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**A STUDY OF NO_x REDUCTION BY FUEL INJECTION
RECIRCULATION**

**Topical Report
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EXECUTIVE SUMMARY

Flue-gas recirculation (FGR) is a well-known method used to control oxides of nitrogen (NO_x) in industrial burner applications. Recent small- and large-scale experiments by Carnot (Tustin, CA) have shown that introducing the recirculated flue gases with the fuel results in a much greater reduction in NO_x , per unit mass of gas recirculated, in comparison to introducing the flue gases with the combustion air. That fuel injection recirculation (FIR) is more effective than windbox FGR is quite remarkable. At present, however, there is no definitive understanding of why FIR is more effective than conventional FGR. One speculation is that introducing the diluent gases on the fuel side of the flame affects the prompt-NO mechanism causing the greater effectiveness.

The objective of our research is to ascertain whether or not chemical and/or molecular transport effects alone can explain the differences in NO_x reduction observed between FIR and FGR. This knowledge will aid in the rational application and optimization of FIR in a wide variety of industrial applications.

A combined modeling and experimental program is in progress to achieve the research objectives. This report discusses, first, computer modeling studies of counterflow diffusion flames employing detailed chemical kinetics for methane combustion and NO_x formation, and, second, experimental studies of laminar, CH_4 -air, jet flames.

The numerical simulations were used to calculate NO_x emission indices for various conditions. Studies were conducted in which a N_2 diluent was added either on the fuel or air side of the flame for conditions of either fixed initial velocities or fixed fuel mass flux. Results from these simulation studies indicate that a major factor in FIR effectiveness is the differential effect on flame zone residence times associated with fuel-side versus air-side dilution. Simulations in which flow velocities were fixed as diluent was added either to the air or fuel stream showed lower NO_x emissions for air-side dilution; however, if instead, fuel mass fluxes were fixed as diluent was added, which results in an increase in the velocity of the streams, fuel-side dilution was more effective. Fixing the fuel mass flux is consistent with the practical application of FIR in a boiler, for example.

In the experimental studies, the following quantities were measured: NO_x and CO emission indices, NO_2 -to- NO_x ratios, and total visible and soot-free flame lengths. As in the simulations, experiments were conducted in which either the air or fuel stream was diluted with N_2 . The experiments showed that fuel-side dilution results in somewhat greater NO_x emission indices than air-side dilution. Since these jet flames are dominated by buoyancy, the flowfield is not greatly influenced by the initial jet velocity; thus, we speculate that the differences in flame lengths associated with air-side versus fuel-side dilution result in longer mean residence times for fuel-dilution. The longer residence times at high temperatures results in higher NO emission. Higher flame temperatures with fuel dilution may also be a cause of the higher emissions. Since fuel dilution is more effective than air dilution in suppressing in-flame soot formation, radiant heat losses with fuel dilution may be less and, consequently, temperatures somewhat higher. Future experiments are planned to measure the temperatures distributions in both diluted-fuel and diluted-air flames.

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RESEARCH OBJECTIVES

A combined theoretical and experimental program is in progress with the overall objective of determining why FIR is more effective than conventional FGR in reducing NO_x emissions from nonpremixed combustion systems. As a result of this understanding, we will also be able to provide guidance as to how to most fully exploit the use of FIR. Specific objectives directed at achieving the overall objective are as follows:

- Incorporate the appropriate detailed chemical kinetics for methane combustion and NO_x formation in a numerical simulation of counterflow diffusion flames.
- Using the model above, conduct parametric studies to determine how adding the diluent in either the fuel or airstream affects NO_x formation.
- Conduct an experimental study of NO_x formation in laminar jet flames investigating the effects of the same parameters used in the theoretical study. NO_x and carbon monoxide emission indices will be measured.
- Measure detailed temperature and species profiles for the flames determined to be most interesting from the parametric investigation.

ACCOMPLISHMENTS JUNE - DECEMBER 1995

Work for this period involved both detailed simulations of counterflow flames and experimental studies of laminar jet flames. Accomplishments include the following:

Numerical Studies

- Discovered an artifactual heat loss in some of the previous simulations where the fuel-side velocity was deliberately made larger than the air-side velocity.
- Re-ran calculations for air and fuel dilution with fixed velocities (CH_4 -air flames) at conditions where there were no artifactual heat losses out the boundaries.
- Ran calculations as above for elevated (500 K) reactant temperature.
- Developed an understanding of why NO emission indices are affected by the location of diluent addition (air-side versus fuel-side).
- Designed, fabricated, and assembled flow metering, heating, and control systems for the coflow, laminar, jet-flame burner.
- Performed flow calibrations for fuel, air, and diluent delivery systems.
- Established the stable operating regime for the laminar-flame burner.

- Conducted parametric tests at room temperature and at elevated reactants temperature (~ 413 K) for fixed fuel rate with either air or fuel dilution. Measured quantities include NO_x and CO emission indices, NO_2 -to- NO_x ratios, visible flame lengths, and fraction of the flame length that is soot free.
- Applied understanding developed from numerical studies to interpreting experimental results.
- Designed, fabricated, and assembled burner traversing system for probe measurements.

PROBLEM OVERVIEW

Flue gas recirculation (FGR) is a well-known technique for oxides of nitrogen (NO_x) control in industrial burner applications. With this control technique, the recirculated flue gases reduce flame temperatures, which in turn results in decreased thermal NO production rates. Recently, it has been demonstrated in a small-scale boiler that introducing the recirculated flue gas with the fuel results in a much greater reduction in NO_x , per unit mass of recirculated gas, when compared to mixing the flue gas with the air [1]. This technique is referred to as fuel injection recirculation (FIR). For example, NO_x emissions are reduced from 90 to 30 ppm with 5% FIR, while 23% conventional windbox FGR is required to achieve the same reduction. The qualitative behavior of FIR versus windbox FGR was the same with or without overfire air. Based on the success of the 2 MMBTU/hr boiler demonstration, Southern California Edison Company also equipped a 45 MW utility boiler with FIR. Field trials of this large-scale unit show results consistent with the small-scale boiler [2].

That FIR is more effective than windbox FGR is quite remarkable. On a simple heat-capacity basis, the reduction in flame temperature resulting from recirculated flue gas should not depend on whether the gas is mixed with the air or fuel, but only on the quantity recirculated. Hopkins et al. [1] speculate that Fenimore prompt NO_x is affected. At present, there is no fundamental understanding of how FIR produces the effects demonstrated. The basic question we are addressing is why indeed does FIR have a greater effectiveness, per unit mass recirculated, than ordinary FGR. More specifically, we would like to understand the relative importance of chemical kinetics, molecular transport, and flame structure in this problem. Such understanding would allow the rational application and optimization of FIR in a wide variety of industrial applications.

FLAME MODELING STUDIES

Overview

A counterflow diffusion flame, shown in Fig. 1, offers a convenient geometry for modeling the detailed processes that occur in diffusion flames. In this stagnation flow, where the fuel and oxidizer streams are opposed, a flame is established on the oxidizer side of the stagnation point. The mathematical description of this flow along the stagnation streamline is one-dimensional, i.e., the species mass fractions, temperature,

Conditions specified at $x = L$: u_L , Y_{air} , Y_{dil} , T_L

Conditions specified at $x = 0$: u_0 , Y_F , Y_{dil} , T_0

FIGURE 1. Counterflow diffusion flame geometry showing location of flame and stagnation plane.

and velocity are functions only of the axial coordinate x [3-5]. As a result of this simplification to one-dimensionality, very extensive chemical kinetic mechanisms can be incorporated into numerical flame models, which require only relatively modest run times.

In our previous progress report [6], results were presented for various flame simulations in which either the fuel stream or air stream was diluted with nitrogen. In some cases, the flame was located sufficiently close to either the fuel or air inlet such that conduction losses occurred through the boundary. This heat loss resulted in flame temperatures being artificially low. For conditions where the fuel-side and air-side flow velocities were both equal and fixed as diluent was added to either stream, we found that air-side dilution was more effective than fuel side dilution, unlike the reported effects for turbulent flames in large-scale experiments [4,5]. This conclusion is not affected by the heat-loss artifact. Results presented below, where conditions were selected to prevent boundary heat losses, show the same trend as reported previously [6]. Simulations in which the fuel mass flux was maintained constant with the addition of diluent, however, result in severe heat losses as a consequence of the high fuel-side momentum pushing the flame toward the air nozzle. When the air-stream is diluted, a similar phenomenon occurs; however, the heat loss in this case is much less pronounced because the momentum flux of the air stream is not increased nearly as much as is the fuel stream for equivalent diluent fractions. We previously concluded that for fixed fuel mass flux, fuel-side dilution is more effective than air-side dilution. Furthermore, we pointed out that the fixed fuel mass condition is typical of practical applications [6]. In the present report, we show results of simulations in which the fuel mass flux is fixed as diluent is added, but without introducing an artifactual heat loss. The conclusion from these calculations is that, for this flow situation, fuel dilution is significantly more effective than air dilution in lowering NO_x emissions.

In the following sections, we present results and analyses of various simulations which illuminate how and why NO emissions are differentially affected by the addition of diluent to the fuel or the air streams.

Nonreacting Isothermal Flow

To help understand the counterflow flames, it is instructive first to consider the case of a nonreacting flow. Calculations were performed for fixed inlet velocities (cf. Fig. 1) of $u_0 = u_L = 50$ cm/s. Methane was introduced at $x = 0$ and air at $x = L$. Nitrogen, the diluent, was added either at $x = 0$ or $x = L$.

Figures 2 and 3 show the concentration profiles for nonreacting counterflows. Figure 2 illustrates the case where the fuel stream has been diluted with N_2 , while Fig. 3 shows the diluted-air case. Both flows have the same diluent fraction $Z = 0.15$, where Z is the mass of N_2 per mass of stoichiometric mixture [6]. Of particular interest are the CH_4 concentration profiles. We note that, although the CH_4 -mole fraction drops more rapidly for the pure-fuel case (Fig. 3) than the N_2 -diluted fuel case (Fig. 2), the change from the nozzle concentration ($\chi_{\text{CH}_4} = 1.0$ or 0.3912) to the stoichiometric value ($\chi_{\text{CH}_4,\text{stoic}} = 0.0794$) is accomplished over a greater distance. We will return to this point after examining the velocity fields associated with these two flows.

FIGURE 2. Mole fraction profiles for nonreacting (300 K) counterflow. Diluted CH₄ mixture flows from the left ($x = 0$) and air flows from the right ($x = L$). The N₂-diluent fraction is $Z = 0.15$ and $u_0 = u_L = 50$ cm/s.

FIGURE 3. Mole fraction profiles for nonreacting (300 K) counterflow. Pure CH₄ flows from the left ($x = 0$) and N₂-diluted air flows from the right ($x = L$). The N₂-diluent fraction is $Z = 0.15$ and $u_0 = u_L = 50$ cm/s.

Figure 4 shows these velocity profiles, where a positive velocity indicates a flow from left to right, while a negative velocity corresponds to a flow from right to left. The boundary conditions for the two flows require that the velocities be identically 50 cm/s at $x = 0$ and at $x = 1.5$ cm ($= L$). Between the boundaries, however, we see that the profile for the diluted-fuel case is shifted to the right relative to the diluted-air case, with the stagnation planes ($v = 0$) separated approximately 0.1 cm. This shifting of the stagnation plane to the right with the addition of N_2 to the CH_4 stream can be understood as a consequence of the greater momentum flux of the fuel-side stream when N_2 is added. Since the velocities at both the left and right boundaries are equal and fixed for all cases, the momentum flux issuing from each nozzle is governed solely by the nozzle-fluid density. Table I shows the mixture densities and momentum fluxes for the various streams considered. Since the density of the fuel-side stream, whether diluted or undiluted, is always less than the oxidizer-side stream, the stagnation plane always lies to the left of center (cf. Fig. 4). If the momentum flux left and right were equal, the stagnation plane would lie halfway between the two nozzles ($x = 1.5/2 = 0.75$ cm). Similarly, increasing the density of the fuel-side stream with the addition of N_2 shifts the stagnation plane to the right, but the plane still lies to the left of center.

TABLE I. N_2 Mass Fraction, Mixture Density, Mixture Mass Flux, and Mixture Momentum Flux for Pure and N_2 -Diluted ($Z = 0.15$) Fuel and Air Streams ($T = 300$ K)

Parameter	Flow Stream			
	CH_4	$CH_4 + N_2$	Air	$N_2 + Air$
N_2 Mass Fraction, Y_{N_2}	0	0.731	0.767	0.799
Density, ρ (kg/m ³)	0.652	0.948	1.133	1.128
Mass Flux, ρv (kg/m ² -s)	0.326	0.474	0.567	0.564
Momentum Flux, ρv^2 (N/m ²)	0.163	0.237	0.284	0.282

Figures 5 and 6 show the fuel concentrations and velocity profiles referenced to the stagnation plane ($x = 0$). From Fig. 5, we clearly see that the stoichiometric concentration for the N_2 -diluted fuel stream lies closer to the stagnation plane than the air-diluted case. This position also corresponds to a significantly lower velocity magnitude, as can be seen in Fig. 6, where the x -locations of the stoichiometric points are indicated for the two cases. The importance of this is that the same qualitative behavior occurs for the reacting flows, i.e., the fuel-diluted flames lie in lower velocity regions compared to their air-diluted counterparts. This, in turn, results in larger residence times at high temperatures for the fuel-diluted flames, which is an important factor in NO production. We discuss this in greater detail below.

FIGURE 4. Velocity profiles for nonreacting counterflows corresponding to Figs. 2 and 3. The stagnation plane for the N_2 -diluted CH_4 case is shifted to the right because of the greater momentum flux associated with the N_2 - CH_4 mixture compared to the undiluted CH_4 .

FIGURE 5. CH₄ mole fraction profiles from Figs. 2 and 3 plotted as functions of the distance from the stagnation plane. Also indicated is the stoichiometric CH₄ mole fraction (≈ 0.0794) for these N₂-diluted mixtures.

FIGURE 6. Velocity profiles for nonreacting counterflows with either the fuel or air stream diluted with N₂ (Z = 0.15) where the origin of the axial distance coordinate is the stagnation plane.

Reacting Flows

Two types of flow conditions were considered for the reacting flows: first, variable dilution, but with fixed inlet velocities of 50 cm/s for all cases; and second, variable dilution, but with a fixed fuel mass flux. This second condition of fixed fuel mass flux was met by increasing the velocities at both the exit of the fuel and air nozzles as diluent was added to the fuel stream. For example, with $Z = 0.15$, the nozzle exit velocity is 128 cm/s compared to 50 cm/s with no dilution. The air stream velocity was increased to match the velocity of the fuel stream thus keeping the flame roughly centered between the two nozzles and, thereby, preventing any artifactual heat loss through the boundaries.

Flow and Flame Structure

Calculations were performed with the same nozzle velocities ($u_o = u_L = 50$ cm/s) as the nonreacting flows discussed above, and a parametric investigation conducted in which increasing amounts of N_2 were added to either the fuel stream or oxidizer (air) stream. Calculations were performed with reactants entering at 300 K and at 500 K.

Figures 7, 8 and 9 show CH_4 , O_2 , and N_2 mole fraction profiles between the opposed nozzles for no dilution (Fig. 7), air dilution with $Z = 0.15$ (Fig. 8), and fuel dilution with $Z = 0.15$ (Fig. 9), i.e., test cases 1, 2, and 3 shown in Table II. Nominally, the same qualitative behavior is observed here as for the corresponding nonreacting flows (cf. Figs. 2 and 3). A major difference, however, is the elimination of the relatively large region where CH_4 and O_2 coexist. In the flames, the O_2 concentration drops to near zero levels at the same location as does the CH_4 concentration, as expected, since the fuel and oxidizer are both rapidly consumed at the flame.

TABLE II. Test Conditions for Selected Numerical Simulations of CH_4 -Air Counterflow Diffusion Flames with Reactants at 300 K

Case No.	Reactant Velocity (cm/s)	Methane Mass Flux (kg/s-m ²)	N ₂ Diluent Fraction, Z	
			<u>Fuel Side</u>	<u>Air Side</u>
1	50	0.326	0	0
2	50	0.326	0	0.15
3	50	0.106	0.15	0
4	127.8	0.326	0.15	0

FIGURE 7. Methane, oxygen, and nitrogen mole fraction profiles for undiluted counterflow diffusional flames (Case 1). Reactants enter at 300 K with velocities of 50 cm/s at $x = 0$ and $x = 1.5$ cm.

FIGURE 8. Methane, oxygen, and nitrogen mole fraction profiles for a counterflow diffusion flame with the air stream diluted with N₂ ($Z = 0.15$) (Case 2). Reactants enter at 300 K with velocities of 50 cm/s at $x = 0$ and $x = 1.5$ cm.

FIGURE 9. Methane, oxygen, and nitrogen mole fraction profiles for a counterflow diffusion flame with the fuel stream diluted with N₂ ($Z = 0.15$) (Case 3). Reactants enter at 300 K with velocities of 50 cm/s at $x = 0$ and $x = 1.5$ cm. Note that these are the same velocities as for the zero-dilution (Fig. 7) and N₂-diluted air stream (Fig. 8) flames.

The reactant concentration profiles through the diluted-fuel flame having the same fuel mass flux as the undiluted flame are shown in Fig. 10. The test conditions are those of Case 4 in Table II. The profiles are nominally the same as the lower velocity flame with the same level of fuel dilution (Case 3, $Z = 0.15$); however, some oxygen penetration through the flame into the fuel is apparent, as would be expected as characteristic flow times get shorter and approach characteristic chemical reaction times.

Temperature profiles associated with the same three fixed-velocity flame conditions discussed above are shown in Fig. 11, and velocity profiles are given in Fig. 12. The temperature profile for the fixed fuel mass flux flame with fuel dilution (cf. Table II, Case 4) is presented in Fig. 13, while the corresponding velocity profile is shown in Fig. 14 along with the profile for the other fuel-diluted (Case 3) flame for comparison.

A key to understanding NO formation is the time-temperature relationship for gases flowing through the flame zone. To quantify this relationship in a meaningful way, we define a residence time for NO_x formation as the time that a fluid particle exists at a temperature above 1500 K. The choice of 1500 K is somewhat arbitrary, but this value is a reasonable lower-limit temperature for NO production. The 1500 K level is shown as a horizontal line passing through the temperature profiles of the simulated flames (Figs. 11 and 13). This residence time is calculated by integrating the reciprocal of the velocity from the axial location where the temperature first reaches 1500 K, through the peak, and terminating the calculation at the location where the temperature again falls to 1500 K, i.e.,

$$\text{Residence time, } \tau \equiv \int_{x_1(T=1500 \text{ K})}^{x_2(T=1500 \text{ K})} u^{-1}(x) dx \quad (1)$$

Table III shows residence times for the four cases considered. The interesting observation here is that air-side dilution decreases residence times over the no-dilution case, while fuel-side dilution increases residence times for the same initial velocity (50 cm/s). On the other hand, fuel dilution with a fixed fuel flow rate shows a reduced residence time compared to no dilution. In fact, the 1.2 ms residence time is smaller than the 2.6 ms value for the air-diluted flame. The increased residence time for the Case 3 ($u_0 = 50$ cm/s) fuel-diluted flame can be understood as a result of the fuel dilution causing the flame to move closer to the stagnation plane, i.e., to move into a region of lower velocity. This is principally a flow phenomenon, since we saw previously for the nonreacting flow (cf. Fig. 4) that location of the stoichiometric fuel mole fraction moves into a lower velocity region when the fuel stream is diluted. For the Case 4 fuel-diluted flame, however, the decreased residence time is a consequence of the generally much greater velocities occurring in this flame. (See Fig. 14 for a comparison of the two fuel-diluted flames.) The location of the flame relative to the stagnation plane and the velocities at the flame are shown quantitatively in Table IV. The flame location is defined as the axial position where the temperature reaches a maximum.

Also presented in Table IV are the peak flame temperatures and the N_2 mole fraction at the peak-temperature location. Here we see that fuel dilution is more effective than air dilution in reducing the peak temperatures (cf. Cases 2, 3, and 4), with the fixed fuel mass flux case having the lowest temperature (1687 K) of the three. The

N₂ mole fractions are not significantly different among the three flames, but the small differences do correlate with the differences in flame temperature, i.e., the lowest temperature coincides with the highest N₂ concentration, and vice-versa.

TABLE III. Rate of Fuel Supplied from Nozzle, Residence Time, Fuel Consumption Rate, and Fraction of Fuel Burned (CH₄-air, T = 300 K)

Parameter	————— $u_0 = 50$ cm/s —————			— $u_0 = 128$ cm/s —
	No Dilution	Air Dilution	Fuel Dilution	Fuel Dilution
Case No.	1	2	3	4
Residence Time for T>1500 K (ms)	3.2	2.6	3.6	1.2
Total Fuel Supplied (mol/cm ² -s)	$2.03 \cdot 10^{-3}$	$2.03 \cdot 10^{-3}$	$7.95 \cdot 10^{-4}$	$2.03 \cdot 10^{-3}$
Fuel Consumption (mol/cm ² -s)	$5.87 \cdot 10^{-5}$	$5.08 \cdot 10^{-5}$	$4.20 \cdot 10^{-5}$	$6.34 \cdot 10^{-5}$
Percentage of Fuel Burned (%)	2.89	2.50	5.28	3.12

TABLE IV. Locations of Stagnation Plane and Flame, Peak Flame Temperature, and Velocity and N₂ Mole Fractions at Peak Flame Temperature (CH₄-air, T = 300 K)

Parameter	————— $u_0 = 50$ cm/s —————			— $u_0 = 128$ cm/s —
	No Dilution (Z = 0)	Air Dilution (Z = 0.15)	Fuel Dilution (Z = 0.15)	Fuel Dilution (Z = 0.15)
Case No.	1	2	3	4
Stagnation Plane Location (cm)	0.580	0.584	0.650	0.676
Flame Location (cm)	0.744	0.750	0.745	0.736
Distance between Flame and Stagnation Plane (cm)	0.164	0.166	0.095	0.060
Temperature at Flame (K)	1927	1802	1762	1672
Velocity at Flame (cm/s)	-55.5	-54.4	-31.0	-65.6
N ₂ Mole Fraction at Flame	0.683	0.726	0.737	0.737

FIGURE 10. Methane, oxygen, and nitrogen mole fraction profiles for a counterflow diffusion flame with fuel dilution ($Z = 0.15$) (Case 4). The fuel mass flux is identical to the zero-dilution flame (Fig. 7) thus requiring the inlet velocities to be higher. Reactants enter at 300 K with velocities of 128 cm/s at $x = 0$ and $x = 1.5$ cm.

FIGURE 11. Temperature profiles for counterflow diffusion flames with no dilution (solid curve without symbols (Case 1)), the air stream diluted with N_2 for $Z = 0.15$ (open symbols (Case 2)), and the fuel stream diluted with N_2 for $Z = 0.15$ (solid symbols (Case 3)). Reactants enter at 300 K with velocities of 50 cm/s at $x = 0$ and $x = 1.5$ cm.

FIGURE 12. Velocity profiles for counterflow diffusion flames with the air stream diluted with N_2 for $Z = 0.15$ (open symbols (Case 2)), and with the fuel stream diluted with N_2 for $Z = 0.15$ (solid symbols (Case 3)).

FIGURE 13. Temperature profile for counterflow diffusion flame with fuel stream diluted with N_2 for $Z = 0.15$ (Case 4). Reactants enter at 300 K with velocities of 128 cm/s at $x = 0$ and $x = 1.5$ cm.

FIGURE 14. Comparison of velocity profiles for the two cases where the fuel stream is diluted with N_2 for $Z = 0.15$. Case 3 (open symbols). Case 4 (solid symbols).

Nitric Oxide Emissions

Figure 15 compares the NO emission indices for the four cases discussed above. Here we see that the addition of the N₂ diluent decreases NO emissions for either air- or fuel-side dilution as expected. Comparing the results for fixed fuel velocity (Cases 2 and 3), we see that, for these conditions, air-side dilution is more effective than fuel-side dilution. Comparing the results for fixed fuel mass flux (Cases 2 and 4), however, we see that fuel-side dilution is now more effective than air-side dilution.

Insights into the differential effects of air-side versus fuel-side dilution are obtained by looking at the various factors involved in the NO emission index calculation. To determine the NO emission index, both the net NO formation rate and fuel burning rate are required, i.e.,

$$EI_{NO} = \frac{\dot{m}_{NO,net}''}{\dot{m}_{fuel}''} = \frac{\dot{N}_{NO,net}'' MW_{NO}}{\dot{N}_{fuel}'' MW_{fuel}} \quad (2)$$

where $\dot{m}''$ is the mass flux (g/cm²-s) and $\dot{N}''$ is the molar flux (mol/cm²-s). Table V shows the values of both the numerators and denominators of Eqn. 2 for the four conditions considered here. Also shown in Table V is a breakdown of the net NO formation into production and destruction components for each flame condition. These two components are the positive and negative areas, respectively, under the volumetric NO production rate-versus-distance curves. These curves for the three cases with Z = 0.15 are shown in Fig. 16.

TABLE V. Contributions of Various Factors to NO Emission Index (CH₄-air, T = 300 K)

Parameter	————— u ₀ = 50 cm/s —————			— u ₀ = 128 cm/s —
	No Dilution (Z = 0)	Air Dilution (Z = 0.15)	Fuel Dilution (Z = 0.15)	Fuel Dilution (Z = 0.15)
Case No.	1	2	3	4
Fuel Consumption (mol/cm ² -s)	5.87·10 ⁻⁵	5.00·10 ⁻⁵	4.20·10 ⁻⁵	6.34·10 ⁻⁵
NO Production (mol/cm ² -s)	35.9·10 ⁻⁹	16.4·10 ⁻⁹	13.6·10 ⁻⁹	3.10·10 ⁻⁹
NO Destruction (mol/cm ² -s)	23.6·10 ⁻⁹	9.55·10 ⁻⁹	7.08·10 ⁻⁹	1.17·10 ⁻⁹
Net NO Formation (mol/cm ² -s)	12.3·10 ⁻⁹	6.85·10 ⁻⁹	6.52·10 ⁻⁹	3.93·10 ⁻⁹
Ratio of Production to Destruction	1.52	1.72	1.92	3.50
NO Emission Index (g/kg)	0.39	0.25	0.29	0.086

FIGURE 15. Nitric oxide emission indices for counterflow diffusion flames for selected conditions (cf. Table II).

FIGURE 16. Nitric oxide volumetric production rates for the three flame cases with N₂-dilution with Z = 0.15.

From Table V, we see for both air- and fuel-dilution at the $u_0 = 50$ cm/s condition that the fuel consumption rates are decreased from the no-dilution case, with the greater decrease associated with fuel dilution. These reduced fuel consumption rates tend to increase the NO emission indices. However, since the net NO formation rates are also decreased, the combined effect is a lowering of the emission indices, as expected with dilution. Note that since the NO formation rates are nominally equal for air- and fuel-dilution (Cases 2 and 3), the factor causing the fuel-dilution to be less effective is the decreased fuel consumption rate.

For fuel dilution with a fixed fuel mass flux (Case 4), however, the fuel consumption rate increases. This has the effect of decreasing the NO emission index. The steeper concentration and velocity gradients associated with this higher-velocity fixed-fuel-mass-flux flame are the cause of its increased fuel consumption rate. Furthermore, the net NO formation rate is also lower; thus, both increased fuel consumption and reduced NO formation factors combine to yield a lower NO emission index for the fixed-fuel-mass-flux flame. Specifically, the emission index for this flame ($EI_{NO} = 0.086$ g/kg) is 3.4 times lower than the fixed-velocity fuel-dilution flame and 2.9 times lower than the corresponding air-dilution flame. It is interesting to point out that, although this reduced net NO formation rate is dominated by residence time considerations (cf. Table III), the ratio of NO production-to-destruction for the Case 4 flame, compared to the other three cases, is quite large, i.e., 3.50 versus 1.92 and 1.72. This suggests that the relative importance of the various NO-formation pathways changes significantly between the 128 cm/s and 50 cm/s conditions. Further research is required to elucidate the details of such effects.

Parametric Studies

Calculations were performed for both air- and fuel-dilution with N_2 over a range of diluent fractions. Two levels of reactants temperatures were considered, 300 K and 500 K, and the fuel dilution was accomplished for both fixed-velocity conditions ($u_0 = 50$ cm/s) and for fixed fuel mass flux (0.326 kg/m²-s at 300K and 0.189 kg/m²-s at 500 K). The previously discussed results were a subset of the calculations performed for 300 K reactants.

Nitric oxide emission indices are shown as functions of diluent fraction in Fig. 17. The corresponding residence times (see Eqn. 1) are presented in Fig. 18. In these figures, we observe that fuel dilution is more effective than air dilution when the fuel mass flux is fixed. Fixed fuel mass flux is the condition that is most applicable to practice; however, one must be cautious in extrapolating the laminar flame results to real boilers both because the geometries are different and, most importantly, the practical flow is governed by turbulent mixing. Nevertheless, we gain the insight that local residence times for NO formation in a flame are affected by how the diluent is added to the system.

Maximum flame temperatures and the N_2 mole fraction at the maximum temperature location are shown in Fig. 19 for the 300 K simulations and in Fig. 20 for the 500 K calculations. From these figures, we see that fuel dilution results in slightly greater N_2 fractions at the flame and, correspondingly, somewhat lower flame

FIGURE 17. Calculated nitric oxide emission indices for counterflow CH₄-air flames for N₂ addition to either the air or fuel streams with reactants at 500 K (upper curves) and 300 K (lower curves). Fuel-stream dilution is accomplished either with fixed nozzle exit velocities (● ■ symbols) or fixed fuel mass flux (▲ ▼ symbols).

FIGURE 18. Calculated residence times above 1500 K for counterflow CH₄-air flames for N₂ addition to either the air or fuel streams with reactants at 500 K (upper curves) and 300 K (lower curves).

temperatures for the fixed-velocity comparison. The fixed fuel mass flux case of fuel dilution, however, shows N_2 fractions similar to the fixed-velocity fuel dilution cases, but temperature levels are significantly lower. This greater temperature depression is thought to be an additional consequence of the shorter residence times in such flames which cause a greater departure from chemical equilibrium. It is well known that high strain rates can cause superequilibrium concentrations of flame radicals, which, in turn, cause temperatures to be below equilibrium levels [7].

EXPERIMENTAL STUDIES

As a complement to the numerical simulations, experiments were conducted using a laminar jet flame. Although the jet flame geometry is significantly different from the counterflow studied numerically, they do share common features. For example, at low-velocity conditions for the counterflow, the structure of both flames are dominated by diffusional processes and, hence, comparable. Furthermore, the jet-flame geometry offers the advantage over the counterflow that NO emission indices are easily measured, since all of the fuel burns in the jet, unlike the opposed-flow flame where much of the fuel escapes. The sections below describe the apparatus used and present and discuss the results of the experiments.

Apparatus

The laminar jet-flame burner used in the experiments is illustrated in Fig. 21. The burner design is that used by Santoro and coworkers [8,9] in soot studies. A laminar fuel jet issues from a tube (10.9-mm i.d., 12.7-mm o.d., 10.6-mm length) into a uniform low-velocity coannular air flow producing stable conical flames. A 12.7-mm thick bed of 3.4-mm diameter glass beads distributes the airflow over the annular space, while a 25.4-mm thick honeycomb provides a laminar flow. The fuel tube protrudes 4.8 mm through the honeycomb. For the present experiments, a 105-mm i.d., 230-mm long glass duct surrounds the flames. This duct prevents any room drafts from influencing the flame and allows the flames to be easily photographed. The products of combustion are mixed by a series of baffle plates at the top of the glass duct before being sampled at the outlet of a contracting section. The burner assembly is mounted on a three-axis position controller. Although not used in the present experiments, this traversing system will be used for in-flame temperature and species probings in future efforts.

The air, fuel, and diluent (N_2) flow control, metering, and heating arrangements are schematically shown in Fig. 22. Calibrated rotameters are used to measure the mass flowrate of each gas at room temperature before the gases are heated. The CH_4 fuel (technical grade, 98% purity) and its diluent is heated, when desired, by variac-controlled heating tapes. The air stream and any diluent is heated by a 950 W process heater with a PID controller. The burner base assembly is well insulated to minimize heat loss to the surroundings. The maximum attainable gas temperature with this arrangement is approximately 140°C (413 K).

The product gas sampling and analysis systems are illustrated in Fig. 23. Samples are withdrawn through a stainless-steel, water-cooled sampled probe. Water cooling temperatures are maintained above the dew point of the product gases to avoid

FIGURE 19. Calculated maximum temperature and N₂ mole fraction at the location of maximum temperature as functions of N₂ addition. Reactants enter at 300 K.

FIGURE 20. Calculated maximum temperature and N₂ mole fraction at the location of maximum temperature as functions of N₂ addition. Reactants enter at 500 K.

FIGURE 21. Laminar jet flame burner.

FIGURE 22. Air, fuel, and N₂ diluent flow control, metering, and heating schematic.

FIGURE 23. Gas sampling and analysis systems.

water condensation within the probe. Moisture is removed by an ice bath water trap before the sampled gases enter the analyzers. NO and NO_x concentration measurements were made with a chemiluminescent analyzer (TECO Model 10-A with factory-installed cooled PMT) equipped with a stainless-steel NO₂-to-NO converter. Measured converter efficiencies exceed 97%. Carbon dioxide concentrations are measured using either a long- or a short-path nondispersive infrared analyzer (Horiba PIR-2000). The long-path CO₂ analyzer permits accurate measurements to a parts-per-million level. A gas-filter correlation analyzer (TECO Model 48) was used to measure CO emissions. A strip chart recorder was used to ascertain when a steady-state output of the NO_x analyzer was attained, while an AT&T 6300 micro-computer collected the data from the analyzers.

Procedures

NO and NO_x emission indices are calculated from measured mole fractions of NO, NO_x, CO, and CO₂ in the product gas using the following relation derived from overall mass and species conservation principles:

$$EI_{NO_x} = \frac{\chi_{NO_x}}{\chi_{CO_2} + \chi_{CO}} = \left[\frac{MW_{NO_x}}{MW_{CH_4}} + \frac{\dot{m}_{air}}{\dot{m}_{CH_4}} \frac{MW_{NO_x}}{MW_{air}} \chi_{CO_2,\infty} \right] \quad (3)$$

where $\chi_{CO_2,\infty}$ is the CO₂ mole fraction in the air stream. NO_x emission indices are based on the assumption that all of the NO_x eventually oxidizes to NO₂; thus, the NO_x molecular weight used in Eqn. 3 is that of NO₂. In general, both χ_{CO} and the second term in the brackets of Eqn. 3 are negligible; thus, NO_x and CO emission indices are readily calculated without a knowledge of the air and fuel stream flowrates, i.e.,

$$EI_{NO_x} = \frac{\chi_{NO_x}}{\chi_{CO_2}} \frac{MW_{NO_x}}{MW_{CH_4}} \quad (4)$$

$$EI_{CO} = \frac{\chi_{CO}}{\chi_{CO_2}} \frac{MW_{CO}}{MW_{CH_4}} \quad (5)$$

Mass-balance tests were conducted to assure that the measured air-fuel ratios were in agreement with those obtained solely by gas analysis. After remedying problems, consistent agreement was obtained.

Visual flame length measurements were obtained from color flame photographs. Although all flames were nonsooting, i.e., no soot escaped the flame, the appearance of a yellow luminosity indicated the presence of in-flame soot. Typically, the region closest to the fuel tube exit was blue (soot free), while the remainder of the flame exhibited a yellow luminosity. Therefore, in addition to the total flame length, a measurement of the soot-free length of the flame at each condition was conducted.

Test Conditions

Preliminary tests were conducted to ascertain fuel and air flow velocities such that stable flames could be obtained when either the fuel or air stream was diluted with N_2 . The baseline test conditions selected for the present investigation are shown in Table VI. Two basic flame conditions were studied: one with unheated reactants, and one with the reactants heated to nominally 400 K. Tests were conducted, starting at the baseline condition (Table VI), by adding N_2 diluent to the fuel stream or to the air stream while maintaining the fuel and air flowrates fixed. Emissions measurements and flame photographs were obtained for various levels of dilution. The maximum diluent fraction employed was approximately 0.2. The following relations can be used to relate the diluent fraction, Z , to the N_2 mass fraction in either the fuel stream or air stream:

$$Y_{N_2, \text{fuel}} = \frac{Z}{f_s + Z}, \quad (6)$$

$$Y_{N_2, \text{air}} = \frac{Z}{1 - f_s + Z}, \quad (7)$$

where f_s is the stoichiometric mixture fraction, i.e., the mass of fuel per mass of mixture at stoichiometric conditions. For methane, f_s equals 0.05518; thus, for the maximum Z ($= 0.2$), $Y_{N_2, \text{fuel}}$ is 0.78 and $Y_{N_2, \text{air}}$ is 0.175.

TABLE VI. Baseline Experimental Flame Conditions (No Diluent)

Flame Designation	A	B
Fuel Temperature (K)	293	413
Air Temperature (K)	293	398
Fuel Flowrate (mg/s)	3.0	3.3
Air Flowrate (mg/s)	243	243
Mean Fuel Velocity (cm/s)	5.0	7.8
Mean Air Velocity (cm/s)	2.4	3.5

Results and Discussion

NO_x emission indices as functions of diluent fraction are shown in Fig. 24 for the flames with heated and unheated reactants. For both cases, air dilution was more effective than fuel dilution in reducing NO_x emissions. For the room-temperature reactants, however, the differences between air and fuel dilution were small. The trends shown are thought to be real since the uncertainty associated with the data is rather small. For example, the high-temperature $Z = 0.10$ fuel-dilution test condition was repeated multiple times during the course of one day's operation, and the 95%-confidence interval for the NO_x emission index was 3.34 ± 0.03 g/kg based on Student *t*-statistics for five samples. Another measure of uncertainty is indicated in Fig. 24, where the high-temperature fuel-dilution data set was repeated after several weeks of acquiring the first data set. As can be seen in the figure, data replication is quite good.

At the present time, it is not possible to give a complete explanation of why the NO_x emission indices are lower with air dilution than with fuel dilution; however, the insights gained from the numerical studies allow some speculation at this point. First, it is likely that the physics of the fuel- and air-dilution experiments resemble that of the fixed initial-velocity simulations, rather than the fixed mass flux. This may seem paradoxical, since the experiments were conducted with a fixed fuel mass flux, conditions under which the numerical simulations showed greater NO_x -reduction effectiveness as fuel dilution. This can be explained by the fact that the experimental jet flames are dominated by buoyancy, hence, the velocity field of the flame is only weakly related to the initial velocity of the jet. Velocity measurements in similar flames by Santoro et al. [8] show that the jet rapidly accelerates as the buoyant force increases as more and more hot products are formed. Near the flame tip, the velocities are many times greater than the exit velocity; for example, at 4.5 cm downstream from the nozzle, a position near the tip of the flame, Santoro et al. [8] measured a velocity of approximately 165 cm/s, a value some 33 times larger than the initial jet velocity.

Based on the discussion above, we would anticipate that the longer the flame, the larger the mean velocity, since buoyancy causes the velocity to increase monotonically from the jet exit to well beyond the flame tip. As a consequence, mean flame-zone residence times should be smaller with the longer flame. Figures 25 and 26 show that, indeed, the flames with air dilution are longer than those with fuel dilution. Thus, if the temperature distributions are similar in the air- and fuel-diluted flames, the decreased residence times of the longer air-diluted flames result in lower NO_x emissions. Measurements of temperature distributions are planned for the future. Such measurements should help clarify this issue. Work is also in progress to model the flowfields of the jet flames to test the hypothesis that residence times are shorter with air dilution.

Although we have just argued that residence time rather than temperature effects explain the experimental NO_x trends, there is also the possibility that the air-dilution flames are somewhat cooler than the fuel-dilution flames. The suggestion for this is that the luminosity of the diluted-air flames is greater than that of the fuel-diluted flames at equal diluent fractions. Here we assume that a greater luminosity implies greater heat

FIGURE 24. NO_x emission indices for laminar CH₄ jet flames with various levels of N₂ dilution in either the fuel or air stream. The fuel flowrate is held constant as the diluent is added.

FIGURE 25. Visible flame lengths for laminar jet flames with various levels of N₂ dilution in either the fuel or air stream. Reactants enter at 293 K with the fuel mass flowrate fixed at 3.0 mg/s.

FIGURE 26. Visible flame lengths for laminar CH₄-air jet flames with various levels of N₂ dilution in either the fuel or air stream. Reactants enter at 400 K (nominal) with the fuel mass flowrate fixed at 3.3 mg/s.

losses and, hence, lower flame temperatures. Figures 27 and 28 show the fraction of the total flame length that is blue, i.e., ostensibly soot-free. In these figures, we see that the soot-free fraction of the diluted-fuel flames increases dramatically with increasing diluent fraction, while the increase is much more modest with air-dilution. At the highest diluent fraction tested ($Z = 0.2$), the flame with fuel dilution is entirely blue with no visual evidence of any in-flame soot. Whether or not the flame temperatures are affected by these visible differences in the flame is not known. The amount of soot formed in a CH_4 flame is quite small and, although the appearance of the flame may be significantly affected, it is possible that there is very little temperature depression associated with the in-flame soot. Again, the planned temperature measurements should answer this question.

Other measurements in the present investigation include molar NO_2 -to- NO_x ratios and CO emission indices. These are shown in Figs. 29 and 30, respectively. In Fig. 29, we see that increased dilution slightly increases the NO_2 proportion of the total NO_x . Although two separate curves are shown for the 400 K reactants flames, the differences between the data for air- and fuel-dilution are small and are within the statistical uncertainty associated with the measurements. The NO_2 -to- NO_x ratios range from about 0.16 to 0.23. These values are similar to measurements from turbulent jet flames [10]. Carbon monoxide emission indices increase with added dilution, as is typically found in practical applications of flue gas recirculation. No consistent difference in CO emissions between air- and fuel-dilution are seen for the unheated reactants, while, for 400 K reactants, fuel-dilution result in slightly lower CO emission indices. The CO levels shown in Fig. 30 also are within the same range as those measured in turbulent CH_4 -air jet flames [11].

CONCLUSIONS

Numerical Modeling

Nonreacting CH_4 -air- N_2 counterflows and counterflow flames were simulated. In these calculations, either the air stream or the fuel stream was diluted with N_2 as a means of simulating some of the possible chemical and molecular transport effects related to the observed increased NO_x -reduction effectiveness of FIR over conventional FGR. All conditions run were free from any heat losses through the boundaries. From these investigations, we draw the following conclusions:

- When the nozzle exit velocities are maintained at fixed values as N_2 is added to either the air or fuel streams, fuel-side dilution results in significantly higher NO emission indices than for air-side dilution. Detailed analysis of the results indicate that the higher NO is a consequence of the N_2 addition to the fuel causing the flame to lie closer to the stagnation plane in a region of lower velocity. The lower velocities, in turn, result in longer residence times for NO formation.
- When the fuel mass flux is maintained constant as diluent is added to the fuel, and the air stream velocity is simultaneously increased to match that of the diluted fuel stream, NO emission indices are considerably lower than for equivalent air-side dilution. This case more realistically represents the situation in practice than does

FIGURE 27. Fraction of the visible flame length that is soot-free (blue) with various levels of N_2 dilution in either the fuel or air stream. Reactants enter at 273 K with the fuel mass flowrate fixed at 3.0 mg/s.

FIGURE 28. Fraction of the visible flame length that is soot-free (blue) with various levels of N_2 dilution in either the fuel or air stream. Reactants enter at 400 K (nominal) with the fuel mass flowrate fixed at 3.3 mg/s.

FIGURE 29. NO₂-to-NO_x molar ratios for laminar jet flames with various levels of N₂ dilution in either the fuel or air stream.

FIGURE 30. Carbon monoxide emission indices for laminar jet flames with various levels of N₂ dilution in either the fuel or air stream.

the fixed-velocity case above. For fuel dilution with a fixed fuel mass flux, all major factors contributing to NO formation are affected: temperatures are lower, residence times are shorter, and the detailed chemical pathways producing NO are altered.

- When the fuel mass flux is maintained constant as diluent is added to the fuel and the air stream velocity is simultaneously increased to match that of the diluted fuel stream, NO emission indices are considerably lower than for equivalent air-side dilution. This case more realistically represents the situation in practice than does the fixed-velocity case above. For fuel dilution with a fixed fuel mass flux, all major factors contributing to NO formation are affected: temperatures are lower, residence times are shorter, and the detailed chemical pathways producing NO are altered.
- The conclusions above are independent of reactant temperature over the range of 300 K to 500 K.

Experiments

NO_x and CO emission indices, NO₂-to-NO_x ratios, and visible and soot-free flame lengths associated with laminar CH₄-air jet flames were measured for a variety of flame conditions. Experiments were conducted in which either the air stream or fuel stream was diluted with N₂ with the range of diluent fractions nominally the same as in the numerical simulations. Conclusions drawn from these experiments are the following:

- Fuel-side dilution results in somewhat greater NO_x emission indices than air-side dilution. The effect is more pronounced at the higher reactants temperature investigated (400 K versus 293 K).
- Although more investigation is required, higher NO emissions with fuel-side dilution may be the consequence of the fuel-diluted flame having slightly larger residence times in the high-temperature flame regions than for the equivalent air-diluted flame. Alternatively, fuel-side dilution decreases in-flame soot levels over air-side dilution, which may result in somewhat higher temperatures.

FUTURE PLANS

The following tasks are planned for the final five months of the project:

- Perform detailed temperature profile measurements in selected flames.
- Continue to analyze both the numerical and experimental results to date.
- Prepare final report.

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