AN INVESTIGATION TO DEFINE THE PHYSICAL/CHEMICAL CONSTRAINTS WHICH LIMIT NO_x EMISSION REDUCTION ACHIEVABLE BY REBURNING

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TABLE OF CONTENTS

1.0 INTRODUCTION

Reburning is an NO_x control technology which uses fuel to reduce No. 1-4 Thus, the main heat release zone can be operated normally to achieve optimum combustion conditions without regard for NO_x control. A schematic of the reburning process is shown in Figure 1-1. With reburning, a fraction of the fuel is injected above the main heat release zone. Hydrocarbon radicals from combustion of reburning fuel react with nitric oxide to form molecular nitrogen. This process occurs best in the absence of oxygen. Thus sufficient reburning fuel, between 15 and 20 percent of the total heat input, must be added to produce an oxygen deficient reburning zone. Subsequently, air is provided to combust fuel fragments which remain at the exit of this zone. Since reduced nitrogen species NH_3 and HCN are also present, air addition allows a further NO_x reduction.

Previous studies have shown that 60 percent reduction in NO_x emissions can be achieved with natural gas reburning. This is considerably less than the limits imposed by thermodynamics on NO formation under fuel-rich conditions. Figure 1-2 is a plot of equilibrium levels of total fixed nitrogen species (HCN, NH_3, and NO) as a function of stoichiometry and temperature. Except for high temperatures (greater than $3100^{o}F$) and extremely rich conditions ($SR<0.5$), the equilibrium levels are less than 10 ppm. Equilibrium considerations would dictate operation of a combustor at moderate temperatures under rich conditions such as the reburning zone or low temperatures near stoichiometric conditions.

The purpose of the studies described in this quarterly report was to define the chemical constraints which prevent 85 percent NO_x reduction with reburning. Tests were conducted in a bench scale tunnel furnace to independently examine the formation of N_2 in the reburning zone and the conversion of XN species in the burnout zone. Detailed measurements were performed at the reburning zone exit to characterize unburned hydrocarbons, CO, NO, NH_3 and HCN. The influence of the concentrations of reactive species was examined as were temperature effects for both the reburning and burnout zone.

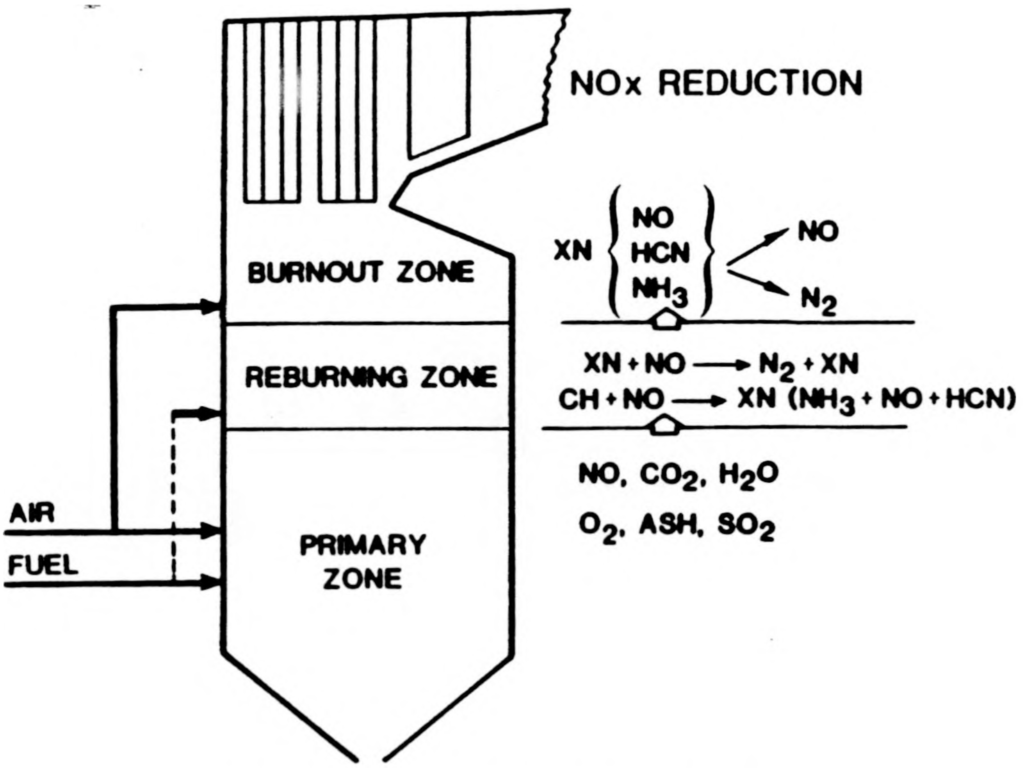


Figure 1-1. The reburning process.

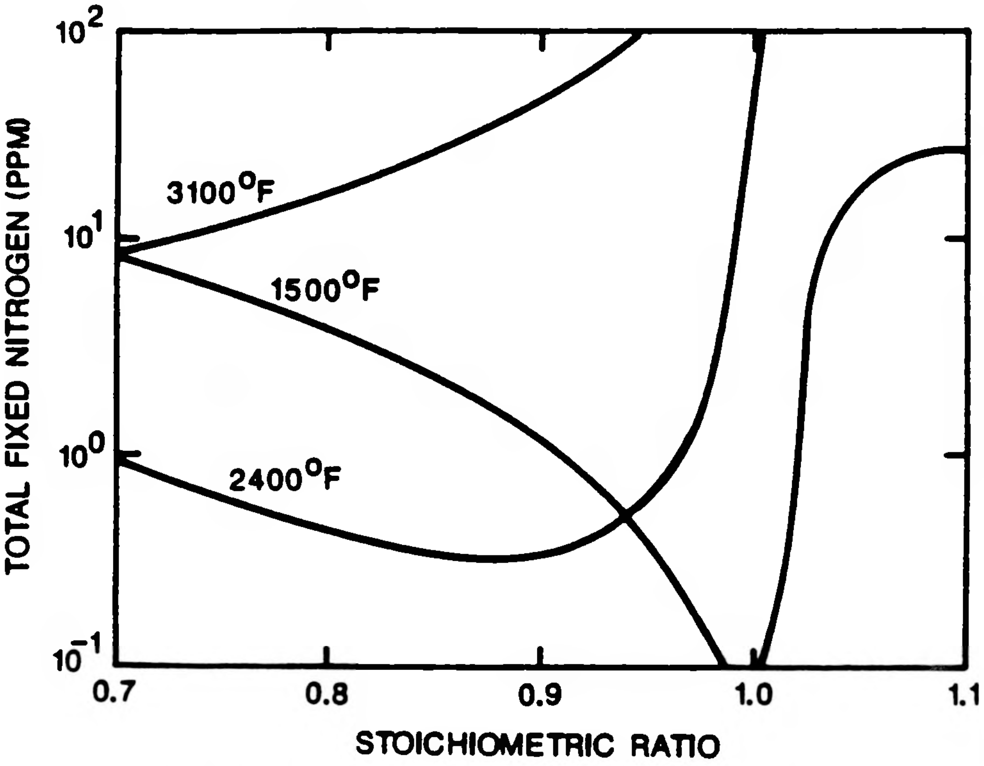


Figure 1-2. Equilibrium considerations.

2.0 EXPERIMENTAL

2.1 Furnace System

The experimental studies were conducted in the 2.5 m refractory-lined Control Temperature Tower (CTT). This 25 kW furnace, as shown in Figure 2-1, is 20.3 cm in diameter and the time/temperature profile can be adjusted using backfired heating channels within refractory walls. The primary fuel, natural gas, was fired at 17.6 kW using a premixed burner. The reburning fuels were injected with a 90° injector located at the centerline of the furnace. This injector allowed the reburning fuel, diluted/transported with argon, to flow radially outward through four 0.5 cm holes and mix rapidly with the oncoming primary effluent. A refractory choke was inserted downstream to isolate the fuel-rich reburning zone from the fuel-lean burnout zone. Burnout air was also injected radially.

2.2 Analytical Methods

Exhaust gas samples were withdrawn through a stainless steel, water-jacketed probe and analyzed for NO_x (chemiluminescence). O_2 (paramagnetic), CO/CO_2 (NDIR), and SO_2 (NDUV). A water-jacketed probe with an internal water quench spray near the front end was used for extracting in-flame samples. Gas phase HCN and NH_3 species were collected in a gas washing unit and subsequently analyzed for CN^- and dissolved ammonia using specific ion electrodes.

2.3 Baseline Conditions

The baseline conditions for the experiments were:

- Primary fuel/natural gas at 80 x 10^3 Btu/hr; primary NO_x, $(NO_x)_p$ = 240 or 600 ppm (dry, 0% O_2) by doping; SR_1 = 1.1.
- Reburning gas injection at 2550°F (T_1); reburning zone residence time (τ_2) = 400 ms.
- Burnout air injection at 2300°F (T_2); SR_3 = 1.25.

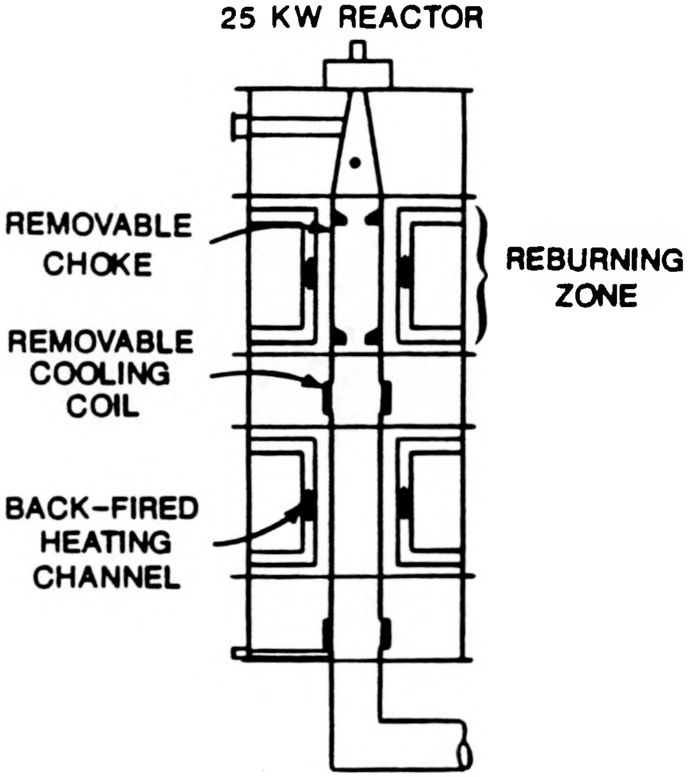


Figure 2-1. Experimental facility--CTT.

3.0 RESULTS

The focus of the first series of testing was on the formation of N_2 in the reburning zone, in particular, the availability of CH radicals. The second series of testing examined the chemistry of XN conversion in the burnout zone. Finally experiment were conducted to verify the performance under the optimum reburning and burnout zone conditions.

3.1 N_2 Formation in Reburning Zone

Upon injection to the furnace, the reburning fuel must first decompose to CH radicals:

$$CH_4 + OH \longrightarrow CH + H_2O$$

These radicals can then react with NO to form HCN:

$$CH + NO \longrightarrow HCN + O$$

The HCN then decays through $NCO \longrightarrow NH_2 \longrightarrow N$ and ultimately reaches N_2 via the reverse Zeldovich reaction:

$$N + NO \longrightarrow N_2 + O$$

3.1.1 Reactant Contracting

Reaction of primary NO species with CH radicals activates the reburning process. Thus, a goal in reburning optimization is to maximize the exposure of NO to CH and minimize CH interaction with oxygen via:

$$CH + O \longrightarrow CO + H$$

To investigate reactant contacting, tests were run with oxygen and/or NO species (which were usually present in the primary zone effluent) premixed with the reburning natural gas prior to furnace injection. The results are shown in Figure 3-1. With preferential contacting between the reburning gas and NO, exhaust NO_x emissions were lower than the baseline case. When oxygen was premixed with the reburning fuel, a substantial increase in NO_x emissions was witnessed, regardless of whether NO_x was premixed with the gases. Higher primary NO_x concentrations resulted in increased reduction in all cases. The results, which demonstrated the competition between primary NO_x and oxygen species for hydrocarbon radicals, showed that NO_x-CH contacting was not rate limiting.

3.1.2 Fuel Composition

The presence of CH radicals is necessary for the reburning process to proceed. An approach to improve CH availability is to use a reburning fuel which favors CH as a decomposition product. Several gaseous hydrocarbon fuels were tested to investigate CH generation. The fuels included acetylene, ethylene (an olefin), isobutane (a parafin), and natural gas, which was primarily methane. The fuels had an H/C ratio of one to four. The data are presented in Figure 3-2 and indicated the reduction efficiency with all of the fuels was similar. Acetylene, the closest stable hydrocarbon to CH (as illustrated in the decomposition chemistry shown in Figure 3-2, did not appear superior to natural gas as a reburning fuel.

Another method to improve interaction between NO and CH is to slow the rate of reburning fuel oxidation. A solid hydrocarbon fuel, naphthalene ($C_{10}H_8$), was selected and tested as the reburning fuel. Lower reduction efficiency was obtained with the solid fuel, however. Figure 3-2 also shows results obtained with methanol as the reburning fuel. Methanol, which favored CO as a decomposition product, yielded substantially lower reduction efficiency. As expected, reburning with CO resulted in the lowest reduction in NO_x emissions.

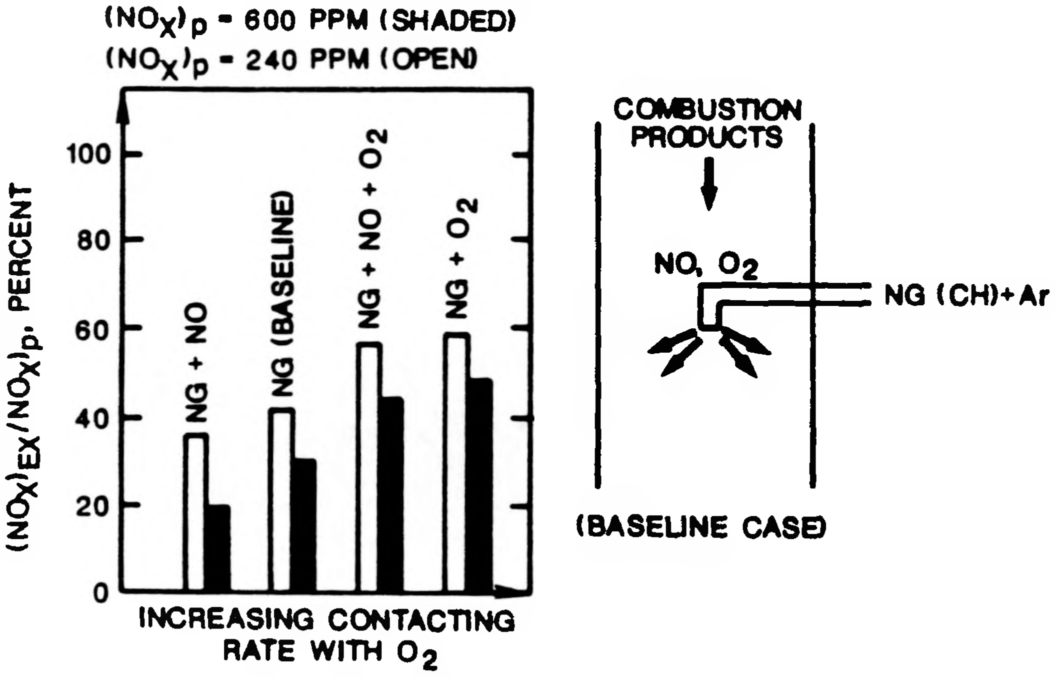


Figure 3-1. Influence of reactant contacting.

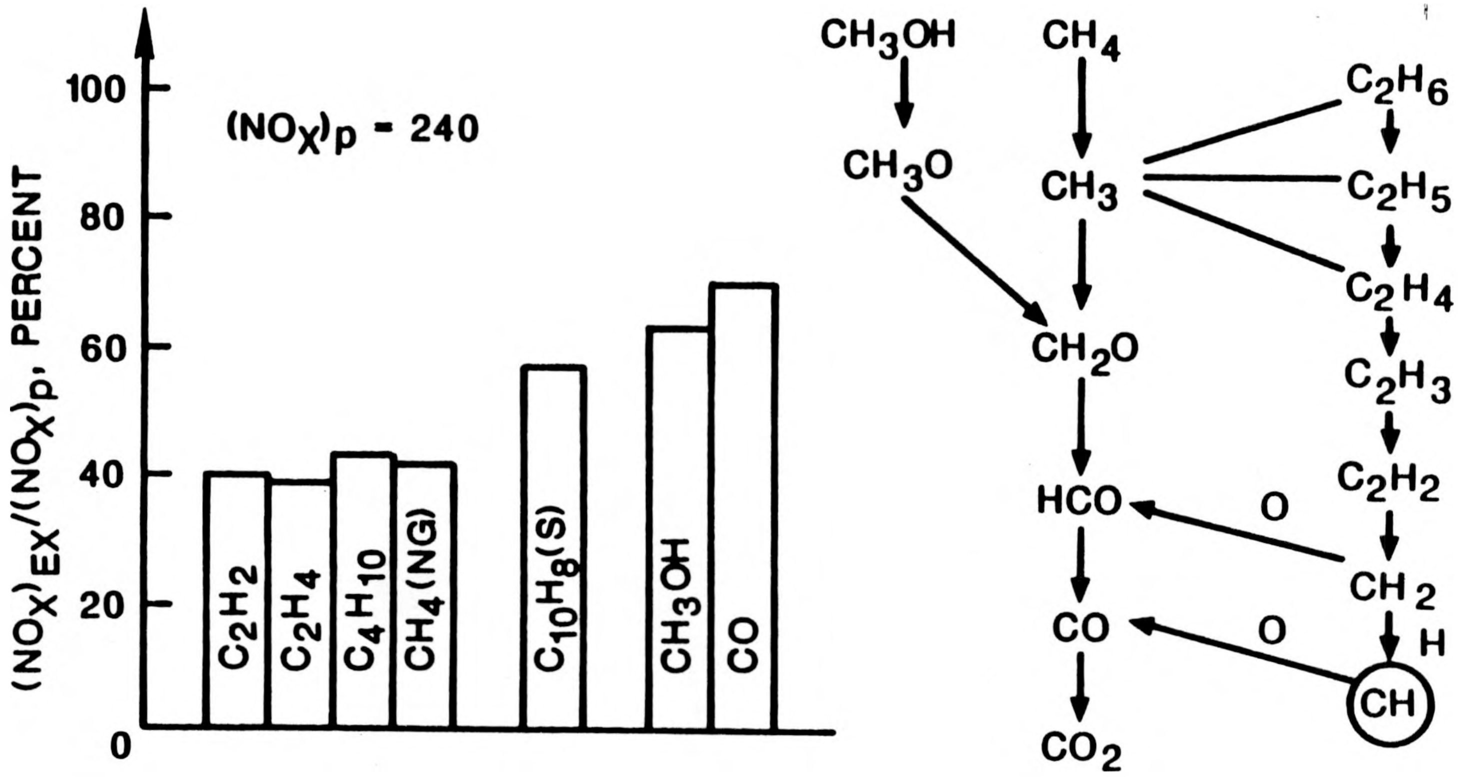


Figure 3-2. Influence of reburning fuel composition.

3.1.3 Fenimore Mechanism

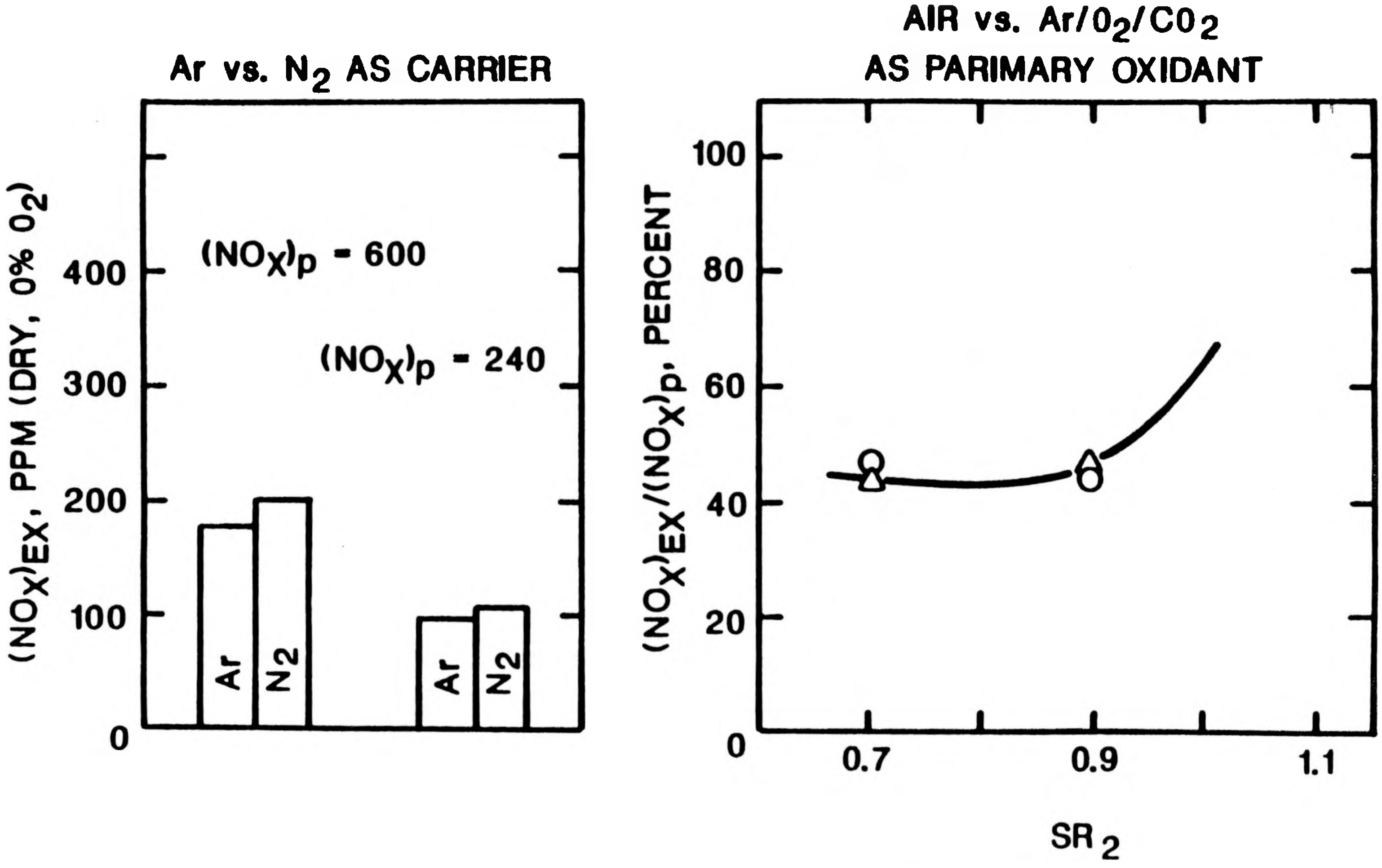
The formation of HCN via CH reaction with NO was discussed in the previous section. Another step which yields HCN is the reaction between CH and molecular nitrogen; i.e., the Fenimore mechanism:

$$CH + N_2 \rightarrow HCN + N$$

The nitrogen which contributes to the Fenimore mechanism could come from primary combustion air, burnout air, or reburning fuel diluent. This mechanism, which causes the formation of thermal NO_x, occurs most readily at high temperatures. Tests were completed with nitrogen dilution of the reburning gas, and a nitrogen-free primary zone oxidant composed of argon, oxygen, and carbon dioxide. The results are presented in Figure 3-3. The data showed that the primary zone nitrogen did not contribute to the Fenimore mechanism in the reburning zone. A slight increase in NO_x emissions was observed when the argon diluent was replaced by nitrogen. The results implied that the Fenimore mechanism was not important in the reburning process.

3.1.4 Reburning Temperature

The results discussed above were obtained with the reburning fuel injected at 2550°F. A series of experiments were carried out to investigate the influence of temperature on rich zone NO reduction. The reburning fuel was injected at temperatures ranging from 2550°F to 1600°F. At the optimum stoichiometry of 0.9, the concentrations of NO were measured at 400 ms downstream of the reburning fuel injection location. Figure 3-4 presents these data and indicates that the NO reduction efficiency in the reburning zone decreased with temperature, with NO concentration measured at 2550°F approximately half of that seen at 1800°F. However, the effect of temperature diminished when the reburning fuel was injected above 2200°F. It is believed that the formation of thermal NO would become important at temperatures above 2600°F.



Fiqure 3-3. Importance of Fenimore mechanism: $CH + N_2 \longrightarrow HCN + N$.

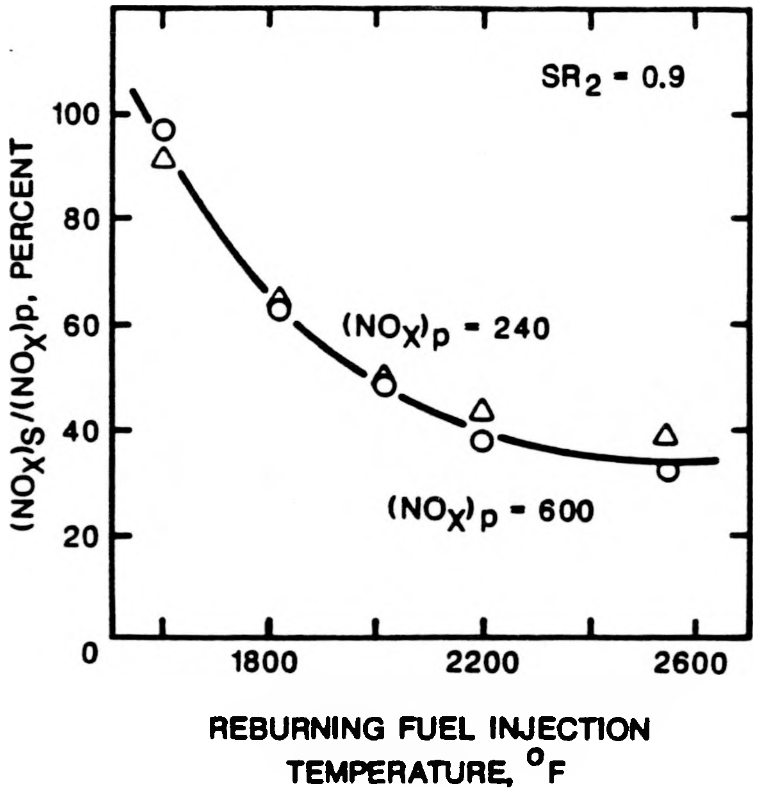


Figure 3-4. Influence of reburning temperature on NO reduction.

3.2 XN Conversion in Burnout Zone

The burnout zone can be considered as an excess-air "flame" burning the remaining fuel fragments from the reburning zone. Oxidation of the fuel fragments, particularly CO, could generate a significant amount of radicals via chain branching:

$$CO + OH = CO_2 + H$$
$$H + O_2 = OH + O$$
$$O + H_2O = OH + OH$$

These radicals play an important role on the conversion of XN species to N_2 or NO during burnout.

3.2.1 Reactive Species

The fuel fragments were characterized initially. CO and total hydrocarbon (THC) concentrations at the reburning zone exit are presented in Figure 3-5 as a function of rich-zone stoichiometry. It can be seen that the amount of CO was considerably higher than THC at all stoichiometries, indicating extensive destruction of the natural gas CH constituents.

XN speciation at the reburning zone exit was subsequently characterized and shown in Figure 3-6. The concentration of NO decreased with stoichiometry, while the concentrations of intermediate species arose. When SR_2 was decreased from 0.9 to 0.7, the amount of HCN rose dramatically, while NH_3 levels exhibited little change. This is an indication of a lack of oxidizing radicals available at the richer stoichiometry for processing HCN through NCO to HH_3. Primary NO_x concentration had only a minor impact on the percent conversion of NO to nitrogenous intermediates. At an SR_2 of 0.9, the ratio of NH_3 plus HCN to NO was approximately 0.9 for both cases.

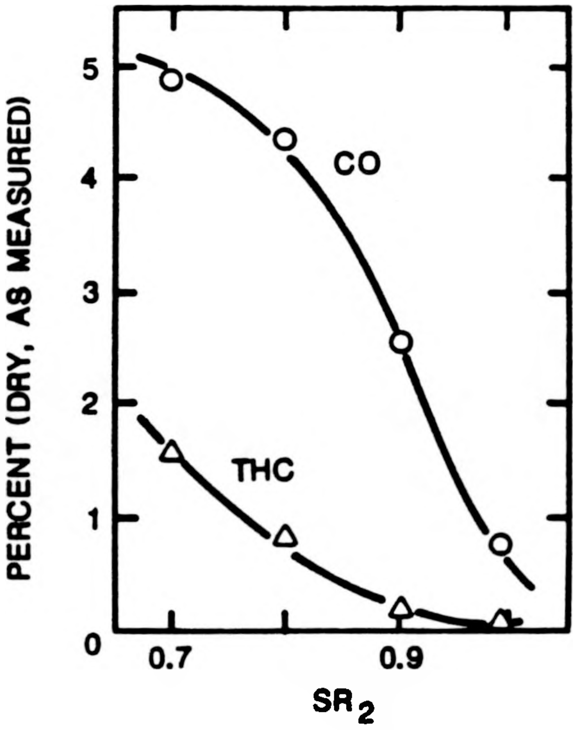


Figure 3-5. Fuel fragments at exit of reburning zone.

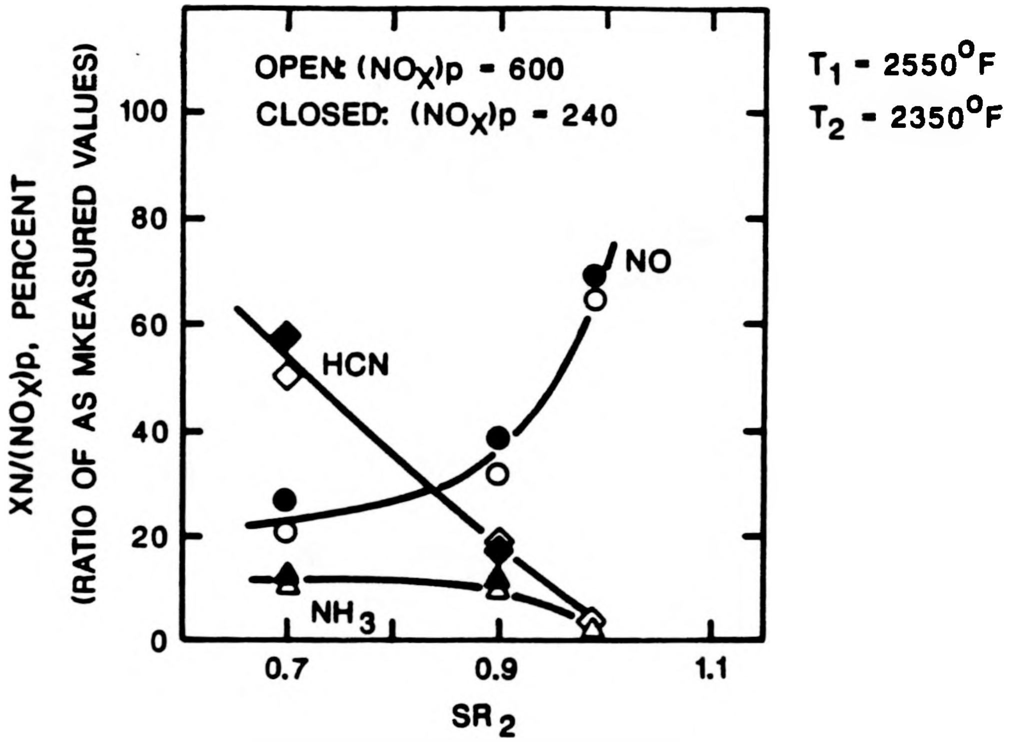


Figure 3-6. XN species at exit of reburning zone.

3.2.2 Conversion Efficiency

Figure 3-7 is an experimental examination of the burnout zone chemistry, in particular, the conversion efficiency of NH_3 to N_2. The rich zone was assumed to supply 600 ppm each of NO and NH_3, or an N to NO ratio of 1.0. Under excess air conditions, ammonia gas was mixed with various amounts of CO and injected at temperatures between 1300 and 2200°F. The solid symbols represent the injection of NH_3 alone, which is basically a simulation of Thermal De-NO_x. For the open symbols, 0.2 percent CO was included with NH_3, thereby yielding a burnout-like environment. The presence of CO lowered the optimum temperature for NO_x reduction from 1800°F to 1500°F. It is readily apparent that a reduction in the burnout temperature from the 2200-2400°F normally employed would increase the conversion efficiency of NH_3 + NO to N_2 because of the presence of CO. However, it was found that the conversion efficiency was also dependent upon the concentration of CO. As shown in Figure 3-8 at the optimum reaction temperature of 1500°F the optimum CO level was approximately 0.5 percent, or less, equivalent to a rich-zone stoichiometry between 0.95 and 1.0.

Figure 3-9 shows the corresponding results for HCN conversion. Note first that the NO reductions obtained with HCN alone were not as high as those with XH_3. Secondly the presence of CO lowered the reduction efficiency. It is obvious that NH_3 is the preferred reducing species for the burnout zone.

3.2.3 Process Optimization

The above results suggest that the key parameters for the enhancement of burnout zone chemistry are:

- reaction temperature (1500°F),
- CO level (0.5% or less), and
- NH_3 species.

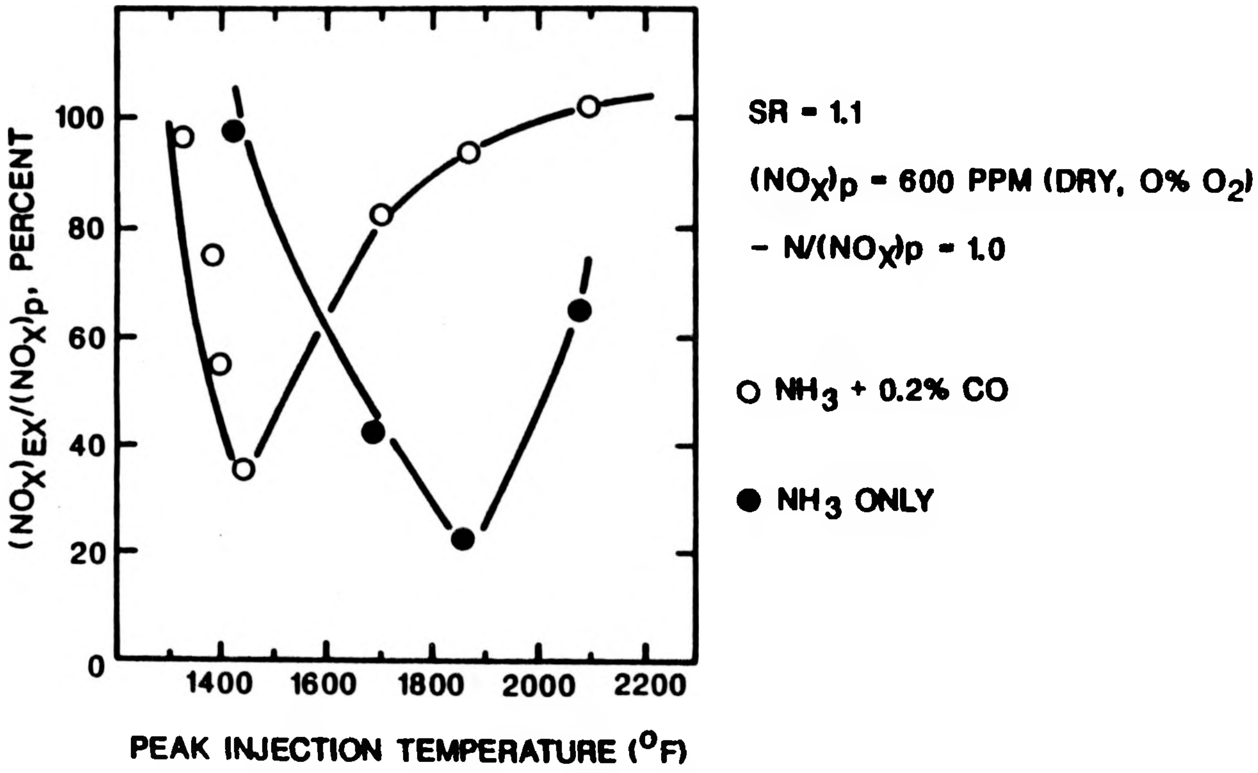


Figure 3-7. NH_3 conversion.

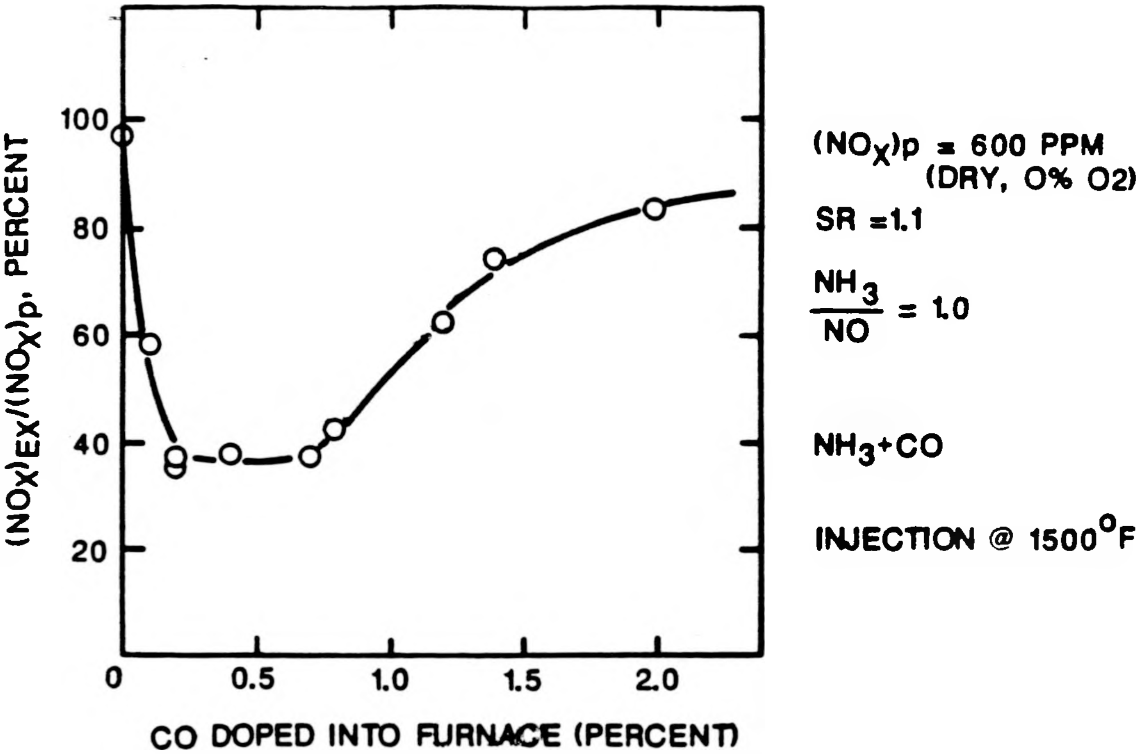


Figure 3-8. Optimum CO for NH_3 conversion.

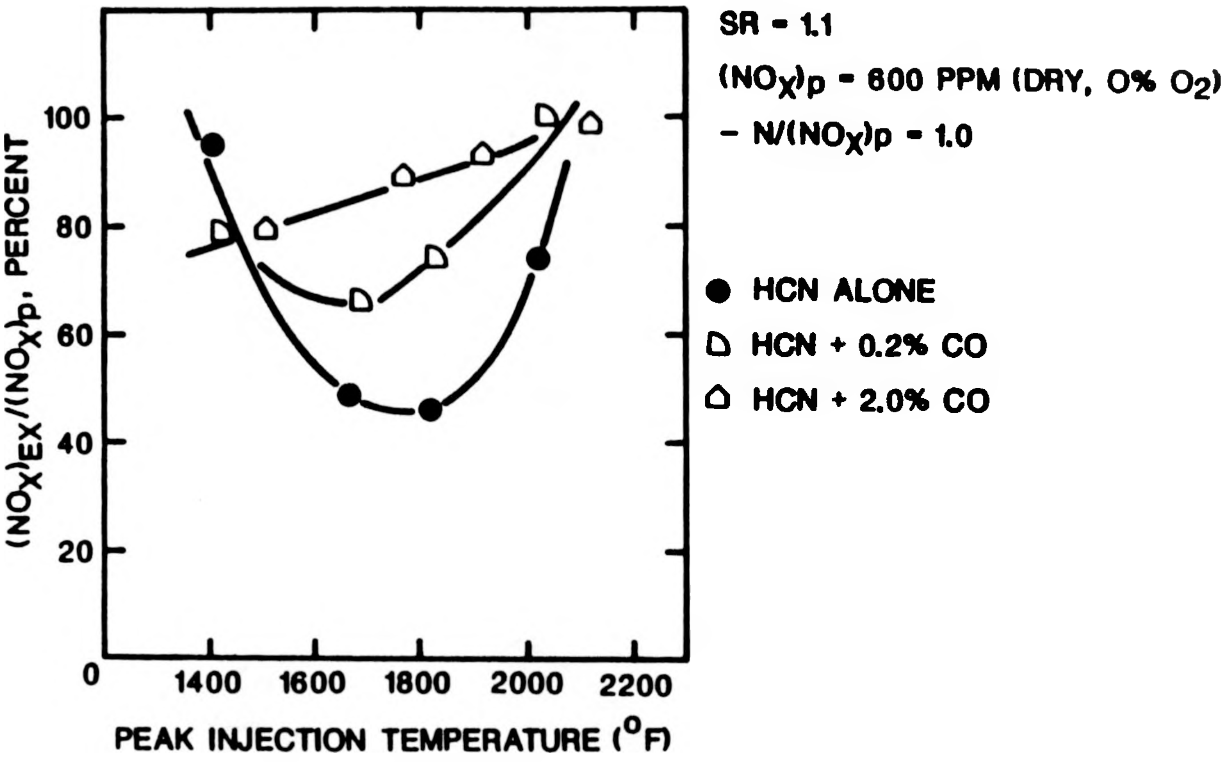


Figure 3-9. HCN conversion.

Apparently the conventional reburning process does not provide the required environment. An optimized process was designed and tested. The results are presented in Figure 3-10. In these experiments, the burnout air was split into two streams. The first stream remained at the normal injection location to reduce the CO concentration from 2.5 percent to approximately 0.2 percent. The second stream was injected downstream at a lower temperature, i.e. 1500°F, to complete the burnout. Little improvement over the conventional process was obtained due to the lack of NH_3 species at an SR_3 of 0.99. However, when an aqueous ammonium sulfate solution was added with the second burnout air to provide the required NH_i species, an additional 50 percent reduction was dramatically achieved, resulting in an overall reduction of 84 percent in NO_x emissions.

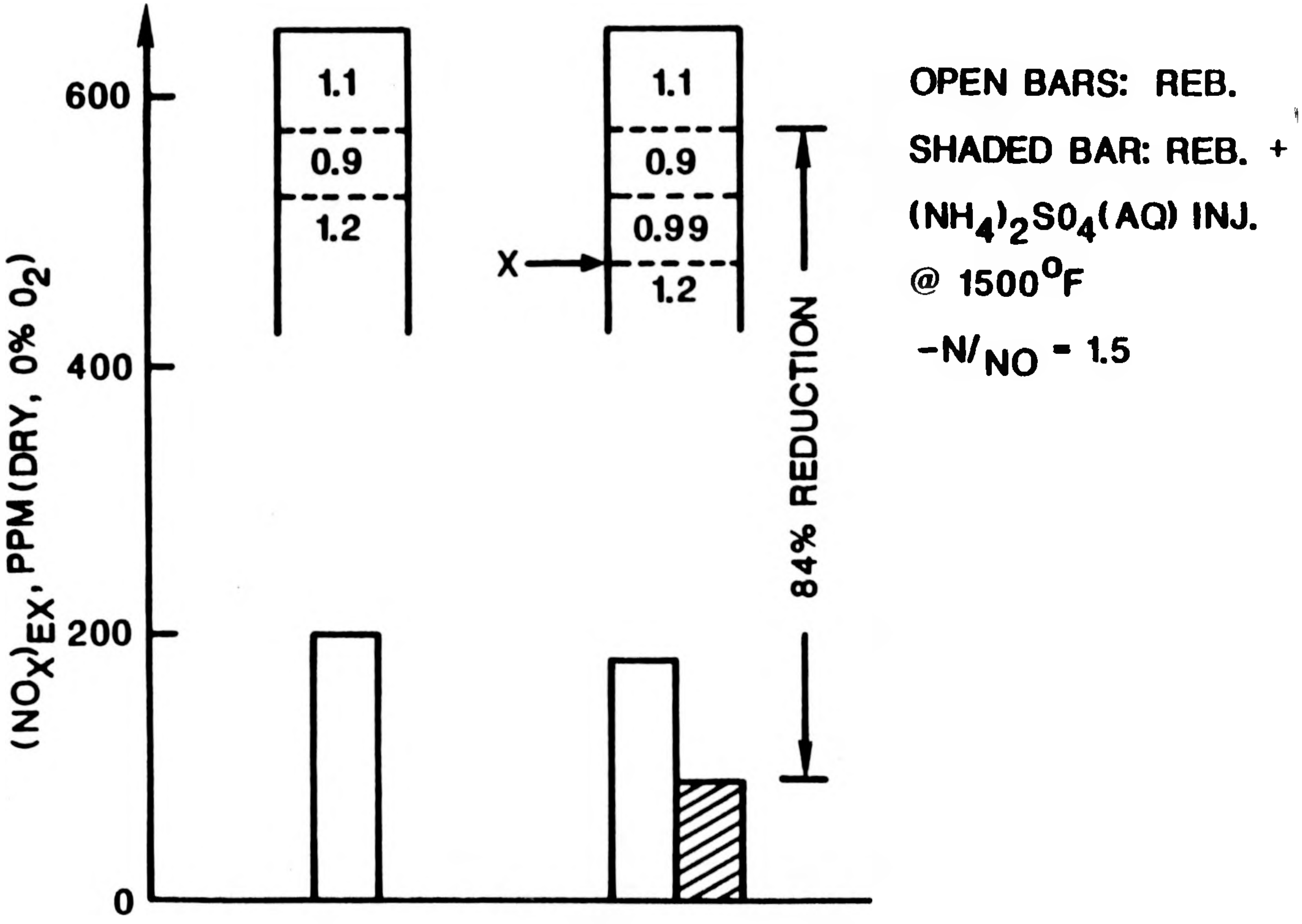


Figure 3-10. Optimized reburning process.

4.0 CONCLUSIONS

The experimental results have shown that in the reburning zone the reactant contacting is not rate limiting, the CH radical pool appears to be sufficient, and the Fenimore HCN formation is not of major importance at $SR_2 = 0.9$. In addition, accelerating the decay of HCN in the reburning zone has proved to be ineffective under the available time and temperature environment. The results have also shown that the addition of reducing agents in the reburning zone does not promote the formation of molecular nitrogen. However, the addition of reducing agents, such as ammonium sulfate in the burnout zone can significantly enhance the conversion of XN species to N_2 and result in greater than 80 percent overall reduction in NO_x emissions. The efficiency of the reducing agent appears to be dependent upon the local stoichiometry and temperature.