DOE/PC/91025--T10

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

JUN 23 1990
DOE/PC/91025--T10

DE90 012404

Quarterly Report 3

DE-AC22-86PC91025

Prepared for:

Richard Tischer
U.S. Department of Energy
Pittsburgh Energy Technology Center

Prepared by:

J. M. McCarthy
L. Ho
S. L. Chen

Energy and Environmental Research Corporation
18 Mason
Irvine, California 92718

January 1988

MASTER *mg*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1.0 INTRODUCTION	1-1
2.0 N ₂ FORMATION IN REBURNING ZONE	2-1
3.0 XN CONVERSION IN BURNOUT ZONE.	3-1
3.1 Reduction of Local Oxygen	3-1
3.2 Addition of Reducing Agent.	3-3
4.0 FUTURE WORK.	4-1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

LIST OF FIGURES

<u>Number</u>		<u>Page</u>
2-1	Injection configurations of reducing agents.	2-2
2-2	Addition of reducing agents in the reburning zone.	2-3
3-1	Effects of local O_2 partial pressure and CH radical pool . . .	3-2
3-2	Injection of reducing agents w/burnout air at $SR_2 = 0.9$	3-4
3-3	Importance of local stoichiometry for de- NO_x reaction.	3-5
3-4	Importance of local temperature for de- NO_x reaction.	3-7

Reburning is a combustion modification technique which removes NO_x from combustion products by using fuel as a reducing agent. Previous studies have shown that natural gas is more effective than coal as a reburning fuel. It is believed that 60 percent reduction in NO_x emission can be achieved with natural gas reburning. However, kinetic calculations indicate that emission reductions greater than 80 percent are possible using the reburning process.

The objectives of this program are to define the chemical and physical constraints which prevent the attainment of 85 percent NO_x reduction with reburning and to test improved configurations for reburning as an advanced NO_x control technique for coal-fired boilers. The program has been divided into two experimental scales. Bench scale studies are designed to screen the chemical and physical means for enhancing reburning efficiency. Subsequent pilot studies will evaluate the impacts of finite rate mixing on the effectiveness of the various concepts. These studies will be supported with chemical kinetics and boiler performance modeling to generalize the experimental data to full scale boilers. Specifically, the program consists of the following tasks:

- Task 1 - Project Work Plan
- Task 2 - Chemical Enhancement of Reburning
- Task 3 - Physical Enhancement of Reburning
- Task 4 - Concept Verification
- Task 5 - Interpretation and Generalization
- Task 6 - Final Report

This quarterly report documents the experimental results obtained in this period on Task 2. The focus of this task is to study the chemical means of maximizing N_2 formation both in the reburning zone and in the burnout zone. The experiments were conducted in the bench scale Control Temperature Tower (CTT). The CTT is a downfired, refractory lined tunnel furnace which is 20 cm in diameter and 2.4 m in length. The baseline conditions for these tests were:

- Primary fuel-natural gas at 80×10^3 Btu/hr; primary NO_x , $(\text{NO}_x)_p = 240$ or 600 ppm (dry, 0% O_2) by doping; $\text{SR}_1 = 1.1$.
- Reburning gas injection at 2600°F (T_1); reburning zone residence time (τ_2) = 400 ms.
- Burnout air injection at 2300°F (T_2), $\text{SR}_3 = 1.25$.

2.0 N₂ FORMATION IN REBURNING ZONE

The chemical enhancement results, as reported in the last Quarterly Report, have indicated that in the reburning zone the reactant contacting is not rate limiting, the CH radical pool appears to be sufficient, and nitrogen fixation via Fenimore HCN formation is not of major importance at SR₂ = 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.

In this reporting period a series of testing was conducted to examine the influence of the addition of -CN and -NH compounds in the reburning zone. In particular, the following reactions were studied:

As shown in Figure 2-1, the reducing agent was either injected with the reburning fuel (natural gas) or injected in the reburning zone approximately 250 ms downstream of the reburning fuel. Figure 2-2 summarizes the results. The addition of the solid reducing agents (transported by argon) to the reburning fuel at a -N (additive)/NO (primary NO_x) molar ratio of 1.5 resulted in a slight increase of the NO_x emissions, probably because of the hot thermal environment (about 2550°F). Little difference was observed when the reducing agents, added as aqueous solutions, were injected in the fuel rich reburning zone. At these temperatures (about 2200°F) the reduction of NO was countered by the production of NO. Therefore, it appears that the conversion of nitrogen species to molecular nitrogen cannot be promoted in the reburning zone by the addition of reducing agents.

Figure 2-1. Injection configurations of reducing agents.

Figure 2-2. Addition of reducing agents in the reburning zone.

3.0 XN CONVERSION IN BURNOUT ZONE

In the burnout zone, air is added to produce overall lean conditions and oxidize the remaining fuel fragments. Oxidation of the remaining fuel, primarily CO, generates free radicals via chain branching:

These radicals determine the fate of the fixed nitrogen species, XN (NO, NH₃, HCN). The XN species are either oxidized to NO via

or reduced to molecular nitrogen via

3.1 Reduction of Local Oxygen

The purpose of this series of testing was to minimize the oxidation of nitrogen species via combustion modifications such as mixing the burnout air with flue gas or with supplemental fuel. The burnout air stream was diluted with inert argon (flue gas simulation) to investigate the influence of burnout air oxygen concentration. The results are presented in Figure 3-1. With the volumetric flowrate constant, no effect was seen for oxygen concentrations ranging from 7 to 21 percent. Figure 3-1 also shows the results with supplemental natural gas added to the burnout air. Only a

Figure 3-1. Effects of local O₂ partial pressure and CH radical pool.

results with supplemental natural gas added to the burnout air. Only a negligible effect was observed, even at natural gas flows as high as the reburning fuel firing rate.

3.2 Addition of Reducing Agent

The focus of this series of testing was on the conversion of NO to N₂ via the addition of reducing agents in the burnout zone. Specifically, the following reactions were examined:

Figure 3-2 presents the data obtained with the reducing agents injected with the burnout air. The reducing agents were transported with the burnout air when introduced as powders and atomized via the burnout air when added as aqueous solutions. In each case each reducing agent was added in an amount to produce a -N/NO molar ratio of 1.5. Increased NO_x emissions were seen at standard reburning conditions, i.e., a stoichiometry of 0.9 (SR₂) prior to the addition of final burnout air. At SR₂ of 0.9, the rich zone was expected to have high concentrations of CO. Upon introduction of the burnout air the oxidation of CO generated an excess amount of radicals, which promoted the formation of NO from the additives.

Tests were also conducted at alternative reburning configurations. Figure 3-3 shows results obtained at three stoichiometries (SR₂ = 0.9, SR₃ = 1.05, SR₂ = 0.99) prior to the addition of final burnout air at 1900°F. With the burnout air split into two separate streams (SR₃ = 1.05, SR_t = 1.2), no enhancement in reburning efficiency was observed, probably due to the reduction of the rich zone residence time. However, the addition of a urea solution with the final air stream resulted in 50 percent reduction in NO_x emissions. Figure 3-3 also shows the results with 10 percent reburning (SR₂ = 0.99). As expected, the reburning process was not as effective as the

Figure 3-2. Injection of reducing agents w/burnout air at SR₂ = 0.9.

Figure 3.3. Importance of local stoichiometry for de- NO_x reaction.

standard conditions ($SR_2 = 0.9$, $SR_t = 1.05$). Surprisingly, the addition of the reducing agent with the burnout air yielded a dramatic reduction in NO_x emissions (83 percent overall). These results illustrate the importance of local stoichiometry for the $deNO_x$ process and suggest that there exists an optimum amount of CO for the generation of radicals during oxidation in the burnout zone.

Finally the influence of reagent injection temperature was investigated. Tests were conducted under "fuel lean" reburning conditions (The reburning zone is fuel lean and no burnout air is added) with and without the addition of ammonium sulfate. The reburning zone temperatures (and the reagent injection temperatures) were varied from 1400 to 2000°F by moving the injection location along the furnace length. Figure 3-4 shows these results and indicates that the reburning process was more efficient at higher temperatures. However, when ammonium sulfate was added with the reburning fuel, lowest emissions occurred at 1600°F.

Figure 3-4. Importance of local temperature for de- NO_x reaction.

4.0 FUTURE WORK

Based on the test results obtained to date, it is hypothesized that a high temperature (T_1) favors N_2 formation in the reburning zone whereas a low temperature (T_2) maximize the conversion of XN to N_2 in the burnout zone. The next test sequence will quantify the concentrations of reactive species (NO , NH_3 , HCN , CO , THC) at the exit of the reburning zone. Tests will subsequently be carried out to determine the temperature dependence of the following reaction steps: