

Nitrogen Oxide Abatement by Distributed Fuel Addition

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ABSTRACT

This program is designed to develop techniques for NO_x abatement by distributed fuel addition. It is expected that multiple fuel and air addition in the post flame of a combustion process will increase free radical concentrations which destroy nitrogenous species as they decay toward their equilibrium concentrations. This concept will be investigated under both fuel rich and fuel lean conditions in the reburn zone.

This report is a brief description of the proposed experimental plan. Results of two preliminary experiments are reported which show the effect of reburning or distributed fuel addition on nitric oxide concentrations.

INTRODUCTION

Nitrogen oxides are major pollutants from pulverized coal combustion. They have a damaging effect on the environment and are contributors to the acid rain problem. The major nitrogen oxides are nitric oxide (NO), Nitrogen Dioxide (NO₂) and nitrous oxide (N₂O). N₂O has been receiving increased attention because of its role in ozone depletion reactions and as a greenhouse gas. There are no known atmospheric sinks for N₂O and it has a lifetime of more than 100 years.

Several investigators (5) reported direct correlations between NO_x emissions and N₂O emissions. Therefore, it is possible that techniques that are effective in reducing NO concentrations would also be effective in reducing N₂O concentrations.

Modifications in the combustion process to reduce nitrogen oxides emissions include a wide range of well-defined techniques. Reburning is one such measure which focuses on the destruction of nitrogenous species in the post-flame zone in a fuel-rich environment. A typical reburning process would involve burning fuel with moderate excess air, sufficient to suppress soot and to maintain a stable flame. Additional fuel is introduced downstream of the primary combustion zone. A large fraction of NO_x formed in the primary zone would then be destroyed in the secondary zone. Additional air is introduced downstream of the reburn zone to complete the combustion process. Less NO_x is produced in the primary zone due to reduced fuel load and reduced excess air and consequently reduced heat release. In the reburn zone, some NO is chemically destroyed and HCN and NH₃ are formed and destroyed. In the burnout

zone, some nitrogenous species can be oxidized to NO or further reduced to produce inert products. Most of the destruction of nitrogenous species is expected to occur rapidly within the first few milliseconds in the reburn zone.

The advantage of reburning over other modes of combustion modification, such as air staging, is that the reburn zone, although fuel rich, is of short duration and is heavily diluted by combustion gaseous products. The result is less problems due to corrosion or flame instability.

The idea of introducing fuel downstream of the main combustion zone to reduce NO_x emissions was first introduced by Wendt et al. (6). Reductions of approximately 50% of NO_x leaving the primary combustion zone were reported. A major reburning parametric study was conducted by Greene et al. (2). The reduction process was found to be less favorable at lower primary NO_x levels and more favorable at higher reburning fuel injection temperatures and longer reburning zone residence times. The study indicated that high initial reburn temperatures were necessary to decompose HCN to NH₃ and low burnout temperatures could facilitate the ultimate destruction of all nitrogenous species. In addition, reburning effectiveness was found to be a strong function of reburning fuel nitrogen and hydrocarbon contents. A more recent study by Miyamae et al. (4) confirms the significance of hydrocarbon radicals in the reduction of NO_x. Using gas phase volatile matter evolved from pulverized coal as reburn fuel, 80% reduction in NO_x emissions were reported at low initial NO_x levels of around 100 ppm. A strong dependence on coal pyrolysis temperature which affects the decomposition of hydrocarbons to CO and H₂ was established. Yang et al. (7) conducted a study on a gas-fired heater in

which reburning with multiple segmented fuel addition was investigated. Reductions of up to 90% in NO emissions were reported as compared to 60% reduction by simple reburning on air staging.

It is expected that under reburning conditions, large quantities of free radicals would be produced at concentrations that are above their equilibrium values. These radicals are essential in the destruction of nitrogen species. In this research project, the concept of continuously generating free radicals along the combustion path by distributed secondary fuel addition will be investigated. It is expected that maintaining a large population of free radicals will keep the destruction mechanisms in force resulting in much lower NO_x emissions.

EXPERIMENTAL APPROACH

The proposed experiments will be conducted on two existing down-fired laboratory pulverized coal combustors having capacities of 2-4 kg of coal per hour. The combustors can be operated in a premixed plug-flow mode or in a turbulent diffusion flame mode. Pulverized coal will be used as the primary combustion fuel.

The research plan is broken down into three tasks:

Task 1

Task 1 would involve screening experiments to define an optimum configuration for distributed fuel and air addition and to have a better understanding of the reburning process. Three primary zone stoichiometries will be investigated as seen in Table 1. The secondary (reburn) zone variables are also listed in Table 1. The experimental conditions of the reburn zone

might be adjusted after each stage of experimentation as more insight is gained regarding the reduction process. The primary coal combustion stage will be in the premixed plug-flow mode and methane will be used as the reburn fuel.

Task 2

In Task 2, the effects of coal composition, reburn fuel nitrogen content and reburn fuel type would be investigated under the conditions defined by Task 1. The primary coal combustion stage will also be in the premixed plug-flow mode.

Task 3

The results obtained from the previous tasks would be extended to investigate the effect of distributed fuel and air addition in the post-flame zone of pulverized coal turbulent diffusion flames. Two types of flames will be investigated: A type A long axial diffusion flame without secondary air swirl and a type C short swirling flame with internal recirculation zone. These flame types are more related to practical applications.

Time-resolved profiles of T, concentrations of O₂, CO₂, CO, H₂, CH₄, C₂H₂, C₂H₆, NO, N₂O, HCN and NH₃ will be measured before and after each combustion zone.

EXPERIMENTAL FACILITIES

The combustors that are available for this research project have similar designs. One will be referred to as combustor A and the other as combustor B. Combustor A was designed by Glass (1) and its characteristics have been well-

defined in previous studies. It has been shown that it has the capability to simulate both full-scale wall-fired units and tangentially-fired units. Figures 1 and 2 show schematic diagrams of these two combustors.

Combustor A burns pulverized coal at a rate of 2-4 kg/hr with gas residence times of 1-3 seconds in the radiant section. The latter is 15 cm I.D. and 2m long, constructed from Zircar alumina cylinders and insulated with Kaowool loose insulation. The structure is enclosed within a 76 cm O.D. steel shell. Seven utility ports provide access to the combustor with connections made of 5 cm I.D. mullite tubes. Wall effects have been shown to be negligible (1), and the system has been shown to be one-dimensional in the post-flame region when operated in the plug-flow mode.

Combustor B is similar to the one described above, but has the advantage of twice as many ports and three times the length with gas residence times of 3-10 seconds. It is designed to study the combustion process at longer times over a wider span of temperatures.

Sampling of the combustion gases is done with a water-cooled, water-quenched stainless steel probe which can be inserted into the furnace from the utility ports. The quench water plus sample flow under vacuum into a separator where water is removed from the sample stream by a barometric leg and a refrigerated condensate separator. Any particulate matter remaining in the gases is removed in a fiberglass filter. The clean, dry gases are then supplied to the continuous analyzer section and to the gas chromatographs for analysis. A water/solid sample is collected from the barometric leg, the solids are filtered out and the water sample is analyzed with ammonia and

cyanide electrodes. The continuous analytical systems consist of a Paramagnetic oxygen analyzer, infrared CO and CO₂ analyzers and a Chemiluminescent NO/NO_x analyzer.

Gas chromatographic analysis of combustion gases (except N₂O) will be performed using a Perkin-Elmer Sigma I analysis system. The permanent gases are separated on a 12 x 1/8 SS 5A molecular sieve column. CO₂ and HCN are separated on a 6 x 1/8 SS Porapak T column. Argon is used as a carrier gas. This gas chromatograph is equipped with a hot wire detector for H₂, N₂, Co and CO₂ measurements, a nitrogen phosphorous detector for HCN measurements and a flame ionization detector for hydrocarbon measurements. The details of these analyses are outlined by Glass (1).

Gas chromatographic analysis of N₂O will be performed using a Shimadzu GC-8A, equipped with an electron capture detector that will be entirely devoted to N₂O measurements. A 12 x 1/8 SS Porapak Q column will be used to separate CO and N₂O gases. The procedure that will be followed in N₂O measurements is similar to the procedure described by Lanier and Robinson (3), except for the use of carrier gas. Nitrogen carrier gas may have a long-term effect on the sensitivity of the detector (5). Consequently, Argon/5% methane will be the carrier gas of choice.

EXPERIMENTAL RESULTS

Two preliminary experiments were performed to investigate the range of NO reduction by reburning under fuel-rich and fuel-lean conditions. The results are listed in Tables 2 and 3. The percentage of NO reduction due to reburning

was plotted versus the overall stoichiometric ratio as seen in Figures 3 and 4. The addition of reburn fuel reduces NO concentration due to dilution. Consequently, NO concentrations should be corrected for this effect.

Figure 3 shows NO reductions for classical reburning in which the reburn fuel was introduced at different locations along the axis of the furnace. The data obtained show a strong dependence of reburning effectiveness on the location of the reburn zone. This dependence was greatly reduced by reducing the primary fuel load by about 40% as seen in Figure 4. Thus, it appears that mixing has a significant effect on the reburning effectiveness.

An important observations from these simple runs is that significant reductions in NO emissions can be achieved at relatively low temperatures and under fuel-lean conditions. For example, by reducing the stoichiometric ratio from 1.2 to 1, about 25% reduction in NO emissions was achieved at temperatures of the order of 1500°K (Figure 3). Similar reduction of about 27% (by interpolation) was observed at lower temperatures (due to reduced primary fuel load) of the order of 1300°K (Figure 4). NO reduction under fuel-lean conditions is significant because only traces of NH₃ and HCN are expected under these conditions.

CONCLUSION

It appears that better reductions can be achieved under well-mixed conditions. Consequently, the design of an appropriate injection system becomes a primary concern. The present injection system consists of a water-cooled stainless steel tube with 1/16" holes that would introduce the reburn fuel radially in all directions from a center point along the axis of the

combustor. In addition, NO reduction under fuel-lean conditions appears to be promising and will be further investigated. Detailed experiments are needed to determine the effect of temperature on NO reduction.

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TASK I: SCREENING EXPERIMENTS

Primary Fuel: Bituminous Coal

Reburn Fuel: Methane

Premixed Configuration

PRIMARY ZONE VARIABLES

1. Stoichiometric Ratio:
 - a. $SR_1 = 1.2$
Classical reburning configuration distributed fuel in reburning zone.
 - b. $SR_1 = 0.8$
Reburning under staged conditions high yield of NO in primary zone.
 - c. $SR_1 = 0.6$
Reburning under staged conditions high yields of HCN and NH_3 in primary zone.

REBURN ZONE VARIABLES

1. Stoichiometric Ratio:
 - a. $SR_2 = 1.2$
Both fuel and air added at leaning out points to investigate additional radical production at leaning out zone.
 - b. $SR_2 = 1.0$
Unchanged overall stoichiometry to investigate the effect of free radical production under overall fuel rich environment when $SR_1 > 1$.
 - c. $SR_2 = 0.8$
Reburning in an enriching environment classical reburning when $SR > 1$.
2. Temperature:
This variable is coupled with time and the location at which reburning occurs.
3. Injection System:
4. Location of Reburn Zone:
5. Number of Injection Points:
1-3 injection points will be tested.

TASK II: TECHNOLOGY DEFINITION
Optimum Configuration
Premixed Configuration

PRIMARY ZONE VARIABLES

1. Coal (Primary Fuel) Composition:
 - a. Bituminous Coal
high yields of HCN
 - b. Lignite Coal
high yields of NH₃

REBURN ZONE VARIABLES

1. Reburn Fuel Nitrogen Content:
Different mixtures of methane/ammonia will be investigated
2. Reburn Fuel Type:
Bituminous and Lignite coals to test the role of coal volatility.

TASK III: TURBULENT DIFFUSION FLAMES

Diffusion flames may be more beneficial in promoting superequilibrium concentrations of free radicals, especially at low temperature

Two types of Flames:

1. Type A, tangentially-fired furnace flame.
2. Type B, wall-fired furnace flame

Reburn Fuel: Bituminous/Lignite coals

Table 2
Data for Classical Reburning

| SCFM Reburn Fuel | SR2 | Dilution Correction Factor | ----INJECTION PORT 3---- | | | | ----INJECTION PORT 4---- | | | |
|------------------------|------|----------------------------------|--------------------------|------------------------|------------|-------------------------|--------------------------|------------------------|------------|-------------------------|
| | | | ppm NO | Vol% O ₂ | Vol% CO | Vol% CO ₂ | ppm NO | Vol% O ₂ | Vol% CO | Vol% CO ₂ |
| 0 | 1.19 | ----- | 925 | 3.25 | 0.1 | 15.8 | 925 | 3.25 | 0.1 | 15.8 |
| 0.064 | 1.05 | 0.988 | 715 | 1.90 | 0.3 | 16.3 | 810 | 2.70 | 0.2 | 15.8 |
| 0.129 | 0.93 | 0.991 | 575 | 1.40 | 0.9 | 16.0 | 690 | 1.75 | 0.6 | 16.0 |
| 0.230 | 0.79 | 1.011 | 360 | 1.00 | 5.2 | 14.4 | 570 | 1.35 | 1.3 | 15.3 |
| 0.410 | 0.63 | 1.045 | 130 | 0.40 | 6.7 | 10.8 | 380 | 0.90 | 5.2 | 13.7 |
| 0 | 1.19 | ----- | 925 | 3.25 | 0.1 | 15.8 | 925 | 3.25 | 0.1 | 15.8 |
| 0.064 | 1.05 | 0.988 | 890 | 2.90 | 0.1 | 15.8 | 950 | 3.20 | 0.1 | 15.8 |
| 0.129 | 0.93 | 0.991 | 840 | 2.90 | 0.2 | 15.7 | 930 | 2.85 | 0.1 | 15.9 |
| 0.230 | 0.79 | 1.011 | 730 | 2.35 | 0.7 | 15.7 | 875 | 2.65 | 0.3 | 16.0 |
| 0.410 | 0.63 | 1.045 | 520 | 1.35 | 1.9 | 14.4 | --- | ---- | --- | ---- |

Coal Feed Rate = 26.90 g/min.

Table 3

Data for Low Temperature Fuel Lean Reburning

| SCFM Reburn Fuel | SR2 | Dilution Correction Factor* | ----INJECTION PORT 3---- | | | | ----INJECTION PORT 6---- | | | |
|------------------------|------|-----------------------------------|--------------------------|------------------------|------------|-------------------------|--------------------------|------------------------|------------|-------------------------|
| | | | ppm NO | Vol% O ₂ | Vol% CO | Vol% CO ₂ | ppm NO | Vol% O ₂ | Vol% CO | Vol% CO ₂ |
| 0 | 1.56 | ----- | 760 | 7.60 | 0.0 | 11.4 | 760 | 7.60 | 0.0 | 11.4 |
| 0.013 | 1.50 | 0.997 | 730 | 6.35 | 0.0 | 12.0 | 770 | 7.20 | 0.0 | 11.6 |
| 0.020 | 1.46 | 0.996 | 725 | 6.20 | 0.0 | 11.7 | 765 | 7.15 | 0.0 | 11.6 |
| 0.043 | 1.37 | 0.990 | 725 | 6.00 | 0.0 | 12.2 | 745 | 6.75 | 0.0 | 12.0 |
| 0.070 | 1.27 | 0.984 | 665 | 5.95 | 0.0 | 12.3 | 690 | 5.75 | 0.2 | 12.4 |
| 0.101 | 1.17 | 0.978 | 620 | 5.05 | 0.0 | 12.7 | 600 | 4.45 | 0.4 | 12.7 |
| 0.138 | 1.07 | 0.969 | 530 | 2.70 | 0.1 | 14.0 | 555 | 3.75 | 0.8 | 13.0 |
| 0.184 | 0.97 | 0.965 | 430 | 1.45 | 0.2 | 14.6 | 470 | 2.75 | 1.4 | 13.0 |
| 0.236 | 0.88 | 0.977 | 305 | 0.45 | 0.7 | 14.8 | 360 | 1.50 | 2.3 | 13.0 |

Primary Fuel: Beulah Lignite, low Na coal

Coal Composition:

45.47% C
 3.19% H
 20.25% O
 0.60% N
 1.73% S
 9.80% ash
 18.98% moisture

Reburn Fuel: Methane

*Dilution Correction Factor is ratio of dry effluent flowrates (total/primary)

$$\% \text{ NO reduction} = 100 - \left[\frac{\text{ppm NO after reburning}}{\text{ppm NO with no reburning}} \right] \times \left[\frac{\text{dilution correction factor}}{\text{factor}} \right] \times 100$$

Coal Feed Rate = 17.84 g/min

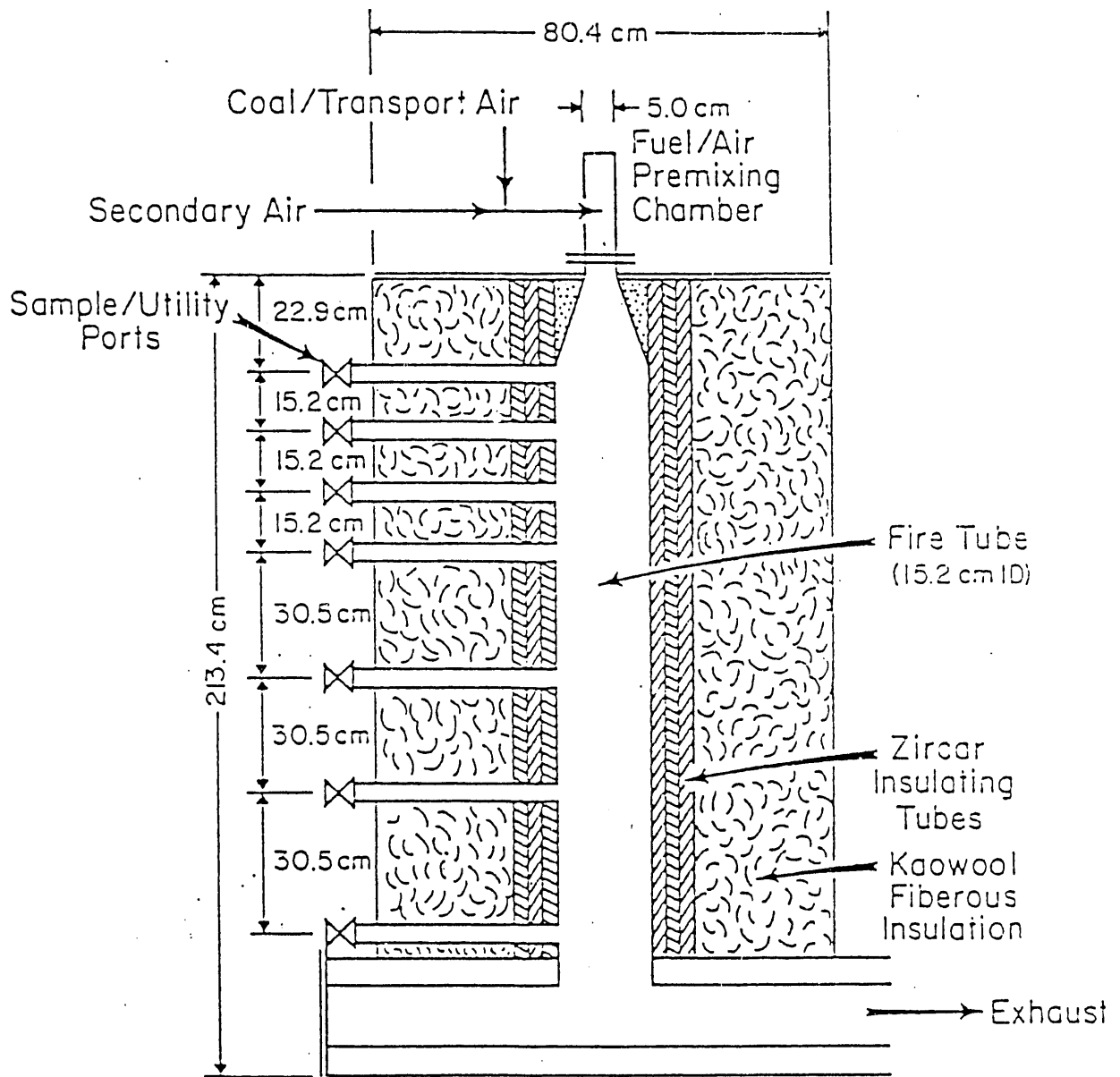


Figure 1. Experimental Combustor A

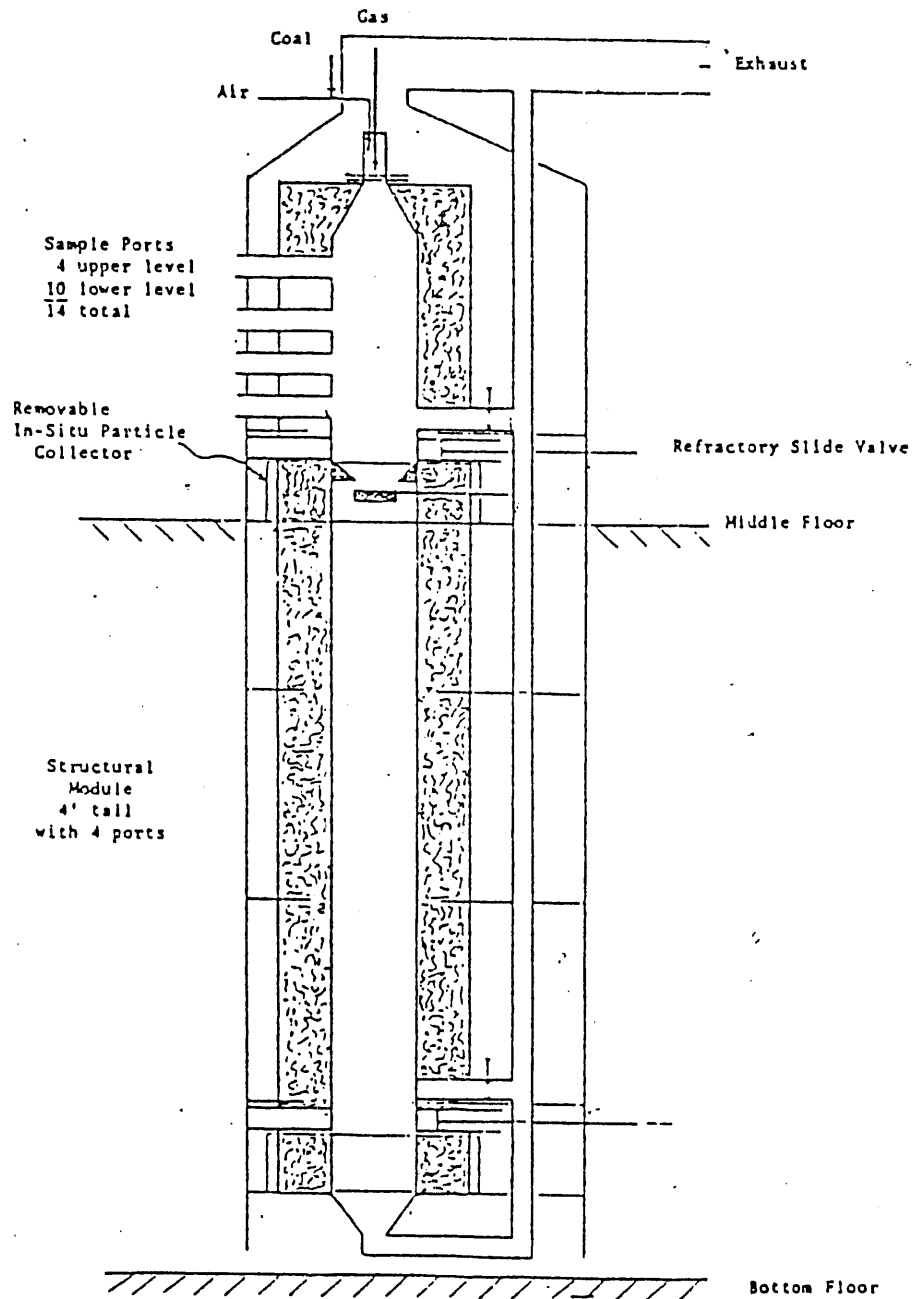


FIGURE 2. Schematic Elevation of
Downflow Combustor B

- reburning at port 3 (21 inches from burner)
- reburning at port 4 (27 inches from burner)
- reburning at port 5 (39 inches from burner)
- reburning at port 6 (51 inches from burner)

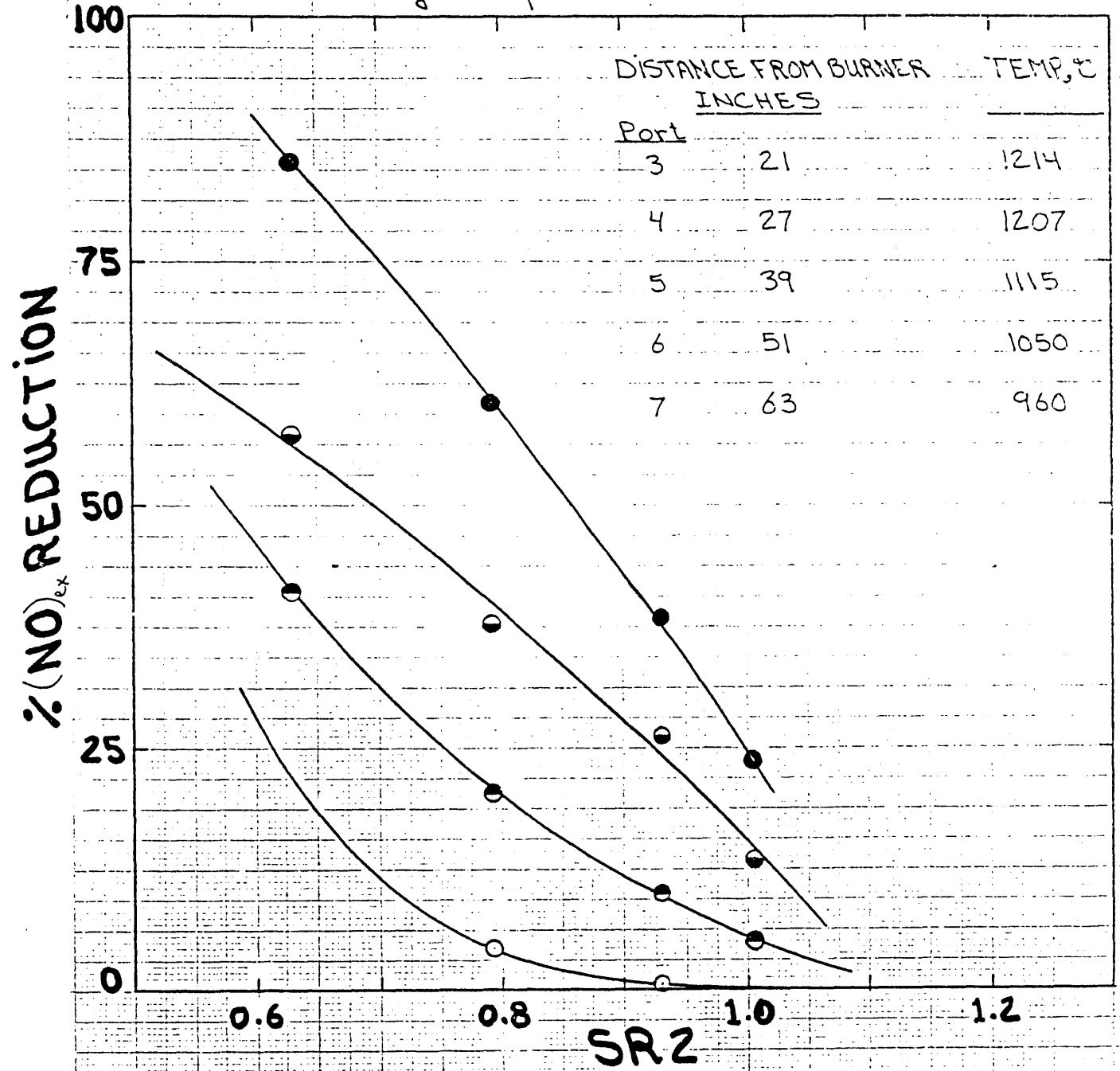


Fig 3: $(NO)_{ex}$ reduction at various reburn fuel loads

reburn fuel : Methane
 primary fuel : Beulah Lignite - low Na coal
 $SR_1 = 1.19$
 base $(NO)_{ex}$ concentration = 925 ppm

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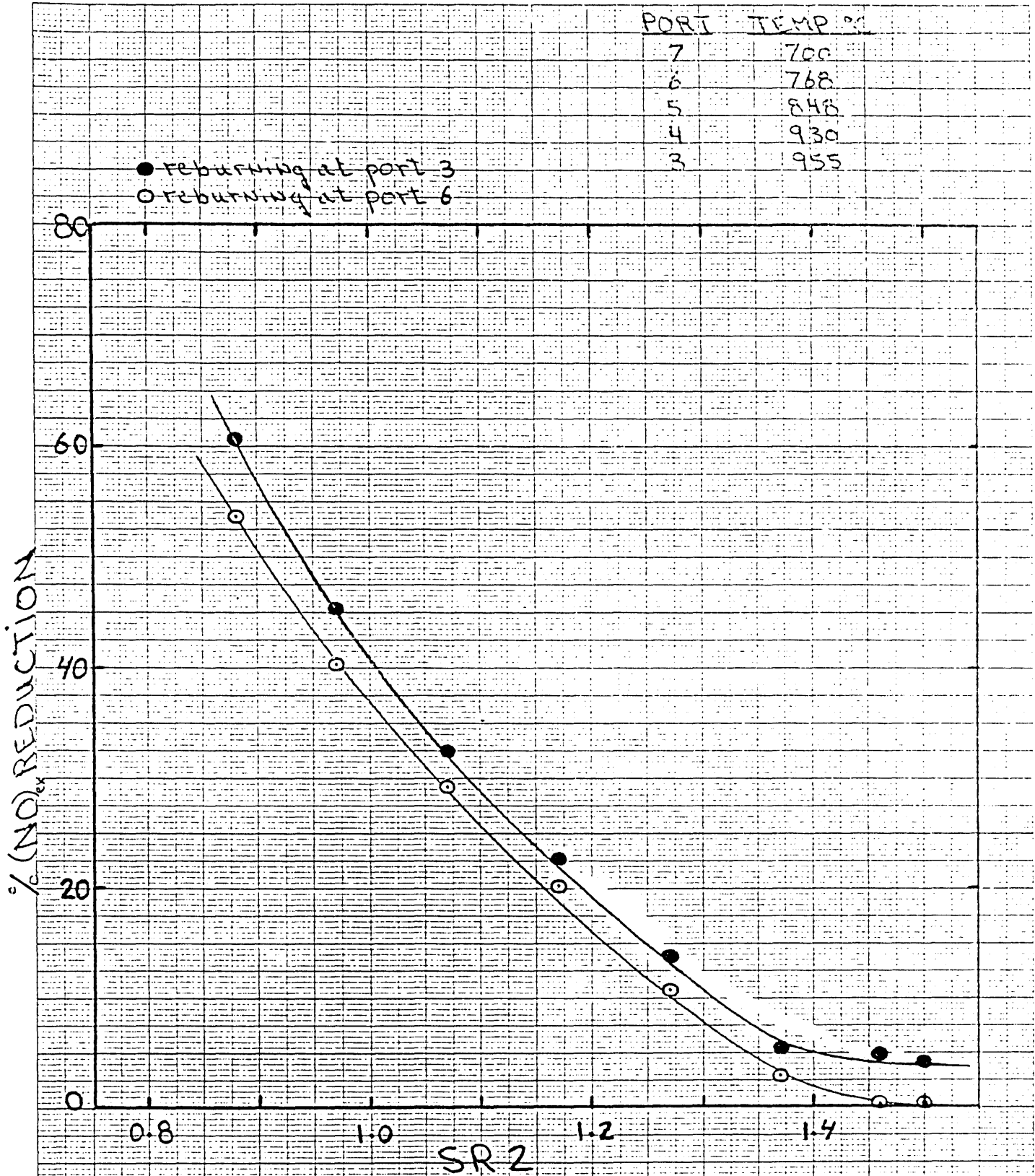


Fig 4 : (NO_x) Reduction at Various Reburn Fuel Loads
 low Temperature - Fuel lean conditions
 reburn fuel : Methane
 primary fuel : Beulah Lignite - low Na coal
 SRF = 1.56
 base : No reburning (NO_x) concentration = 760 ppm

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