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DOE/PC/91025--T11

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

Quarterly Report 2.

DOE/PC/91025--T11

DE90 012405

DE-AC22-86PC91025

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October 1987

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TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
LIST OF FIGURES.	ii
1.0 INTRODUCTION	1-1
1.1 Background.	1-1
1.2 Purpose and Scope	1-2
1.2.1 Task 2 - Chemical Enhancement of Reburning	1-5
1.2.2 Task 3 - Physical Enhancement of Reburning	1-6
1.2.3 Task 4 - Concept Verification.	1-6
1.2.4 Task 5 - Interpretation and Generalization	1-6
1.2.5 Task 6 - Final Report.	1-7
2.0 EXPERIMENTAL FACILITIES.	2-1
2.1 Controlled Temperature Tower.	2-1
2.2 Measurement Systems	2-3
2.2.1 Flue Gas Sampling.	2-3
2.2.2 Gas Temperature Measurement.	2-4
2.3 Thermal Profile	2-4
3.0 CHEMICAL ENHANCEMENT OF REBURNING.	3-1
3.1 Reactant Contacting	3-1
3.2 CH Availability	3-1
3.3 HCN Processing.	3-14
4.0 EQUILIBRIUM CONSIDERATIONS	4-1
4.1 Free Radical Concentrations	4-1
4.2 CH Species Concentration.	4-1
5.0 FUTURE WORK.	5-1

LIST OF FIGURES

<u>Number</u>		<u>Page</u>
1-1	The reburning process.	1-2
1-2	Application of reburning for NO _x control	1-3
2-1	Cross-sectional views of the controlled temperature tower. . .	2-2
2-2	Reburning fuel and burnout air injection scheme.	2-4
2-3	Continuous monitoring flue gas sampling system	2-6
2-4	Gas temperature measurement system	2-7
2-5	Bench scale temperature profile.	2-8
3-1	Hydrocarbon and nitrogen chemistry relevant to reburning . . .	3-2
3-2	Influence of reactant contacting on NO _x emissions.	3-3
3-3	Influence of oxygen availability on reburning efficiency . . .	3-5
3-4	Influence of reburning fuel H/C ratio on reburning efficiency. .	3-6
3-5	Influence of primary NO _x on reburning efficiency	3-7
3-6	Influence of reburning fuel diluent on reburning efficiency. .	3-8
3-7	Influence of solid fuels on reburning efficiency	3-10
3-8	Influence of flame inhibitor on reburning efficiency	3-11
3-9	Influence of CO on reburning efficiency.	3-12
3-10	Influence of H ₂ on reburning efficiency.	3-13
3-11	NO _x formation from Fenimore mechanism.	3-15
3-12	Influence of CO ₂ on reburning efficiency	3-16
3-13	Influence of H ₂ O ₂ or O ₂ injection on reburning efficiency. . .	3-17
4-1	Equilibrium radical concentrations	4-2
4-2	Influence of fuel H/C ratio on equilibrium CH pool	4-3
4-3	Influence of stoichiometry on equilibrium CH pool.	4-4
4-4	Influence of flame inhibitor on equilibrium CH pool.	4-5

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1.0 INTRODUCTION

1.1 Background

Reburning is a NO_x control technology which uses fuel to reduce NO . 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 this 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 present, air addition methodology may allow a further NO_x reduction.

The Gas Research Institute (GRI) is promoting the select use of natural gas as a reburning fuel. It is believed that 60 percent reduction in NO_x emissions can be achieved using natural gas as a reburning fuel. Natural gas has several advantages as a reburning fuel. It does not contain nitrogen and there are no problems with carbon burnout. However, kinetic calculations indicate that emission reductions greater than 80 percent are possible using the reburning process.

1.2 Purpose and Scope

Figure 1-2 illustrates the application of reburning to a conventional pulverized coal fired boilers. NO_x emissions are shown as a function of percent oxygen in the exhaust gas and:

- Curve a is the normal full load operating curve of NO_x against excess oxygen typical of pulverized coal fired utility boilers;
- Curve b illustrates the impact of a reduction in load;

Figure 1-1. The reburning process.

1-3

Figure 1-2. Application of reburning for NO_x control.

- Curve c, d and e are operating curves representative of the application of reburning.
- Point 1 represents NO_x and oxygen concentration under uncontrolled conditions. The application of reburning involves a reduction in fuel input to the main heat release zone of approximately 20 percent. This is equivalent to a drop in load and NO_x emissions fall to Point 2. Excess air is now reduced to give operation at almost stoichiometric conditions (Point 3). The reburning fuel and burnout air are applied bringing overall oxygen to the original operating point but much lower NO_x emissions.
- Point 4 is typical of current estimates of reburning applications.
- Point 5 is illustrative of the kinetic limit for reburning.
- Point 6 is illustrative of emission levels that might be obtained using a combination of reburning with in-situ deNO_x or urea injection.

The objectives of this program are to define the physical and/or chemical constraints which prevent realization of Point 5 (85 percent NO_x reduction) with reburning, to use this information to identify and test improved configurations for reburning as an NO_x control technique on coal-fired boilers, and to test various methods which could be used in practice to reduce NO_x during the burnout step of the reburning process. The program will be performed at two experimental scales. Bench scale studies will be carried out in a 100×10^3 Btu/hr tunnel furnace to evaluate the importance of chemical and physical constraints in the absence of mixing limitations. A 10×10^6 Btu/hr pilot scale facility will subsequently be used to investigate the impacts of finite rate mixing and determine methods of minimizing them. Finally, a series of experiments will be conducted to verify the various concepts and demonstrate the optimum configuration for an advanced reburning process to achieve 85 percent NO_x reduction at a cost lower than SCR. Intensive use will be made of the kinetic and boiler performance models to

allow generalization of the test data to full scale pulverized coal fired boilers.

In order to accomplish these objectives, the program will be carried out in six 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

In the first task, a project work plan was prepared which described experimental test plans and management and cost plans. Experimental tests for tasks 2 and 3 will be conducted at bench scale, and the pilot scale facility will be used for task 4. Details of the subsequent tasks are presented in the following sections.

1.2.1 Task 2 - Chemical Enhancement of Reburning

Experimental work for this task is near completion. The task has focused on the testing of chemical means of enhancing reburning chemistry. Enhancement of NO_x reduction in the reburning and burnout zones are being investigated. The goals of this task are:

- Enhancement of NO_x reduction in the reburning zone by modifying the reburning fuel composition and concentration of reactant species in the NO reduction process;
- Examination of the possibility for additional NO_x destruction during the final burnout air addition.

1.2.2 Task 3 - Physical Enhancement of Reburning

The purpose of this task is to evaluate the use of advanced fuel and air contacting patterns as a physical means for reburning enhancement. Distribution of the reburning fuel may result in better exposure of NO to CH radicals, while air distribution may increase the conversion of XN species to molecular nitrogen. Alternative fuel and air distribution will also be investigated.

1.2.3 Task 4 - Concept Verification

After completion of bench scale tests, this task will evaluate the most promising concepts at a larger scale. The task will evaluate impacts of finite rate mixing on the effectiveness of advanced reburning concepts, determine the means for mixing enhancement, and verify the process performance with coal. Design of the injectors for reburning fuel and burnout air addition will be based on jet trajectory calculations and cold flow modeling. Several injection configurations chosen from the modeling results will ultimately be screened to determine mixing impacts. The most successful concepts from a chemical and physical standpoint will then be applied to evaluate the full potential of the advanced reburning process.

1.2.4 Task 5 - Interpretation and Generalization

Experimental results throughout the program will be evaluated and eventually extrapolated to full scale. Data will be compared to predictions on a process model which includes kinetic modeling, complex flow modeling and furnace heat transfer modeling.

This methodology will first be applied to the pilot scale configuration as a means of verifying the procedure. The methodology will then be applied to a typical wall fired configuration and a typical tangentially fired configuration. These results will provide some estimation of the effect of scaling up the findings of this research, and will provide direction to future application work.

1.2.5 Task 6 - Final Report

A final report covering all technical activities of the program will be prepared. Included in the report will be a description of the practical and design implications of the results for a full scale application.

2.0 EXPERIMENTAL FACILITIES

The program will be performed at two experimental scales. Bench scale studies are being conducted in the 100×10^3 Btu/hr Controlled Temperature Tower (CTT). These tests evaluate the significance of chemical and physical constraints in the absence of mixing limitations. Subsequently, pilot scale tests will be undertaken on the 10×10^6 Btu/hr reburning tower. These tests will investigate the impacts of finite rate mixing and verify the bench scale concepts and optimum reburning configuration. The bench scale facility is described in the following section.

2.1 Controlled Temperature Tower

The CTT is a downfired, refractory lined tunnel furnace. The combustion passageway is 20 cm in diameter, and is illustrated in Figure 2-1. Coal or natural gas and air are downfired through the quarl at the top of the furnace. The refractory lined channel contains two pairs of backheated zones. These are fired by auxiliary burners to provide a higher temperature than would be possible with only insulation. Further manipulation of the thermal profile can be accomplished by inserting cooling coils or rods in the combustion chamber. The furnace is designed to provide a thermal quench rate, or time-temperature history, that is similar to that of typical American boilers. Thus, a parcel of furnace gas will experience the same thermal environment in the CTT as would occur in the high temperature portions of a U.S. designed coal fired boiler. Numerous ports located along the furnace axis allow the insertion of supplementary equipment. The advantages of CTT testing include:

- The small scale allows mixing limitations to be avoided. Thus, the furnace allows the chemical limits of reburning behavior to be examined;
- The small scale allows greater flexibility in selecting test conditions than would be available from a larger or full-scale furnace;

Figure 2-1. Cross-sectional views of the control temperature tower.

- The backfired design allows an adequate variation of stoichiometry and temperature;
- The ability to stage fuel and air into the primary combustion stream in any configuration desired.

The baseline conditions for bench scale experiments are:

- ~~Primary NOx = 240 ppm~~ ^{1425°C}
- ~~Reburning fuel dilution with argon to promote rapid mixing without an influence on chemistry.~~ ^{1200°C}
- ~~Reburning fuel dilution with argon to promote rapid mixing without an influence on chemistry.~~
- ~~Reburning fuel dilution with argon to promote rapid mixing without an influence on chemistry.~~

The reburning fuel and burnout air injectors were designed to provide rapid dispersion of the streams and yield a well defined reburning zone entrance and exit. The injectors introduce respective streams radially into the furnace. The jet size was determined from trajectory calculations. The injector configuration and calculated jet trajectories are shown in Figure 2.2. The desired trajectory was such that the stream would mix rapidly with the furnace flow and impact the furnace wall at a low angle of incidence to avoid possible backmixing. A choke was placed immediately upstream of the burnout air injection location to physically separate the reburning and burnout zones and enhance mixing.

2.2 Measurement Systems

Figure 2-2. Reburning fuel and burnout air injection scheme.

2.2.1 Flue Gas Sampling

In bench scale tests, flue gas sampling was continuously conducted in the exhaust. The gas sample was pulled through a stainless steel water-jacketed probe, two chilled condensers, and a particulate filter. The gas sample was then pumped to the control room and the following gas species were continuously measured by the method indicated:

- NO_x - chemiluminescence,
- O_2 - paramagnetism,
- CO/CO_2 - nondispersive infrared.

A schematic of the sampling system is shown in Figure 2-3.

2.2.2 Gas Temperature Measurement

Gas temperatures were measured with a B-type thermocouple in a suction pyrometer jacket as shown in Figure 2-4. The pyrometer was placed in the flue gas stream with the opening in the alumina sheath pointing downstream. A sufficient gas sample was drawn around the thermocouple tip such that the convective heat transfer of the gas to the thermocouple dominated over the radiation heat loss of the thermocouple tip to the surroundings.

2.3 Thermal Profile

Initial tests performed on the CTT involved the characterization of the furnace thermal history. The main burner was fired at 80×10^3 Btu/hr and both the upper and lower back-fired heating channels were fired to obtain the proper temperatures and quench rate. The resultant temperature profile is shown in Figure 2-5. The reburning fuel injection temperature was 2600°F with a burnout air injection temperature of 2300°F . The reburning zone residence time was 0.4 seconds.

Figure 2-3. Continuous monitoring flue gas sampling system.

Figure 2-4. Gas temperature measurement system.

CTT

Natural Gas Firing

$$SR_1 = 1.1$$

$$SR_2 = 0.9$$

$$SR_3 = 1.25$$

Figure 2-5. Bench scale temperature profile.

3.0 CHEMICAL ENHANCEMENT OF REBURNING

The chemistry that controls the reburning process is illustrated in Figure 3-1. The reburning fuel must first decompose to CH radicals. These radicals can then react with NO to form HCN which decays through amines to ultimately form molecular nitrogen. ~~Experimental results presented in this section show that the ratio of exhaust to primary NO_x is on a concentration (ppm) basis. Thus, a portion of the reduction recorded was due to dilution by the reburning fuel-argon mixture and burnout air and was not chemical reduction.~~

3.1 Reactant Contacting

Reaction of primary NO species with CH radicals activates the reburning process. ~~Thus, a goal in the design of the reburning process is to maximize the contact between the reburning fuel and the primary NO species.~~ 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 3-2. 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 reburning fuel hydrocarbon radicals, showed that even with the most advantageous NO_x-CH contacting, the kinetic limit of 85 percent reduction was not attained.

3.2 CH Availability

The presence of CH radicals is necessary for the reburning process to proceed. A series of tests were performed to investigate the availability of this radical on reburning efficiency. Tests examined oxygen effects, fuel

Figure 3-1. Hydrocarbon and nitrogen chemistry relevant to reburning.

3-3

Figure 3-2. Influence of reactant contacting on NO_x emissions.

Figure 3-3. Influence of oxygen availability on reburning efficiency.

Figure 3-4. Influence of reburning fuel H/C ratio on reburning efficiency.

Figure 3-5. Influence of primary NO_x on reburning efficiency.

CTT

$$SR_1 = 1.1$$

$$SR_2 = 0.9$$

$$SR_3 = 1.25$$

$$(NO_x)_p = 240 \text{ ppm (dry, 0\% O}_2\text{)}$$

$$FGR = 4.4\% \text{ O}_2, 71.7\% \text{ N}_2, 23.9\% \text{ CO}_2$$

$$(\% \text{ CO}_2)_{sim} = (\% \text{ CO}_2)_{actual} + (\% \text{ H}_2\text{O})_{actual}$$

Figure 3-6. Influence of reburning fuel diluent on reburning efficiency.

flue gas stream, which was composed of oxygen, nitrogen and carbon dioxide was a hydrogen sink as well as a hydrocarbon oxidizer. Nitrogen effects will be discussed in the next section.

The effect of a solid fuel-natural gas mixture as reburning fuel is displayed in Figure 3-7. Either pulverized coal or naphthalene ($C_{10}H_8$), a nitrogen-free fuel with an H/C ratio similar to coal, were fed along with natural gas. The ~~reduction in NO_x emissions was not significant.~~ Since reduction efficiencies did not exceed that of the baseline test, these data imply that primary NO_x -CH contacting is not problematic.

A flame inhibitor and non-hydrocarbon gases were also added with the reburning fuel as oxygen scavengers. The data are shown in Figure 3-8 for the flame inhibitor. With up to 10 percent of the reburning fuel as methyl bromide, little change in the reduction efficiency was noted. Tests were also conducted with CO as a portion of the reburning fuel. The results, presented in Figure 3-9, show that NO_x reduction remains constant until high levels of CO are added. The data were not linear between the pure CO and pure natural gas case. Equilibrium calculations for CH concentration, also shown in Figure 3-9, substantiate the experimental results by indicating a relatively constant CH pool at less than 50 percent CO in the reburning fuel.

With hydrogen-natural gas mixtures as a reburning fuel, shown in Figure 3-10, NO_x emissions were higher than baseline for all cases.

Figure 3-7. Influence of solid fuels on reburning efficiency.

Figure 3-8. Influence of flame inhibitor on reburning efficiency.

Figure 3-9. Influence of CO on reburning efficiency.

Figure 3-10. Influence of H₂ on reburning efficiency.

The formation of HCN via CH reduction of NO was discussed in the previous section. [REDACTED] OH as [REDACTED] This step, and the subsequent decay of HCN by reaction with a hydroxide radical, were investigated.

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 temperature. 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 3-11. The data show 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. [REDACTED] in [REDACTED] was not [REDACTED] burning [REDACTED] S.

The [REDACTED]. Potential sources of OH were added in the reburning zone to attempt to enhance this reaction and investigate its role as a possible rate limiting step. Hydrogen peroxide, oxygen and carbon dioxide will form OH by reacting with a hydrogen radical. All three species were added downstream of the reburning fuel to allow time for HCN formation. The results for CO_2 addition are shown in Figure 3-12. Oxygen and hydrogen peroxide data are presented in Figure 3-13. Carbon dioxide had a negative impact, while the lower volumes of H_2O_2 and O_2 showed little effect. Since CO_2 was injected in larger quantities, it may have depleted hydrogen radicals, thus resulting in a NO_x emissions increase.

Figure 3-11. NO_x formation from Fenimore mechanism.

Figure 3-12. Influence of CO₂ on reburning efficiency.

Figure 3-13. Influence of H₂O₂ or O₂ injection on reburning efficiency.

4.0 EQUILIBRIUM CONSIDERATIONS

Although reburning zone residence times are limited, equilibrium calculations can support experimental results. Equilibrium concentrations of various reburning zone species by model calculations are presented here.

4.1 Free Radical Concentrations

Hydrogen, hydroxyl and oxygen radicals all influence reburning chemistry. Experimental results indicated that the H/C ratio of gaseous reburning fuels had little impact on emissions, while rich zone stoichiometry was important. The equilibrium radical concentrations, shown in Figure 4-1, substantiate these results. Essentially no dependence of radical concentrations on H/C is seen. Stoichiometry, however, has a large effect. At the optimum stoichiometry of about 0.9, trace amounts of oxygen are available to aid in hydrocarbon decay, while substantial levels of both hydrogen and hydroxyl radicals are present.

4.2 CH Species Concentration

The dependence of the equilibrium CH radical pool on CO, H/C ratio, stoichiometry, and a flame inhibitor were determined. The dependence on CO, shown in Figure 3-9, indicated that CH levels remained approximately constant when the percentage of reburning fuel as CO was less than 50 percent. The H/C ratio also has little influence on the CH concentration when the ratio exceeds one, as shown in Figure 4-2. The effect of stoichiometry, presented in Figure 4-3, is substantial from 1.0 to 0.9, with a lower stoichiometry resulting in a much larger CH pool. The influence of CH₃Cl, a flame inhibitor similar to the CH₃Br tested, is shown in Figure 4-4. Only a negligible influence is seen. ~~At 1.0 stoichiometry, the CH concentration is approximately 1.0 x 10⁻¹⁰ mole/mole, and at 0.9 stoichiometry, it is approximately 1.5 x 10⁻¹⁰ mole/mole.~~

~~The data obtained on the bench show that the CH concentration is approximately 1.0 x 10⁻¹⁰ mole/mole at 1.0 stoichiometry, and approximately 1.5 x 10⁻¹⁰ mole/mole at 0.9 stoichiometry.~~

Figure 4-1. Equilibrium radical concentrations.

Figure 4-2. Influence of fuel H/C ratio on equilibrium pool.

Figure 4-3. Influence of stoichiometry on equilibrium CH pool.

Figure 4-4. Influence of flame inhibitor on equilibrium CH pool.

5.0 FUTURE WORK

The chemical enhancement results to date have shown that in the reburning process 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 $SR_2 = 0.9$. Future tests will complete investigation of the rich zone by examining the influence of the addition of amine species to the reburning zone. Subsequent tests will investigate the formation of molecular nitrogen in the burnout zone and determine parameters which influence this formation.