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AN ANALYTICAL STUDY OF NITROGEN OXIDES AND CARBON MONOXIDE EMISSIONS IN HYDROCARBON COMBUSTION WITH ADDED NITROGEN — PRELIMINARY RESULTS

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INTRODUCTION

One of the major efforts in the development of gas turbines for ground power generation is their adaptation to the use of coal-derived liquid fuels. The wide range of properties of these synthetic liquid fuels leads to many problems. A recent summary of coal derived liquid fuel properties and their potential problems in turbine combustion is given in Ref. 1. The present paper focuses on the problem of increased emissions. The main question is how much the oxides of nitrogen (NOx) emissions will be increased by the increased amount of organic nitrogen compounds contained in these synthetic liquids. Another question is whether this fuel-bound nitrogen (FBN) will have any significant effect upon the carbon monoxide (CO) emissions from synthetic fuel combustion.

The present work was undertaken to investigate these questions as one part of the Critical Research and Technology program funded by the Department of Energy at the Lewis Research Center. The primary purpose of this work is to analytically determine the effect of combustion operating conditions on the conversion of FBN to NOx. The effect of FBN and of operating conditions on CO emissions was also examined. Propane-air was chosen as the combustible mixture for the first series of computations. The combustor model was assumed to be a two-stage, adiabatic, perfectly-stirred reactor. Chemical modeling of the oxidation of propane and the formation of NOx was done using a fifty-seven reaction mechanism. The use of two-stage combustion to minimize NOx formation has been reported by several investigators (2 to 4).

Results are presented for NOx and CO concentrations as a function of \( \Phi_p, \Phi_s, \) and both primary and secondary residence times, as well as the amount of FBN. A limited comparison of the computed results with experimental results obtained under another task in the Critical Research and Technology program is also given. The comparison will show the good semi-quantitative agreement between our theoretical model and the experimental results. It should be mentioned that neither the theoretical computations nor the experimental work were meant to model a practical turbine combustor.

Moreover, the effects of initial temperature and pressure variation were considered of secondary importance. These conditions were not changed in either the experimental or the theoretical work.

1Numbers in parentheses designate references at end of paper.
CHEMISTRY OF THE COMBUSTION PROCESS

The chemistry of nitrogen oxide formation during combustion has been studied extensively for many years. Two good reviews of this topic are given in Refs. 8 and 9. In this paper we shall define nitrogen oxides or NOx as the sum of nitric oxide (NO) and nitrogen dioxide (NO2) concentrations. Although the mechanism of NOx formation in lean hydrocarbon combustion is fairly well known, our knowledge is still lacking for very rich mixtures (i.e., equivalence ratios from about 1.2 to 2). For lean combustion NOx formation is explained mainly by the extended Zeldovich mechanism

\[ N + O_2 \rightarrow NO + O \quad (39)^2 \]

\[ O + N_2 \rightarrow NO + N \quad (38) \]

\[ N + O_2 \rightarrow NO + O_2 \quad (40) \]

and the additional reaction:

\[ O + NO_2 \rightarrow NO + O_2 \quad (31) \]

To explain experimental NO concentrations higher than computed values for rich mixtures Pesinmore (10) suggested the direct reaction of hydrocarbon fragments with molecular nitrogen:

\[ CH + N_2 \rightarrow HCN + N \quad (41) \]

Both products of this reaction can lead to additional NO formation. The additional reactions of HCN, CN, and NH species are the unknowns in the path of complete understanding of NOx formation. Jachimowski (11) showed that the addition of only reaction (41) to the fairly well known methane oxidation mechanism improved rich combustion NO prediction considerably. And more recently, Wakelam, Jachimowski and Wilson (12) developed a comprehensive propane-air combustion mechanism. It employs not only reaction (41) but those involving HCN, CN, NCO, and NH species. When applied to computing NO concentrations for stirred-reactor combustion of rich propane-air mixtures (up to \( \phi = 1.4 \)), this mechanism gave excellent agreement with experimental results obtained in their laboratory. These investigators also applied the stirred-reactor model and their propane-air chemical model in computations attempting to match experimental flame-tube emission data of Anderson (13). The computed and experimental results agreed quite satisfactorily.

In choosing the mechanism for the present computations we have, therefore, used a modification of the mechanism developed in Ref. 12. One of the key contributions of that work is the fact that the computed NO concentration is very sensitive to the rate constant, \( k_{41} \) for reaction (41). The authors used this fact to derive a new value for \( k_{41} \) which gave the best agreement between their computed and experimental results and this improved value of \( k_{41} \) was used in the present computations. The complete mechanism used in the present computations is given in Table 1, along with rate constants and their sources. The first 40 reactions plus reaction 52 were sufficient for computations at \( \phi_p \) values from 0.5 to 1.0. The full mechanism was used for all \( \phi_p \) values greater than 1.0.

SIMULATION OF FUEL-BOUND NITROGEN

In previous analytical modeling of fuel-bound nitrogen conversion to NOx (4 and 13) the FBN has been simulated by simple species such as N, NH, NH3, HCN, CN. This is necessary because of the complexity of the organic nitrogen compounds in synthetic fuels and the lack of detailed kinetic data on the pyrolysis of these compounds. The rationale for using one of these "model compounds" to represent FBN is detailed in Ref. 14. The basic assumption is that one of these simple species represents the major pyrolysis product of the more complicated molecule that can react to form NOx. The work of Ref. 14 showed that computed results for NO conversion using N, NH, CN, and HCN are semiquantitatively similar. Inasmuch as our combustor model is quite idealized, we chose the simplest species, nitrogen atom, as our model compound for the FBN. It should be mentioned that using N as the model compound gives about 25 percent less conversion to NOx than using the other model compounds. This is due to the importance of the reverse of reaction 38, NO + N → O2 + N2.

RESULTS AND DISCUSSION

Effect of Fuel-Bound Nitrogen

The main interest in this paper is the effect of FBN on both NOx and CO final concentration. This effect is shown in Fig. 1 for NOx and Fig. 2 for CO. In each figure computed final pollutant concentration, with no further dilution in the experimentally obtained primary equivalence ratio, \( \phi_p \), from 0.5 to 1.7 for several different FBN contents. For these computations primary reaction volume was constant at 4360 cm3, the shortest primary-zone residence time; secondary residence time was fixed at nominally 1 msec. These conditions were chosen to correspond to those used in the experimental flame tube work which will be described briefly in a following section. Secondary air was added when necessary to give a \( \phi_s \) value of 0.7. Primary mixtures leaner than \( \phi_p = 0.7 \) were not diluted. It is observed in Fig. 1 that the minimum NOx concentration is always obtained at a \( \phi_p \) value between 1.4 and 1.5 for the range of \( \phi_p \) shown. At the \( \phi_p \) value for this minimum NOx concentration the CO concentration (Fig. 2) always attains its maximum value. Although NOx always increases as FBN is increased, the highest percent conversion of FBN to NOx occurs for 0.5 percent FBN at the rich \( \phi_p \) values. For example, at \( \phi_p = 1.4 \) the FBN conversions are approximately 25, 19, and 15 percent for initial FBN contents of 0.5, 1.0, and 2.0 percent, respectively. The decrease in FBN conversion with increased FBN content has been observed by others (14). The effect of FBN on CO formation is quite different. Figure 2 shows that any FBN decreases the final CO concentration. For \( \phi_p = 1.4 \), the point of greatest CO concentration, any amount of FBN decreases the CO concentration by about 17 percent.

The effect of added FBN on final NOx concentration can be seen better in Fig. 3 where the NOx concentration is plotted against percent of FBN for several different primary equivalence ratios. This plot shows that the greatest percentage increase of NOx concentration with added FBN occurs at the extremely lean and the very rich primary equivalence ratios. The absolute increase in NOx concentration for a fixed addition of FBN does not change greatly with primary equivalence ratio. For example, we can compare NOx concentrations for 0 and 0.5 percent FBN in the following table.

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2Reactions are numbered to correspond to numbers in Table 1.
The absolute changes in NOx concentration are between 230 and 345 ppm. But this translates to a change of about 200 percent at the highest and lowest $\varphi_p$ value. The value of NOx formation is highest without FBN present. Also in Fig. 3, the decrease in NOx concentration is significant by percent FBN rises above 0.5 is particularly noticeable at $\varphi_p = 1.4$, the condition for minimum NOx formation in general.

**Effect of Secondary Dilution**

The effect of additional dilution was studied by repeating the secondary stage computations for a $\varphi_p$ value of 0.5 instead of 0.7. The results for final NOx concentration are shown in Figs. 4 and for CO concentration in Fig. 5. All other conditions are the same as in Figs. 1 and 2. Final pollutant concentration is again plotted against $\varphi_p$ for various amounts of FBN. Examination of Figs. 4 and 1 and Figs. 5 and 2 show that the trends are very much the same. However, both pollutant concentration levels have been significantly reduced by the added dilution. For a better quantitative comparison of dilution effects we have replotted the 1 percent FBN NOx formation curves from Figs. 1 and 4 together in Fig. 6(a). Likewise the 1 percent FBN CO formation curves from Figs. 2 and 5 are replotted together in Fig. 6(b). From these plots it is seen that as percent FBN rises above 0.5 is particularly noticeable at $\varphi_p = 1.4$, the value for minimum NOx. NOx is reduced by about 67 percent and CO by 57 percent due to the additional dilution.

The observed concentration reductions are, of course, the combined effect of physical dilution of the primary gas and the chemical reaction in the secondary-stage combustion. It is of interest to compare these two effects for the present model and this can be done with the help of Table II. In this table we have listed three different values of NOx and CO concentration for several $(P, T)$ values from 0.8 to 1.7 when $\varphi_p = 0.7$. This drop in temperature could easily quench the NOx formation reactions which are very temperature dependent. The situation is quite different for CO.

Table II shows that the final CO concentration is determined mainly by secondary stage chemical reaction for all conditions. This is especially true for the rich primary mixtures in which CO concentration is very high. The reason for the quite different behavior of CO concentration is the lack of temperature dependence of the main CO oxidation reaction:

$$CO + OH + \text{H}_2O + \text{H} \rightarrow \text{CO}_2 \text{O}$$

A drop of 300 K in temperature, as shown in Fig. 7, has a negligible effect on the rate constant of this reaction.

**Effect of Primary and Secondary Residence Times**

Primary zone residence time was increased by changing the reaction volume by factors of 1.2 and 1.4. Thus a typical residence time of 12 msec at the smallest reaction volume was changed to about 17 msec for the largest volume. No significant effect on primary residence time was predicted for either pollutant. Typical examples of the variation of NOx and CO with primary residence time are shown in Figs. 8 and 9. Pollutant concentration is plotted against primary equivalence ratio for mixtures containing 1.0 percent fuel-bound nitrogen using three different primary residence times.

All secondary-stage computations were performed using these different reaction volumes. They were chosen to give nominal secondary residence time values of 1.2, 2, and 3 msec. Typical plots of NOx concentration versus secondary residence time with $\varphi_p$ as a parameter are shown in Figs. 10(a) and (b). For Fig. 10(a) the secondary stage $\varphi_p$ value is 0.7 and for Fig. 10(b) it is 0.5. Mixtures containing 1 percent FBN were used for the computations. For dilution to $\varphi_p = 0.7$, we see that the NOx results are somewhat sensitive to residence time variation for the very rich mixtures ($\varphi_p = 1.4$ and 1.7). There is a 35 percent increase in NOx concentration as residence time increases to 3 msec for Fig. 10(b). The secondary dilution is to $\varphi_p = 0.5$, however, Fig. 10(b) shows that final NOx concentration is completely independent of secondary residence time.

These results are explained by the temperature effect on NOx formation reactions just discussed. There can only be an effect of secondary residence time on NOx concentration where there is chemical reaction in the secondary zone. It has just been shown that NOx concentration increases in the secondary zone only for rich mixtures diluted to $\varphi_p = 0.7$. The effect of secondary residence time on CO concentration is shown in Figs. 11(a) and (b). The plots are exactly analogous to Figs. 10(a) and (b). In contrast to NOx, the CO concentration decreases as residence time increases for all values of $\varphi_p$ and both secondary dilutions. Moreover, the rate of decrease of CO concentration with residence time is fairly independent of both primary equivalence ratio and amount of secondary dilution. The trends shown here for 1.0 percent FBN in the fuel, are similar to those for other added amounts of FBN. When no added FBN is present, the trends are the same especially for secondary dilution to $\varphi_p = 0.5$. The only difference is observed for $\varphi_p = 0.7$. For this dilution the NOx concentration increases more sharply with increasing secondary residence time for $\varphi_p = 1.4$ and 1.7 than shown in Fig. 10(a).
Comparison with Experimental Data

Experimental emission measurements are being made by G. Wolfbrandt and D. Schultz at the Lewis Research Center in another part of the CRT program. Their apparatus is a two-stage flame tube. A highly turbulent hydrocarbon-air mixture is burned in two stages, with dilution in the second stage exactly as described for the present idealized stirred-reactor model. Both propane-air and propane-toluene-air mixtures are being used in this program and pyridine is added to simulate fuel bound nitrogen. The purpose of this experimental work is the same as for the present theoretical study; that is, to determine the effect of operating conditions on FBN conversion to NOx. To test whether the idealized stirred-reactor model predicts the qualitative experimental trends we have made plots comparing experimental and computed results. Figure 12 shows experimental and computed NOx concentration vs. \( \phi_p \) and Fig. 13 shows CO concentration vs. \( \phi_p \). These results are for propane-air with no added FBN. The experimental points are the first data from the flame-tube experiment. For both pollutants the qualitative agreement can be seen to be quite good. Moreover, the quantitative agreement steadily improves as we go to rich primary equivalence ratios. For this latter region agreement is within ±50 percent.

Some possible sources of discrepancy are: (1) an incomplete chemical model of the combustion; (2) experimental heat losses; and (3) mixing nonhomogeneity during the experiment. The present chemical model should be equivalent to the model of Ref. 12 in matching the data of Anderson (13). We find this to be true when we compare the results of this primary zone computations with the experimental results of Anderson. Our computed primary zone NOx and CO concentrations are in good agreement with Anderson's results for all equivalence ratios. Therefore the observed discrepancies between computed and experimental second-stage pollutant concentrations are probably due to mixing nonhomogeneity and heat losses in the second stage combustion. One important point is the fact that there is a finite length of mixing and chemical reaction at the entrance to the secondary zone for the experiment. The computational model assumes instantaneous mixing of the dilution air with the primary exhaust gases before the secondary reaction begins. Apparently the experimental effects are less important when the primary-zone burning is rich.

SUMMARY OF RESULTS

In this study we have predicted analytically the effect of operating conditions on pollutant formation in two-stage combustion. In particular we have studied the effect of these conditions on the fuel bound nitrogen conversion to NOx and also on CO formation. Propane-air mixtures were assumed to burn in a two-stage, adiabatic, perfectly-stirred reactor. Various amounts of fuel-bound nitrogen, up to 2 percent by weight as nitrogen atoms, were used. The product gases of the primary stage were diluted by added air in the second stage to an overall equivalence ratio of either 0.7 or 0.5. The computed results were compared with a limited amount of experimental data. The important results of this work may be summarized as follows:

1. Minimum NOx formation occurs in general when the primary zone equivalence ratio is between 1.4 and 1.5. However, for this range of values, the CO formation is at its highest level.

2. The percentage conversion of fuel bound nitrogen to NOx is greatest for small percentages of FBN and decreases as FBN content is raised above 0.5 percent by weight.

3. The final concentrations of NOx and CO are significantly reduced by additional secondary dilution from \( \phi_s = 0.7 \) to \( \phi_s = 0.5 \). The extra dilution lowers the secondary reaction temperature by about 300 K and thus suppresses all secondary-stage NOx reactions. Therefore, the change in NOx concentration due to the added dilution is another good of more dilution to the primary mixture. For CO, however, the final CO concentration is always a combined result of diluting the primary mixture and secondary-zone chemical reaction. This is because temperature has very little effect on CO destruction chemistry in the present model.

4. For secondary dilution to \( \phi_s = 0.5 \), NOx concentration is completely independent of secondary residence time. This is because of the suppression of NOx reactions due to the low secondary zone reaction temperatures. For secondary dilution of rich primary mixtures to \( \phi_s = 0.7 \), NOx forms in the secondary zone due to chemical reaction. Therefore NOx concentration increases with increasing secondary residence time for these rich primary mixtures only. Only in this region is chemical reaction important in the secondary zone. The final CO concentration always decreases with increasing secondary residence time because, in the present model, chemical reaction to destroy CO is not strongly affected by temperature.

5. Final NOx and CO concentrations show negligible dependence on primary zone residence time.

6. Comparison of computed results with limited experimental data indicates that there is good agreement in trends between the idealized theoretical model and the experiment. The quantitative agreement steadily improves as the primary equivalence ratio increases. For the values of greatest interest (\( \phi_p \geq 1.4 \)) the agreement between theory and experiment is within ±50 percent. Apparently, effects of experimental heat transfer losses and mixing nonhomogeneity are less for these rich primary mixtures. These last two factors were not considered in the theoretical combustion model.

CONCLUDING REMARKS

This theoretical study reinforces the well-known idea that emissions of NOx and CO can be reduced by two-stage combustion, burning rich in the primary zone and lean in the secondary. Our computations indicate that modest additional secondary dilution, from equivalence ratio 0.7 to 0.5, has a strong effect in reducing the absolute level of NOx and CO concentrations. Also it was found that there is a large increase in NOx formation due to a small amount (0.5 percent) of added FBN in the fuel. Our computed emission concentrations do not have a direct correlation with actual combustor emissions. However, the trends do indicate that removing only a moderate amount of the FBN from a real fuel during refining may not be sufficient to meet government emission standards.

Future synthetic fuels contain higher amounts of olefins and aromatic hydrocarbons than current petroleum fuels. The lower hydrogen/carbon ratio of the synthetic fuels will also affect pollutant formation. Therefore, we hope to perform additional computations using as the fuel a mixture of toluene (C7H8) and propane. The results for NOx and CO emissions can then be compared with experimental flame tube results using the same fuel mixture.
ACKNOWLEDGEMENT

I wish to express my appreciation to Gary Wolfbrandt and Don Schulte for allowing me to publish some of their experimental data.

REFERENCES


**TABLE 1. REACTION MECHANISM FOR PROPANE-AIR COMBUSTION**

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
<th>Rate constant ( k ) ( \times 10^{12} )</th>
<th>Reference</th>
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<tr>
<td>1</td>
<td>( \text{H} + \text{C}<em>{2}\text{H}</em>{4} \rightarrow \text{C}<em>{2}\text{H}</em>{4} + \text{H} )</td>
<td>( 3.0 \times 10^{15} )</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>( \text{C}<em>{2}\text{H}</em>{4} \rightarrow \text{C}<em>{2}\text{H}</em>{4} )</td>
<td>( 3.1 \times 10^{12} )</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>( \text{O} + \text{C}<em>{2}\text{H}</em>{4} \rightarrow \text{C}<em>{2}\text{H}</em>{2} + \text{H} + \text{O} )</td>
<td>( 2.3 \times 10^{13} )</td>
<td>12</td>
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<tr>
<td>4</td>
<td>( \text{O} + \text{C}<em>{2}\text{H}</em>{4} \rightarrow \text{C}<em>{2}\text{H}</em>{2} + \text{O} )</td>
<td>( 2.0 \times 10^{13} )</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>( \text{CH}_{2} + \text{O} \rightarrow \text{HCO} + \text{OH} )</td>
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<td>6</td>
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<td>( 3.0 \times 10^{13} )</td>
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</tr>
<tr>
<td>7</td>
<td>( \text{C}<em>{2}\text{H}</em>{4} \rightarrow \text{CH}_{3} + \text{H} + \text{H} )</td>
<td>( 4.6 \times 10^{13} )</td>
<td>15</td>
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<tr>
<td>8</td>
<td>( \text{CH} + \text{CH}<em>{2} \rightarrow \text{CH}</em>{3} + \text{H} )</td>
<td>( 5.1 \times 10^{12} )</td>
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<td>9</td>
<td>( \text{CH} + \text{CH}<em>{2} \rightarrow \text{CH}</em>{3} + \text{H} )</td>
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<td>20</td>
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<td>( 2.5 \times 10^{10} )</td>
<td>15</td>
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Note: Rate constants are given by the equation \( k = A \exp (-E_a/RT) \) where \( T \) is temperature in K and \( E_a \) is the ratio of the reaction activation energy to the universal gas constant.

Units of \( k \) for a unimolecular reaction are \( \text{cm}^3/\text{mole sec} \); for a bimolecular reaction, units are \( \text{cm}^3/\text{mole}^2 \text{sec} \); and for a termolecular reaction, units are \( \text{cm}^3/\text{mole}^3 \text{sec} \).
<table>
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<th>NO$_x$ concentration, ppm</th>
<th>CO concentration, ppm</th>
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<td></td>
<td>Primary exhaust gas</td>
<td>Diluted primary exhaust gas</td>
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<tr>
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<td>2 019</td>
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<tr>
<td>1.0</td>
<td>3 139</td>
<td>2 242</td>
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<td>1.2</td>
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<tr>
<td>1.4</td>
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<table>
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(b) Dilution to $\phi_s = 0.5$.

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<tr>
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<td>57 763</td>
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<tr>
<td>1.4</td>
<td>96 213</td>
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Figure 4. NO\textsubscript{x} concentration versus primary equivalence ratio for additional secondary dilution.

Figure 3. Effect of fuel-bound nitrogen on final NO\textsubscript{x} concentration.
Figure 5. - CO concentration versus primary equivalence ratio for added secondary dilution.

Figure 6. - Effect of secondary dilution.
Figure 6. Effect of secondary dilution.

Figure 7. Effect of secondary dilution on secondary reaction temperature.
Figure 8. - Effect of primary residence time on NO\textsubscript{x} formation for 1.0 percent fuel-bound nitrogen content.

Figure 9. - Effect of primary residence time on CO formation for 1.0 percent fuel bound nitrogen content.
Figure 10. - Effect of secondary residence time on final NOx concentration.

(a) Secondary equivalence ratio = 0.7.
(b) Secondary equivalence ratio = 0.5.
Figure 11. Effect of second-stage residence time on final CO concentration.

(a) SECONDARY EQUIVALENCE RATIO = 0.7.

(b) SECONDARY EQUIVALENCE RATIO = 0.5.
Figure 12. - Comparison of computed and experimental NO\textsubscript{x} concentrations.

Figure 13. - Comparison of computed and experimental CO concentrations.