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Work performed for  
**U.S. DEPARTMENT OF ENERGY**  
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# EFFECT OF FUEL NITROGEN AND HYDROGEN CONTENT ON EMISSIONS IN HYDROCARBON COMBUSTION

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## INTRODUCTION

This paper presents the results of a study of the effects of operating conditions and fuel properties on emissions during the two-stage combustion of hydrocarbon fuels. This work is part of a theoretical and experimental basic research effort in support of a major Department of Energy program to adapt ground-power gas turbines to use coal derived liquid fuels (1).<sup>1</sup> The importance of this syncrude-burning capability to the development of the gas turbine for ground power is discussed at length in reference (1). One of the important questions is how the emissions of nitrogen oxides ( $\text{NO}_x$ ) and carbon monoxide (CO) will be affected by (1) the increased content of low percentage hydrogen aromatic hydrocarbons and (2) the increased content of organic nitrogen compounds in these coal-derived fuels.

The present work is part of the Critical Research and Technology (CRT) project funded by the Department of Energy at the Lewis Research Center (DOE/NASA Interagency Agreement No. DEAI-01-77ET10350). Its main purpose is to determine, theoretically and experimentally, the effect of operating conditions on nitrogen oxides emissions during syncrude combustion. Under normal combustion conditions most of the chemically bound nitrogen in hydrocarbon fuels will be converted to nitrogen oxides ( $\text{NO}_x$ ) (2 and 3). Two-stage combustion has

been suggested by several investigators (4, 5 and 6) as a technique for reducing  $\text{NO}_x$  emissions. The control of  $\text{NO}_x$  is achieved by rich primary burning followed by very lean secondary combustion. Lack of oxygen in the rich primary zone reduces the formation of  $\text{NO}_x$  while the fuel-bound nitrogen (FBN) forms molecular nitrogen and other compounds. In the very lean secondary zone thermal  $\text{NO}_x$  formation from  $\text{N}_2$  is limited by the reduced temperature, while the other nitrogen compounds present react less rapidly to form  $\text{NO}_x$  than the original FBN. Therefore, a two-stage combustor model was used in a parametric study to extend current knowledge by determining the relationship between operating conditions, fuel properties and exhaust emissions. Although  $\text{NO}_x$  emissions are the main focus of this work, effects of variables on CO emissions were also investigated.

The preliminary analytical part of this study was reported in reference (7) and the experimental part of the work was reported in reference (8). The present paper reports additional theoretical computations and gives comparisons of theoretical and experimental results for a variety of conditions. The operating conditions used in this work include a primary equivalence ratio,  $\phi_p$ , range of 0.6 to 1.8 and one secondary equivalence ratio,  $\phi_s$ , of 0.5. The primary zone residence time ranged from 12 to 20 msec and secondary residence times from 1 to 3 msec. Fuel-bound nitrogen contents of 0.5 and 1.0 percent were used and fuel hydrogen varied from 9 to 18 weight percent. Initial temperature and pressure were not primary variables in this work. Pressure was generally maintained at 5 atm. However, a limited number of computations was performed at a pressure of 12 atm. Initial temperatures ranged from 600 to 650 K, depending upon composition.

## ANALYTICAL COMBUSTOR MODEL AND EXPERIMENTAL DETAILS

Two-stage combustion was studied experimentally in a flame tube with secondary air injection. A diagram of the apparatus is given in figure 1. Fuel

<sup>1</sup>Numbers in parentheses designate references at end of paper.

mixtures of propane, toluene and pyridine were blended to give a range of carbon-hydrogen ratios and fuel nitrogen contents matching syncrude fuel properties. Exhaust gases were sampled for emissions of nitrogen oxides, carbon monoxide, carbon dioxide and unburned hydrocarbons. From these data combustion efficiencies and percent conversion of FBN to  $\text{NO}_x$  were computed. Complete details of the experimental apparatus and procedure are given in reference (8).

The two-stage flame tube was modeled theoretically by a two-stage, adiabatic well-stirred reactor. A description of the mathematical technique is given in reference (7). This highly back-mixed, idealized system was assumed to approximate the turbulent mixing in the flame tube. The fuels used were propane, toluene and one mixture of these two fuels. The exhaust gases from the primary-stage reactor were assumed to be instantaneously diluted with the required amount of air and then enter the second-stage reactor. This assumption is one of the major differences between the theoretical model and the experimental flame tube. In the latter there are mixing inhomogeneities caused by the dilution and mixing zone between the end of the primary combustion zone the start of secondary combustion. A second difference between the idealized model and the experimental flame tube is the heat transfer losses for the experiment, which are not considered in the analytical model.

A third difference between the theoretical model and the experiment is the method of adding chemically bound nitrogen to the fuel. In the experiment the organic compound pyridine was blended with the hydrocarbon fuels. For the computations, FBN was added in the form of free nitrogen atoms. The rationale for using this simple "model compound" to represent organic fuel bound nitrogen is described in reference (7). Another difference between the experiment and the computational model is the fact that the chemical model does not take into account smoke formation. In the experimental study (8) a few smoke measurements were made. The results showed relatively high smoking tendencies even at the relatively low pressures used, and with high dilution in the secondary zone. Reference (7) showed that, in spite of these differences between experiment and analytical model, certain experimental trends for propane-air mixtures could be theoretically predicted. In reference (7), comparisons were done only for some preliminary experimental data. In this report a more extensive comparison is given between computed results and experimental data.

#### CHEMICAL MODEL

The chemistry of nitrogen oxide formation during hydrocarbon combustion has been studied extensively (9 and 10). For the computations of reference (7), a fifty-seven reaction mechanism was used for the propane-air combustion system. The important nitric oxide forming reactions are, first of all, the extended Zeldovich mechanism:



For rich mixtures, the direct reaction of hydrocarbon fragments with molecular nitrogen:



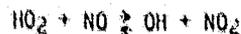
has been found to be important (10 and 11). This reaction is followed by radical attack on HCN and further reactions involving the oxidation of CN, NCO and NH species to NO. For the computations to be reported in this paper several reactions have been added to the mechanism. First of all, two reactions involving hydrocarbon fragments and NO have been added:



These reactions are important for rich primary mixtures. In addition the following three radical attacks on  $\text{HO}_2$  radical have been added:



These reactions are important mainly for lean and stoichiometric primary mixtures. The nitrogen oxides are mostly nitric oxide, NO, especially for rich primary mixtures. For lean and stoichiometric mixtures some NO is converted to nitrogen dioxide,  $\text{NO}_2$ , by the reactions



Total  $\text{NO}_x$  was always taken as the sum of the NO and  $\text{NO}_2$  concentrations. The complete mechanism used for propane-air combustion and  $\text{NO}_x$  formation is given in table I. When toluene is included in the fuel, additional reactions are needed in the oxidation mechanism. The recent work of McLain, Jachimowski and Wilson (12) has provided the first detailed oxidation mechanism for toluene. The additional reactions used in the present computation, when toluene is in the fuel mixture, are given in table II.

#### RESULTS AND DISCUSSION

##### Effect of Fuel-Bound Nitrogen on $\text{NO}_x$ Formation

The results of this study are presented for three different fuels, A, B and C. Fuel A contains nominally 18 percent hydrogen by weight, fuel B is 11 percent and fuel C contains 9 percent hydrogen. Fuel A is pure propane both for the computations and the experimental work. Fuel B is, for the computations, a mixture of 26.74 percent propane and 73.26 percent toluene by weight. Nitrogen atoms are added to give the appropriate amount of fuel bound nitrogen. Experimentally, fuel B is either the stated mixture of propane and toluene (for zero percent FBN) or the appropriate mixture of propane, toluene and pyridine when FBN is present. Fuel C is, computationally, pure toluene with nitrogen atoms added for FBN. Experimentally, fuel C is a mixture of either toluene and propane or toluene, pyridine and propane.

Figure 2(a) shows computed final (second-stage)  $\text{NO}_x$  concentration as a function of primary equivalence ratio,  $\phi_p$ , for fuel A with 0, 0.5 and 1.0 percent fuel-bound nitrogen (FBN) contents. These

results are slightly different from those presented in reference (7) because of the expanded chemical model used here. However, the same trends are shown. Minimum  $\text{NO}_x$  formation occurs for a  $\phi_p$  value of about 1.5. Although  $\text{NO}_x$  emission increases with FBN content, the conversion of FBN to  $\text{NO}_x$  decreases as the amount of FBN increases. This is shown by the curves' getting closer together as FBN content increases. Computed  $\text{NO}_x$  emissions for fuel B are shown in figure 2(b). The general trends with  $\phi_p$  and FBN content are similar to those for fuel A. Although results could not be obtained for rich  $\phi_p$  values above 1.5, the  $\phi_p$  values for minimum  $\text{NO}_x$  formation are definitely greater than 1.5 for all three nitrogen contents. For fuel C, the lowest hydrogen content fuel, computed  $\text{NO}_x$  concentration vs  $\phi_p$  results were obtained up to  $\phi_p = 1.6$ . The plots in figure 2(c) show trends with  $\phi_p$  and FBN content similar to the other fuels. However, it appears that the  $\phi_p$  value for minimum  $\text{NO}_x$  emission is now greater than 1.6. Thus the computed results indicate an increase in the  $\phi_p$  for minimum  $\text{NO}_x$  with decreasing hydrogen content of the fuel. This trend agrees with the experimental results previously published (8). A full comparison of computed and experimental  $\text{NO}_x$  emission concentrations will be given in the next section.

A detailed study of the computed results indicates a possible explanation for the shift of the  $\phi_p$  value for minimum  $\text{NO}_x$  as the amount of aromatic hydrocarbon in the fuel increases. The pyrolysis reactions of toluene (see table II) form significant amounts of hydrocarbon fragments that are not present during the pyrolysis and oxidation of propane. The reactions of these fragments form CH radicals which destroy NO directly via reactions 58 and 59 of table I. We have determined that the importance of these reactions increases significantly as the percentage of toluene in the fuel increases. This additional path for NO reaction increases the ratio between its destruction and its formation by reactions such as the oxidation of nitrogen atoms and HCN species by hydroxyl radical, OH. Therefore, as more toluene is added to the fuel, the minimum  $\text{NO}_x$  concentration occurs at increasingly higher  $\phi_p$  values.

We have shown directly the effect of  $\phi_p$  on percent FBN conversion to  $\text{NO}_x$  in figure 3, which gives this percent conversion plotted against  $\phi_p$  for all three fuels. Computed results for fuel A are shown in figure 3(a). FBN conversion is lower for the 1.0 percent fuel nitrogen content than for the 0.5 percent content. Moreover, the conversion is smallest in the rich  $\phi_p$  region of 1.4 to 1.5 where  $\text{NO}_x$  emissions are at their minimum. No flame tube experiments with added fuel nitrogen were performed for fuel A, so only computed results are shown. In figure 3(b) it is seen that, for fuel B, the computed difference in fuel nitrogen conversion between 0.5 and 1.0 percent FBN contents is quite small, even though the 1.0 percent FBN values are still lower. Experimental flame tube data are also plotted. The two points that can be compared with the computed lines are in excellent agreement with them. All the experimental data are consistent with the computed trend of slightly lower FBN conversion for the higher FBN content fuel. A much better comparison of experimental and computed conversions is shown in figure 3(c) for fuel C. The computed results for  $\phi_p$  values  $\leq 1.1$  indicate the conversion to  $\text{NO}_x$  is significantly lower for 1.0 percent FBN content than for 0.5 percent FBN. However for

$\phi_p$  values greater than 1.1, the percents conversion are very close for the two FBN contents. The experimental data points shown are in good qualitative agreement with these computed trends and also in good quantitative agreement with the computed results for rich primary equivalence ratios. It is significant to note that FBN conversion rates of less than 10 percent can be achieved with rich-lean, two-stage combustion.

#### Effect of Hydrogen Content on $\text{NO}_x$ Formation

The computed effect of hydrogen content on  $\text{NO}_x$  emissions is shown in figure 4. The final  $\text{NO}_x$  concentration, plotted against primary equivalence ratio for the three fuels used, is shown in figure 4(a) for no fuel bound nitrogen content. For  $\phi_p$  values up to about 1.5,  $\text{NO}_x$  concentration increases as the fuel hydrogen content decreases. However, at  $\phi_p = 1.6$ , the computed  $\text{NO}_x$  concentration is the same for the 9 percent and the 18 percent hydrogen fuels. Similar situations can be seen in figures 4(b) and (c) which show the same type of plot for the three fuels with 0.5 and 1.0 percent FBN content. In these plots two trends are noticeable. First, the effect of decreasing the hydrogen content becomes smaller as the hydrogen percentage decreases. Second, the presence of fuel nitrogen appears to lessen the  $\text{NO}_x$  increase caused by lowering the fuel hydrogen content. Therefore, the computations predict that hydrogen content has a small effect on  $\text{NO}_x$  emission at rich equivalence ratios in this two-stage combustion. The experimental results agree with this predicted trend, as can be seen by examining the experimental data also plotted in figures 4(a) to (c). For rich primary mixtures these data indicate essentially the same  $\text{NO}_x$  emissions for fuels B and C, whose hydrogen contents are 11 and 9 percent. Quantitatively, the theoretical model predicts too little  $\text{NO}_x$  for rich primary mixtures and over predicts  $\text{NO}_x$  for lean primary mixtures. The lean side effect is mainly due to lack of heat-loss corrections in the model. This results in higher computed reaction temperatures and thus too much thermal  $\text{NO}_x$  formation. For the rich primary mixtures deficiencies in the gas-phase chemical mechanism for the conversion of fuel nitrogen to  $\text{NO}_x$  may explain a good part of the discrepancies. In figure 4(c) we have also shown experimental data (the filled-in diamond symbols) for  $\text{NO}_x$  emissions using an actual coal syncrude fuel. The fuel was made by the SRC-II process and is a 2.9:1 blend of middle and heavy distillates. The hydrogen content is 8.64 weight percent and the bound nitrogen content is 0.95 percent. Detailed properties of this fuel are given in table I of reference (8). It can be seen that there is good agreement between measured  $\text{NO}_x$  for the actual syncrude fuel and for the toluene-propane-pyridine simulated syncrude fuel.

#### Effect of Fuel Nitrogen and Hydrogen Content on CO Emission

The effect of both hydrogen and nitrogen content of the fuel on CO emission is shown in figure 5. Final CO concentration is plotted against  $\phi_p$  for the three different fuels. In figure 5(a) the fuels contain no nitrogen. In figures 5(b) and (c) the fuels contain 0.5 and 1.0 percent FBN. For all nitrogen contents we see that the computed CO concentration increases significantly as hydrogen content of the fuel decreases. By comparing curves for the same fuel in figures 5(a) to (c) it can readily be seen that computed CO concentration is independ-

ent of fuel-bound nitrogen content. Theoretically, it would be expected that CO formation would increase with decreasing hydrogen to carbon ratio of a hydrocarbon fuel from equilibrium thermodynamic considerations, without any chemical kinetics. Therefore, the observed increase in CO emissions with decreasing hydrogen content of our three fuels is not surprising. Experimental verification of this trend for two-stage combustion can be seen in figure 5(a). The data points plotted show considerable scatter. However, they follow the trend of the computed curves with  $\phi_p$ . For this condition of no added fuel bound nitrogen, the data indicate a generally increasing CO level as hydrogen content decreases. The experimental data in figures 5(b) and (c) are insufficient to determine any CO trend with hydrogen content. However, they follow the computed trend with  $\phi_p$  and also verify the lack of dependence of CO concentration on fuel bound nitrogen content found theoretically.

#### Effect of Residence Times on $\text{NO}_x$ and CO Emissions

Previous theoretical computations (7) for fuel A showed that  $\text{NO}_x$  and CO emissions are independent of primary-stage residence time. The experimental results (8) showed an increase of  $\text{NO}_x$  concentration with increasing primary-zone residence time for fuel C. These experimental results are shown in figure 6 along with theoretical computations for fuel C. The data shown are for a primary equivalence ratio of 1.0. The computations show the same  $\text{NO}_x$  independence of primary-zone volume (i.e., residence time) as found for fuel A. The experimental results show an increase of about 16 percent in  $\text{NO}_x$  formation when the primary-zone residence time increases by about 19 percent. The failure of the model to predict this trend is no doubt due to its lack of heat-loss corrections and inability to simulate the finite experimental mixing of air with the primary combustion gases.

The theoretical computations (7) for fuel A indicated some increase of  $\text{NO}_x$  formation with increasing secondary residence time. This was true only for rich primary mixtures, diluted to a secondary equivalence ratio of 0.7. When these rich mixtures were diluted to  $\phi_s = 0.5$ , the  $\text{NO}_x$  formation was found to be constant as secondary residence time increased. In figures 7(a) and (b) we have plotted  $\text{NO}_x$  concentration vs. secondary residence time for fuels B and C to see the effect of fuel hydrogen content. Only  $\phi_s = 0.5$  was used for the computations. It is apparent that  $\text{NO}_x$  concentration is generally independent of secondary residence time for these lower hydrogen-content fuels. Very slight increases can be seen for the richest  $\phi_p$  values of 1.4 and 1.6. Experimental results for fuel B are shown in figure 8, where  $\text{NO}_x$  concentration is plotted against secondary equivalence ratio for several secondary residence times and  $\phi_p = 1.5$ . These data show a very slight effect of secondary residence times at  $\phi_s = 0.5$  and a significant increase in  $\text{NO}_x$  with secondary residence time for  $\phi_s = 0.6$  and 0.7. These experimental results are in agreement with the computed trends. We have found that fuel hydrogen content has no effect on the  $\text{NO}_x$  trend with secondary residence time.

Figures 9(a) and (b) show plots of computed CO concentration against secondary residence time for fuels B and C. Fuel nitrogen content is 0.5 percent, as in figure 7. The trends are the same as found for fuel A in reference (7). The CO emission decreases significantly with increasing residence

time. Thus, one can decrease the CO emission without increasing  $\text{NO}_x$  by increasing the secondary residence time. This is particularly important because of the increased level of CO emissions in these lower hydrogen content fuels.

#### Effect of Pressure on $\text{NO}_x$ Formation

Although pressure was not a primary variable in this study, a limited number of computations was performed at a higher pressure of 12 atm. Fuel B was used. Computations were performed for fuel nitrogen contents of 0 and 0.5 percent over a  $\phi_p$  range of 0.8 to 1.5. Plots of final  $\text{NO}_x$  and CO concentration vs.  $\phi_p$  for pressures of 5 and 12 atm are shown in figures 10 and 11 for the two nitrogen contents. Results show that increasing the pressure causes a small to moderate increase in  $\text{NO}_x$  concentration at most  $\phi_p$  values. For the rich  $\phi_p$  values of most interest the increase is 30 percent for no FBN and only 3 percent for 0.5 percent FBN. All the  $\text{NO}_x$  increase is due to the thermal  $\text{NO}_x$ . The computed percent conversion of fuel nitrogen to  $\text{NO}_x$  are slightly lower at 12 atmospheres pressure than at 5 atm. Carbon monoxide formation decreases at the higher pressure. It was not possible to perform experiments at high pressure to obtain data to compare with the computed results.

#### SUMMARY OF RESULTS

An experimental and theoretical study has been made of the effect of operating conditions and fuel properties on emissions during two-stage syncrude combustion. The hydrogen content of the fuel was varied from 18 percent (pure propane) to 9 percent (pure toluene). Nitrogen content of each fuel was changed from zero up to 1.0 percent by weight. Primary-stage equivalence ratio was varied from 0.6 to 1.8 and second-stage dilution was always to an equivalence ratio of 0.5. Pressure was usually held constant at 0.48 MPa (5 atm) and inlet mixture temperatures varied from 600 to 650 K, depending upon its composition. Nitrogen oxides and carbon monoxide emissions were computed using a two-stage, well-stirred reactor combustor model and were measured experimentally using a two-stage, highly turbulent flame tube. The results of this study may be summarized as follows:

1. The simple stirred-reactor model was able to predict several of the important trends for the emissions from two-stage hydrocarbon combustion.

2. Two-stage, rich-lean combustion gives experimental conversion rates of fuel-bound nitrogen to  $\text{NO}_x$  of 10 percent or less for rich equivalence ratios of 1.5 to 1.7 and fuel-bound nitrogen contents of 0.5 and 1.0 percent by weight. These results of the experimental flame-tube work are the same as those predicted by the two-stage well-stirred reactor computations.

3. Both experiment and theory show that decreasing fuel hydrogen content causes a small increase in  $\text{NO}_x$  emission level. The presence of fuel nitrogen may decrease the effect of hydrogen content on  $\text{NO}_x$ .

4. Although the absolute level of  $\text{NO}_x$  emission increases with fuel-bound nitrogen content, the percent conversion of the fuel nitrogen decreases slightly as the amount of fuel nitrogen increases. This is found both experimentally and theoretically.

5. Both experimentally and theoretically, the rich primary equivalence ratio for minimum  $\text{NO}_x$  formation shifts to higher values as the amount of aromatic hydrocarbon (toluene) in the fuel is increased. This can be explained by the reaction of

the pyrolysis products of toluene directly with NO to increase the NO destruction rate.

6. Carbon monoxide emissions increase significantly with decreasing fuel hydrogen content, as shown by both the experiments and the theoretical computations. Also CO emissions are highest at the rich primary equivalence ratios that give minimum  $\text{NO}_x$ .

7. Both experiments and theoretical computations show that carbon monoxide emissions are independent of fuel-bound nitrogen content.

8. The formation of  $\text{NO}_x$  increases slightly at most primary equivalence ratios when the pressure is increased from 5 to 12 atm. The increase is between 3 and 30 percent at the rich equivalence ratios for minimum  $\text{NO}_x$  formation. All the increase is due to thermal  $\text{NO}_x$ . The percent conversion of fuel-bound nitrogen at 12 atm is slightly less than at 5 atm.

9. Computed  $\text{NO}_x$  emissions are essentially independent of secondary residence time for all fuels used, when the secondary equivalence ratio is 0.5.

10. Computed CO emission decreases significantly as secondary residence time increases for all fuels used and all operating conditions.

11. Computed  $\text{NO}_x$  and CO emissions are independent of primary-zone residence time. Experimental  $\text{NO}_x$  emissions, however, increase moderately with primary residence time.

#### CONCLUDING REMARKS

Although the theoretical and experimental combustors used in this study are not actual gas turbine combustors, the results obtained have some application to more practical combustors. Experimentally, a coal syncrude distillate of the SRC-II process gave  $\text{NO}_x$  emissions that matched very well those from the fuel blends used to simulate the actual fuels in both hydrogen and nitrogen content. Limited measurements of smoke from the rich-lean combustion of these simulated syncrude fuels indicated relatively high smoke emissions in spite of the very lean second-stage burning. This fact, along with the high observed carbon monoxide emissions, indicates that trade-offs will be necessary between the conditions that minimize  $\text{NO}_x$  and those that control CO and smoke emissions.

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TABLE I. - REACTIONS FOR PROPANE-AIR COMBUSTION AND NO<sub>x</sub> FORMATION

Reaction number	Reaction	Rate constant <sup>a, b</sup>			Reference
		A	n	ε	
1	M + C <sub>3</sub> H <sub>8</sub> → C <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub> + M	5.0x10 <sup>15</sup>	0.0	32 713	13
2	C <sub>2</sub> H <sub>5</sub> → C <sub>2</sub> H <sub>4</sub> + H	3.16x10 <sup>13</sup>		20 483	
3	O + C <sub>2</sub> H <sub>4</sub> → CH <sub>3</sub> + HCO	2.26x10 <sup>13</sup>		1 359	
4	O + C <sub>2</sub> H <sub>4</sub> → CH <sub>2</sub> O + CH <sub>2</sub>	2.5x10 <sup>13</sup>		2 516	
5	CH <sub>3</sub> C <sub>3</sub> H <sub>8</sub> → CH <sub>4</sub> + C <sub>3</sub> H <sub>7</sub>	2.0x10 <sup>13</sup>		5 184	
6	C <sub>3</sub> H <sub>7</sub> → C <sub>2</sub> H <sub>4</sub> + CH <sub>3</sub>	4.0x10 <sup>13</sup>		16 658	
7	H + C <sub>2</sub> H <sub>4</sub> → H <sub>2</sub> + C <sub>2</sub> H <sub>3</sub>	1.1x10 <sup>14</sup>		4 278	
8	OH + C <sub>2</sub> H <sub>4</sub> → H <sub>2</sub> O + C <sub>2</sub> H <sub>3</sub>	1.0x10 <sup>14</sup>		1 761	
9	M + C <sub>2</sub> H <sub>3</sub> → C <sub>2</sub> H <sub>2</sub> + H + M	3.0x10 <sup>16</sup>		20 382	
10	O + C <sub>2</sub> H <sub>2</sub> → CH <sub>2</sub> + CO	5.2x10 <sup>13</sup>		1 862	14
11	M + CH <sub>4</sub> → CH <sub>3</sub> + H + M	4.7x10 <sup>17</sup>		46 900	15
12	H + CH <sub>4</sub> → CH <sub>3</sub> + H <sub>2</sub>	1.26x10 <sup>14</sup>		5 989	13
13	O + CH <sub>4</sub> → CH <sub>3</sub> + OH	2.0x10 <sup>13</sup>		4 640	
14	OH + CH <sub>4</sub> → CH <sub>3</sub> + H <sub>2</sub> O	3.0x10 <sup>13</sup>		3 020	
15	CH + O <sub>2</sub> → HCO + O	1.0x10 <sup>13</sup>		0.0	
16	CH <sub>2</sub> + O <sub>2</sub> → CH <sub>2</sub> O + O	1.0x10 <sup>14</sup>		1 862	15
17	CH <sub>3</sub> + O <sub>2</sub> → CH <sub>2</sub> O + OH	1.7x10 <sup>12</sup>		7 045	13
18	CH <sub>3</sub> + O → CH <sub>2</sub> O + H	6.8x10 <sup>13</sup>		0.0	15
19	CH <sub>2</sub> O + H → HCO + H <sub>2</sub>	2.0x10 <sup>13</sup>		1 660	
20	CH <sub>2</sub> O + O → HCO + OH	5.0x10 <sup>13</sup>		2 300	
21	CH <sub>2</sub> O + OH → HCO + H <sub>2</sub> O	5.0x10 <sup>15</sup>		6 540	
22	HCO + O → CO + OH	3.0x10 <sup>13</sup>		0.0	
23	HCO + H → CO + H <sub>2</sub>	2.0x10 <sup>13</sup>		0.0	
24	HCO + OH → CO + H <sub>2</sub> O	3.0x10 <sup>13</sup>		0.0	
25	M + HCO → H + CO + M	3.0x10 <sup>14</sup>		7 397	
26	CO + OH → CO <sub>2</sub> + H	4.0x10 <sup>12</sup>		4 026	
27	M + CO + O → CO <sub>2</sub> + M	2.8x10 <sup>13</sup>		-2 285	
28	CO + O <sub>2</sub> → CO <sub>2</sub> + O	1.2x10 <sup>11</sup>		17 615	
29	H + O <sub>2</sub> → OH + O	2.2x10 <sup>14</sup>		8 450	16
30	O + H <sub>2</sub> → OH + H	1.8x10 <sup>10</sup>	1.0	4 480	16
31	H <sub>2</sub> + OH → H <sub>2</sub> O + H	5.2x10 <sup>13</sup>	.0	3 270	15
32	OH + OH → O + H <sub>2</sub> O	6.3x10 <sup>12</sup>		550	16
33	H + O <sub>2</sub> + M → HO <sub>2</sub> + M	1.5x20 <sup>15</sup>		-503	16
34	O + O + M → O <sub>2</sub> + M	5.7x10 <sup>13</sup>		-900	17
35	H + H + M → H <sub>2</sub> + M	8.3x10 <sup>17</sup>	-1.0	0.0	16
36	H + OH + M → H <sub>2</sub> O + M	8.4x10 <sup>21</sup>	-2.0	0.0	16
37	H + CH <sub>3</sub> → H <sub>2</sub> + CH <sub>2</sub>	2.7x10 <sup>11</sup>	.67	12 930	13
38	O + CH <sub>3</sub> → OH + CH <sub>2</sub>	1.9x10 <sup>11</sup>	.68	12 930	13
39	OH + CH <sub>3</sub> → H <sub>2</sub> O + CH <sub>2</sub>	2.7x10 <sup>11</sup>	.67	12 930	13
40	HO <sub>2</sub> + NO → NO <sub>2</sub> + OH	1.2x10 <sup>13</sup>	.0	1 200	18
41	O + NO <sub>2</sub> → NO + O <sub>2</sub>	1.0x10 <sup>13</sup>		300	
42	NO + O + M → NO <sub>2</sub> + M	5.6x10 <sup>15</sup>		-584	
43	NO <sub>2</sub> + H → NO + OH	2.9x10 <sup>14</sup>		400	
44	N + O <sub>2</sub> → NO + O	6.4x10 <sup>9</sup>	1.0	3 145	13
45	O + N <sub>2</sub> → NO + N	1.8x10 <sup>14</sup>	.0	38 370	19
46	N + OH → NO + H	4.0x10 <sup>13</sup>		0.0	20
47	CH + N <sub>2</sub> → HCN + N	1.5x10 <sup>11</sup>		9 562	13
48	CN + H <sub>2</sub> → HCN + H	6.0x10 <sup>13</sup>		2 669	
49	O + HCN → OH + CN	1.4x10 <sup>11</sup>	.68	8 506	
50	OH + HCN → H <sub>2</sub> O + CN	2.0x10 <sup>11</sup>	.60	2 516	
51	CN + O <sub>2</sub> → NCO + O	3.2x10 <sup>13</sup>		503	
52	CN + CO <sub>2</sub> → NCO + CO	3.7x10 <sup>12</sup>		0.0	
53	O + NCO → NO + CO	2.0x10 <sup>13</sup>			
54	N + NCO → N <sub>2</sub> + CO	1.0x10 <sup>13</sup>			
55	H + NCO → NH + CO	2.0x10 <sup>13</sup>			
56	NH + OH → N + H <sub>2</sub> O	5.0x10 <sup>11</sup>	.5	1 006	
57	CH + NO → N + HCO	1.0x10 <sup>14</sup>	.0	0.0	21
58	CH + NO → O + HCN	1.0x10 <sup>13</sup>	.0	0.0	21
59	CH + CO <sub>2</sub> → HCO + CO	3.7x10 <sup>12</sup>	.0	0.0	13
60	H + CH <sub>2</sub> → H <sub>2</sub> + CH	2.9x10 <sup>11</sup>	.7	13 080	22
61	O + CH <sub>2</sub> → OH + CH	3.2x10 <sup>11</sup>	.5	13 080	22
62	OH + CH <sub>2</sub> → H <sub>2</sub> O + CH	5.0x10 <sup>11</sup>	.5	3 019	22
63	H + HO <sub>2</sub> → OH + OH	2.5x10 <sup>14</sup>	.0	960	15
64	O + HO <sub>2</sub> → OH + O <sub>2</sub>	5.0x10 <sup>13</sup>	.0	503	15
65	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	5.0x10 <sup>13</sup>	.0	503	15

<sup>a</sup>Rate constant is given by the equation  $k = AT^n \exp(-\epsilon/T)$ , where T is temperature in K and  $\epsilon$  is the ratio of the reaction activation energy to the universal gas constant, also in K.

<sup>b</sup>Units of k are sec<sup>-1</sup> for a unimolecular reaction; for a bimolecular reaction they are cm<sup>3</sup>/mole-sec and for a termolecular reaction cm<sup>6</sup>/mole<sup>2</sup>-sec.

TABLE II. - REACTIONS FOR TOLUENE OXIDATION

Reaction number	Reaction	Rate constant <sup>a, b</sup>			Reference
		A	n	e	
66	$C_7H_8 + O_2 \rightleftharpoons C_7H_7 + HO_2$	$1.0 \times 10^{14}$	0.0	20 130	12
67	$C_7H_8 \rightleftharpoons C_7H_7 + H$	$3.2 \times 10^{15}$	↓	44 440	
68	$H + C_7H_8 \rightleftharpoons C_7H_7 + H_2$	$1.0 \times 10^{14}$			
69	$O + C_7H_8 \rightleftharpoons C_7H_7 + OH$	$1.0 \times 10^{14}$			
70	$OH + C_7H_8 \rightleftharpoons C_7H_7 + H_2O$	$1.0 \times 10^{13}$			
71	$O + C_7H_7 \rightleftharpoons CH_2O + C_6H_5$	$1.0 \times 10^{13}$		0.0	
72	$C_7H_7 \rightleftharpoons C_4H_3 + C_3H_4$	$1.0 \times 10^{15}$		51 330	
73	$C_3H_4 \rightleftharpoons C_2H_2 + CH_2$	$1.0 \times 10^{15}$		51 330	
74	$C_3H_4 \rightleftharpoons CH_3 + C_2H$	$1.0 \times 10^{15}$		51 330	
75	$O + C_3H_4 \rightleftharpoons C_2H_3 + HCO$	$1.0 \times 10^{13}$		0.0	
76	$O_2 + C_2H_7 \rightleftharpoons 2CO + C_3H_5 + C_2H_2$	$5.0 \times 10^{12}$		7 550	
77	$C_3H_6 \rightleftharpoons CH_3 + C_2H_2$	$1.0 \times 10^{14}$		27 180	
78	$C_3H_5 \rightleftharpoons C_3H_4 + H$	$1.3 \times 10^{13}$		30 790	
79	$C_2H + O_2 \rightleftharpoons HCO + CO$	$1.0 \times 10^{13}$		3 523	
80	$C_7H_8 \rightleftharpoons C_6H_5 + CH_3$	$1.0 \times 10^{17}$		52 550	12
81	$C_6H_6 \rightleftharpoons C_4H_3 + C_2H_2$	$3.2 \times 10^{14}$	43 280	14	
82	$C_4H_3 \rightleftharpoons C_2H + C_2H_2$	$1.0 \times 10^{14}$	29 700		
83	$C_4H_3 \rightleftharpoons C_4H_2 + H$	$1.0 \times 10^{14}$	29 700		
84	$O_2 + C_6H_5 \rightleftharpoons 2CO + C_2H_3 + C_2H_2$	$7.5 \times 10^{13}$	7 550		
85	$H + C_2H_2 \rightleftharpoons C_2H + H_2$	$2.0 \times 10^{14}$	9 562		
86	$O + C_2H_2 \rightleftharpoons C_2H + OH$	$3.2 \times 10^{15}$	8 556		
87	$OH + C_2H_2 \rightleftharpoons C_2H + H_2O$	$6.0 \times 10^{12}$	3 523		
88	$O + C_2H \rightleftharpoons CO + CH$	$5.0 \times 10^{13}$	0.0		
89	$O_2 + C_2H_2 \rightleftharpoons 2HCO$	$4.0 \times 10^{12}$	14 090		
90	$M + C_2H_2 \rightleftharpoons C_2H + H + M$	$1.0 \times 10^{14}$	57 370		
91	$O + C_3H_5 \rightleftharpoons C_2H_4 + HCO$	$1.0 \times 10^{13}$	↓	0.0	c

<sup>a</sup>Rate constant is given by the equation  $k = AT^n \exp(-e/T)$ , where T is temperature in K and e is the ratio of the reaction activation energy to the universal gas constant, also in K.

<sup>b</sup>Units of k are  $\text{sec}^{-1}$  for a unimolecular reaction; for a bimolecular reaction they are  $\text{cm}^3/\text{mole-sec}$  and for a termolecular reaction  $\text{cm}^6/\text{mole}^2\text{-sec}$ .

<sup>c</sup>Estimate - by analogy with reaction 75.

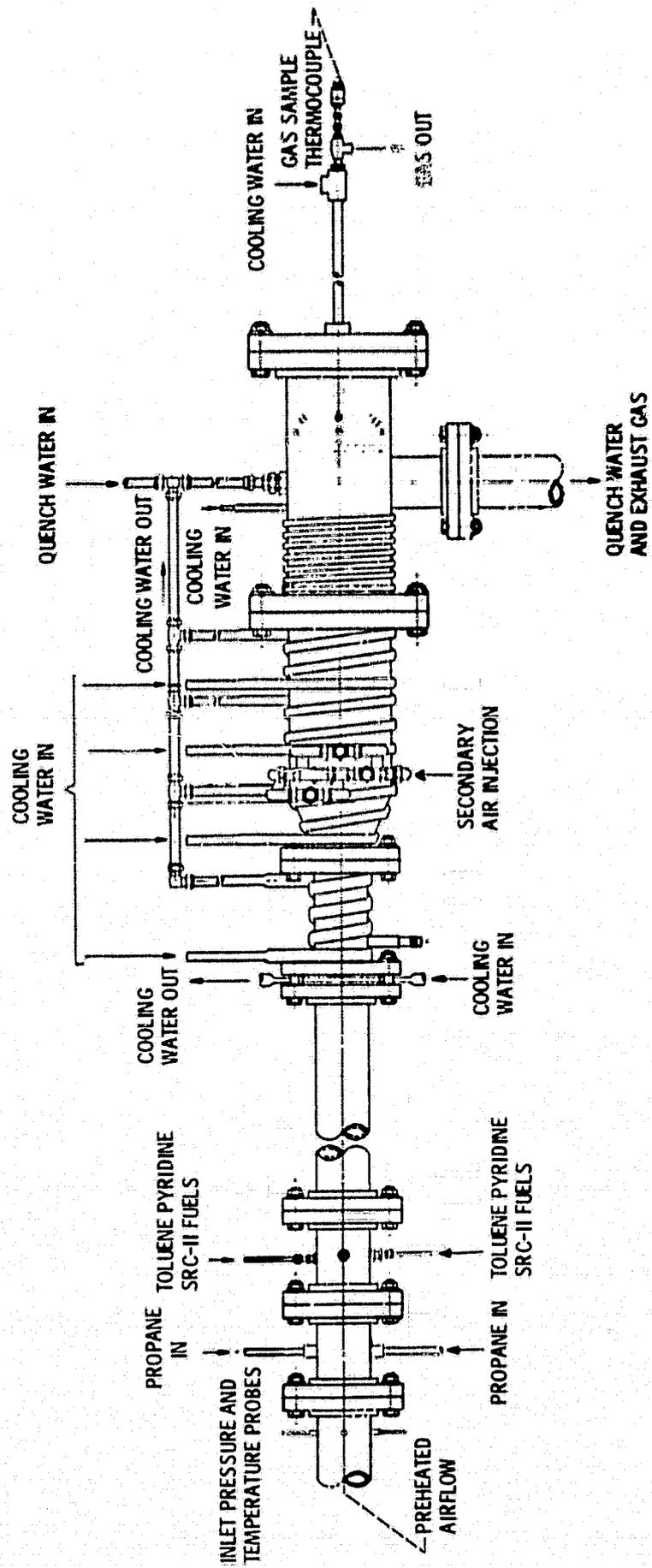


Figure 1. - CRT Flame tube apparatus.

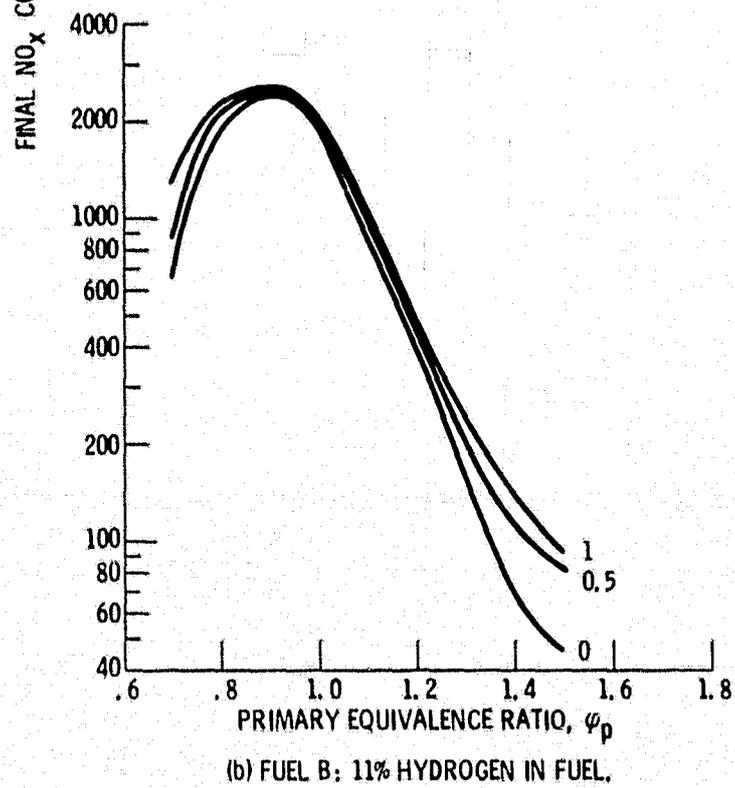
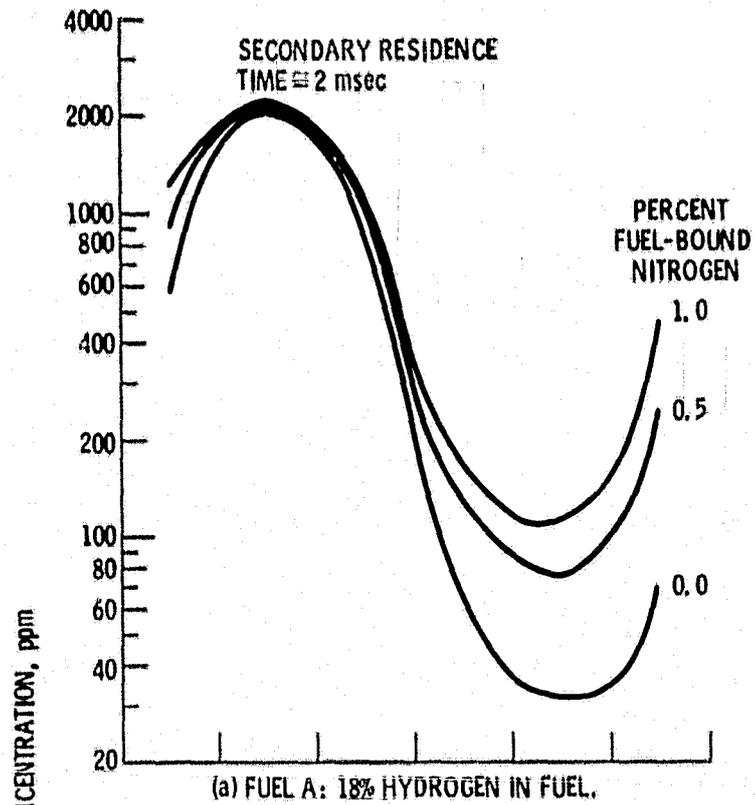
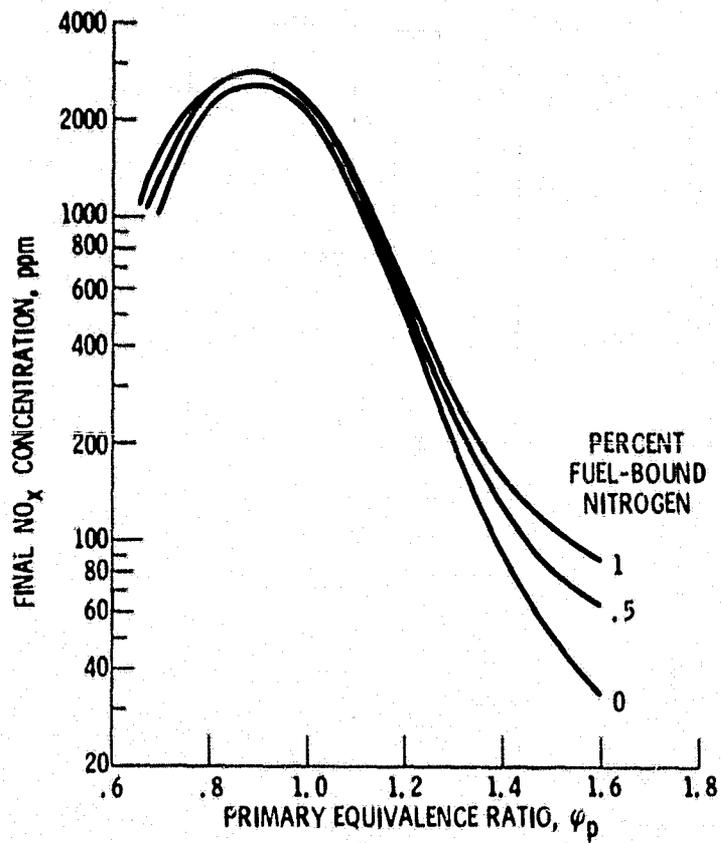


Figure 2. - Computed  $\text{NO}_x$  concentration vs. primary equivalence ratio. Secondary equivalence ratio = 0.5.



(c) FUEL C: 9 PERCENT HYDROGEN.

Figure 2. - Concluded.

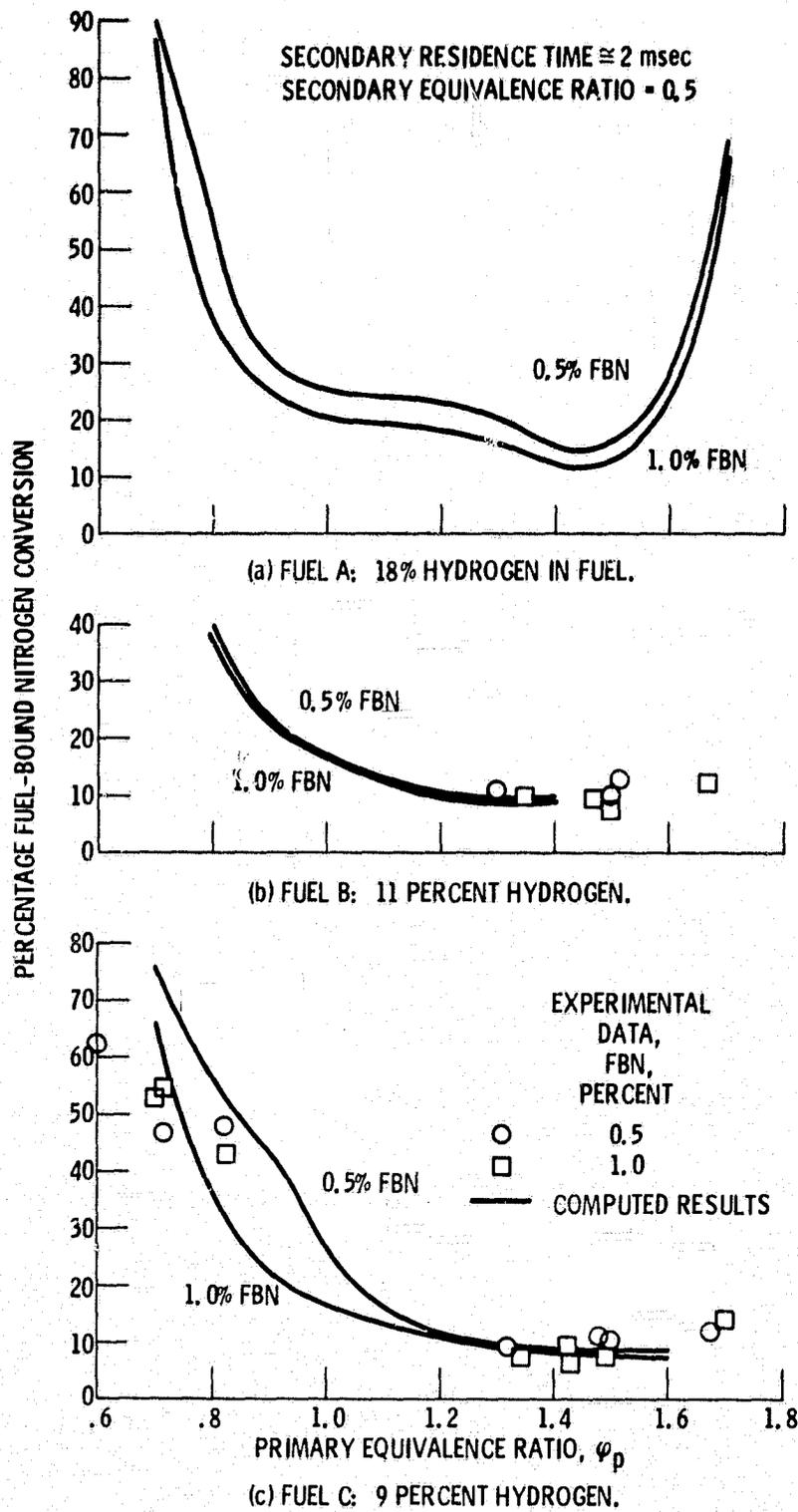


Figure 3. - Fuel-bound nitrogen conversion vs. primary equivalence ratio.

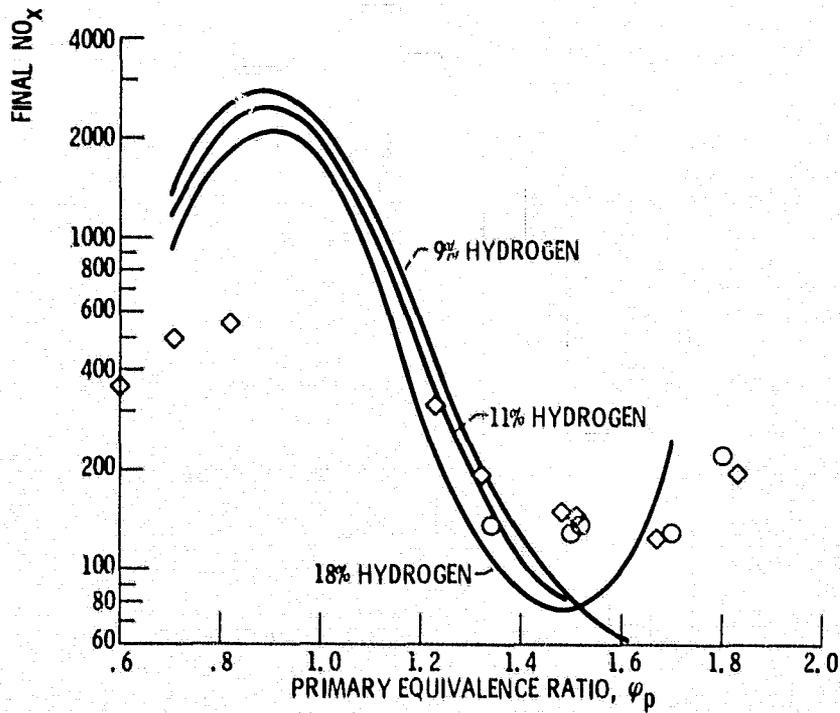
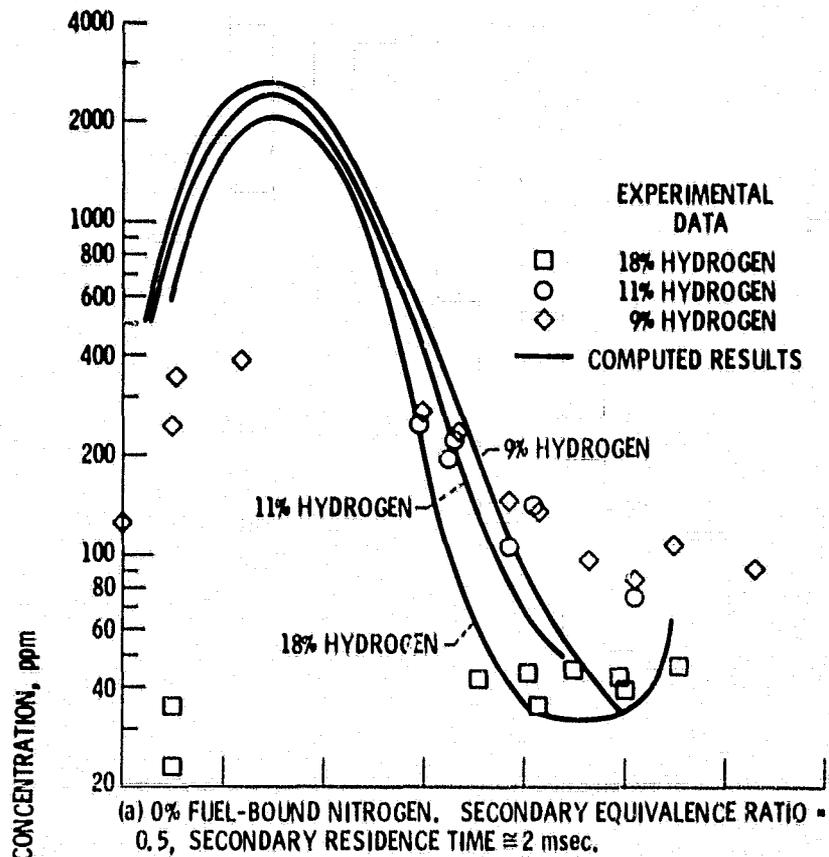
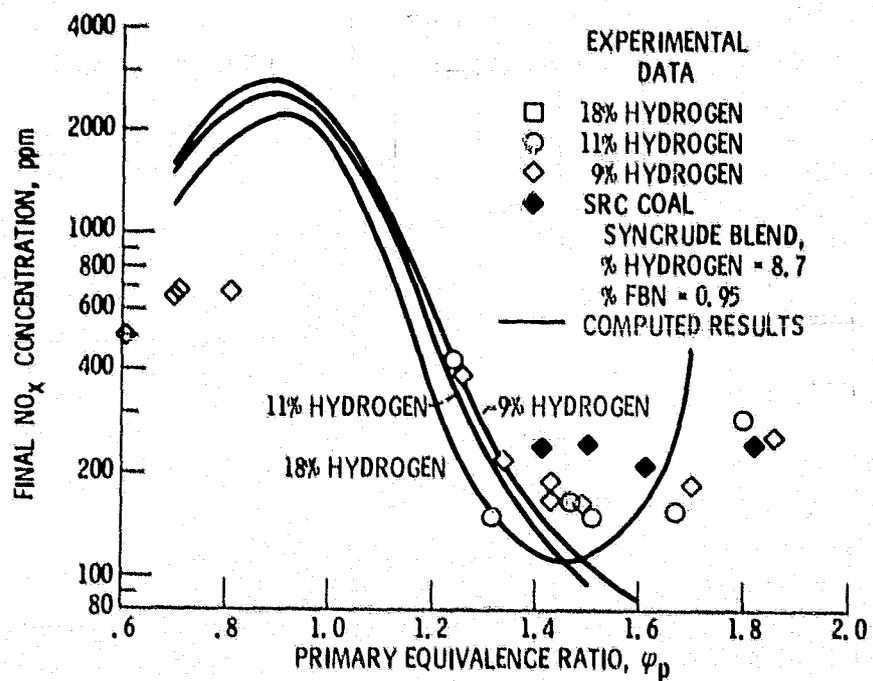


Figure 4. - Effect of hydrogen content on  $\text{NO}_x$  emissions.



(c) 1.0% FUEL-BOUND NITROGEN. SECONDARY EQUIVALENCE RATIO = 0.5, SECONDARY RESIDENCE TIME  $\approx$  2 msec.

Figure 4. - Concluded.

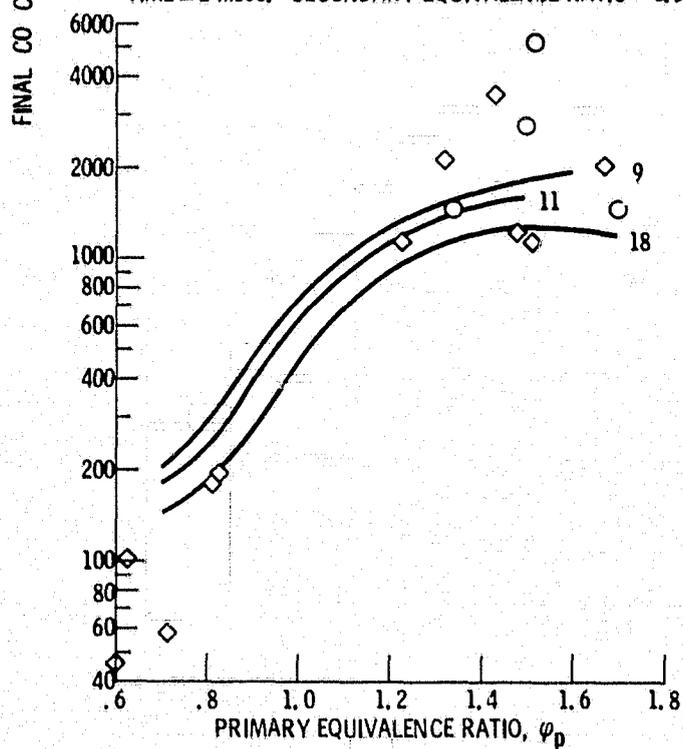
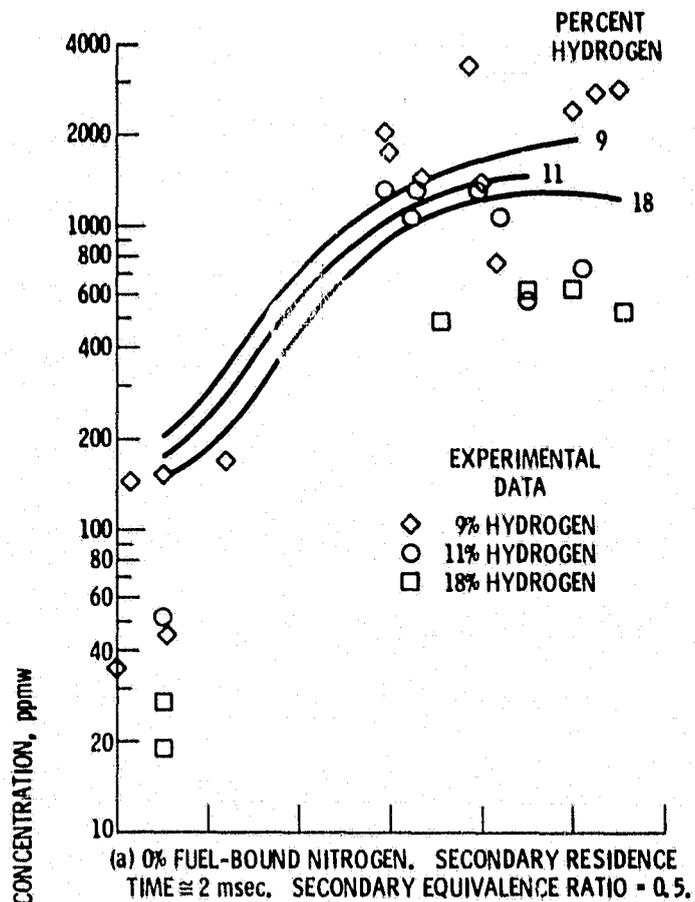


Figure 5. - Effect of percent hydrogen on carbon monoxide emissions for hydrocarbon combustion.

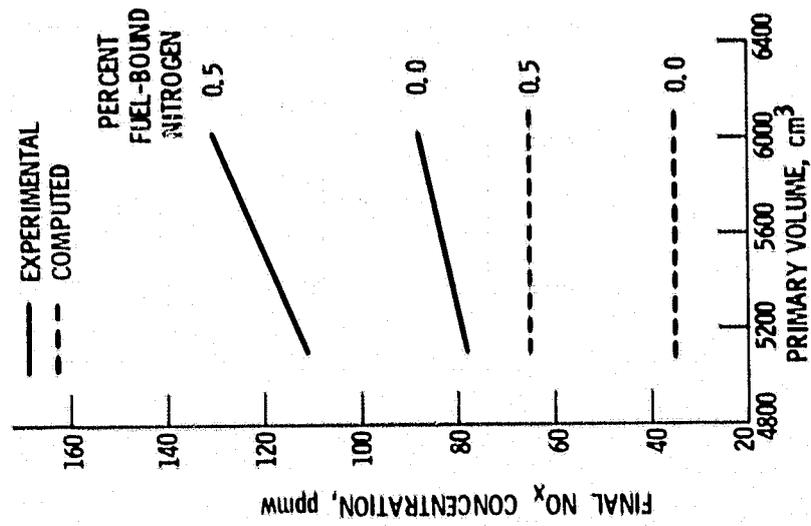
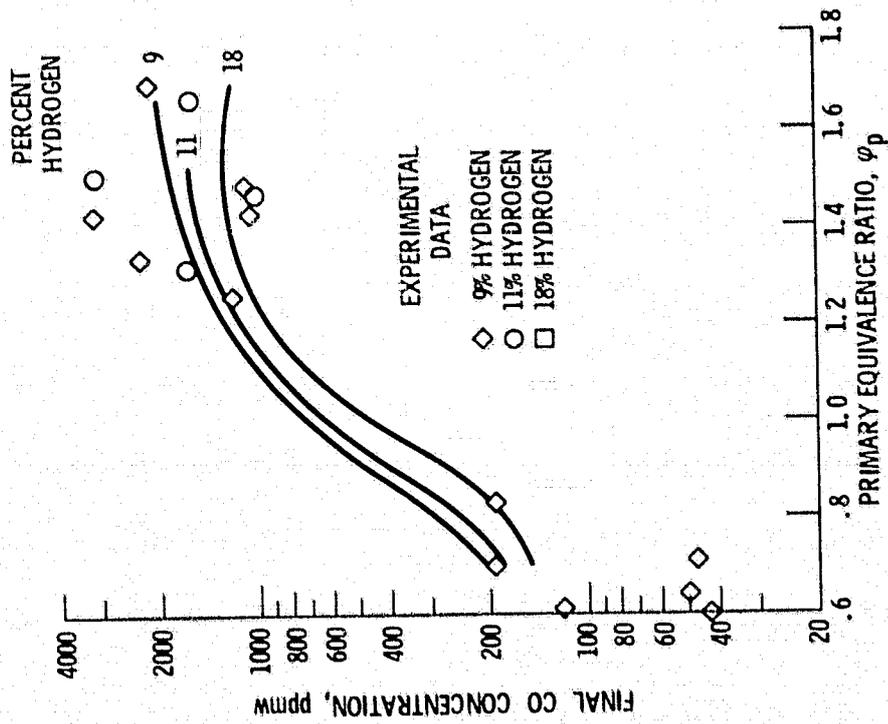
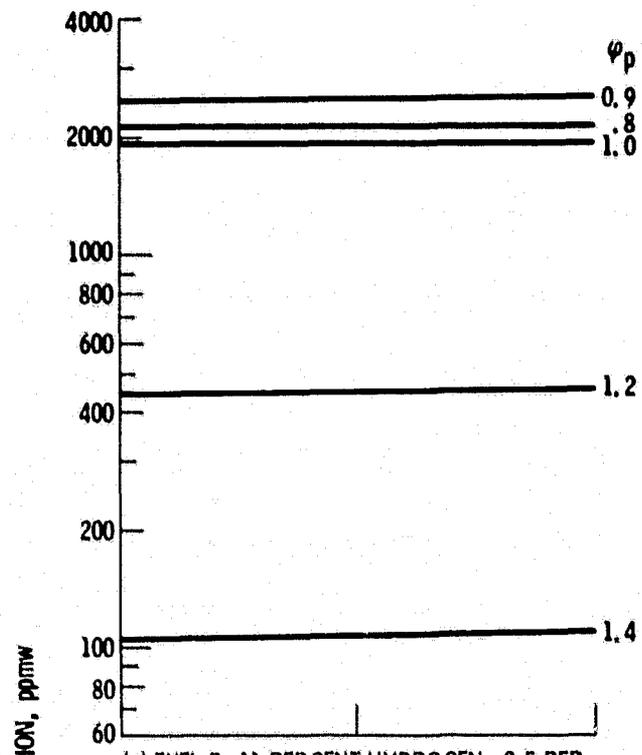


Figure 6. -  $\text{NO}_x$  concentration vs. primary volume. Fuel C: 9 percent hydrogen; primary equivalence ratio = 1.6, secondary residence time  $\approx$  2 msec, secondary equivalence ratio = 0.5.

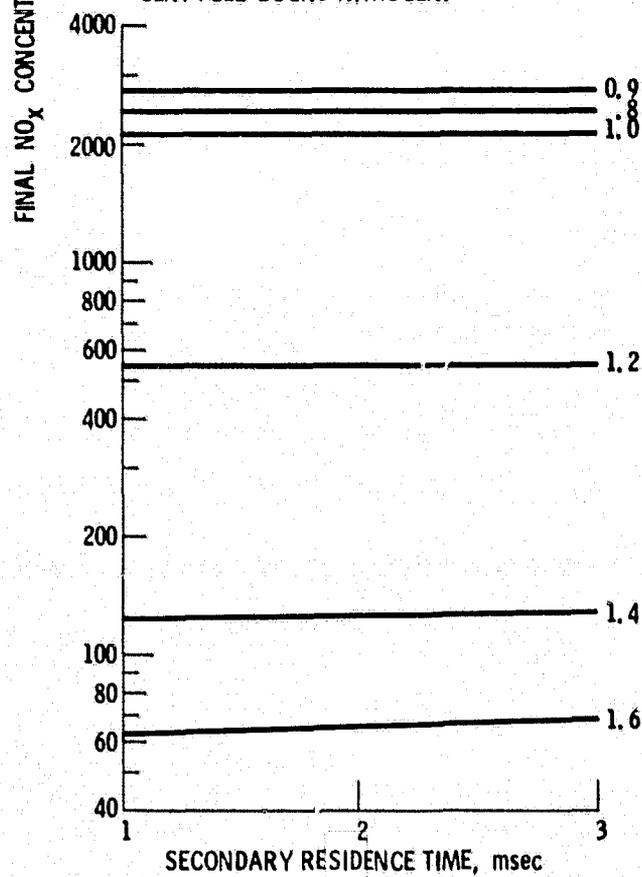


(c) 1.0% FUEL-BOUND NITROGEN. SECONDARY RESIDENCE TIME  $\approx$  2 msec. SECONDARY EQUIVALENCE RATIO = 0.5.

Figure 5. - Concluded.



(a) FUEL B: 11 PERCENT HYDROGEN; 0.5 PERCENT FUEL-BOUND NITROGEN.



(b) FUEL C: 9 PERCENT HYDROGEN; 0.5 PERCENT FUEL-BOUND NITROGEN.

Figure 7. - Effect of secondary residence time on  $\text{NO}_x$  formation. Secondary equivalence ratio = 0.5.

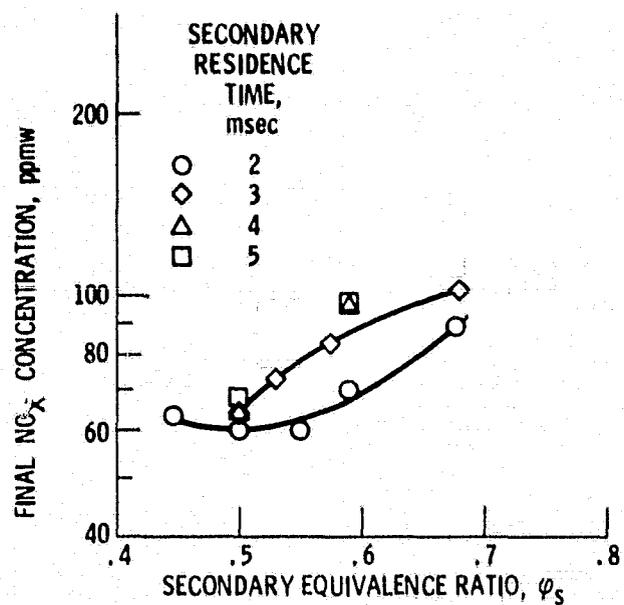
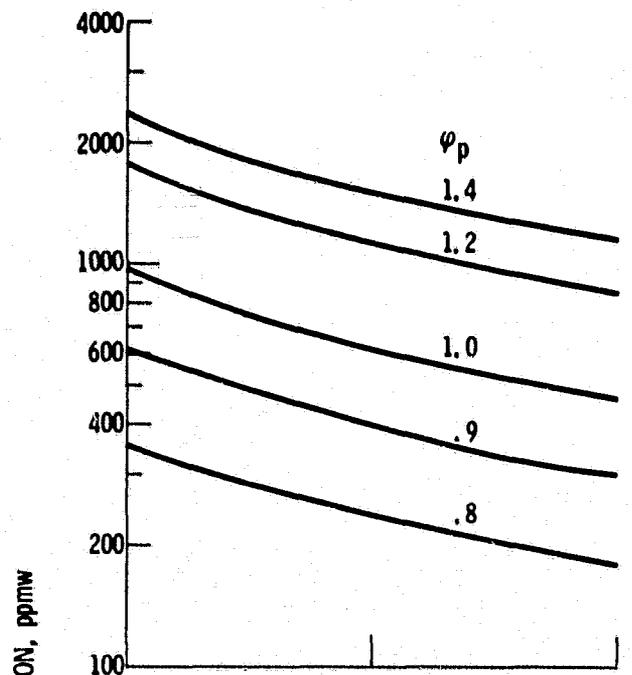
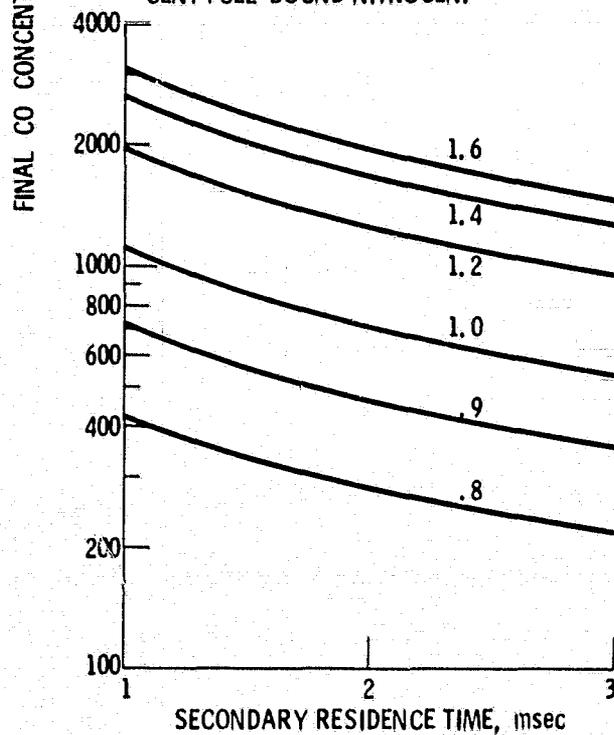


Figure 8. - Experimental final NO<sub>x</sub> concentration vs. secondary equivalence ratio for various secondary residence times. Fuel B: 11 percent hydrogen; primary equivalence ratio = 1.5; 0.0 percent fuel-bound nitrogen.



(a) FUEL B: 11 PERCENT HYDROGEN. 0.5 PERCENT FUEL-BOUND NITROGEN.



(b) FUEL C: 9 PERCENT HYDROGEN. 0.5 PERCENT FUEL-BOUND NITROGEN.

Figure 9. - Effect of secondary residence time on CO formation. Secondary equivalence ratio = 0.5.

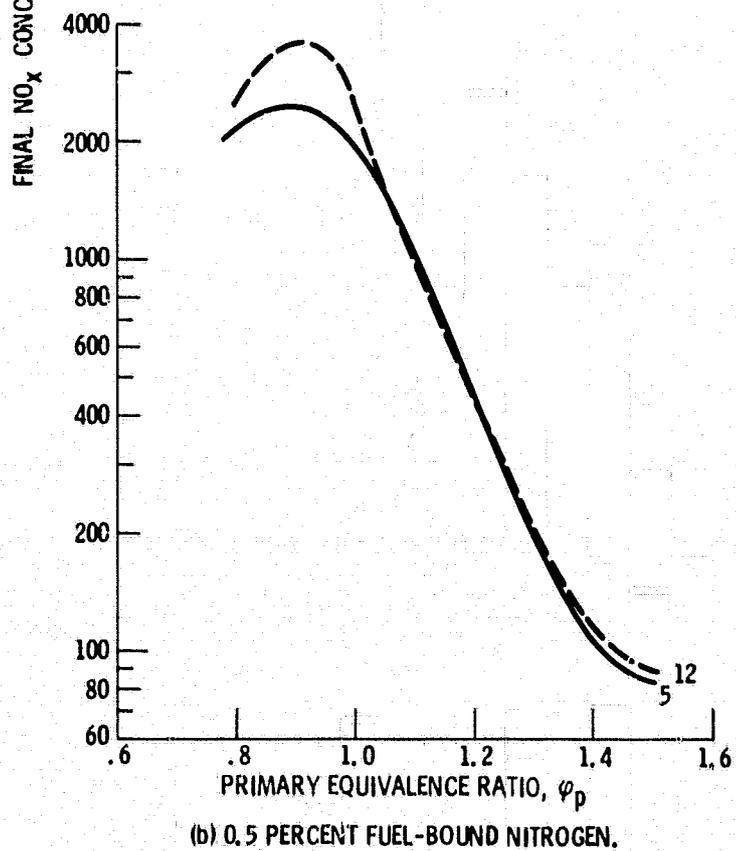
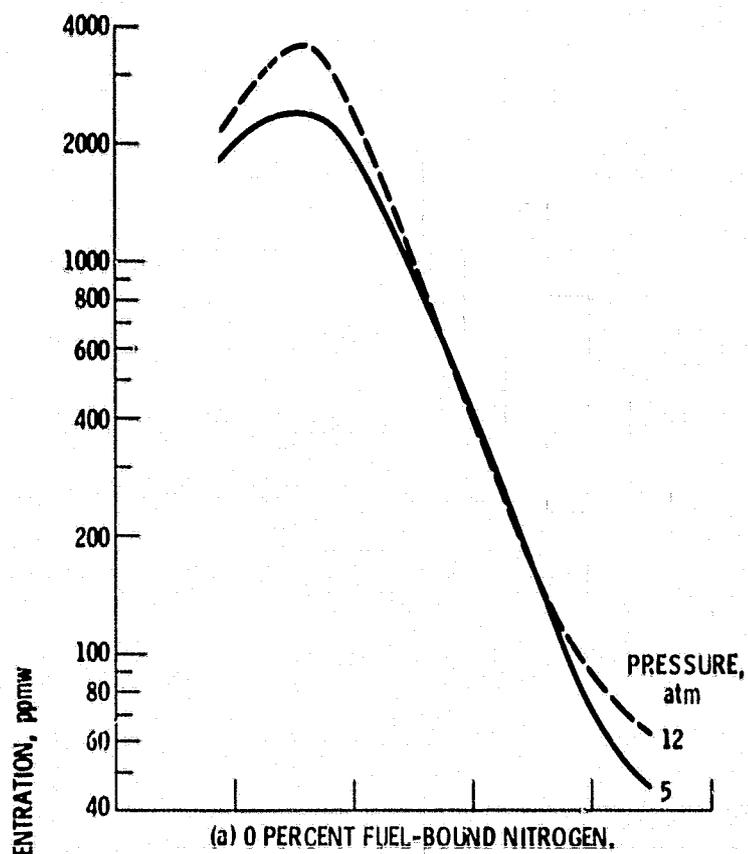


Figure 10. - Effect of pressure on  $\text{NO}_x$  formation. Fuel B: 11 percent hydrogen; residence time  $\cong$  2 msec. Secondary equivalence ratio = 0.5.

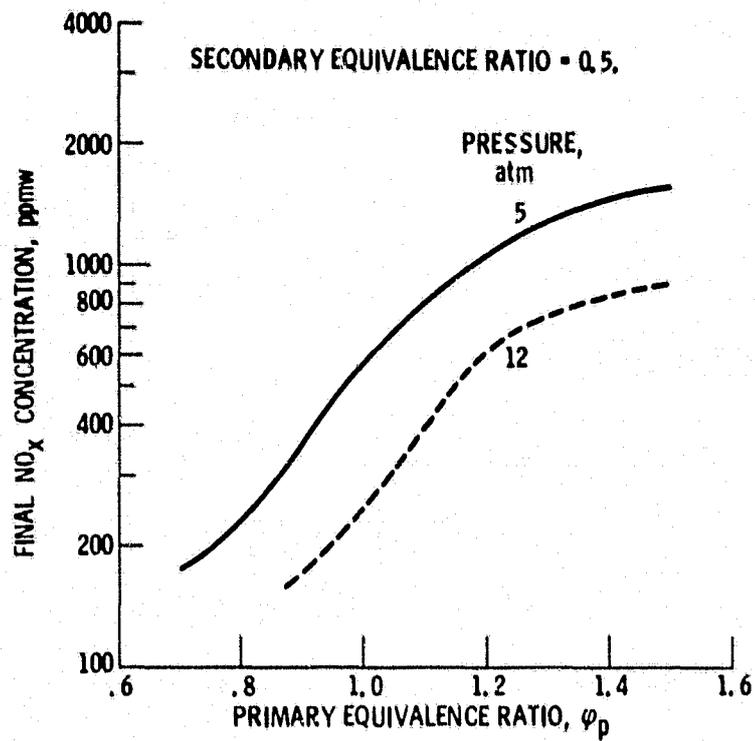


Figure 11. - Effect of pressure on carbon monoxide formation. Fuel B; 11 percent hydrogen; residence time  $\cong$  2 msec; 0.0 percent fuel-bound nitrogen.