Title
CHARACTERIZATION STUDIES OF THE SELECTIVE REDUCTION OF NO by NH3

Author
Brown, N.J.

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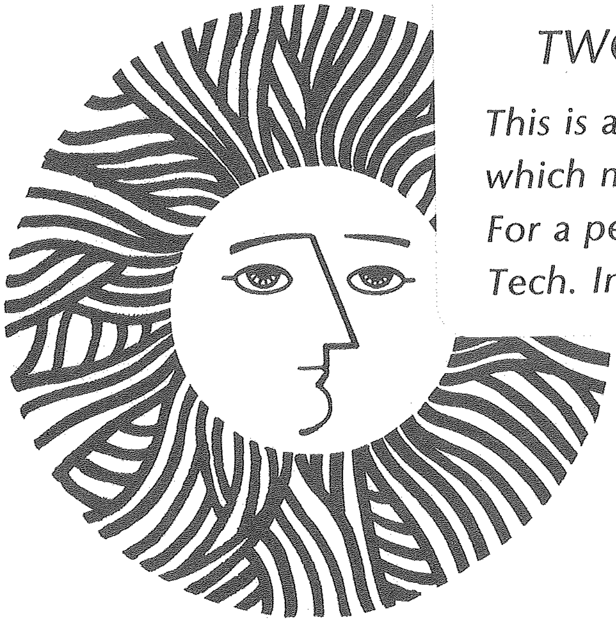

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DISCLAIMER

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CHARACTERIZATION STUDIES OF THE SELECTIVE REDUCTION OF NO by NH_3

N.J. Brown and R.F. Sawyer
Principal Investigators

and

T.S. Eitzen
Staff Scientist

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

This report describes a set of experiments which characterize, in part, the selective reduction of NO via NH_3 in the post combustion gases of propane/air in a laboratory scale combustion tunnel. The newly constructed tunnel supports steady state reproducible turbulent combustion under a variety of operating conditions. The prototype fuel nitrogen compound used throughout the study was NO. The important experimental variables considered in the study are: equivalence ratio, NO concentration prior to reduction, temperature, and NH_3 concentration added to the product gases. Results are analyzed in terms of NO survival and NH_3 emissions. The NO survival was found to be in the range 97 to 13 percent for the variables considered. The survival of NO and the NH_3 emissions were found to be especially sensitive to operating conditions.

EXECUTIVE SUMMARY

This report describes a set of experiments which characterize, in part, the selective reduction of NO via NH_3 in the post combustion gases of propane/air in a laboratory scale combustion tunnel. The combustion tunnel has been designed, constructed and characterized for the laboratory study of the selective reduction of NO. The combustion products of propane and air are diluted by nitrogen injection to provide precise temperature control. Nitric oxide levels at the inlet of the test section are fixed by nitric oxide addition to the reactant gases. Boiler combustion gases are thereby simulated in the laboratory with independent control of equivalence ratio, temperature, and nitric oxide level. Special attention was paid to the uniformity of the hot test gases and to the completeness of the mixing of the injection of ammonia so that the effects of system parameters (combustion product equivalence ratio, temperature at point of ammonia injection, nitric oxide level at ammonia injection, and ammonia to nitric oxide ratio) could be independently determined. In practical applications these parameters are largely interdependent and their uniformity in space (across the plane of ammonia injection) or time is unlikely. The residence times in the laboratory combustion tunnel (about 20 msec) are less than those associated with the practical application which are at least an order of magnitude greater. While such a difficulty is unavoidable in laboratory scale experimentation, the observation that reactions in practically all cases were complete within our test section suggests that the results are applicable to larger scale devices. The effectiveness of the process was characterized primarily in terms of nitric oxide survival and ammonia breakthrough with particular attention to off-design operating conditions.

At excess air operating conditions the observed behavior of the ammonia injection process for nitric oxide control was consistent with previous investigators. An optimum temperature and ammonia addition level for maximum nitric oxide removal were observed. Nitric oxide survival was somewhat greater than had been obtained by other investigators. This difference is probably attributable to differences in experimental configuration.

The effectiveness of nitric oxide removal improves as the stoichiometric mixture is approached from the lean side but is very sensitive to the mixture ratio at near stoichiometric conditions. Once the stoichiometric condition is reached and (apparently) there is no excess oxygen available, the effectiveness of nitric oxide removal drops rapidly. Under fuel rich conditions ammonia addition is ineffective for nitric oxide removal.

Ammonia breakthrough was not determined to be a problem for operating conditions near those at which the ammonia injection process is intended to be used. Ammonia breakthrough occurs under conditions of excess fuel (absence of excess oxygen), low temperature at the point of injection, and high ammonia to nitric oxide ratios.

The optimization of the process in practical applications may prove difficult because of expected variations in space and time of parameters to which process effectiveness is sensitive (temperature, excess oxygen, and nitric oxide level). Trade-offs exist between nitric oxide removal and ammonia breakthrough which suggest that optimization also must involve an assessment of the relative importance

of nitric oxide and ammonia emissions. For a large scale application the desirability of monitoring temperature, nitric oxide level, and excess oxygen as a means of selecting the amount and possibly location of ammonia injection should be investigated. Because of the sensitivity of the process to system parameters, monitoring of exhaust nitric oxide and ammonia would appear advisable (particularly in large scale applications).

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NOMENCLATURE

DF = The dilution factor. This is the ratio of the molar flow rate of N_2 injected into the combustion effluent to the total flow rate of the fuel and air reactants.

T^* = The temperature of the combustion effluent in degrees Kelvin 5 cm upstream of NH_3 injection.

i = An NH_3 measurement which was indeterminate but whose concentration is expected to be less than 100 ppm.

c = The designation for complete NO - NH_3 reduction prior to the final combustion effluent sampling station.

nc = The designation for incomplete NO - NH_3 reduction prior to the final combustion effluent sampling station.

β = The molar ratio of the quantity of NH_3 injected into the combustion effluent to the quantity of NO initially present at the NH_3 injection plane prior to NH_3 addition.

σ_{CO_2} = The standard deviation in a particular set of CO_2 measurements.

ϕ = The equivalence ratio of the reactants.

[ ] = The designation of molar concentration.

Superscripts

i = The designation of an initial value.

f = The designation of a final value.

ACKNOWLEDGEMENT

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I. INTRODUCTION

Combustion sources both of the mobile and stationary types are recognized as the primary sources of the nitrogen oxides, NO and NO_2. Two mechanistic paths are responsible for NO production during combustion, one involves the oxidation of atmospheric nitrogen (thermal NO) and the other results in NO production from the nitrogen chemically bound to fuel molecules (fuel NO_x). In combustion systems burning the heavier fossil fuels, the fuel and thermal mechanisms are of nearly equal importance in NO generation. The two formation mechanisms depend differently on temperature and have characteristically different reaction times. Conventional abatement technologies that are based upon reducing combustion temperatures to prevent the formation of thermal NO are less effective in reducing fuel NO.

A new NO control technology has been described by Lyon and Longwell[1] which selectively removes NO from combustion effluent gases through homogeneous reactions with ammonia and oxygen. The process is different from conventional NO abatement techniques since it does not prevent or limit NO formation but rather removes the NO through reaction in the post combustion gases. Since the process does not differentiate between thermal and fuel NO, and selectively removes NO after its formation, it reduces both thermal and fuel NO_x.

The present paper is concerned with characterizing the selective reduction of NO through the addition of NH_3 to the post combustion gases. The study was undertaken in a laboratory scale combustion tunnel that suppports steady state reproducible combustion under a variety of operating conditions. Propane fuel was premixed with air and the prototype fuel nitrogen compound, NO, prior to combustion. Experimental variables considered in the study are: (1) equivalence ratio, (2) NO concentration prior to ammonia addition, (3) temperature of the combustion products prior to ammonia addition, and (4) ammonia concentrations added to the product gases. Results are analyzed in terms of NO survival yields and the concentration of NH_3 emissions.

It is important to characterize new pollution control technologies prior to their large scale application. The characterization process for the selective reduction of NO through reaction with NH_3 added to the post combustion gases has involved kinetic studies, laboratory scale combustor studies and demonstration studies in utilities, and these provide different but complementary information. The kinetic studies have been undertaken by Lyon and his co-workers[2-4] to elucidate mechanistic details of the $NH_3/NO/O_2$ reactions. These have been conducted in a quartz plug flow reactor of conventional design and have yielded some interesting mechanistic information regarding the reaction sequence. A recent modelling study has been undertaken by Branch et al[5] who attempted to model reported experimental results. These authors indicated that the reaction $NH_2 + NO \rightarrow N_2 + OH$ was of crucial importance in effecting the reduction of NO. It is somewhat difficult to accept that the $NH_2 + NO$ reaction is an elementary reaction and responsible for the reduction of NO. There are no measured rate coefficients for this reaction and kinetic data had to be estimated to model observed experimental behavior. Investigations of the second type are laboratory scale combustion studies which have been conducted by Muzio et al.[6,7] and by Banna and Branch[8]. Laboratory scale combustion studies allow careful control of experimental variables and provide a post combustion environment in which the selective reduction can be investigated. These studies provide some mechanistic information and have resulted in the determination of optimum conditions for the selective NO reduction. Demonstration studies of the selective reductions in utilities have occurred in Japan and are reported by Sema et al.[9] and Woo and Goodly[10] and these have indicated that the selective reduction is viable for commercial application.

This report has the following organization. The combustion tunnel and analytical procedures used throughout the study are described in Section II. Results are given in Section III, and data supporting the steady state, reproducible nature of the combustion tunnel are given. The reduction of NO in lean, near stoichiometric and rich mixtures is also discussed. Data are presented which summarize the NH_3 emissions problem associated with the reduction of NO. Conclusions of our study are given in Section IV.

II. EXPERIMENTAL SYSTEM

The combustion tunnel used throughout the collection of experiements discussed in this report is described in this section. The analytical techniques used to measure temperature, CO, CO_2, NO and NH_3 are also discussed.

A. Combustion Tunnel

The combustion tunnel supports reproducible, steady state turbulent combustion over a range of operating conditions. Figure 1 is a schematic diagram which illustrates the five component parts of the experimental system. The first of these is the gas metering and mixing section for fuel and oxidizer. Calibrated rotameters with temperature and pressure indication at the inlet metered the mass flow rates of all gases used in this investigation. Air was supplied from a laboratory compressor and was introduced into a 5 cm inside diameter low alloy steel tube at the upstream end of the combustion tunnel. The air mass flow rate could be varied from 3.3 to 35.0 gm/sec; however, it was convenient to maintain the air flow rate constant at 9.0 gm/sec and to vary equivalence ratio by adjusting the fuel flow. The fuel used throughout this study was NGPA grade HD-5 propane which was supplied in 45.3 kg cylinders from Allied Propane Service. The fuel tanks were immersed in steam heated water baths to aid in vaporizing the fuel. The fuel flow was monitored with a rotameter, and pressure and temperature were measured at the rotameter inlet to provide necessary fuel density information. Fuel flows were varied from 0.46 g/sec to 0.68 g/sec to achieve equivalence ratios in the range of 0.8 to 1.2, respectively. The fuel and air were combined using a conventional mixing venturi. The resulting fuel/air mixture then passed

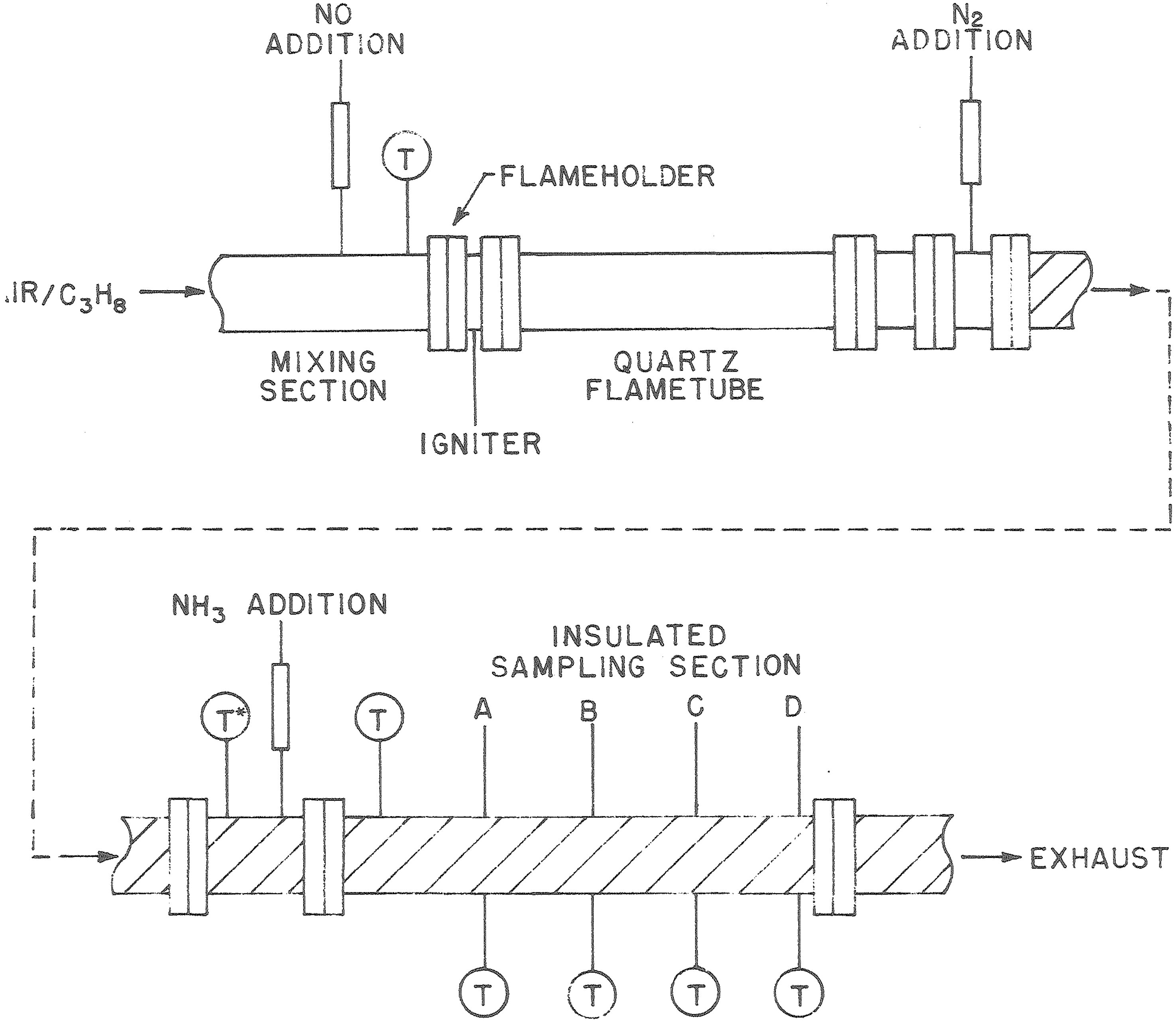

Figure 1. Schematic diagram of the laboratory scale combustion tunnel.

through a 5 cm inside diameter stainless steel flow straightening tube of length 69 cm to allow fully developed flow.

The second segment of the tunnel is the combustion section consisting of a flame holder, igniter and a quartz flame tube. The flame holder was a 1.5 mm thick, 5.6 cm diameter sintered stainless steel disc of 50 to 100 micron porosity. The absolute pressure upstream of the flameholder was typically 150 KPa, and the differential pressure across the flameholder was approximately 45 KPa. Under these conditions, the flameholder has proven to be very stable over a range of equivalence ratios from 0.8 to 1.2. The igniter initiated combustion approximately 3 cm downstream of the flameholder through use of a spark gap powered by a conventional automotive ignition coil. Following ignition, the combustion products flowed through a 5.3 cm inside diameter quartz section 60 cm in length. The Reynold's number in this region was approximately 7500.

To achieve the desired combustion product temperature for the injection of NH_3, secondary N_2 was introduced at the third axial component of the combustor. The nitrogen was supplied in liquid form from a 160 liter dewar to a heat exchanger for vaporization. The gaseous N_2 flow was then metered through a rotameter to the N_2 injector supply tubing. The N_2 was introduced into the combustion tunnel through four stainless steel injectors displaced 90° from one another circumferentially in a plane perpendicular to the combustor axis located 67 cm downstream of the flameholder (Figure 2). Each 0.95 cm diameter injector protruded 1.75 cm radially into the flow field, and supplied N_2 to the combustion product stream through five 1.6 mm holes separated axially by 3.2 mm. The orifices of each injector were oriented to supply N_2 counterflow to the combustion product stream.

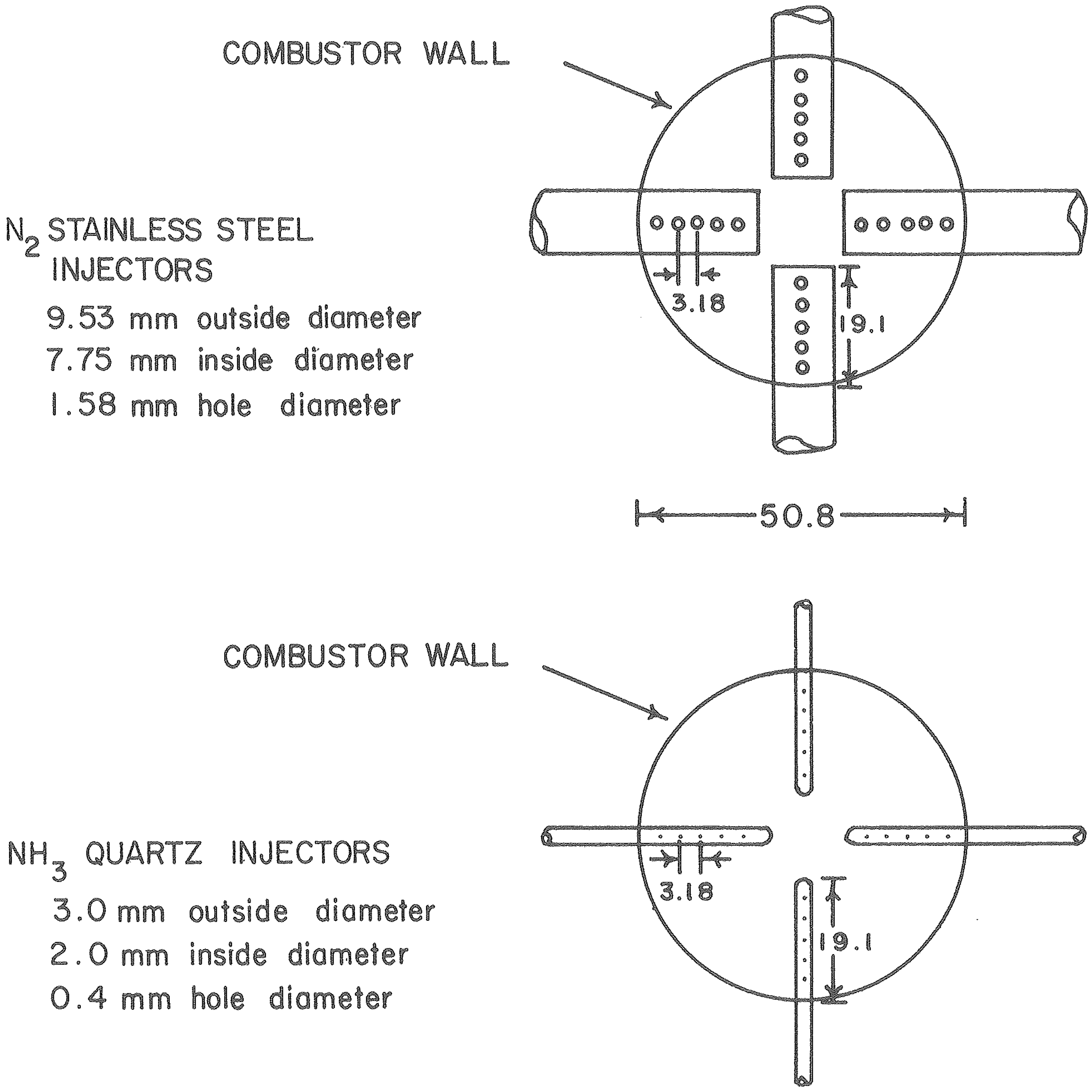

Figure 2. Schematic diagram of the N_2 and NH_3 injectors.

These opposed flow jets and the bluff body nature of the injectors induced additional turbulence which resulted in rapid mixing. The N_2 flows were varied with equivalence ratio to achieve the desired combustion effluent temperature.

The NH_3 injection system (Figure 2) located 88 cm downstream of the flameholder is the fourth component of the tunnel. Mass flow rates of Matheson CP grade anhydrous NH_3 were determined with a rotameter and by monitoring the gas temperature and pressure at the rotameter inlet. The salient construction and geometric orientation features of the N_2 injection system were incorporated into the basic design of the NH_3 injection system. Different materials and dimensions were used for the NH_3 injectors, however. The four NH_3 injectors were fabricated from 2 mm inside diameter quartz tubes which were sealed at one end. These injectors were inserted 1.9 cm into the tunnel, and NH_3/N_2 mixtures were discharged through five 0.4 mm holes separated by 3.2 mm along the injector axis. A series of experiments were performed to ascertain whether catalytic decomposition of the NH_3 occured in this uncooled quartz injection configuration. An apparatus was constructed to pass carefully metered mixtures of either NH_3/air or NH_3/N_2 through tubes of either stainless steel or quartz which could be heated to a desired temperature. The tube temperature and the gas mixture residence time in the tubes were selected to simulate the conditions of NH_3 injection into the combustion tunnel during normal operation. After passing through the heated length of tube, the resulting mixture was bubbled through a flask containing 20 mℓ of acetic acid of known concentration which absorbed any undecomposed NH_3. The unreacted acetic acid was then titrated with ammonium hydroxide of known concentration in the presence of an indicator to determine the quantity of ammonia which had decomposed in the tube. Quantitative transfer of NH_3 occurred when: 1) NH_3/N_2 mixtures were passed through an unheated quartz tube, 2) NH_3/N_2 mixtures were passed through a heated quartz tube, 3) NH_3/Air mixtures were passed through an unheated quartz tube, and 4) NH_3/Air mixtures were passed through an unheated stainless steel tube. Mixtures of NH_3/N_2 passed through an unheated stainless steel tube were not checked for quantitative transfer; however, no significant NH_3 decomposition would be expected under such circumstances. Significant decomposition of NH_3 (60 to 80 percent) occured when: 1) NH_3/Air mixtures were passed through a heated quartz tube, 2) NH_3/Air mixtures were passed through a heated stainless steel tube, and 3) NH_3/N_2 mixtures were passed through a heated stainless steel tube. Since the decomposition of NH_3 was negligible when NH_3/N_2 mixtures were passed through a heated quartz tube, quartz was chosen as the material for the NH_3 injectors.

Matheson CP Grade NO was used as the prototype fuel nitrogen compound in this study. The NO injection manifold was constructed to allow the introduction of NO into the combustion tunnel through any one of three axial locations: 1) upstream of the flameholder, 2) through the N_2 injectors, and 3) through the ammonia injectors. This capability facilitated both the evaluation of the survival of NO in combustion at various equivalence ratios and the determination of the mixing efficiency of gases introduced through the N_2 and NH_3 injectors.

The final segment of the combustor is the test section which begins 9 cm downstream of the ammonia injectors, and is approximately 60 cm in length. Composition and temperature measurements may be performed in this section at five axial locations separated by approximately 12 cm. At each of these axial sampling planes, there were four 19.1 mm tapped access ports in the combustion tunnel wall displaced circumferentially from one another by 90°. At each access port, a probe can be positioned on the test section centerline, or at any one of seven radial locations between the centerline and the combustion tunnel wall. Errors in probe positioning were estimated to be ± 1 mm. The test section and the portions of the tunnel 20 cm upstream and downstream of the test section were wrapped with 2.54 cm thick Fiberfrax Alumina Silica insulation to reduce heat losses. Upon exiting the test section, the combustion product gases passed through a convoluted expansion section to the main laboratory exhaust system.

B. Analytical Techniques

Temperatures were measured with Chromel/Alumel thermocouples. Corrections for thermocouple radiation losses were made through calibration with a suction pyrometer (aspirated thermocouple). Figure 3 is a schematic diagram of the suction pyrometer. Thermocouple and suction pyrometer measurements were taken simultaneously during the calibration process. The bare wire thermocouple temperature measurements were then subtracted from the more accurate temperatures extrapolated from suction pyrometer data to obtain a correction for thermocouple readings. These resulting radiation corrections were typically 25 K for temperatures between 1200 and 1250 K. All temperatures reported here were corrected for radiation losses by adding the appropriate radiation correction to the respective bare wire thermocouple measurement.

A schematic diagram of the sample gas flow path is shown in Figure 4. Gas samples were extracted from the test section through aerodynamically quenched microprobes. The probes were constructed from 2.0 mm I.D. quartz tubing and were approximately 25 cm in length with orifice diameters of 0.3 mm to 0.4 mm. Samples were drawn through one of three microprobes using a Metal Bellows Corporation model 155 vacuum pump which provided absolute pressures of 24 to 34 KPa to the microprobe. The sample gas was

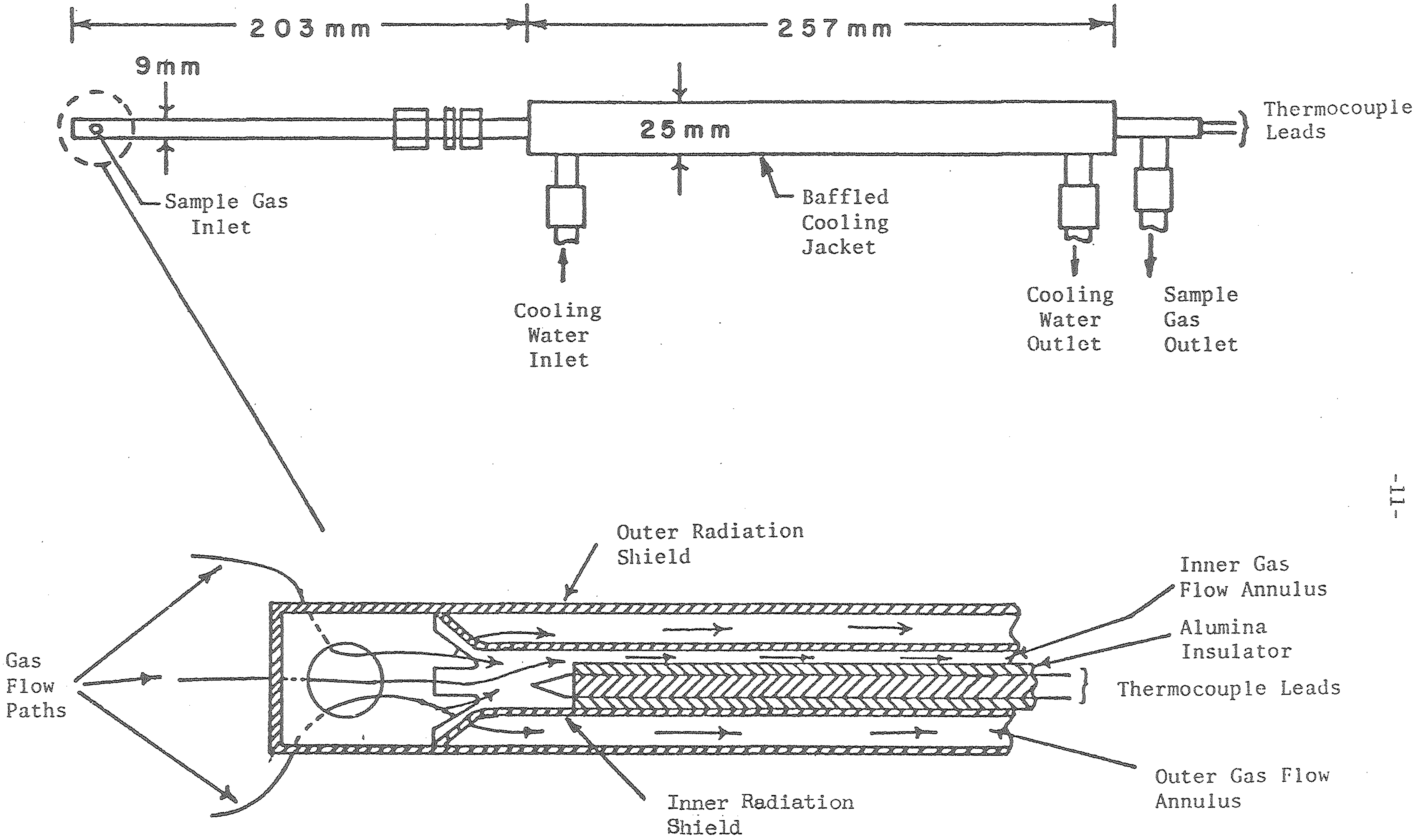

Figure 3. Schematic diagram of the suction pyrometer.

then passed through a heated sample line to the sample gas manifold which routed the sample through either analytical instruments for measurement of CO, CO_2, and NO/NO_x or to the NH_3 collection apparatus. Water was removed from the sample gas routed to CO, CO_2 and NO/NO_x analyzers with a two stage condenser and an anhydrous $Mg\ (C\ell O_4)_2$ moisture trap.

Measurement of dry CO and CO_2 concentrations was accomplished using Beckman Model 315 Non-Dispersive Infrared (NDIR) continuous gas analyzers. Calibration gases were obtained from a commercial vendor and new calibration curves were constructed for the CO instrument. The calibration gas concentration was verified by gas chromatography. Calibration of each instrument was performed immediately before each measurement.

A Thermoelectron Model 12A Chemiluminescent Analyzer was used to measure NO and NO_x concentrations. Calibration gases of NO in N_2 were purchased from commercial sources and the specified concentrations were then checked by mass spectrometric analyses. The concentrations determined by mass spectrometric analyses were used for calibrating the chemiluminescent analyzer. Good agreement was found between our values of concentration and those specified by the vendor for NO/N_2 mixtures stored in aluminum tanks. However, mass spectrometric analyses of NO/N_2 mixtures stored in iron tanks consistently revealed concentrations of NO approximately 30 percent lower than the concentration specified by the vendor. It is possible that NO reacts with iron, and causes a reduction in NO concentration.

Ammonia samples were collected for measurement using the sample gas flow path shown in Figure 4. The samples analyzed were collected through a microprobe positioned at the test section access port located 59 cm downstream of ammonia injection. The gas sample then passed through a 100 mm pyrex drying tube filled with 3 mm diameter, spherical glass beads

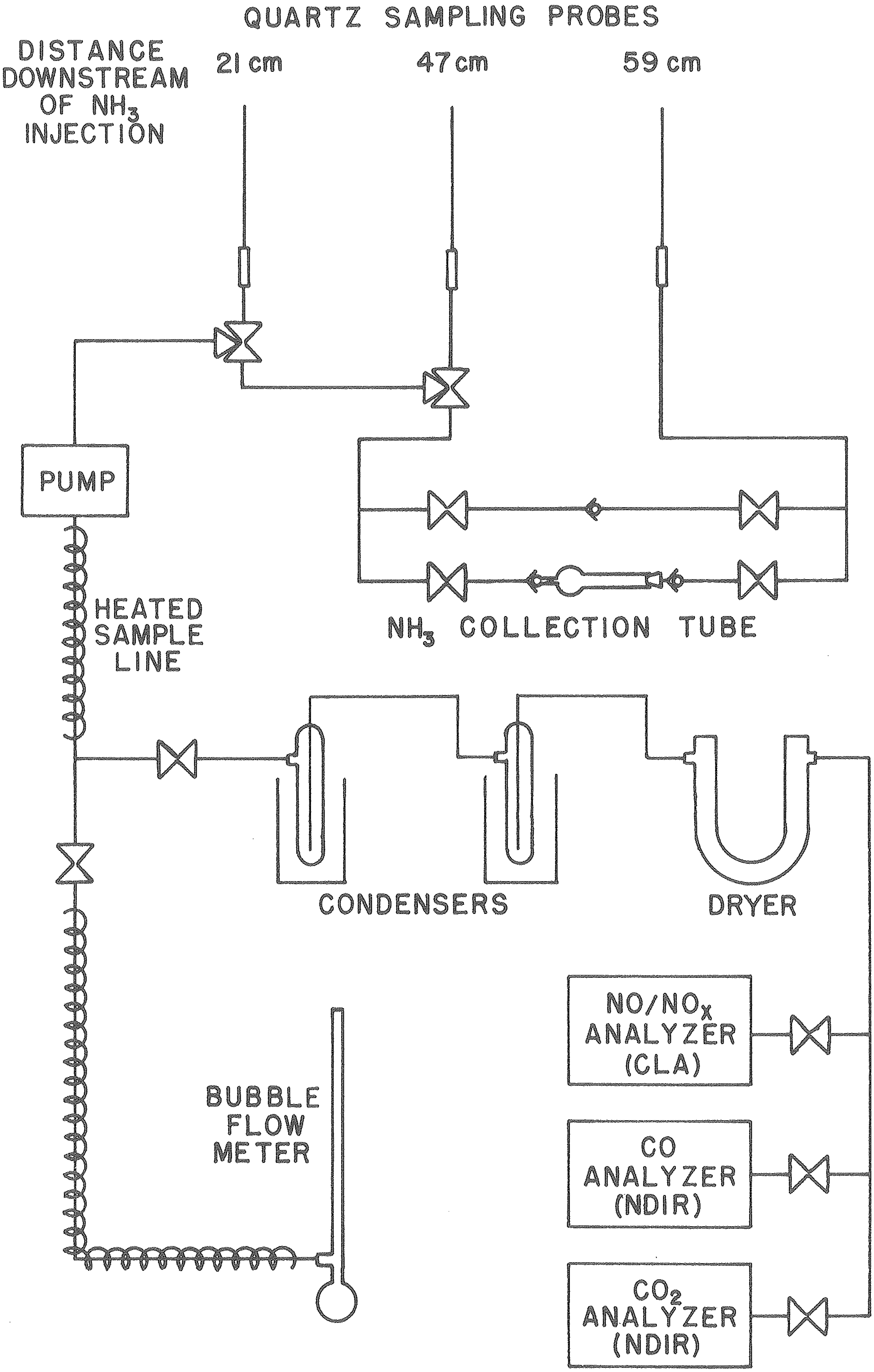

Figure 4. Schematic diagram of the sampling system and analytical train.

which were coated with a weak H_3PO_4 solution. The NH_3 passing through the collection tube adhered to the surface coating on the glass beads. Sample system valving downstream of the collection tube routed the sample gas to the bubble flow meter for measurement of sample gas volumetric flow rate. This measurement was required to determine the volume of sample gas routed through the collection tube. A bypass around the NH_3 collection tube was provided to allow for collection tube isolation. This arrangement facilitated accurate measurement of the sample volume and replacement of the NH_3 collection tube.

The volume of sample gas passing through the NH_3 collection tube was determined by measuring the total time of collection while simultaneously measuring the sample gas flow rate with a bubble flow meter. No attempt was made to correct the resulting total sample gas volume measurement for any H_2O removal that might have occurred when the sample passed through the collection tube.

After a measured volume of sample gas was passed through the collection tube, the tube was removed from the collection flowpath and washed with NH_3-free de-ionized H_2O to dissolve the collected NH_3 in an aqueous solution. Two washes of each collection tube were performed for the majority of the measurements reported here. The washes were accomplished by filling the collection tube with the de-ionized H_2O, agitating the tube and glass beads for one minute, soaking for four minutes and draining the resulting solution into a test tube.

The quantitative measurement of the dissolved NH_3 present in the collection tube wash water was determined using the sodium phenolate method.[11-14] The method was developed for our work by Newton.[15] Briefly, the dissolved NH_3 is chlorinated to chloramine, NH_2Cl, which is then reacted with sodium phenolate to form an indophenol dye of unknown structure. The optical density of this dye is measured using a Beckman Model DU Spectrophotometer operating at a wavelength of 632 nm. The concentration of NH_3 is determined by comparing the optical density of the sample to the optical density of a known standard. The sensitivity of the technique increases as the total sample gas volume passed through the collection tube increases. If 100 $m\ell$ of sample gas flows through the collection tube, the range of applicability of the technique is between 70 and 600 ppm. The possible interference of primary and secondary amines in the ammonia concentration measurement was evaluated by applying the sodium-phenolate method to solutions containing ethyl amine and dimethyl amine. Ethyl amine exhibited a molar extinction coefficient approximately 1/4 that of ammonia, while dimethyl amine produced no observable effect. Consequently, we expect a small interference from any primary amines present in the ammonia collection tube wash water, and no interference from secondary amines.

III. RESULTS

Radial and axial composition profiles have been determined in the test section of the combustion tunnel for lean, near stoichiometric, and rich mixtures. These data provide a framework for assessing the day-to-day reproducibility and combustion characteristics of the tunnel and the degree of mixing of the combustion product gases in the test section of the tunnel. The results of the studies of the selective reduction of NO by NH_3 are also presented and discussed. The NO reduction has been investigated as a function of initial NH_3 concentration, initial NO concentration, combustion product temperature at NH_3 injection, and the equivalence ratio, ϕ. During each run, NO concentrations were monitored at several test section probe stations, and NH_3 was measured at the final probe station located 59 cm downstream of the NH_3 injectors. Temperature, concentrations of CO and CO_2, and total NO_x were also monitored.

A significant and frequently mentioned parameter in the following paragraphs is the combustion product temperature at ammonia injection. To avoid any confustion which might result from abbreviating this description to "NH_3 injection temperature" or "injection temperature," the combustion product temperature at ammonia injection will hereafter be referred to as T* (Figure 1).

A. Combustor Performance

The desired temperature field at the point of the ammonia injection and in the test section of the combustion tunnel is achieved through the addition of an appropriate amount of secondary N_2 to the combustion product gas stream. The quantity of secondary

N_2 introduced is dependent upon the equivalence ratio, ϕ, and the desired value of T*. The amount of diluent added is expressed as a dilution factor, DF, where

$$DF = \frac{\text{number of moles of secondary } N_2 \text{ added per second}}{\text{number of moles of fuel and air added per second}}$$

Table I indicates the variation in DF for various experimental conditions. Concentrations of products of combustion must be corrected by these factors in order to compare them with values associated with normal fuel/air combustion at the same equivalence ratio.

Axial and radial temperature profiles were measured for several equivalence ratios to ascertain the temperature gradients in the combustor and to appraise reproducibility. A typical axial profile is shown in Figure 5 for an equivalence ratio of 0.98 and T* at 1245 K. Axial gradients were nearly linear at approximately 1 K/cm. Typical radial temperature profiles are shown in Figure 6, where the radial distance is measured from the combustor wall to the combustor centerline. The profiles shown were measured at an axial location 47 cm downstream of secondary N_2 injection (axial location A in Figure 1) for equivalence ratios of 0.8, 0.97, and 1.2 with temperatures at T* of 1170 K, 1245 K, and 1320 K. The plots exhibit a shape characteristic of steady-state turbulent pipe flow which demonstrates the well mixed nature of the combustion products downstream of secondary N_2 injection. Since it is necessary to stop the experiment and allow the test section to cool prior to adjusting the thermocouple radial position, the points plotted on the profiles correspond to different experimental runs. The smoothness of the resulting plots provides confidence in the ability of the apparatus to reproduce a desired experimental environment. A temperature decrease of 50 K occurs between the centerline and 3/4 of the distance between the

TABLE I

Dilution Factor for Various Combustor Operating Conditions

Equivalence Ratio	T*(K)	Dilution Factor
0.80	1170	0.38-0.51
	1245	0.35-0.40
	1320	0.21-0.23
0.87	1170	0.66
	1245	0.48
	1320	0.35-0.37
0.98	1170	0.77-0.90
	1245	0.61-0.67
	1320	0.47-0.48
1.2	1170	0.73-0.82
	1245	0.55-0.69
	1320	0.47

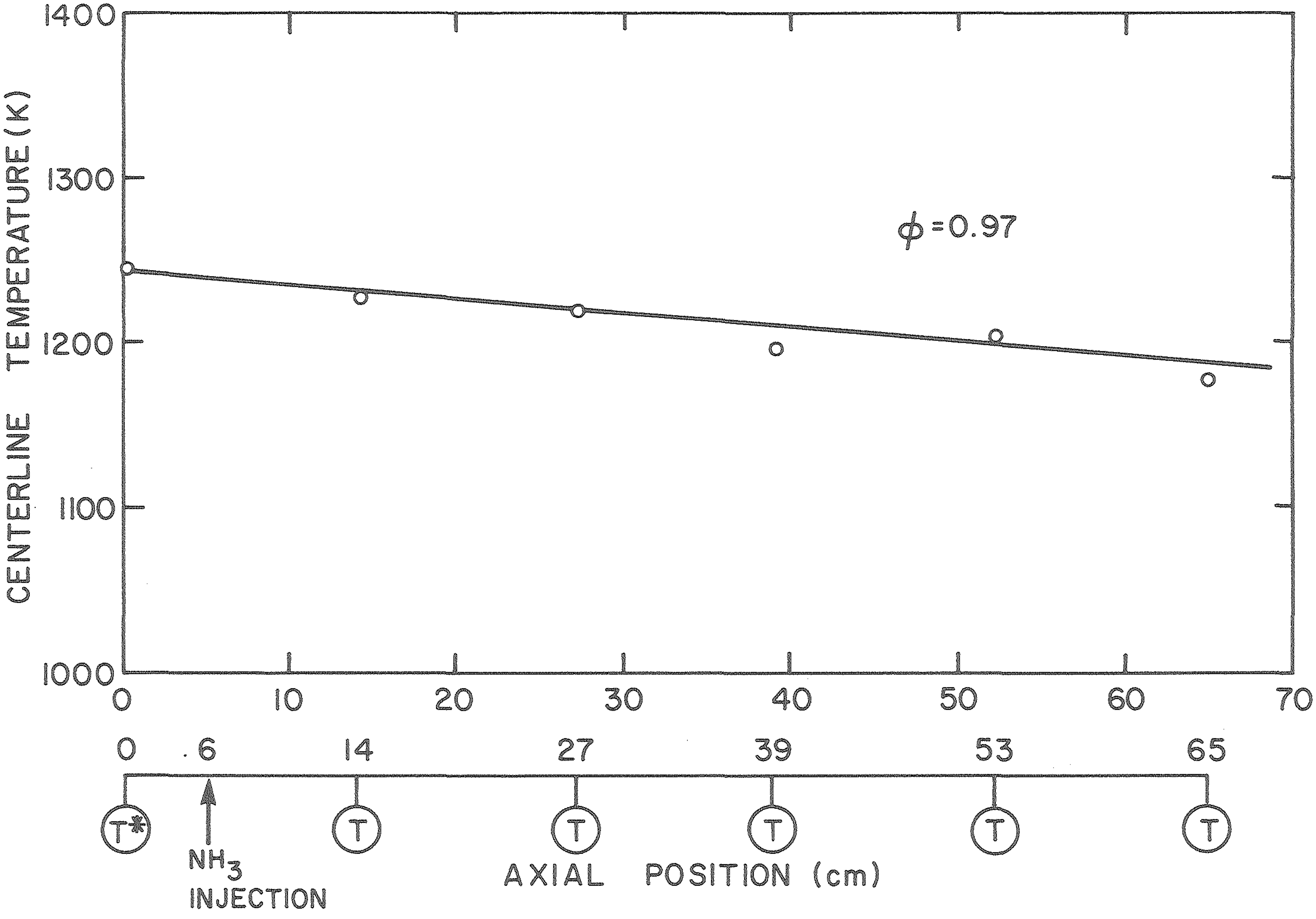

Figure 5. Combustion effluent temperature (K) measured along the combustor test section centerline as a function of axial distance (cm) for an equivalence ratio of ϕ = 0.97 and T* = 1245 K. The axial reference is the T* thermocouple.

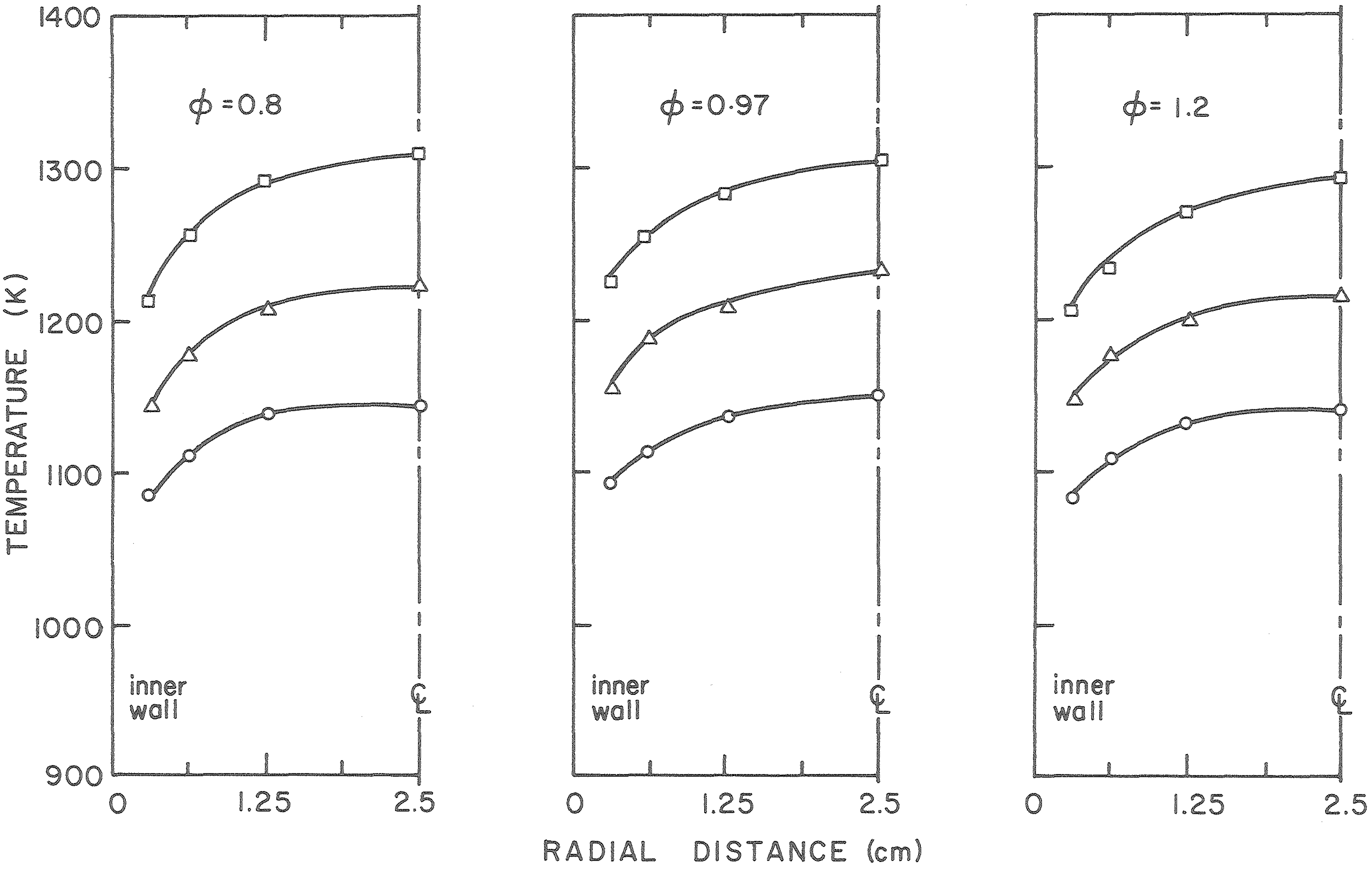

Figure 6. Combustion effluent temperature (K) as a function of radial distance (cm) at an axial position 47 cm downstram of secondary N_2 injection for an equivalence ratio of φ = 0.8, 0.97, 1.2 and T* = 1320 K (□), 1245 (Δ), 1170 K (o).

centerline and wall, and is independent of the dilution factor and equivalence ratio. Larger radial temperature gradients exist in the region very close to the combustor wall.

Radial and axial profiles were measured for CO, CO_2, NO and NO_x for various equivalence ratios and T* values. For the species considered, no appreciable radial or axial gradients were observed. This indicated that mixing of the diluent was satisfactory and that combustion was completed prior to the test section. Figure 7 is a centerline profile for CO_2 at an equivalence ratio of 0.98. This equivalence ratio was the most difficult case investigated, since it was at the interface between fuel lean and rich mixtures. Estimated errors in flow metering with rotameters were on the order of 5 percent, and the maximum and opposite error in the fuel and oxidizer rotameter could alter the equivalence ratio by ± 0.1. The data plotted in this figure were obtained from ten separate experiments performed over a two week period. The average values of CO_2 are indicated by circles in the plot and the percent standard deviations at various probe stations were in the range of 6 to 7 percent. This profile indicates a slight increase in the CO_2 concentration through the test section. Measurements of CO concentrations were higher than calculated equilibrium values at 1245 K and indicated that the CO to CO_2 conversion was not fully equilibrated after cooling the combustion gases via nitrogen dilution.

Thermal NO concentration was measured as a function of equivalence ratio at various radial and axial locations in the test section. No significant dependence of NO concentration on either radial or axial position was observed for the fuel lean and stoichiometric mixtures; however, a slight decrease in NO concentration was noted for the fuel-rich mixture, since NO continues to undergo reduction in the fuel-rich environment.

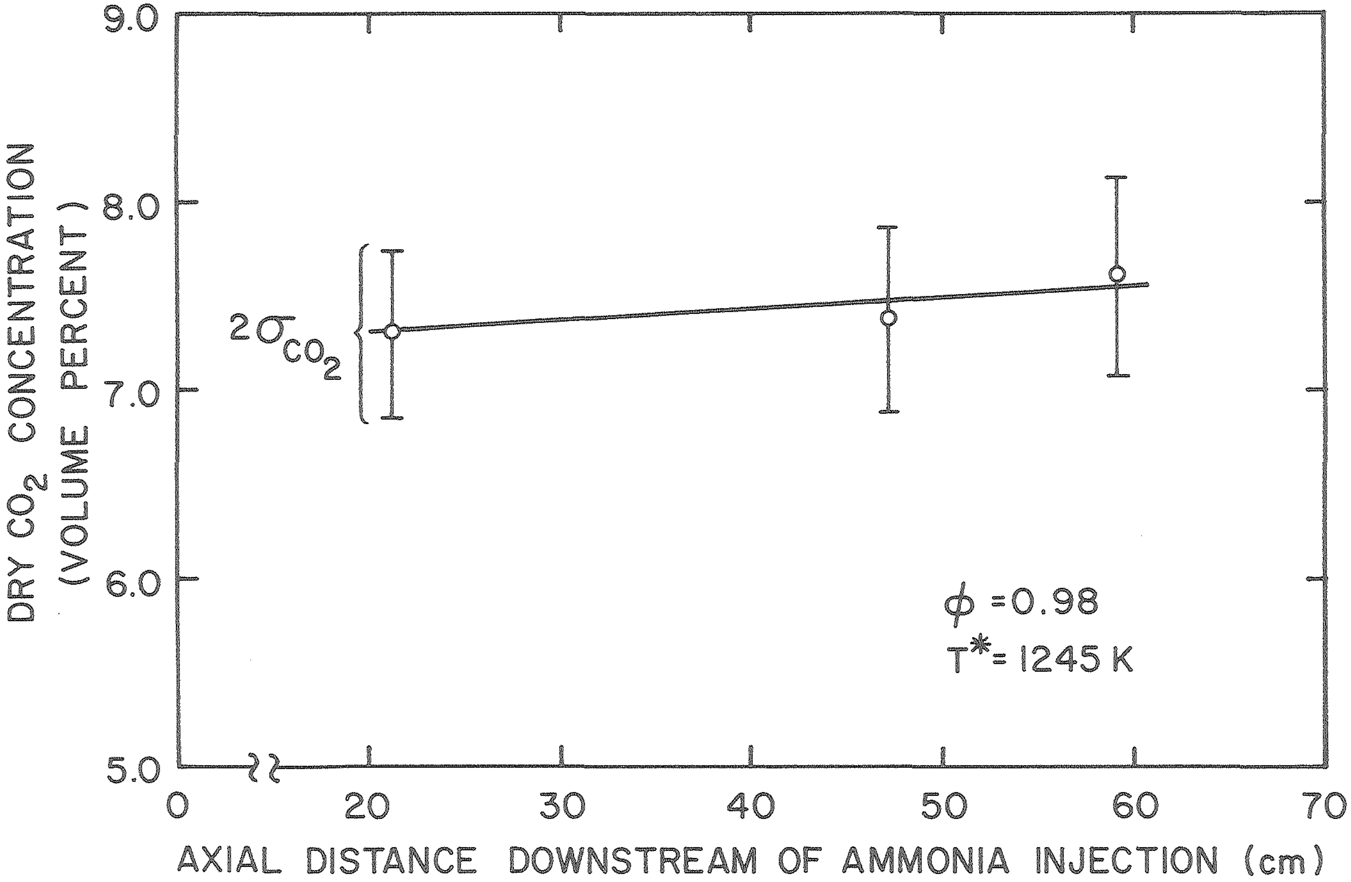

Figure 7. Dry CO_2 concentration (volume percent) as a function of axial distance (cm) downstream of NH_3 injection along the combustion tunnel centerline. The equivalence ratio $\phi = 0.98$, $T^* = 1245$ K, and σ_{CO_2} is the standard deviation in the CO_2 concentration measurements at the particular axial location.

The measured NO concentrations are reasonable and show the correct dependence on equivalence ratio. It is of interest to note that, prior to the addition of NH_3, measurements were made in the NO_x mode of the analyzer. The NO and NO_x measurements are identical within experimental error, thus indicating the unimportance of probe effects.

B. Characterization of NH_3 Mixing

A reliable characterization of the selective reduction of NO through NH_3 addition requires that the injected NH_3 be rapidly and homogeneously mixed into the combustion gases prior to the first probe station. Earlier experiments indicated that NO destruction through the flame zone of lean flames was less than 4.0 percent. Concentrations of NO were metered in at the preflameholder position to achieve concentrations of approximately 500 ppm at the terminal probe station. Measurements indicated that centerline axial profiles in the test section under these conditions were uniform for lean and near stoichiometric mixtures. Identical flows of NO/N_2 were then introduced through NH_3 injectors and axial profiles were then measured at three probe stations throughout the test section. Results of the measurements are shown in Table II. The first row in the table indicates that axial centerline profiles were uniform, thus indicating that rapid mixing occurs prior to the first probe station. To further investigate mixing, a series of experiments were performed whereby the first probe was positioned on the centerline, 21 cm from the NH_3 injectors, and two probes at different axial locations were positioned at a radial distance between the wall and centerline. While the agreement among the three measurements is not quite as good as that among the three centerline measurements, it is quite satisfactory. The agreement between any two measurements at a given radial position but different axial positions is

TABLE II

NH_3 System Mixing Characteristics, Nitric Oxide Concentrations At Various Locations, in ppm

Axial Distance Downstream of NH_3 Injectors		
21 cm	47 cm	59 cm
490 (CL)	482 (CL)	487 (CL)
490 (CL)	522 (CL+½)	517 (CL+½)
480 (CL)	510 (CL+¾)	502 (CL+¾)
482 (CL)	522 (CL+⅞)	517 (CL+⅞)

Operating Conditions: ϕ = 0.80, T* = 1245 K and velocity in test section approximately 25 m/sec. Radial positions are indicated in parenthesis. The centerline position is indicated by CL and fraction indicates, fractional distance between wall and centerline.

within two percent. The mixing ability of the NH_3 injectors tested by the mixing of NO was thus satisfactory.

This procedure was used routinely to check mixing. It is important to note that the method was extremely sensitive to detecting malfunctions in the injectors. Grossly non-uniform profiles resulted when an injector was broken or when injectors were improperly oriented.

C. The Reduction of NO by NH_3

Tables III through VI summarize the results of our investigation of the selective reduction of NO through addition of NH_3 to the post combustion gases of propane/air/nitrogen mixtures. The combustion product temperature, T*, listed in the tables was measured at a location 5 cm upstream of NH_3 injection. It is important to note that the T* value represents the maximum value of the temperature. If one considers centerline axial temperature gradients, a reasonable estimate of the temperature at the final probe station is 60 K less than the T* value. The three addition temperatures considered in this study were 1170, 1245 and 1320 K.

It is important to discuss the meaning of the term <u>initial NO</u> concentration since there is much confusion regarding this term in the literature. There are two sources of NO in this system: one is the result of admixing a prototype fuel nitrogen compound to the fuel and oxidizer, and the other is the thermal NO formed during the combustion process. The prototype fuel nitrogen compound used in all cases was NO. Appropriate quantities of NO were added to the fuel and oxidizer to yield either 250 or 500 ppm at the final probe station, D. Axial profiles of NO were then measured throughout the test section, prior to the addition of NH_3. These measured profiles were uniform for lean and near stoichio-

TABLE III

Summary of NO Survival Measurements with an Initial NO Concentration of 250 ppm.

Equivalence Ratio, ϕ	T* (K)	β	[NO] at 21cm	[NO] at 47cm	[NO] at 59cm	R_x	NO Survival (percent)
0.98	1170	0.5	180	175	175	c	70
		1.0	140	117	110	c	44
		2.0	117	75	67	c	27
	1245	1.0	120	117	115	c	46
		1.5	81	55	48	c	19
		2.0	70	42	52	c	13
	1320	0.5	175	182	180	c	72
		1.0	122	101	98	c	39
		2.0	78	56	49	c	22
1.0	1245	0.5	195	185	185	c	74
		1.0	155	145	145	c	58
		2.0	142	137	135	c	54

All concentrations are in ppm.

TABLE IV

Summary of Selective Reduction of NO Data for $\phi = 0.87$ and an Initial NO Concentration of 500 ppm

T*	β	[NO] at 21 cm	[NO] at 47 cm	[NO] at 59 cm	R_x	NO Survival (percent)	Average Survival (percent)	High $[NH_3]$	Low $[NH_3]$	Average $[NH_3]$
1170	0.5	318	287	284	c	57	57	38	31	35
	1.0	256	204	188	c	38	38	226	198	212
	1.5	223	162	159	c	32	32	416	400	408
	2.0	208	163	150	c	30	30	967	620	794
1245	0.5	378	365	360	c	72	72			i
	1.0	338	304	297	c	59	59			i
	1.5	258	207	188	c	38	38	50	45	47
	2.0	213	145	138	c	28	28	95	68	82
1320	0.5	450	430	445	c	89				i
		450	437	445	c	89	91			i
		460	461	467	c	93				i
		470	465	472	c	94				i
	1.0	458	420	419	c	84				i
		436	415	415	c	83	88			i
		482	457	477	c	95				i
		457	437	457	c	91				i
	1.5	415	380	375	c	75				i
		452	432	430	c	86	81			i
		447	422	407	c	81				i
	2.0	413	372	362	c	72				i
		462	440	420	c	84	79			i
		452	407	403	c	81				i

All concentrations are in ppm.

TABLE V

Summary of Selective Reduction of NO Data for $\phi = 0.98$ at an Initial NO Concentration of 500 ppm.

T*	β	[NO] at 21 cm	[NO] at 47 cm	[NO] at 59 cm	R_x	NO Survival (percent)	Average Survival (percent)	High $[NH_3]$	Low $[NH_3]$	Average $[NH_3]$
1170	0.5	330	294	290	c	58	58			50
	1.0	270	180	147	nc	29		161	126	143
	1.5	252	184	164	c	33	33	648	326	87
	2.0	245	205	200	c	39	39	981	494	738
1245	0.5	313	282	290	c	58	63			i
		317	342	342	c	68				i
	1.0	239	168	161	c	32		159	148	154
		185	137	135	c	27	31			
		180	175	177	c	35				
	1.5	207	143	141	c	28	21			
		145	81	70	c	14		565	350	457
	2.0	172	98	97	c	19		521	456	489
		145		53	c	11	15			
1320	0.5	377	361	374	c	75				i
		417	401	399	c	80	77			i
	1.0	292	263	266	c	53	60			i
		365	341	329	c	66				i
	1.5	235	158	163	c	33				i
		338	293	293	c	59	46			i
	2.0	168	102	115	c	23		169	76	122
		294	259	245	c	49	36	<70	<70	<70

All concentrations in ppm.

TABLE VI

Summary of Selective Reduction of NO Data for $\phi = 1.2$ at an Initial NO Concentration of 500 ppm

T*	β	[NO] at 21 cm	[NO] at 47 cm	[NO] at 59 cm	R_x	NO Survival (percent)	High $[NH_3]$	Low $[NH_3]$	Average $[NH_3]$
1245	0.82	525	490	475	c	95	761	353	557
	1.6	543	505	485	c	97	1115	916	1016
	2.5	535	500	480	c	96	1673	1386	1530
	3.3	535	500	478	nc	98	2002	1184	1590

All concentrations are in ppm.

metric mixtures and indicated that no decomposition of the NO occurred throughout the test section. The case of rich combustion will be discussed separately.

In order to determine the quantity of NH_3 to add through the NH_3 injectors, it was important to investigate NO decomposition across the flame zone, since the amount of NH_3 added was related to the concentration of NO in the test section. A set of experiments was performed to ascertain the fraction of NO decomposing during combustion. These experiments were conducted at a T* value of 1245 K. Lean, near-stoichiometric and rich mixtures were considered. Appropriate quantities of NO were added through the N_2 injectors to give approximately 500 ppm NO at the probe station located 20 cm downstream of the NH_3 injectors. Axial profiles were then measured throughout the test section. The profiles were uniform for lean and near-stoichiometric mixtures, thus indicating that NO was not undergoing decomposition in the test section. A slight decrease of NO concentration with distance was noted for the rich mixture. Next, an identical flow of NO was metered in at the preflameholder position rather than at the N_2 injectors, and the profiles were again measured in the test section. The amount of NO decomposition through the combustion zone could then be determined by taking ratios of the concentration obtained at each probe station for the two methods of addition. The results are shown in Table VII. The survival of NO across the flame is 96% for the lean flame, 82% for the near stoichiometric flame, and 74% for the rich flame.

For lean and near stoichiometric flames, the amount of NH_3 to be added to the combustion product steam was determined through a three-step procedure. First, the centerline thermal NO concentration profile was

TABLE VII

Survival of NO Across the Flame

Probe Position	ϕ	Thermal* NO (ppm)	$[NO]^{(1)}$	$[NO]^{(2)}$	NO Survival (percent)
21 cm	0.8	18	530	510	96
34 cm		17	525	510	97
47 cm		19	530	510	96
21 cm	near stoichiometric	60	515	425	83
34 cm		61	510	420	82
47 cm		54	515	413	80
21 cm	1.2	24	485	360	74
34 cm		23	485	360	74
47 cm		21	455	340	75

*dilution not accounted for.

(1) Concentration of NO in ppm from addition at the N_2 injectors.

(2) Concentrations of NO in ppm from addition at the preflameholder inlet.

measured to provide the background NO level. Secondly, the prototype fuel nitrogen compound NO was introduced through the N_2 injectors at a flow rate which provided an NO concentration of 500 ppm at the terminal probe station. Using the information from these first two steps, the molar flowrate of NO was then determined which corresponded to this uniform, centerline NO profile. The final step involved calculating the NH_3 rotameter setting necessary to inject a desired quantity of NH_3 and achieve a desired ratio of NH_3 to NO molecules. Prior to injecting the NH_3, however, the NO addition location was changed from the N_2 injection plane to a position upstream of the flameholder, and the NO flowrate was again adjusted to produce 500 ppm at the terminal probe station. The NH_3 was then introduced through the NH_3 injection system at the previously calculated rotameter setting to produce the desired ratio of NH_3 to NO in the combustion effluent. This technique of determining the quantity of NH_3 to be injected minimizes the errors resulting from the thermal NO level as well as from the NO decomposition which occured across the flamefront. The parameter β is used to designate the number of moles of NH_3 added through the NH_3 injectors and is defined as

$$\beta = \frac{\left[NH_3{}^{i}\right]}{\left[NO^{i}\right]}$$

where the superscript i designates initial values in the test section prior to reduction.

The probe stations at which composition measurements were performed are designated by the distance from the NH_3 injectors to the particular probe station. The NO-NH_3 reduction reaction is defined as complete (c) when the NO concentration at the final two probe stations (C and D, see Figure 1) are within 20 ppm, otherwise the reaction is not complete (nc). Concentrations of NO in ppm are determined at three different probe stations. The percentage NO survival is the molar ratio of the NO present at the terminal probe station to the NO present there prior to NH_3 addition, multiplied by one hundred.

The NH_3 concentrations listed in the table were measured at the terminal probe station. Collections were repeated twice and average values are tabulated. The symbol (i) in the column associated with the average NH_3 designates an indeterminate concentration of NH_3 which is less than 100 ppm. Measurements of NH_3 for the cases where the concentration was indeterminate resulted from NH_3 sample solutions with optical densities less than 0.1 on the first and subsequent washings. In order to quantify these concentrations, larger sample volumes should be collected. The measurement of NH_3 was extremely difficult and there were many potential sources of error such as:

1) erroneous measurement of the sample volumetric flow rate;
2) leaks in the NH_3 collection lines;
3) failure to wash the NH_3 completely from the glass beads and non-quantitative transfer of the sample;
4) measurement of the optical density in a range where deviations from Beer-Lambert Law were found.

Every attempt was made to minimize the errors; however, it was impossible to eliminate them entirely.

For each experiment listed in the Tables III through VI, measurements at each probe station were taken in sequential order, and the measurements were then repeated at least once. The average of the measured NO concentrations are reported in Tables III through VI. Variations in measured concentrations for a single experiment were on the order of three percent.

An inherent source of error which effects achieving day-to-day reproducibility is associated with flow metering. The error in flow metering with rotameters is approximately five percent and this manifests itself in the determination of equivalence ratio which in turn effects the amount of excess oxygen present for the selective reduction of NO. It is important to recognize that the maximum error in any of the reported equivalence ratios is ± 0.1. This has a most serious effect on the near stoichiometric mixture of equivalence ratio 0.98 since consideration of the error implies that this mixture can, in fact, be either fuel lean, stoichiometric or fuel-rich.

Measurements of the NO_x concentration along the combustor test section axis differed from the measured NO concentrations by 20 ppm at most for the lean and near stoichiometric case. These differences should have been greater and proportional to the axial decay in the NH_3 concentration as the NO - NH_3 reduction process proceeded. The absence of the expected axial variation in the NO_x measurement most likely resulted from the adsorption of NH_3 in the NO sample manifold.

Examination of Tables III through VI reveals that NO survival is in the range from 91 to 13 percent for the cases investigated. Estimated velocities in the test section were between 24 and 31 m/sec and these correspond to residence times on the order of 20 milliseconds. These velocities were fast enough to monitor reaction progress.

C1. Reduction in Lean Mixtures

The data associated with $\phi = 0.87$ are listed in Table III. Reproducibility was checked by performing multiple experiments at T* values of 1320 K for the four values of β. The maximum deviation of the percent NO survival from the mean value occurred for $\beta = 1.0$ and was seven percent. The agreement among multiple measurements is, however, satisfactory, but could be improved with better precision in flow metering.

Figure 8 is a plot of NO survival versus β for three values of T*. Examination of the figure reveals that the survival of NO is inversely proportional to β for the three temperatures. Optimum reductions occurred at T* = 1170 K for a given value of β and were least at 1320 K where survival was greater than 79 percent. The survival of NO is quite similar for $\beta > 1.0$ at the temperatures 1170 and 1245 K.

Ammonia concentrations increased with β and were largest at T* = 1170 K. The concentrations of NH_3 at T* = 1320 K were less than 100 ppm for all values of β. It appears that the excess NH_3 which is not used to reduce the NO is emitted directly in the exhaust gas at T* = 1170 K, while at T* = 1320 K, a significant portion of the NH_3 is likely to be oxidized to NO. The latter speculation is consistent with both the high survival of NO and the low NH_3 emissions determined at 1320 K. Ammonia emissions also increased for $\beta > 1.0$ for T = 1245 K. At 1245 K, the NH_3 oxidation is slower than at 1320 K and is thus less competitive with the reduction of NO. Consequently, the reduction of NO is greater at 1245 K than at 1320 K and the NH_3 oxidation at this temperature is incomplete and NH_3 breakthrough is observed.

The equivalence ratio 0.87 corresponds to an excess oxygen concentration of approximately three percent in the product gases prior to dilution by N_2. It is thus appropriate to compare the results of the selective

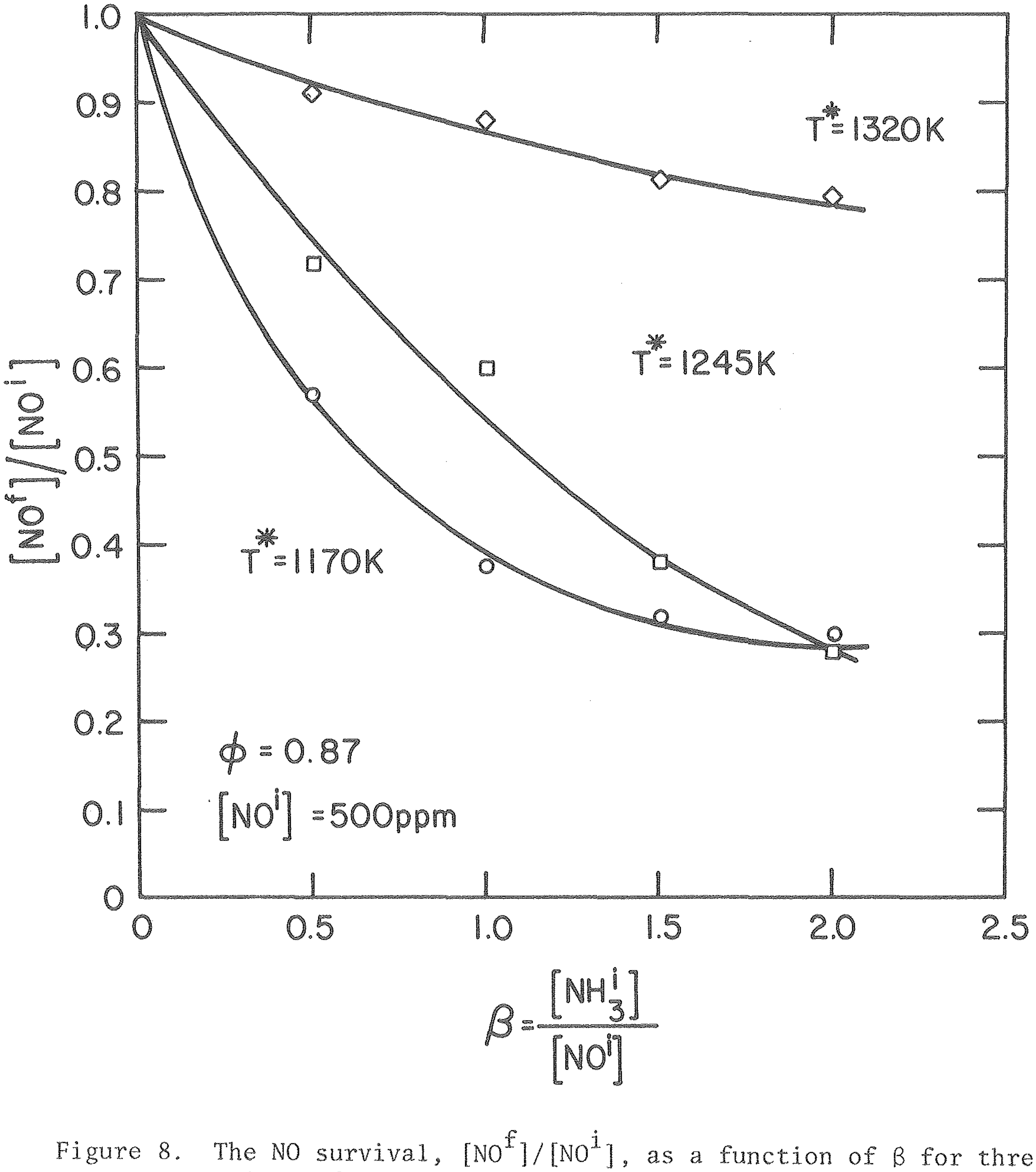

Figure 8. The NO survival, $[NO^f]/[NO^i]$, as a function of β for three values of T*. The initial concentration of NO is 500 ppm and the equivalence ratio $\phi = 0.87$. $[NO^f]$ and $[NO^i]$ signify the final and initial NO concentrations respectively.

reduction studies at this equivalence ratio with the results of Muzio, et al[6], who investigated the reduction of NO at two and four percent excess oxygen in the product gases of methane/air combustion.

Muzio et al[6] report optimum reductions of NO occur at temperatures of 1240 K and that NO survival is approximately five percent for $\beta = 2.0$ In addition, they find that NO survival is approximately 30 percent for a temperature of 1140 K and $\beta = 2.0$. In contrast, our results indicate optimum reduction at $T^* = 1170$ K and NO survival values of 30 percent for $\beta = 2.0$ at temperatures of 1170 and 1245 K. Our measured NO survival values are in agreement with those of Muzio et al[6] at $T^* = 1320$ K, and our conclusions regarding the dependence of NH_3 emissions on addition temperature and the dependence of NO survival on β are also in agreement.

The lack of agreement regarding the optimum temperature and NO survival at the optimum temperature may reflect the great sensitivity of the selective reduction to operating parameters. The addition temperatures of Muzio et al[6] are somewhat different from ours, and the axial temperature gradients in their system are a factor 1.7 greater than ours. The residence time of product gases in their combustion tunnel was a factor of thirty greater than ours and slight decreases in NO concentrations are indicated on their concentration/time profiles measured for $\beta = 2.0$ at 1240 K, which may indicate that reduction was incomplete in our system.

C2. Reduction in Near Stoichiometric Mixtures

The study of the selective reduction of NO by NH_3 at near stoichiometric equivalence ratios was the most difficult case investigated since small errors in the flow rates of fuel and air could transform the product gases from a mildly oxidizing to a mildly reducing environment. These results are summarized in Tables III and V. Reproducibility was assessed at the addition temperatures 1245 and 1320 K. At a temperature of 1245 K, deviations from the average NO survival were less than seven percent; however there was a factor of two difference in NO survival for duplicate measurements for $\beta > 1.0$. Reproducibility was less satisfactory for $\beta > 1.0$ at 1320 K where deviations from the mean NO survival were on the order of 13 percent and NO survival for duplicate measurements varied by approximately a factor of two. We believe that the magnitude of the errors for $\beta > 1.0$ are indicative of the sensitivity of the selective reduction reactions to excess oxygen concentrations.

Figure 9 is a plot of NO survival versus β at the three addition temperatures for an equivalence ratio of 0.98 and an initial NO concentration of 500 ppm. The dependence of the NO survival with respect to β at 1170 K for 500 ppm initial NO concentration was anomalous. Measurements at all other conditions, and in particular, experiments performed on the near stoichiometric mixtures at 1170 K with an initial NO concentration of 250 ppm indicate that NO survival is inversely dependent upon β. The survival of NO was least at $T^* = 1245$ K for $\beta > 1.0$ as seen in Figure 9, and this is in agreement with the results summarized in Table III for similar experiments conducted with initial NO concentrations of 250 ppm.

It is of interest to examine the effect of initial NO concentration on the survival of NO at the different values of β for the three additional temperatures. The NO survival was less for $\beta < 2.0$ for the temperatures 1170 and 1245 K for the experiments with higher initial concentrations of NO, but was greater for the higher initial NO concentration of 500 ppm at 1320 K where there is a competition between the NH_3/NO reduction reactions and NH_3 oxidation reactions.

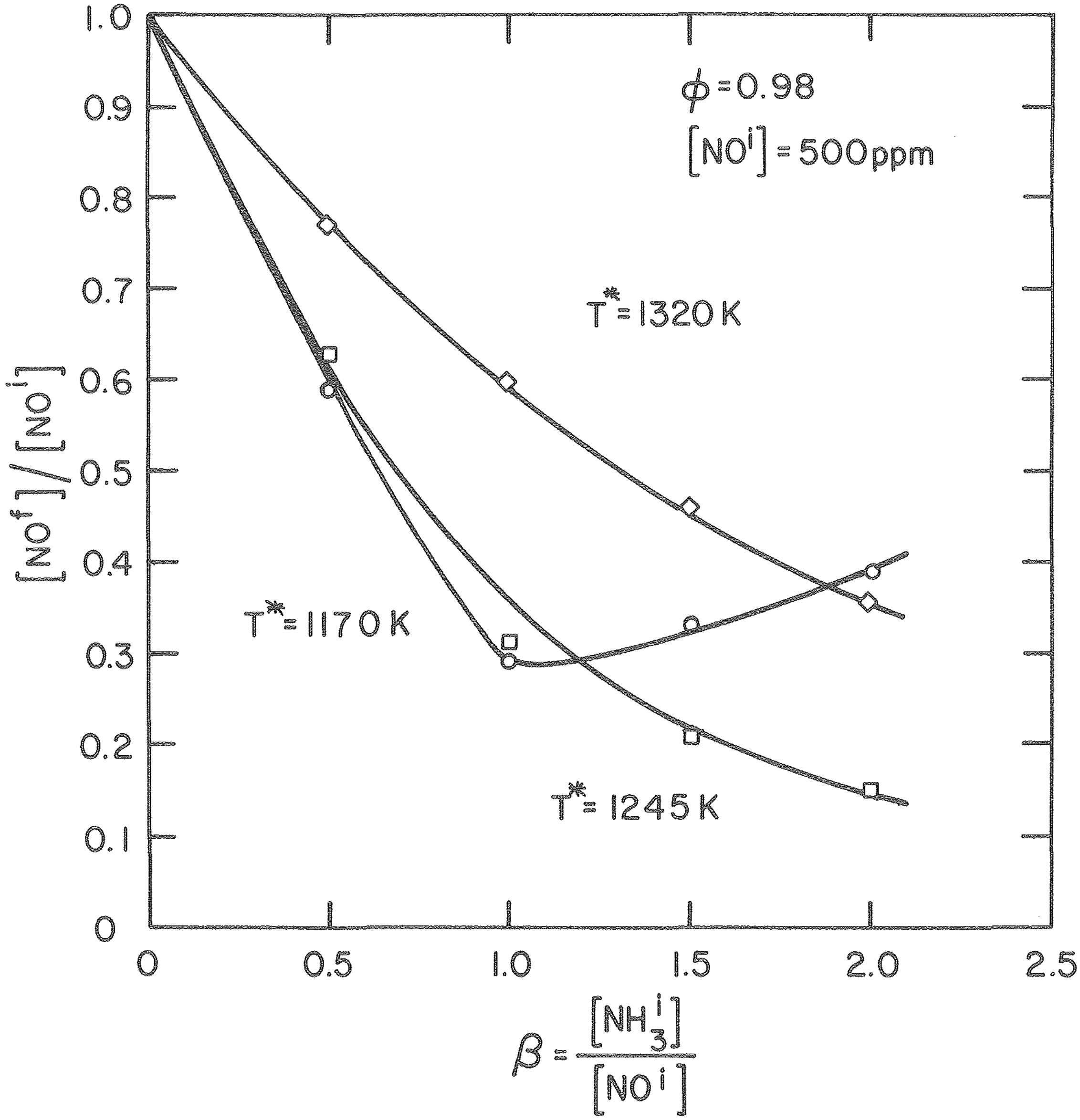

Figure 9. The NO survival, $[NO^f]/[NO^i]$, as a function of β for three values of T^*. The initial concentration of NO is 500 ppm and equivalence ratio $\phi = 0.98$. $[NO^f]$ and $[NO^i]$ signify the final and initial NO concentrations respectively.

It is also important to consider the effect of excess oxygen concentration on the selective reduction process. This effect is illustrated in Figures 10 and 11 where NO survival is plotted versus β for equivalence ratios 0.87 and 0.98 for the addition temperatures 1245 and 1320 K, respectively. The survival of NO is seen to be inversely related to excess oxygen concentration. The survival of NO at 1170 K for the two equivalence ratios was very similar for each value of β. These results are somewhat puzzling when they are compared with results derived from our studies on rich mixtures. If one refers to data given in Table III for the equivalence ratios 0.98 and 1.0, there is an apparent contradiction since NO survival was greatest for the 1.0 mixtures. While there are errors in determining the accurate value of equivalence ratio, the preliminary data associated with measurements of CO, CO_2 and thermal NO, indicates that the 1.0 mixtures were slightly on the rich side of stoichiometric and the 0.98 mixtures were slightly lean. This apparent contradiction will be discussed subsequently. Future characterization measurements of the selective reduction will include a determination of the excess oxygen concentration in the test section. The oxygen concentration will be measured with gas chromatography, and the analysis procedure has been developed and characterized.

The NH_3 concentration measured at the terminal probe station for mixtures of equivalence ratio 0.98 agree qualitatively with those determined for the lean mixture of equivalence ratio 0.87. Ammonia emissions increase with β and are greatest at the lowest addition temperature where the net rate of NH_3 oxidation is much slower than the selective reduction reactions. It is important to recognize that there are errors in the measurement of NH_3 and in the concentration of NH_3

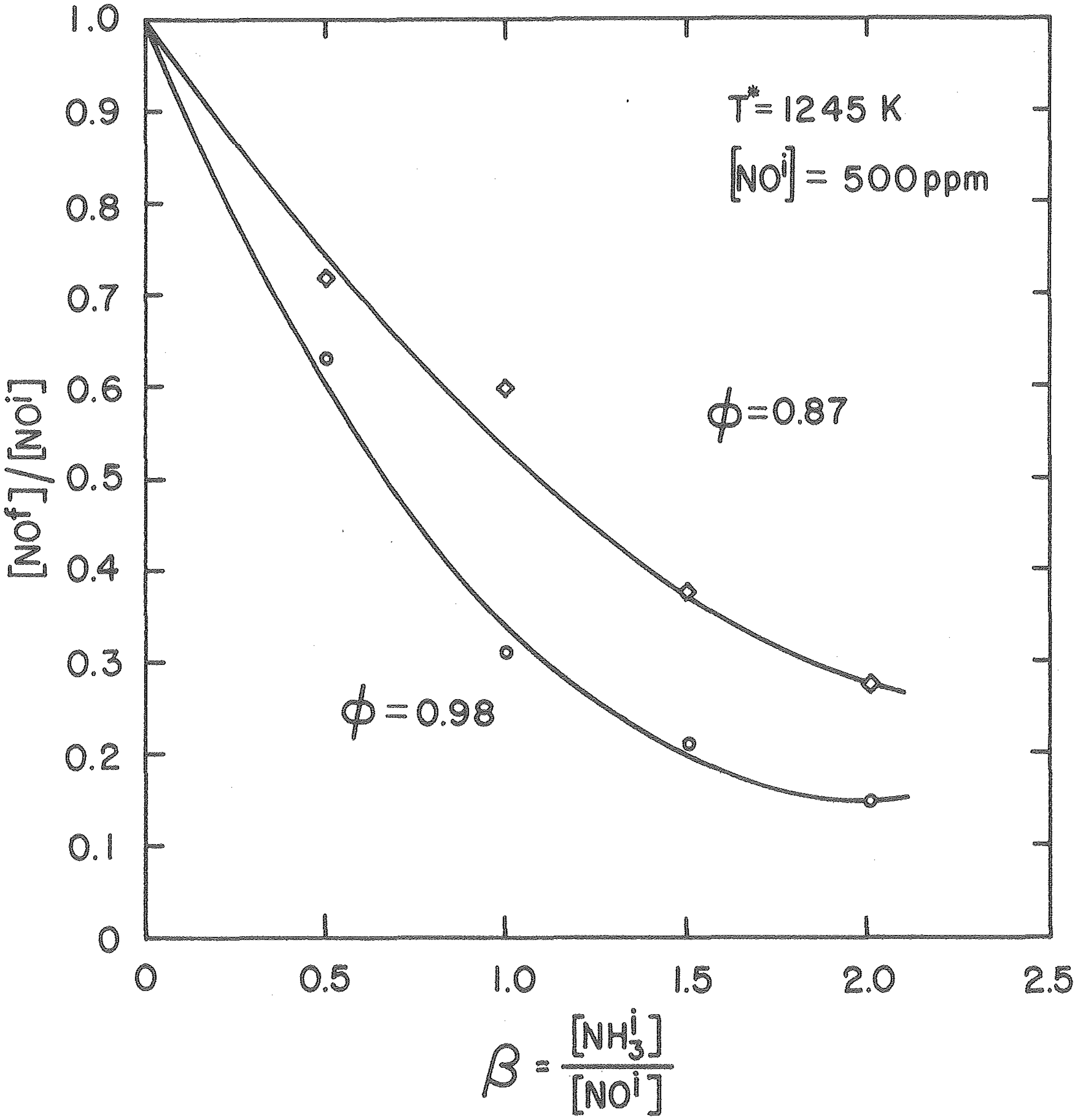

Figure 10. The NO survival, $[NO^f]/[NO^i]$, as a function of β for $T^* = 1245$ K at equivalence ratios of $\phi = 0.87$ and 0.98. The initial NO concentration is 500 ppm. $[NO^f]$ and $[NO^i]$ signify the final and initial NO concentrations respectively.

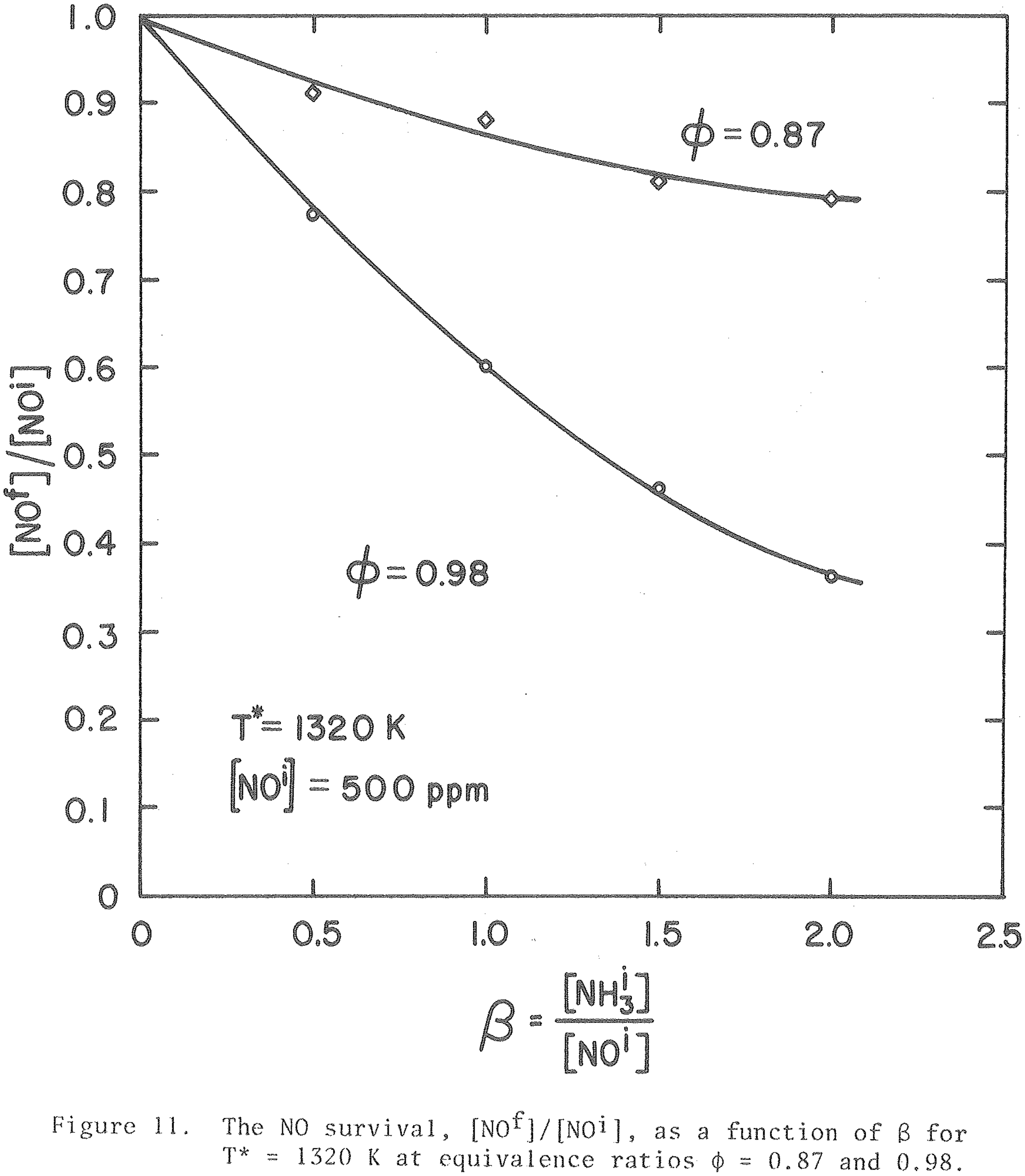

Figure 11. The NO survival, $[NO^f]/[NO^i]$, as a function of β for $T^* = 1320$ K at equivalence ratios $\phi = 0.87$ and 0.98. The initial NO concentration is 500 ppm. $[NO^f]$ and $[NO^i]$ signify the final and initial NO concentrations respectively.

mixed in at the injectors. It does appear, however, that the NH_3 not involved in the selective reduction of NO at 1170 K is likely to be entirely emitted in the exhaust. The NH_3 emissions measured for the near stoichiometric mixture at 1245 K are greater than those for lean mixtures. Ammonia concentrations of approximately 100 ppm were determined for $\beta = 2.0$ at 1320 K. The NH_3 oxidation reactions appeared to be somewhat less competitive with the selective NO reduction reactions at 1320 K for the 0.98 mixtures than the previously discussed mixtures of equivalence ratio 0.87.

The selective reduction is dependent upon the presence of excess oxygen; however, if there is an abundance of excess oxygen, the oxidation of NH_3 is competitive with the reduction of NO at 1245 and 1320 K. There are two observations which support the unimportance of NH_3 oxidation at 1170 K. First, large concentrations of NH_3 are emitted in the exhaust gas for experiments conducted at 1170 K, and these emissions correlate well with the difference in the initial NH_3 concentration and the NH_3 consumed in the reduction of NO. Second, NO survival is nearly identical at 1170 K for the two equivalence ratios 0.87 and 0.98. At the higher addition temperatures, provided that excess oxygen is present, NO survival is greater at the equivalence ratio 0.87 than at 0.98, and NH_3 emissions are also less at the lower equivalence ratio. It appears that the NH_3 oxidation is more competitive at the lower equivalence ratio, 0.87. In contrast, when one compares the 0.98 and slightly richer mixture, NO survival is greater since there is a deficiency of excess oxygen present.

C3. Reduction in Rich Mixtures

The reduction of NO by NH_3 was also investigated for an equivalence ratio of 1.2 at an addition temperature of 1245 K and the data are listed in Table VI. The initial NH_3 concentration was determined differently for the rich mixture and the parameter β represents the ratio of number of molecules of NH_3 admixed through the NH_3 injectors to the number of molecules of NO present there.

The reducing environment of the fuel rich combustion products reduced NO added at the preflameholder inlet. Although a major portion of the NO reduction occurred in the combustion process, reduction continued in the test section. Axial concentration profiles of NO measured along the centerline were not uniform since NO concentrations decreased with distance. Consequently the proper quantity of NH_3 required to achieve a particular value of β was not directly proportional to the NO concentration of 500 ppm measured at the terminal probe station. In order to determine the concentration of NO present at the NH_3 injectors, NO was introduced through the N_2 injectors and centerline axial profiles of NO were measured in the test section. The decay of NO concentration exhibited an exponential dependence on distance, hence an extrapolation utilizing measured concentrations could be used to determine the NO concentration at the NH_3 injectors. The concentration of NO at the NH_3 injectors calculated from extrapolation was 615 ppm, and this was used to determine β.

The data in Table VI indicate that there is no significant reduction of NO by NH_3 in mixtures of equivalence ratio 1.2. Concentrations of NO are measured at the probe station located 59 cm from the NH_3 injectors in the presence and in the absence of NH_3. The survival of NO, determined by computing the ratios of these NO concentrations, is approximately 96 percent and is independent of β.

Ammonia concentrations were determined by collecting samples at the terminal probe station. Duplicate collections were performed, and each sample was washed five times to insure complete transfer of the ammonia. Agreement between duplicate measurements of NH_3 is satisfactory for two values of β, and duplicate measurements for the other two values of β differ by a factor of two. It does appear that a significant fraction of the initial NH_3 is emitted directly in the exhaust. This experiment will be repeated to resolve the discrepancies in the NH_3 measurements. Product gases will also be analyzed with a gas chromatograph/mass spectrometer to determine whether other nitrogeneous compounds are formed.

IV. CONCLUSIONS

A combustion tunnel has been designed, constructed, and characterized for the laboratory study of nitric oxide reduction by ammonia injection. The combustion products of propane and air are diluted by nitrogen injection to provide precise temperature control. Nitric oxide levels at the inlet of the test section are fixed by nitric oxide addition to the reactant gases. Boiler combustion gases are thereby simulated in the laboratory with independent control of equivalence ratio, temperature, and nitric oxide level. Special attention was paid to the uniformity of the hot test gases and to the completeness of the mixing of the injection of ammonia so that the effects of system parameters (combustion product equivalence ratio, temperature at point of ammonia injection, nitric oxide level at ammonia injection, and ammonia to nitric oxide ratio) could be independently determined. In practical applications these parameters are largely interdependent and their uniformity in space (across the plane of ammonia injection) or time is unlikely. The residence times in the laboratory combustion tunnel (about 20 msec) are less than those associated with the practical application which are at least an order of magnitude greater. While such a difficulty is unavoidable in laboratory scale experimentation, the observation that reactions in practically all cases were complete within our test section suggests that the results are applicable to larger scale devices. The effectiveness of the process was characterized primarily in terms of nitric oxide survival and ammonia breakthrough with particular attention to off-design operating conditions.

At excess air operating conditions the observed behavior of the ammonia injection process for nitric oxide control was consistent with previous investigators. An optimum temperature and ammonia addition level for maximum nitric oxide removal were observed. Nitric oxide survival was somewhat greater than had been obtained by other investigators. This difference is probably attributable to differences in experimental configuration.

The effectiveness of nitric oxide removal improves as the stoichiometric mixture is approached from the lean side but is very sensitive to the mixture ratio at near stoichiometric conditions. Once the stoichiometric condition is reached and (apparently) there is no excess oxygen available, the effectiveness of nitric oxide removal drops rapidly. Under fuel rich conditions ammonia addition is ineffective for nitric oxide removal.

Ammonia breakthrough was not determined to be a problem for operating conditions near those at which the ammonia injection process is intended to be used. Ammonia breakthrough occurs under conditions of excess fuel (absence of excess oxygen), low temperature at the point of injection, and high ammonia to nitric oxide ratios.

The optimization of the process in practical applications may prove difficult because of expected variations in space and time of parameters to which process effectiveness is sensitive (temperature, excess oxygen, and nitric oxide level). Trade-offs exist between nitric oxide removal and ammonia breakthrough which suggest that optimization also must involve an assessment of the relative importance of nitric oxide and ammonia emissions. For a large scale application the desirability of monitoring temperature, nitric oxide level, and excess oxygen as a means of selecting the amount and possibly location of ammonia injection should be investigated. Because of the sensitivity of the process to system parameters, monitoring of exhaust nitric oxide and ammonia would appear advisable (particularly in large scale applications).

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