each five minute test with the counterflow burner provides an extinction point for a given Φ and strain rate, which further refines the extinction curve.

In the ASTM E-681 method there is uncertainty associated with the type of ignition source and the vessel size used. The ASTM E-681 - 94 standard states specifically that the vessel wall may cause quenching effects "...for certain amines, halogenated materials, etc. which have large ignition-quenching distances." To reduce these effects, they recommend that tests should be conducted in vessels larger than the typical 5 liters. Finally and most importantly, the ASTM E-681 method introduces the possibility of human subjectivity, since it relies on the operator's observation of a weakly flammable gas to determine if the flame has propagated sufficiently outward from the ignition source. Uncertainty exists in cases when the flame lights but does not evenly or unequivocally travel to the side wall. In the case of the counterflow burner, the only evaluation required is whether or not a twin-flame exists; no ambiguous partial flame is possible. By using a counterflow burner to define an empirical flammability limit at zero strain rate, many experimental and operational variables are avoided and flammability limits of refrigerants will be clearly defined and reliably reproducible.

CONCLUSIONS

Using this counterflow burner in the configuration described, the lean flammability limit of HFC-32 was found to be 12.0 ± 0.6 % by volume in air and the critical flammability ratio of HFC-125 in HFC-32 was determined to be 18.5 ± 0.8 % by volume. These numbers are in good agreement with published values. As preliminary results, they provide strong evidence that counterflow burners can be successfully used to measure global strain rates and

11

lean flammability limits of fuels other than CH_4 and C_3H_8. With refinement of the burner, improved flow control and calibration, and local velocity measurements, it will be possible to define with much greater accuracy fundamental flammability limits of HFC-32 and other refrigerants.

The empirical technique for deriving the critical flammability ratio shows great promise. The maximum attainable strain rates for different mixtures of HFC-125 and HFC-32 decreased linearly with increasing HFC-125, allowing the critical flammability ratio to be determined by the extrapolation to zero strain rate. The broadening of the constant concentration contours assisted this evaluation, indicating that the maximum strain rate is not very sensitive to small changes in the equivalence ratio.

In conclusion, the results here demonstrate that the opposed flow burner and the zero strain rate extrapolation technique can work well with refrigerants and refrigerant mixtures. There are many improvements and modifications that will be required to develop a system with the accuracy required, but this work demonstrates that it is possible using a counterflow burner to define flammability limits and critical flammability ratios as fundamental properties of refrigerants.

COMPLIANCE WITH AGREEMENT

Two modifications of the experimental procedure as described in the contract agreement were made:

The burner was initially tested with methane (CH_4), instead of propane (C_3H_8) as originally proposed. Methane was selected because detailed results using methane on a counterflow have been published and could be referenced for comparison purposes. Measurements with propane were planned, but due to problems with the bottle supplied, they were not completed.

The spacing of between the burners was not varied during these tests. Due to the design of this burner, adjustments of height could not be performed quickly and with consistent repeatability. Because of the need to perform numerous tests with efficiency, testing proceeded with the burner in the position of 15.9 mm spacing.

PRINCIPAL INVESTIGATOR EFFORT

Summary of charges to ARTI MCLR Project Number DE-FG02-91CE23810:

Personnel salary and overhead:

Principal Investigators	$25,400
Technical Support	$19,700
Administrative Support	$2,000
	$47,100

Hardware and consumable supplies:

Equipment and supplies	$11,000
Miscellaneous	$1,900
	$12,900

14
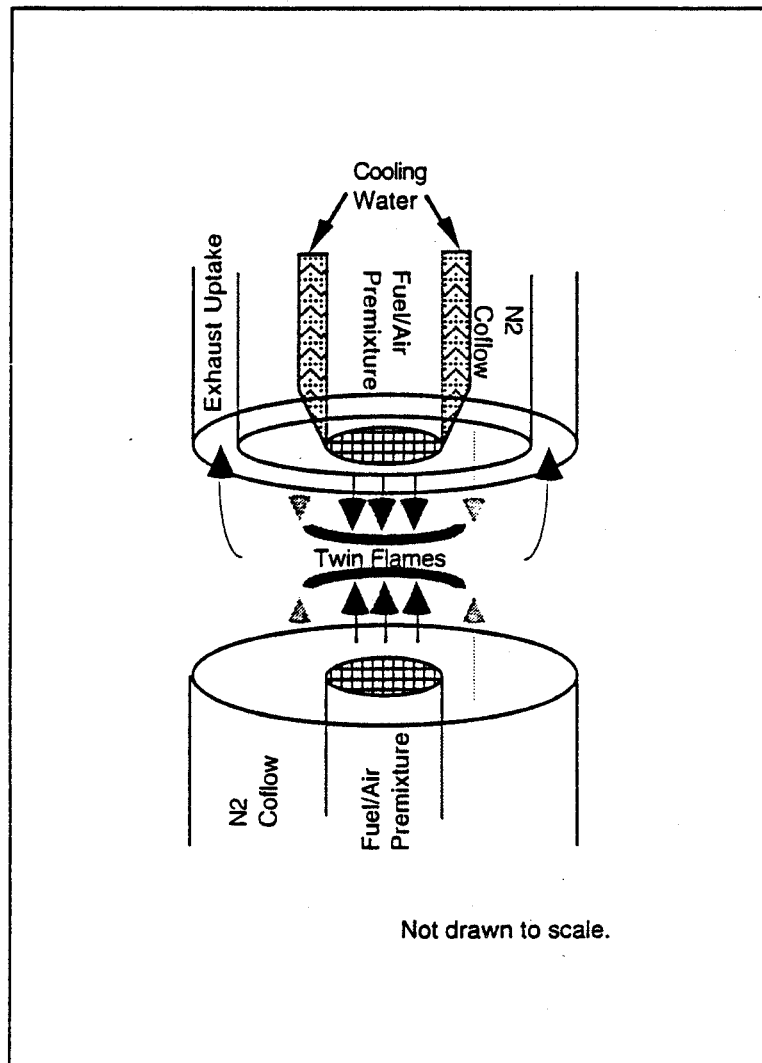
Figure 1: Flow diagram of counterflow burner.
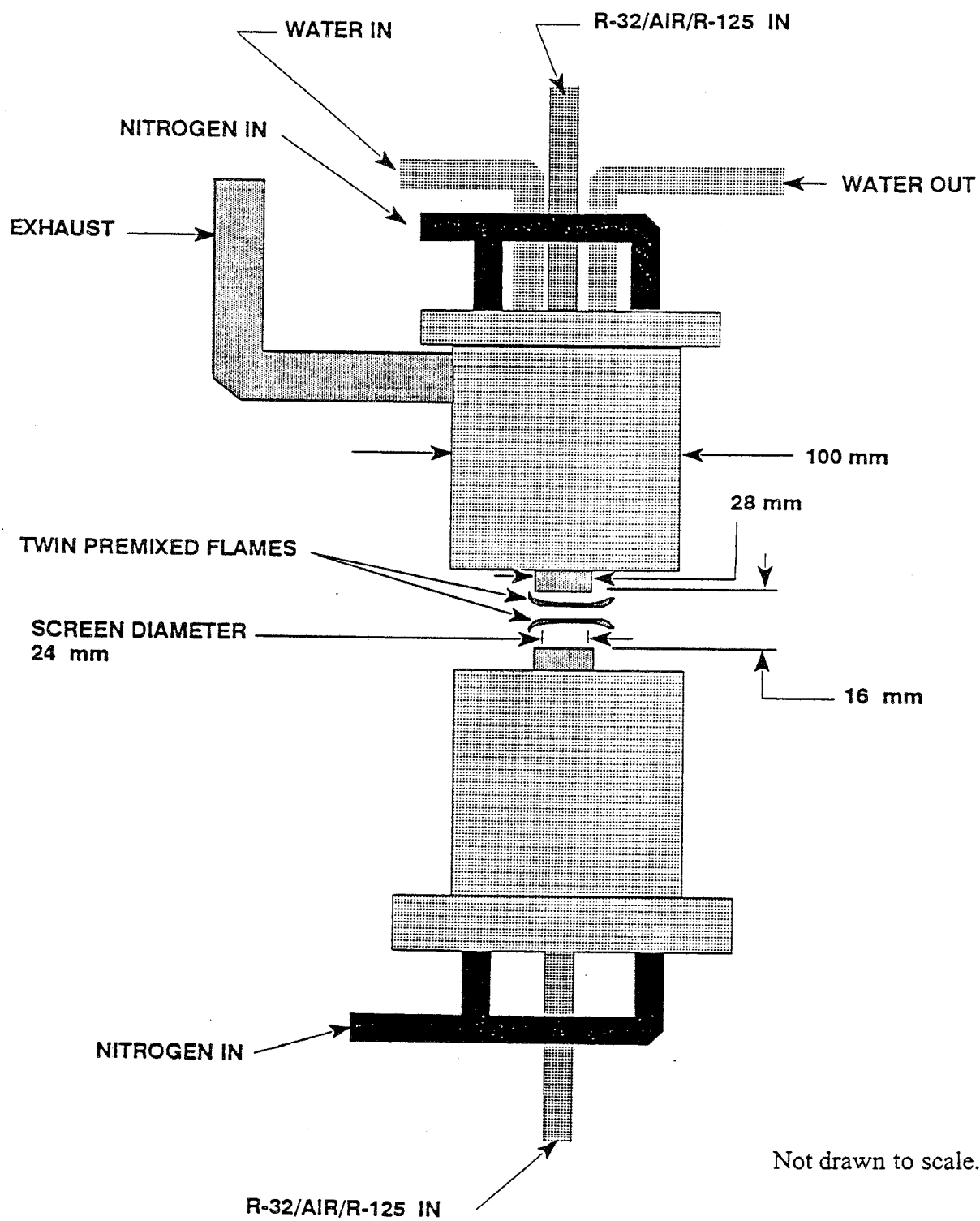
Figure 2: Counterflow premixed flame burner.
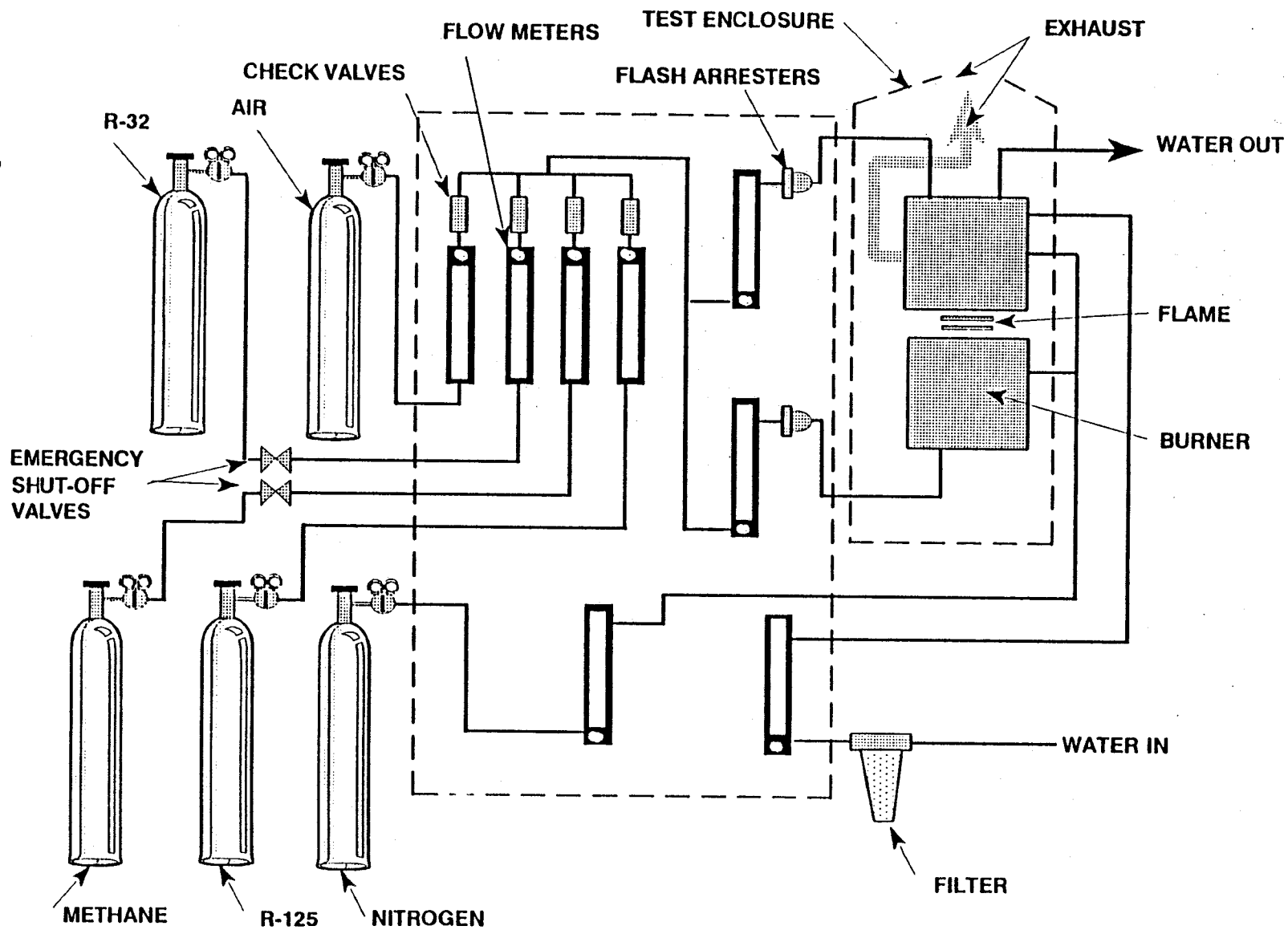
Figure 3 : Burner flow control system.
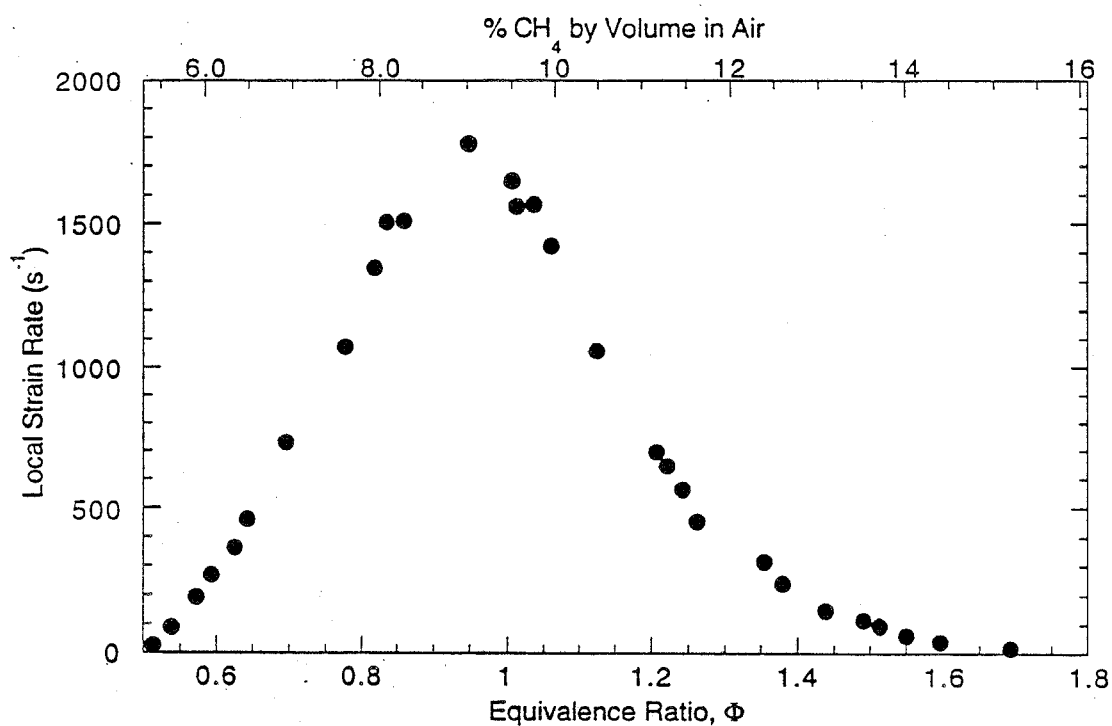
Figure 4: Extinction curve for CH_4 as a function of local strain rate. (Law *et al.*, 1986)
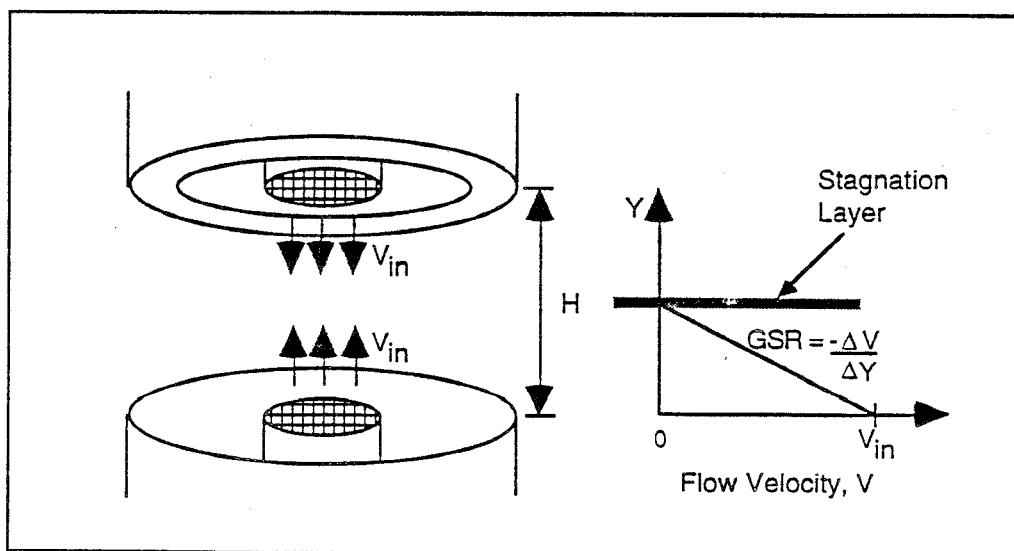
Figure 5: Global strain rate is defined as the gradient of the mean velocity where
GSR = $V_{in}/(H/2)$.
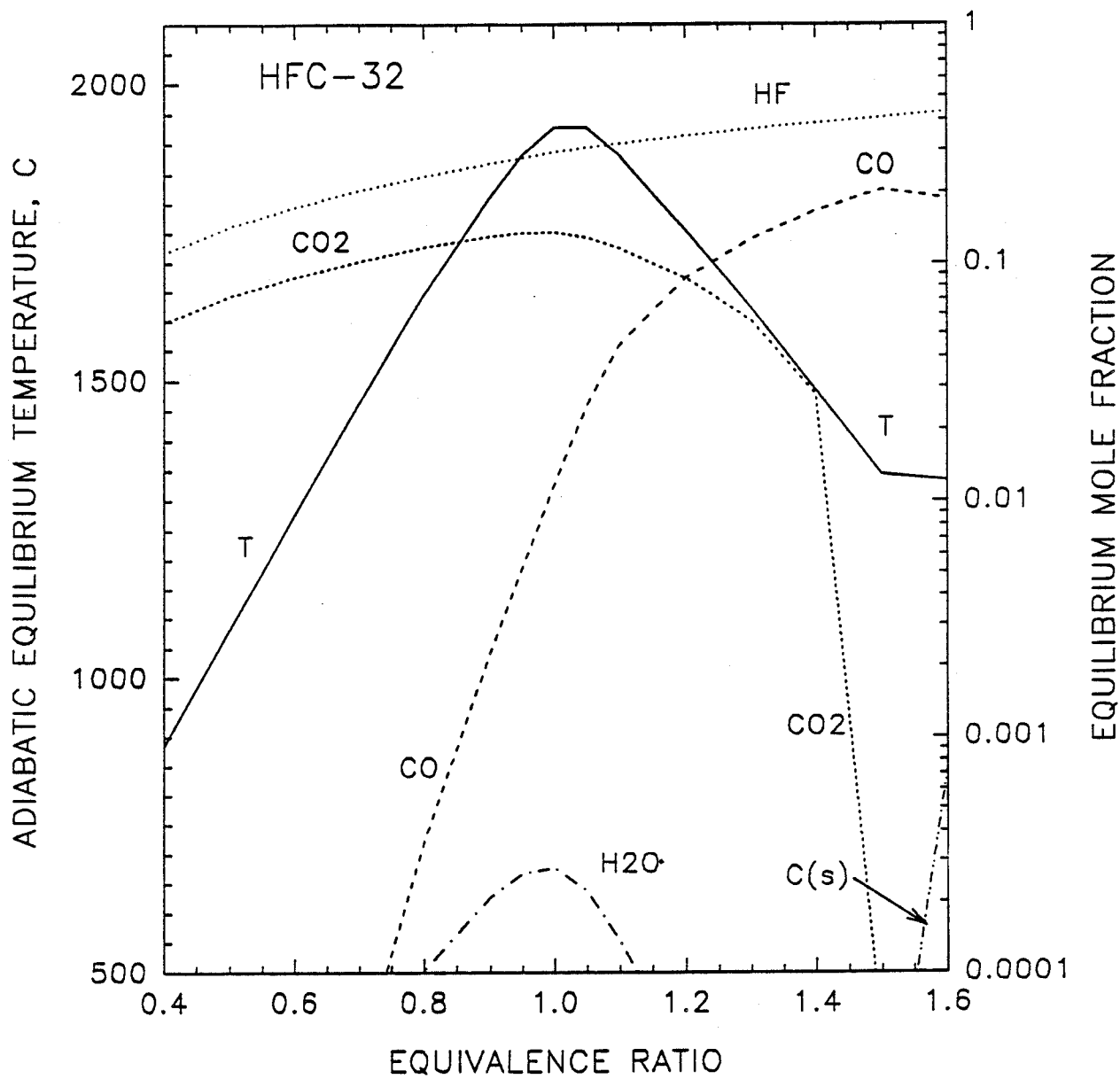
Figure 6: Calculated equilibrium composition and temperature for HFC-32 in air.
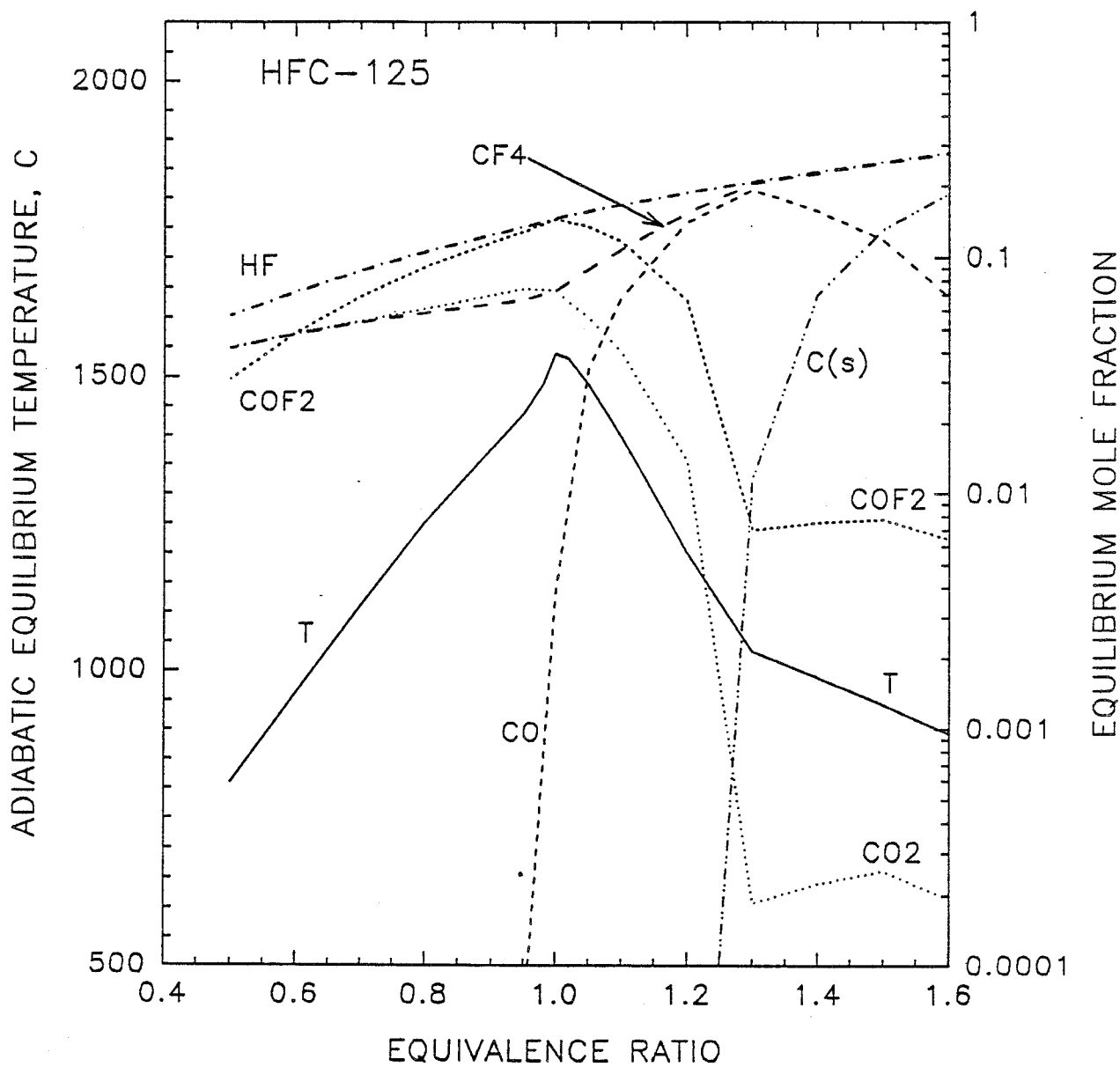
Figure 7: Calculated equilibrium composition and temperature for HFC-125 in air.
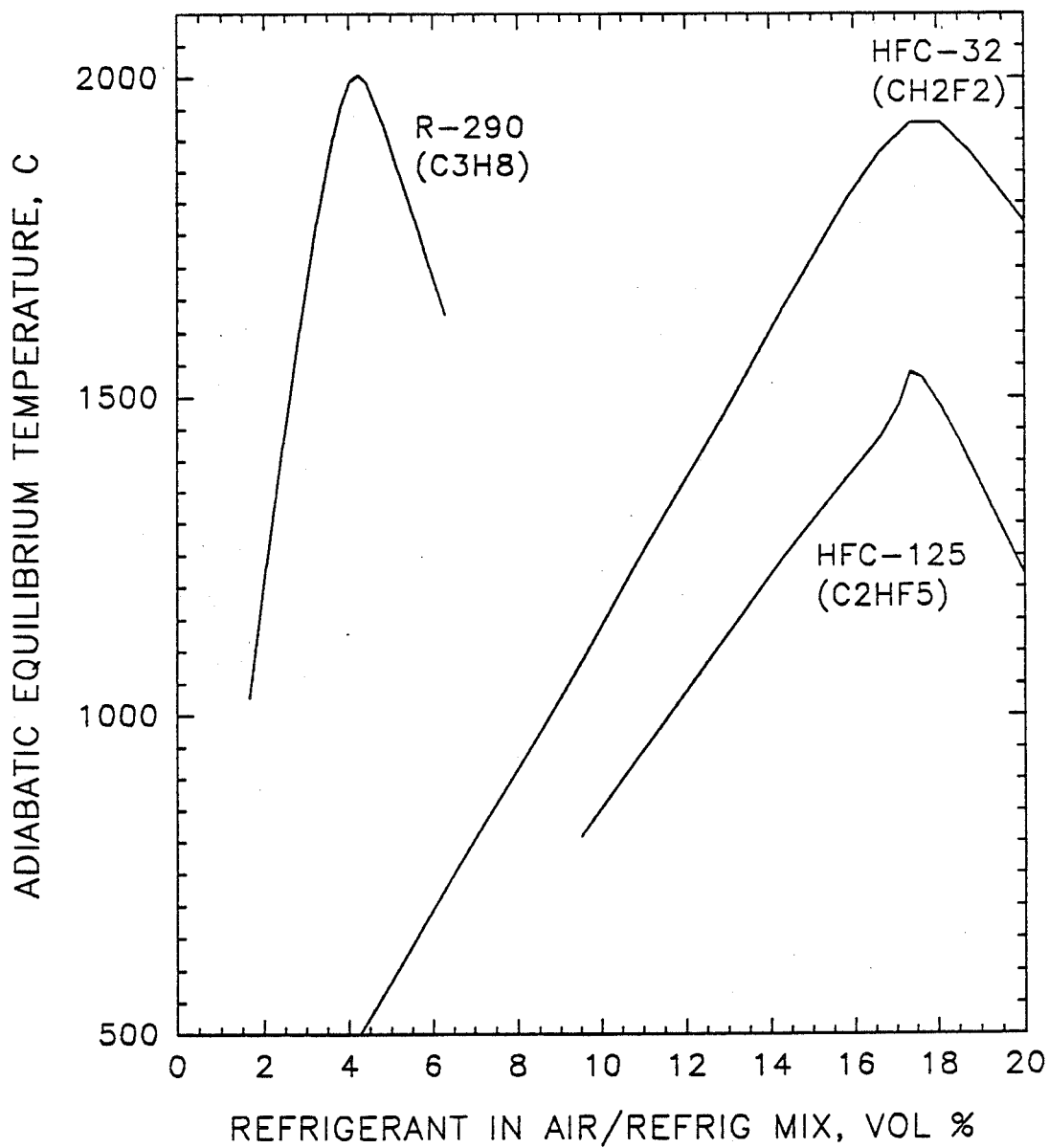
Figure 8: Calculated equilibrium temperatures for R-290, HFC-32, and HFC-125 in air.
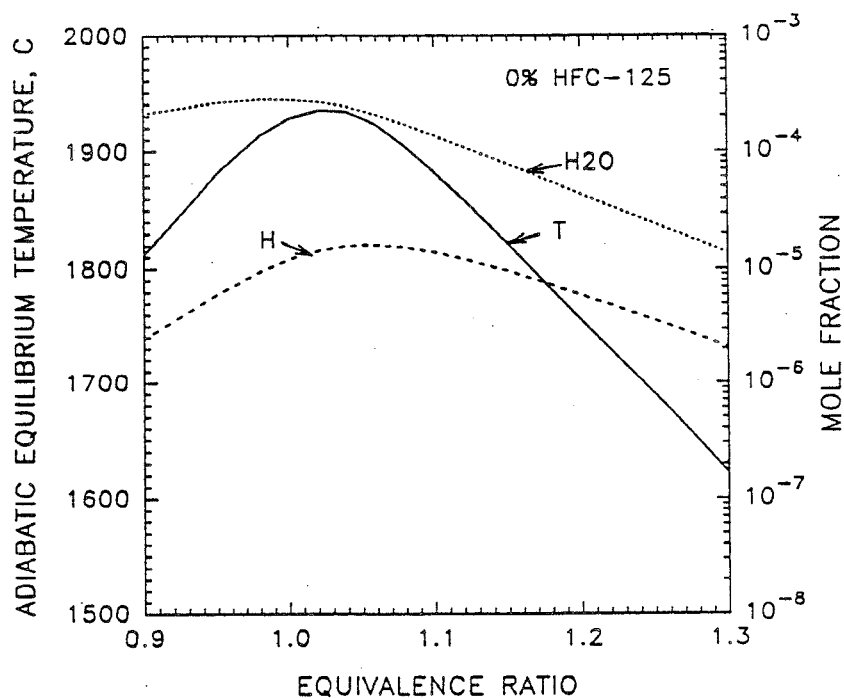
Figure 9a: Calculated equilibrium temperature and mole fractions of H and H_2O for HFC-32 in air (no HFC-125).
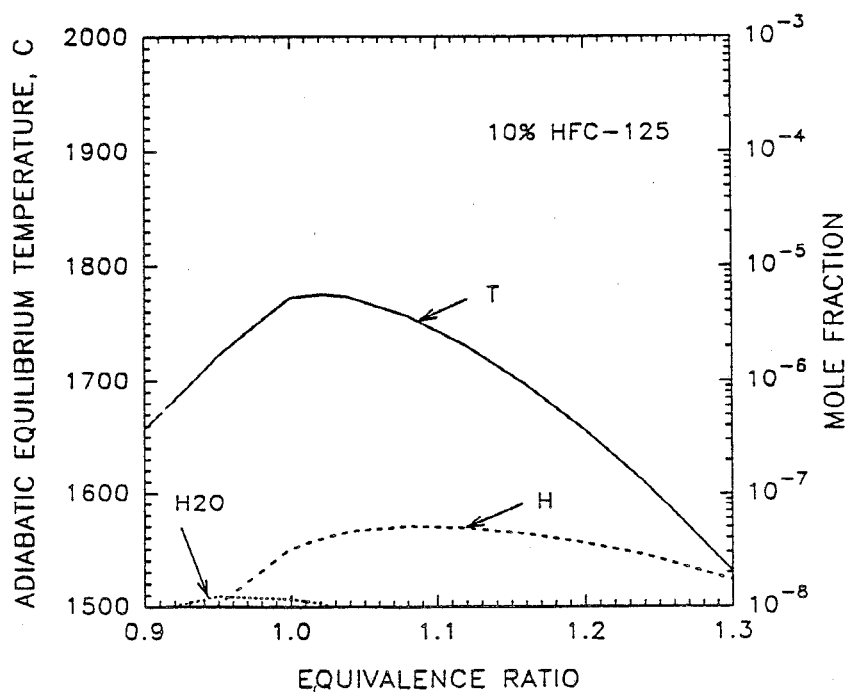
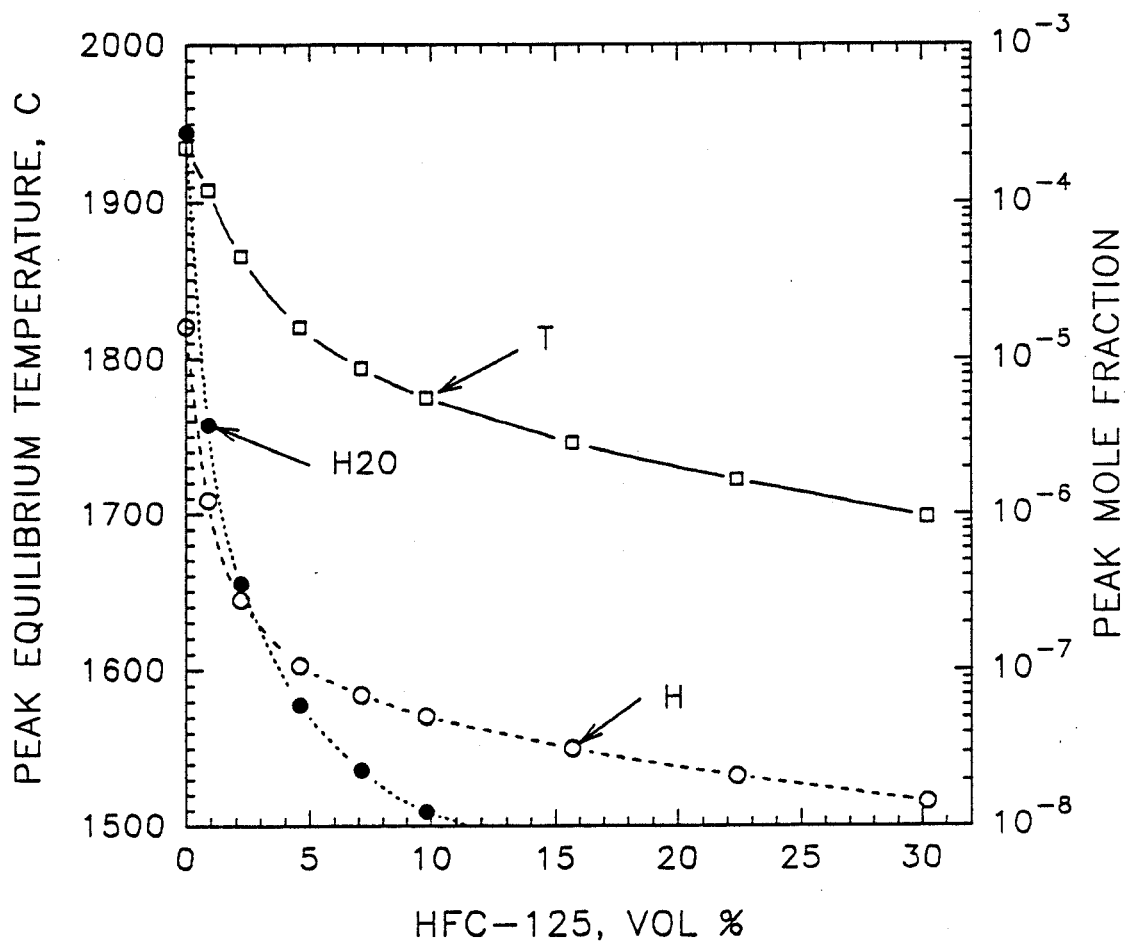Figure 9b: Calculated equilibrium temperature and mole fractions of H and H_2O for 90/10 mixture of HFC-32 and HFC-125 in air.

Figure 10: Peak values of temperature and mole fractions of H and H_2O as a function of HFC-125 percent volume.
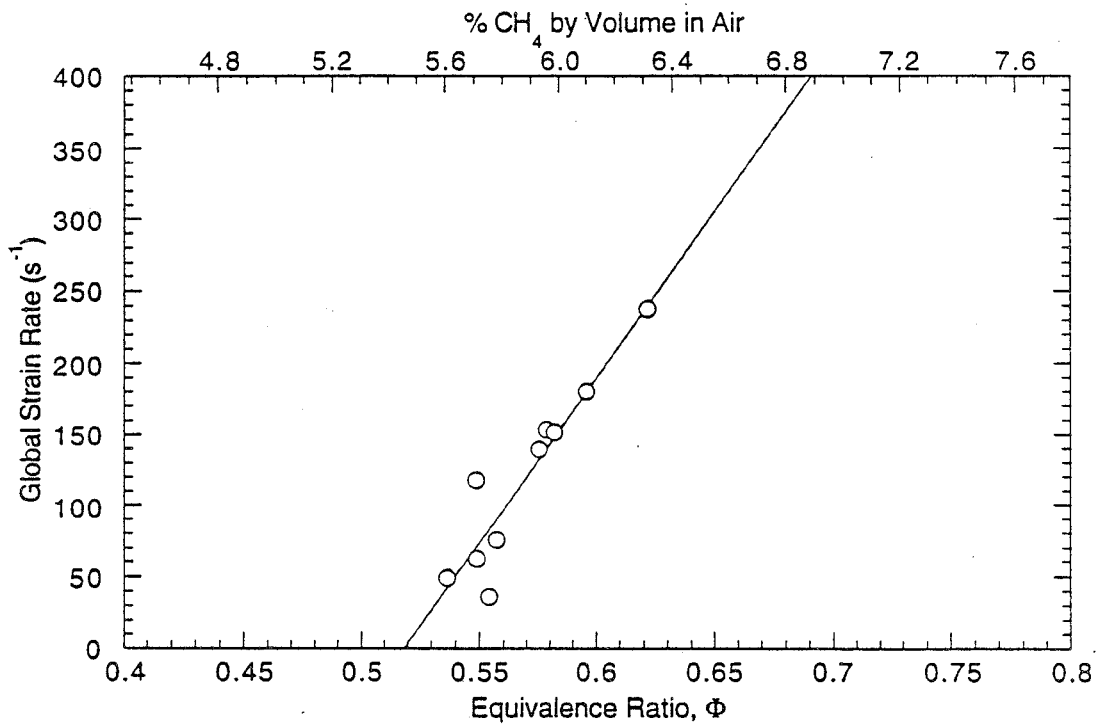
Figure 11: Global strain rate at extinction for a premixed lean CH_4/air flame measured in the NIST burner.
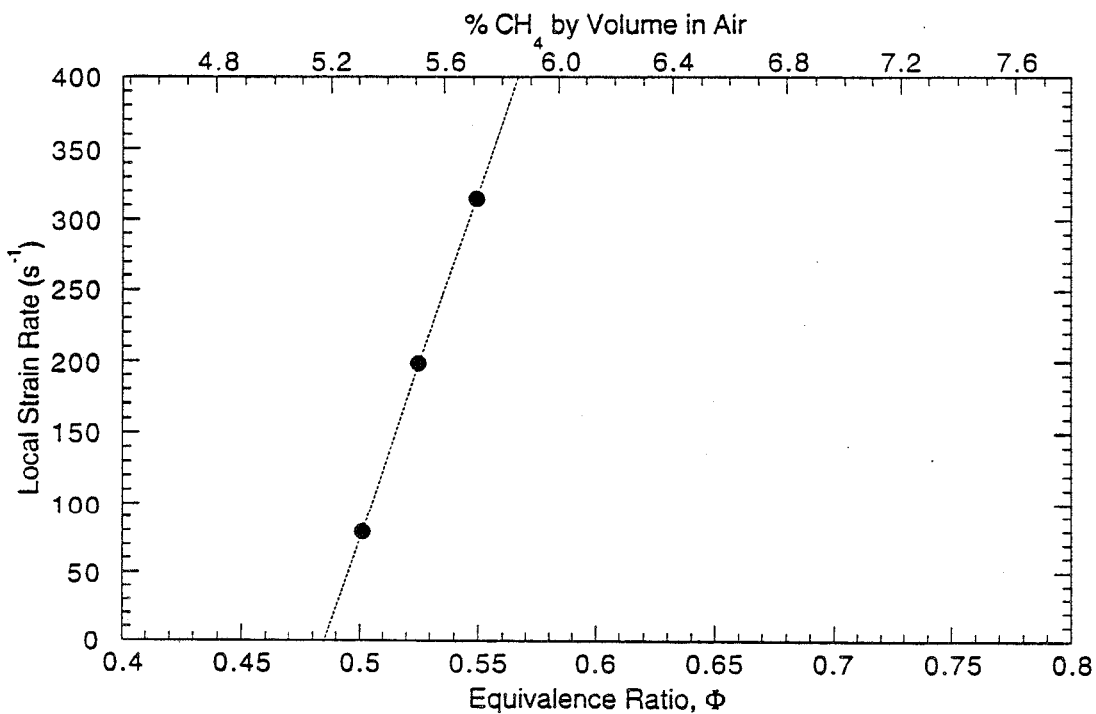

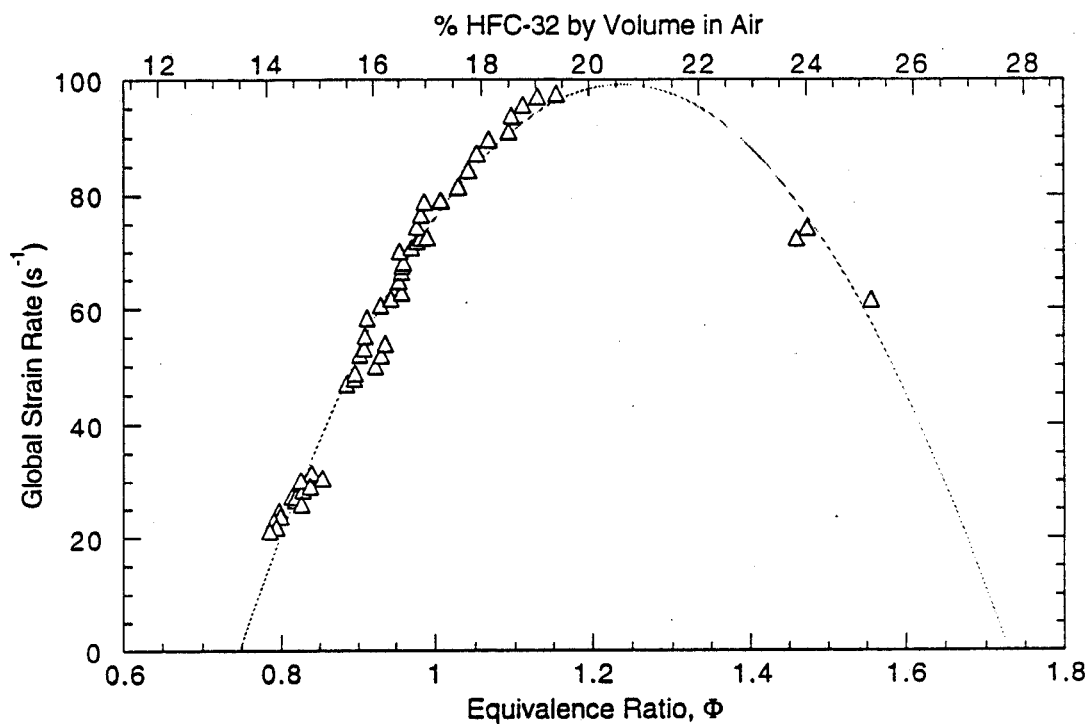Figure 12: Local strain rate at extinction for a premixed lean CH_4/air flame (Law and Egolfopoulos, 1988).

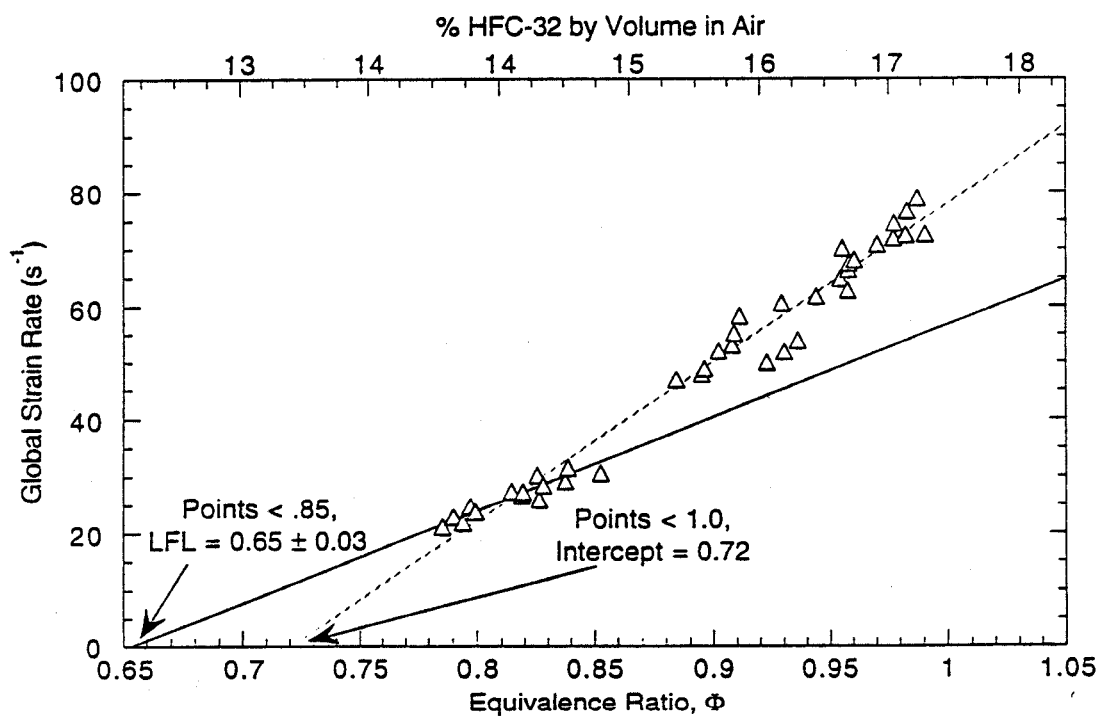Figure 13: Extinction points of HFC-32/air premixed flame.

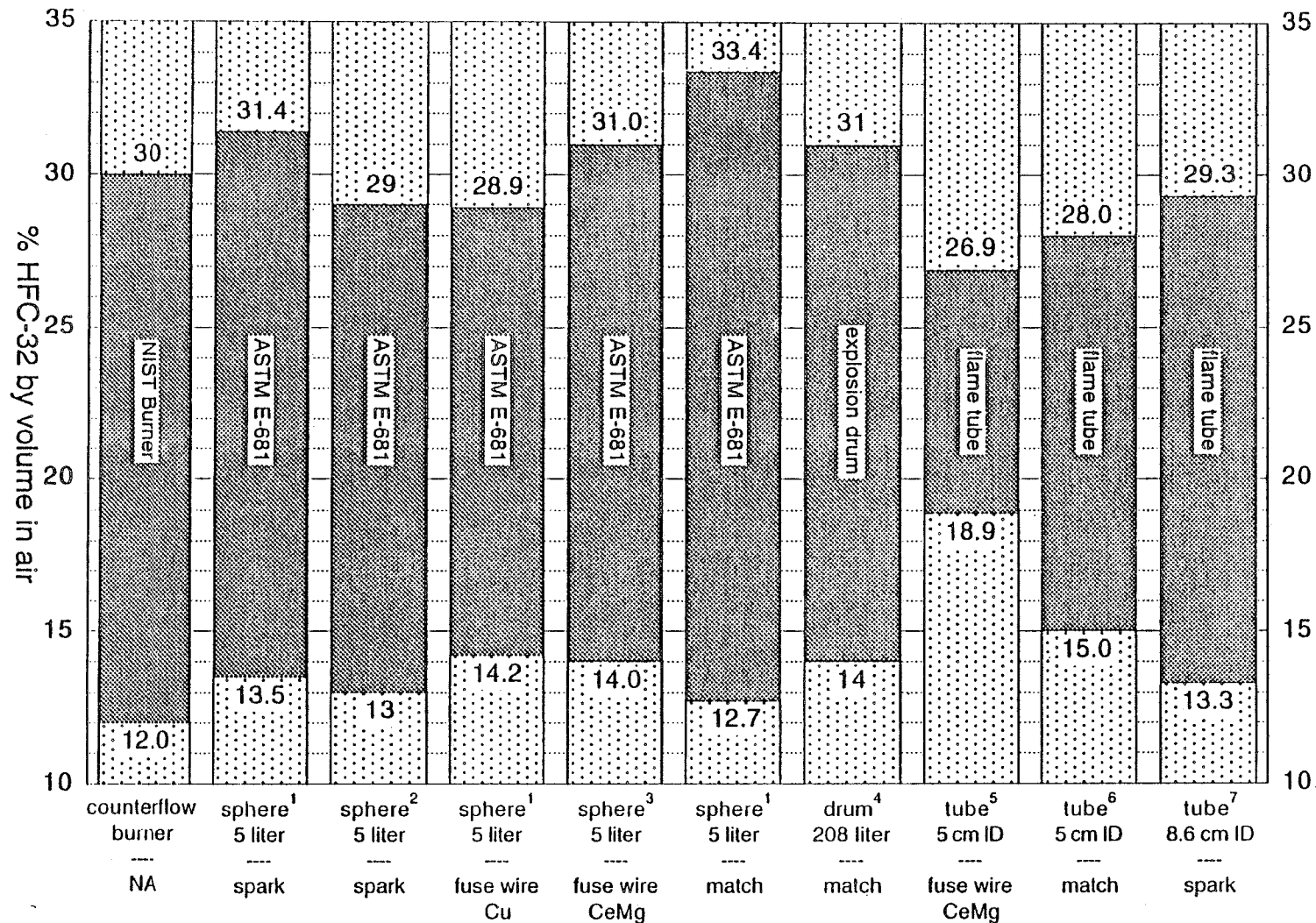Figure 14: Range of Lean Flammability Limit of HFC-32 in air.

25

Figure 15: Flammability Limits for HFC-32 using various methods at ambient temperatures.

References:
1. ASTM E-681 vessel; Richard and Shankland, 1992.
2. ASTM E-681 vessel; Ohnishi et al., 1993.
3. ASTM E-681 vessel; Dekleva et al. 1993.
4. Explosion Drum, Freon Products Laboratory, Dupont; Downing, 1988.
5. Flame Tube (5 cm ID, 200 cm length); Dekleva et al., 1993.
6. Bureau of Mines Eudiometer (5 cm ID, 200 cm length); Richard and Shankland, 1992.
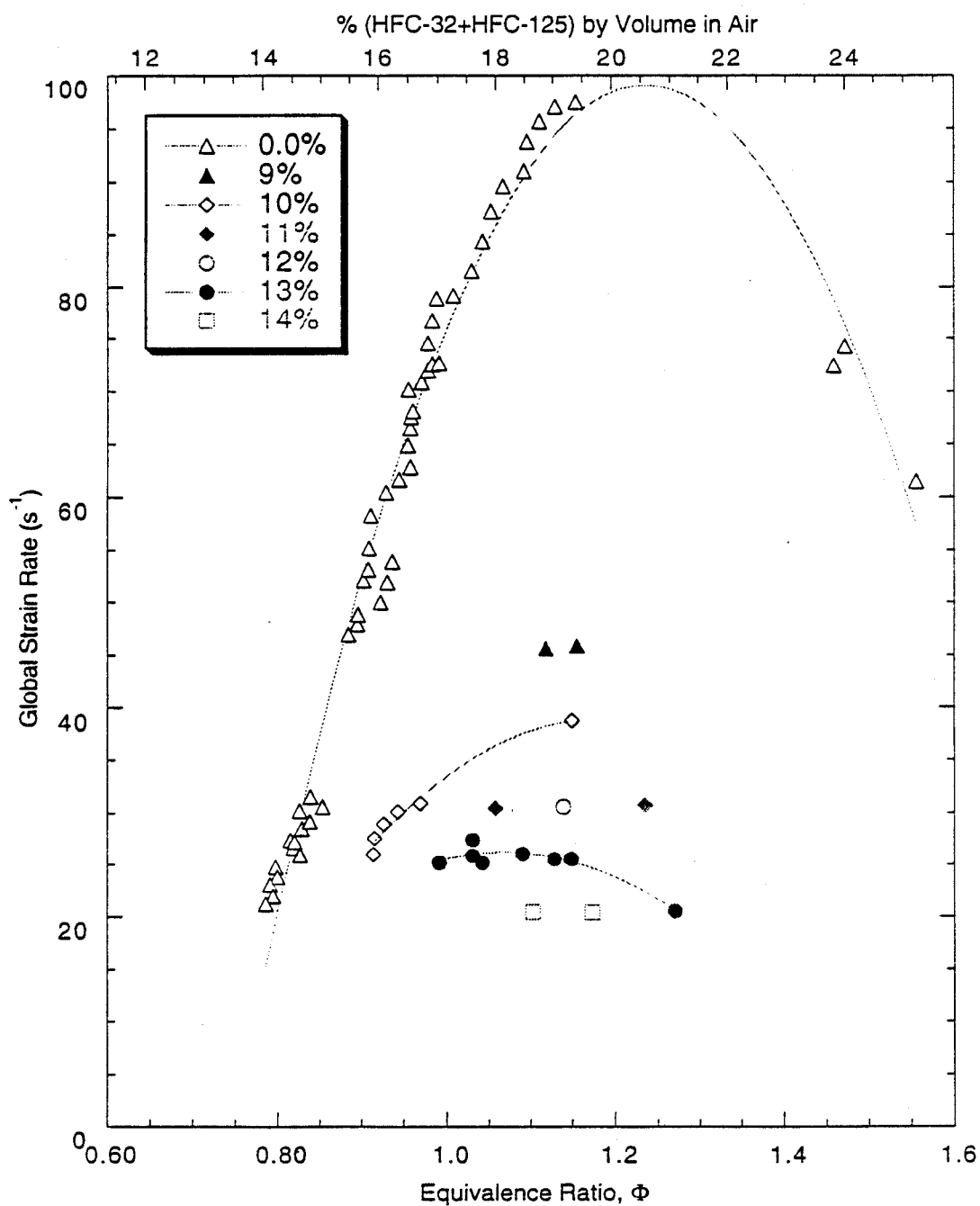7. Explosion Tube (8.6 cm ID, 30 cm length); Urano et al., 1990.

Figure 16: Extinction points for HFC-32 flames with different volume percent of HFC-125 in the refrigerant mixture. Second order curve fits are overlaid to demonstrate the progressive effect of more HFC-125.
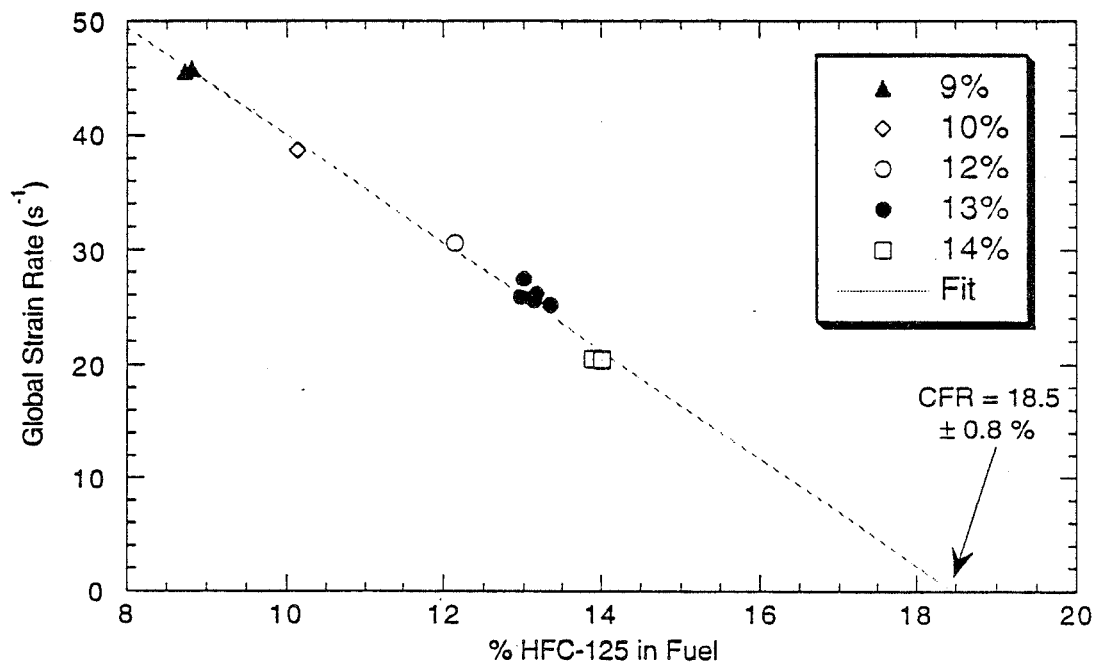
Figure 17: Extrapolation to zero strain rate for critical flammability ratio of HFC-125 in HFC-32.

BIBLIOGRAPHY

ASHRAE Standard 15-1994, "Safety Code for Mechanical Refrigeration"; August 1994, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, GA.

ASHRAE Standard 34-1992, "Number Designation and Safety Classification of Refrigerants"; August 1992. American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, GA.

ASTM E 681 - 94, "Standard Test Method for Concentration Limits of Flammability of Chemicals"; American Society for Testing and Materials, Philadelphia, PA.

Coward H. F.; Jones, G. W. (1952) *Limits of Flammability of Gases and Vapors*; Bulletin 503, Bureau of Mines, National Technical Information Service, Springfield, VA.

Dekleva, T. W.; Lindley A. A.; Powell, P. (1993) "Flammability and Reactivity of Select HFCs and Mixtures"; *ASHRAE Journal*, December 1993, Atlanta, GA.

Downing, R. C. (1988) *Fluorocarbon Refrigerants Handbook*; Prentice-Hall, Englewood Cliffs, NJ, pp 350-365.

Gordon, S.; McBride, B. (1994) *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Application*; NASA Reference Publication 1311, October 1994, NASA Scientific and Technical Information Program.

Ishizuka, S. (1993) "Characteristics of Tubular Flames"; *Progress in Energy and Combustion Science*, Vol. 19, Pergammon Press, pp 187-226.

Ishizuka, S.; Law, C. K. (1982) "An Experimental Study on Extinction and Stability of Stretched Premixed Flames"; Nineteenth Symposium (International) on Combustion: The Combustion Institute, pp 327-335.

Law, C. K.; Egolfopoulos, F. N. (1988) "A Kinetic Criterion of Flammability Limits: Lean Limits of C-H-O-N-Br Systems"; Proceedings of the Chemical and Physical Processes in Combustion: Fall Technical Meeting, 5-7 December 1988, Clearwater Beach, FL.

Law, C. K.; Zhu, D. L.; Yu, G. (1986) "Propagation and Extinction of Stretched Premixed Flames"; Twenty-first Symposium (International) on Combustion: The Combustion Institute, pp 1419-1426.

Ohnishi, H. (1993) "Relationship Between Flammability and Composition Ratio of HFC-32/HFC-134a Blend"; Proceedings of the ASHRAE/NIST Refrigerants Conference: R-22/R-502 Alternatives, Gaithersburg, MD, August 19-20, 1993.

Pannock, J.; Didion, D. A. (1991) *The Performance of Chlorine-Free Binary Zeotropic Refrigerant Mixtures in a Heat Pump*; NISTIR 4748.

Richard, R. G.; Shankland, I. R. (1992) "Flammability of Alternative Refrigerants"; *ASHRAE Journal*, April 1992, Atlanta, GA.

Taylor, B. N.; Kuyatt, C. E. (1994) *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297.

Urano, Y.; Horiguchi, S.; Tokuhashi, K.; Iwasaka, M.; Kondo, S. (1990) "Flammability Limits of Alternative Fluorocarbons"; *High Pressure Gases* (Koatsu Gasu), Vol. 27, No. 6, April 1990, pp 22-28. Published in Japanese.