

**NO_x Emission Reduction by Furnace Cleanliness
and Combustion Management**

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Abstract

This paper highlights two overlooked strategies for NO_x control in fossil fuel fired systems. The first, furnace cleanliness management, is designed to control furnace gas temperatures to minimum acceptable levels by enhancing furnace heat absorption, thereby reducing NO_x. Reductions of 20 to 30% are possible with this control strategy. The second, combustion management, strives to minimize NO_x emissions by optimizing combustion characteristics in each burner. Laboratory test results show that on-line combustion measurements identify proper and improper burner vane settings. NO_x emission levels varied as much as a factor of two as burner vane settings were changed.

Background

The Clean Air Act Amendments of 1990, Titles I and IV, mandate NO_x reduction from stationary sources. The impact on utilities is that by the year 2000, more than 200,000 MW must be retro-fitted with low-NO_x systems. Title IV (acid rain) requires the use of low NO_x combustion technology and Title I (ozone non attainment) requires RACT (reasonable, available control technology) to reduce NO_x.(1)

Introduction

NO_x formation from any combustion process using air has two major components, thermal NO_x and fuel NO_x. The relative contribution of each depends primarily on the nitrogen content of the fuel and the temperature of the combustion process. NO_x is produced at high temperatures by oxidation of the nitrogen from the combustion air (thermal NO_x) and oxidation of the nitrogen from the fuel (fuel NO_x). Thermal NO_x is formed by gas-phase chain reactions between O₂ and N₂. Conversion of fuel bound N depends on the stoichiometry, residence time, and temperature within the flame. NO_x is reduced by depressing combustion zone temperatures and by delaying the admission of sufficient oxygen to complete combustion.

NO_x control methods include: Combustion Modification and Downstream Processes. Examples of each approach are listed below:(2)

Combustion Modification

- Low NO_x burners
- Over fired air
- Flue gas recirculation
- Low excess air

Downstream Processes

- Selective catalytic reduction
- Selective non-catalytic reduction

Furnace cleanliness management and combustion management, while not routinely considered as such, are NO_x control strategies. The remaining sections of the paper discuss NO_x formation and control mechanisms and describe the cleanliness and combustion management strategies for NO_x control.

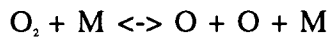
NO_x Formation Mechanisms

Thermal NO_x

NO_x collectively refers to nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O). NO is the only nitrogen oxygen compound that can form, be stable, and exist in significant quantities in the high temperature portions of a utility boiler system (3).

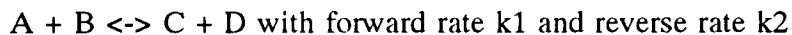
Thermal NO_x is NO derived from heating of air. If one looks at the three equations of the Zel'dovich mechanism, some understanding of thermal NO_x can be obtained.

The first equation:



shows that diatomic oxygen in the presence of a reaction medium M breaks down to or is combined from oxygen radicals. The forward reaction rate is proportional to temperature and on the order of 10 ft³/lb-mol-hr at 2300°F, 100 ft³/lb-mol-hr at 2500°F, and 1000 ft³/lb-mol-hr at 2700°F. The reverse reaction rate is constant on the order of 10¹⁴ ft³/lb-mol-hr regardless of temperature.(4)

If we use these forward and reverse reaction rate constants in the following equation for a reversible reaction:



$$\text{at equilibrium: } k_1[\text{A}][\text{B}] = k_2[\text{C}][\text{D}]$$

Then, for this reaction proportionally few oxygen radicals exist relative to concentration of diatomic oxygen even at high temperatures. Also, since k₁ increases with temperature and k₂ does not, as temperature increases for a constant concentration of diatomic oxygen the radical concentration will increase.

The next equation:



shows that diatomic nitrogen in the presence of oxygen radicals will combine with some of those radicals to form NO and radical N.

The forward reaction rate constant for this equation is also proportional to temperature but on the order of 10⁶ ft³/lb-mol-hr at 2600°F and 10⁷ ft³/lb-mol-hr at 2900°F. The reverse reaction rate is constant with temperature and on the order of 10¹⁵ ft³/lb-mol-hr.(4)

Although the reverse reaction rate constant is much higher than the forward rate constant, the high concentration of diatomic nitrogen relative to NO and N will force the reaction forward as long as sufficient oxygen radicals are present. At temperatures of 2700-2800 the first equation produces a sufficient oxygen radical concentration to drive this second reaction forward.(4)

From these constants one can see that the NO formation rate is also faster than the oxygen radical formation rate of the first equation. This means that the formation rate of NO is limited by the rate of formation of oxygen radicals which is proportional to temperature.

The third equation:



shows that if nitrogen radicals are present with diatomic oxygen, NO can be formed. The forward reaction rate is slightly temperature dependent and is on the order of 10^{14} ft³/lb-mol-hr at 2600°F. The reverse reaction rate is more temperature dependent but on the order of only 10^9 ft³/lb-mol-hr at 2600°F and 10^{10} ft³/lb-mol-hr at 3000°F (4). Both the forward reaction rate constant being higher than the reverse rate constant and the relatively high diatomic oxygen concentration drive this reaction forward where N radicals exist.

Finally, comparing the second and third equations, the reverse reaction rate of the second equation is on the order of 10^{15} ft³/lb-mol-hr compared to the forward reaction rate of the last equation at 10^{14} ft³/lb-mol-hr. This would alone suggest that a nitrogen radical would preferentially combine with NO to form diatomic nitrogen and oxygen radicals over combining with diatomic oxygen to form NO. However, the difference in reaction rates constants is only on the order of 10 while the ratio of diatomic oxygen concentration to the concentration of NO will normally greatly exceed this factor. Therefore, NO is formed by both the second and third equations in the heating of air.

Fuel NO_x

The other major mechanism for the formation of NO_x is derived from the nitrogen in the fuel. Although oils and coals typically contain only 0.5 to 2% of nitrogen by weight (5), it is generally believed that fuel NO_x contributes between 50 and 80% of the total NO_x generated in unstaged firing applications.

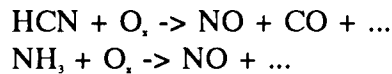
The formation of fuel NO can be further divided into two paths dependent on the location of the nitrogen undergoing reaction: volatile nitrogen which is released with the volatile matter of the coal, and char nitrogen which remains with the char after devolatilization is complete. Figure 1 shows the relative percentages of thermal, volatile based fuel, and

char based fuel NO_x generated versus heat rate (5) and versus stoichiometry ratio for unstaged combustion (4). Low NO_x burners and staged combustion reduce NO_x emissions by reducing the percentage of volatile nitrogen and thermal NO_x .

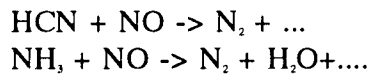
The nitrogen in fuels is usually bound in the form of attached ammonia (NH_2) or pyridine ($\text{C}_5\text{H}_5\text{N}$). Once the fuel is heated it breaks down into nitrogen bound intermediates:

fuel + heat \rightarrow HCN, CN, OCN, HNCO, NH_2 , NH_3 , NH , or N.

These intermediates are released in the volatile mass leaving behind char. Then in the presence of oxygen these intermediates react forming NO as a product:

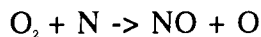


In the absence of sufficient oxygen these intermediates may however react with any NO present to form diatomic nitrogen:

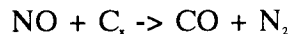


Experimental work of Takagi, et al. indicated that the conversion of HCN and NH_3 was dependent on the local temperature and oxygen radical concentrations (4). The primary factor affecting fuel nitrogen conversion is the oxygen concentration. The formation rate constants are not as temperature dependent as the formation and reaction of oxygen radicals of the Zel'dovich mechanism for thermal NO_x .

The char which remains after the volatile matter is released is high in carbon, low in oxygen and hydrogen, and contains some nitrogen, sulfur, and other minerals. Carbon and nitrogen oxidization of these char particles is heterogeneous as oxygen comes into contact with the hot particle surfaces:



The conversion efficiency of char nitrogen is generally less than 20%, which is lower than for volatile nitrogen. This may relate to the known capability of carbon to reduce NO (5):



NO_x Reduction Principles

Char nitrogen forms a constant baseline NO dependent on coal characteristics which is unavoidable under practical combustion. This is because the reaction of char particles with oxygen is much slower than the oxidization of volatile matter. This makes it impossible to keep char particle combustion in an oxygen lean condition to preclude NO formation.

The remaining sixty to eighty percent of the fuel NO produced during unstaged combustion has been attributed to nitrogen released with volatile matter.

The total nitrogen volatilized in the heating of coal was found to be more sensitive to temperature than the total mass evolved during pyrolysis (6). Thus, at higher temperatures an increase in the amount of nitrogen is evolved with the volatile matter during coal devolatilization. Since the conversion efficiency of fuel nitrogen to NO is higher for volatilized nitrogen than it is for char bound nitrogen, the less volatilized nitrogen the lower the fuel N to NO_x conversion efficiency.

Principle 1: Lower temperatures at the point of coal devolatilization reduce volatilized nitrogen and lower the overall fuel N to NO_x conversion efficiency.

The second principle arises from the fact that in the absence of oxygen the nitrogen bound intermediates react with any NO present to form diatomic nitrogen. This is the principle upon which the technique of staging combustion rests.

Principle 2: If coal devolatilization occurs in an oxygen lean environment then HCN and NH₃ form N₂ rather than NO and react with NO to reduce it to N₂.

The third principle uses the requirement that for the second equation of the Zel'dovich mechanism to be driven forward requires an oxygen radical concentration corresponding to a temperature greater than 2700°F.

Principle 3: If the oxygen lean condition can be extended as long as temperatures are above 2700°F then insufficient oxygen radical concentration will be formed to drive the Zel'dovich mechanism's NO formation equation forward.

The fourth principle is based on the temperature dependence of the rate constant of oxygen radical formation, and the concept that for moving particles residence time is related to flame volume. As the time available for reaction at high temperature increases, the NO concentration can be expected to increase.(7)

Principle 4: In oxygen rich conditions reducing temperatures in as minimum a volume or time as possible to 2700°F will minimize total thermal NO_x produced.

In oil and coal burning plants, the major contributor of NO_x is fuel NO_x. The most significant parameter in fuel NO_x formation mechanisms is oxygen concentration at the location where the nitrogen bound intermediate constituents are reacting. The location can be assumed to be near the location of coal devolatilization as temperatures high enough for devolatilization provide sufficient activation energy for the reactions. If oxygen concentration can be reduced for the majority of the reactions while maintaining temperature to cause devolatilization, the resulting nitrogen product will be diatomic nitrogen rather than NO. Since a given coal particle will principally absorb heat by radiation, the production of a highly radiant, yet small volume, flame surface between the fuel source and the air source will create a desirable condition. This concept may be implemented on wall fired unit burners by the creation of a shell of flame around the fuel. The same concept may be implemented on tangential fired unit burners by the formation of a diffusion flame front with low stoichiometry ratio. Then additional air is introduced after the nitrogen intermediates have reacted. Laboratory tests have indicated that the optimum burner stoichiometric ratio is 0.8.(8)

The second highest producer is thermal NO_x. The most significant factor in the thermal NO_x formation mechanism is temperature. The highest temperature is produced in a flame of stoichiometry ratio near one. Combustion staging can reduce peak temperatures. Controlled admission of air in a reactor which absorbs heat (boiler) allows the temperature to be controlled as combustion is completed. Thus, a low thermal NO_x producing flame would ideally consist of a flame of low peak temperature volume product, a rapid decrease in temperature below 2700, and a larger volume at or near 2700°F to maintain total heat release rate. Practically, this is implemented by rapidly reducing temperatures after the initial reducing zone by flow dynamics. This concept is the basis for recirculation zones (drawing cooler exhaust back into flame) as well as the distribution control of air in staged combustion.

Furnace Cleanliness Management

The concept of NO_x control by furnace cleanliness management is based on controlling gas side temperatures to minimum acceptable values by enhancing furnace heat absorption. In many coal and oil-fired boilers, this can be accomplished by prudent

selection, location and effective operation of furnace cleaning devices. As previously described, thermal NO_x is a major contributor to overall NO_x emission levels. The most significant factor in the formation of thermal NO_x is temperature. Furnace cleanliness management primarily reduces thermal NO_x by reducing furnace gas side temperatures.

Heat transfer to the tube side fluid in the furnace of utility boilers is predominately radiation (~90% of total heat transfer). As furnace heat transfer surface becomes dirty, flame temperatures must increase to maintain constant load conditions.

$$R = \epsilon\tau (T_1^4 - T_2^4)$$

Where:

R	=	Net rate of radiation energy transfer
ϵ	=	Effective Emissivity
τ	=	Constant
T_1	=	Flame Temperature
T_2	=	Furnace Wall Temperature

The above equation can be used to estimate the effect of changing cleanliness conditions on gas side temperatures. For a constant heat transfer rate and the assumptions noted below, the change in flame temperature with variations in furnace cleanliness can be estimated.

Assumptions:

T_{1c}	=	3000°F (flame temperature with clean furnace wall)
ϵ_c	=	0.7 (effective emissivity with clean furnace wall)
T_{2c}	=	750°F (wall temperature with clean furnace wall)
T_{2d}	~	750°F (wall temperature with dirty furnace wall)
ϵ_d	=	0.4 (effective emissivity with dirty furnace wall)
T_{1d}	=	(flame temperature with dirty furnace wall)

Radiation heat transfer is related to temperatures to the fourth power, therefore, for an order of magnitude estimate, T_2 can be eliminated since the value when raised to the fourth power is small compared to T_1 to the fourth power. Therefore, the equation for estimating the change in flame temperature can be simplified to

$$T_{1d} = \left(\frac{\epsilon_c}{\epsilon_d} \right)^{1/4} T_{1c}$$

T_{1d} based on the above equation is ~3500°F or a 500°F increase compared to the temperature required with a clean furnace. In practice, the total change in furnace

temperature would not be seen since convection pass heat transfer surfaces would provide part of the added heat transfer requirement.

Field test results have shown effective wall emittance variations from 0.2 to 0.8 are possible (9) in coal fired units. Figure 2 illustrates the magnitude of furnace exit gas temperature (FEGT) change that can occur in a 500 MW boiler at full load conditions as furnace wall emittance varies. FEGT in this paper refers to the gas side temperature at roughly the nose of the furnace and upstream of any furnace platen or pendent surface. A 500°F increase in FEGT can result with a change in the furnace emittance of 0.4 to 0.7.

Thermal NO_x, which occurs only at high flame temperatures, is formed by the reaction of oxygen and nitrogen found in the air. Generation of thermal NO_x is exponentially dependent on temperature.(10) The NO_x emission at 2700°F is over 40 times greater than at 2200°F.

Several studies (11,12) have shown that FEGT can be controlled by a proper complement and operation of furnace cleaning equipment. Therefore, fossil fuel fired boilers with a significant thermal NO_x component and the need for furnace heat transfer surface cleaning can realize significant reductions in NO_x emissions by furnace cleaning management.

Figure 3 illustrates the measured variation in NO_x emission with changes in FEGT. These results were obtained on a large (>500MW) wall fired unit burning bituminous coal. The variation in NO_x resulted primarily from changes in the operating frequency of furnace wall cleaning devices. Unit load varied from 85-100%. A NO_x reduction of up to 30% was measured corresponding to a FEGT change of 100°F.

FEGT can be controlled to minimum acceptable levels by enhancing furnace heat absorption, thereby reducing NO_x. An integrated system of an on-line FEGT sensor, furnace cleaning devices and controls can effectively manage the cleaning process to realize NO_x reductions of more than 30%. Figure 4 illustrates a comprehensive system to improve furnace heat transfer, reduce FEGT, and thereby reduce NO_x emissions. The system includes: Diamond Power's waterlances and/or steam cleaning devices, BOS™ sootblower control system, and Gastemp™. The integrated system permits condition-based sootblower control to maintain the desired FEGT and thereby the achievable NO_x reduction.

Combustion Management

Combustion management involves dividing the furnace into individual burners or logical combustion segments and verifying operation of each segment in accordance with a NO_x reduction strategy. The strategy may be derived from the design concept of Low NO_x burners or formulated for other burners based on general NO_x reduction principles.

Locations of high NO_x generation are identified and corrected as each segments forward (NO_x formation) reaction rates are minimized and reverse (NO_x destruction or blocking) reaction rates are maximized. Stepwise implementation of combustion management tools and techniques on the logical combustion segments then results in a reduction of the total NO_x generated in the furnace.

Test Case Implementation

A single low NO_x burner shown in Figure 5 was tested in a laboratory facility. The facility was instrumented to record exit gas concentrations including NO_x, CO, O₂, and CO₂ generated from the burner. The facility was also outfitted with a two color pyrometer camera (Flameview™, Diamond Power Specialty Co.) specialized for imaging and thermally mapping utility furnace combustion zones.

This area pyrometer system displayed 15,360 point resolution images of the temperature distribution of the burner flame for each test condition. A data acquisition system also recorded plant settings and monitoring equipment values at each test condition. This arrangement allowed isolated definition and complete instrumentation and recording of what is termed a combustion segment in the combustion management overview.

The burner design splits the secondary air into inner and outer zones around the primary air/coal stream. Both the inner and outer secondary air paths have independently adjustable spin vanes acting from a zero angle (closed) to a 90 degree angle (fully open, no spin).

The controlled parameters for the testing were maintenance of a constant power level and a constant excess oxygen percentage at the stack. Vane settings were changed through a series of graduations. Plant operation and emissions data was taken once the system had stabilized at each new condition of vane settings.

Test Case Results

The conditions of the following presentation are representative samples selected from a larger body of data to present a variety of burner vane settings in a reasonable size paper. For the results presented below, the larger the vane position number the greater the vane opening angle. The same position number for the inner and outer vanes would correspond to equal angular settings.

The temperature contours from the Flameview™ camera (Figure 6), placed above the flame for an inner vane position of 2 and an outer vane position of 4, show the characteristics of good staged combustion. A small volume hot zone exists at the region

of coal devolatilization where a fuel rich condition can be expected. Notice that this hot zone peaks at only 2950°F and the 2900°F volume is small. This is followed by a rapid cooldown downstream. Recirculation is evident by the folding inward of the contours as the air swirls back into the rear of the flame.

Figure 7 presents data for an inner vane setting of 2, same as the previous figure and an outer setting of 3 (reduced angle). The temperature contours from the Flameview™ camera are quite similar to the first case in that temperature ranges and volumes are about the same. The principle difference between the two is the strength of the recirculation evident by the contours. Comparing the 2800°F and the 2750°F contours between the two temperature plots one can see that for the 3 outer vane position a slight rounded folding of the contours occurs compared to the deep folding of the position 4 setting. Also, the general shape of all the contours is more circular. However, the temperature gradient is still steep and the NO_x value has increased to 1.04 (Test Case 2/Test Case 1 NO_x). The O₂ at the stack was decreased for this case indicating that the flattening of the vane setting was not yet fully compensated for by the operator adjusting the fan current before the data was recorded. The data provided here was taken as the mean off of a strip chart for the test condition over a period after the system had stabilized at the new settings.

Figure 8 presents results for an inner and outer vane position of 4. Opening of the inner vane proportions more air into the core of the flame. This increases oxygen concentration in the region of the nitrogen based intermediate reactions resulting in NO versus N₂ formation. Coincident angles with relatively mild spin decreases turbulence and results in a longer tubular versus wedge shaped flame. While the peak temperature is the same as in Figure 6 at 2950°F, the 2900°F volume is larger, and the 2850 and 2800 regions are much larger. These high temperatures are extended to an area of the flame where oxygen concentrations are high resulting in thermal NO_x generation. Between the increased volatile fuel NO_x and thermal NO_x formations the measured NO_x has increased to 1.81 (Test Case 3/Test Case 1 NO_x) while other exit gas conditions are nearly the same. An additional case with the inner vane opened further proportioned more flow to the flame core. This produced the highest NO_x level of 2.10 (Test Case 4/Test Case 1 NO_x).

Summary

Thermal and fuel NO_x formation mechanisms were presented. Four principles for NO_x reduction based on minimizing the forward reaction rates and maximizing the reverse reaction rates were identified.

Two alternative approaches, furnace cleanliness management and combustion management, for NO_x control were presented. Furnace cleanliness management is a control strategy to achieve minimum acceptable gas side temperatures by enhancing furnace heat absorption. Appropriate selection, placement and operation of furnace heat transfer surface cleaning devices can reduce gas side temperatures in many utility boilers and thereby reduce NO_x emissions up to 30%.

A single laboratory burner had vane settings altered while exit gas parameters were monitored to determine the optimal settings for NO_x reduction. A two color pyrometer camera provided temperature distributions for visualization of this component of NO_x formation kinetics. The results indicated that application of the NO_x reduction principles accomplished a variation of NO_x from the worst test condition value to the low NO_x case of 2.1.

This test case illustrates that the application of combustion management tools and techniques can be used to identify and correct locations of high NO_x generation. The periodic verification that each furnace combustion segment operates in accordance with a NO_x reduction strategy, whether this strategy is design based for low NO_x burners or general principle based for other burners, is an effective means of reducing total NO_x generation within the furnace.

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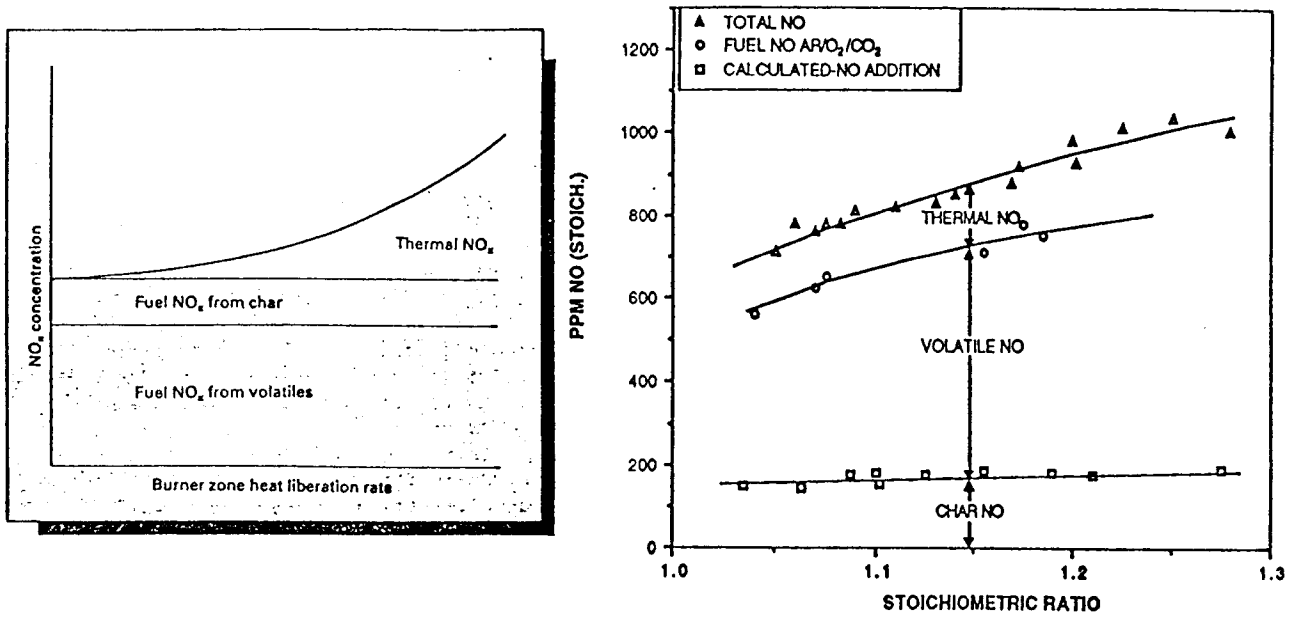


Figure 1
Contributions to NO_x from Coal Combustion

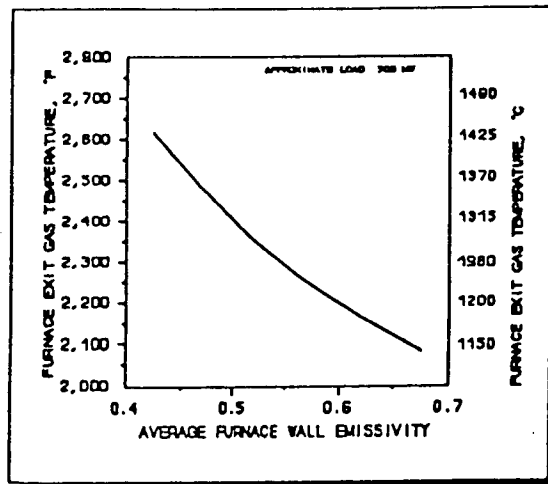


Figure 2
Effect of Furnace Emissivity with Constant Power

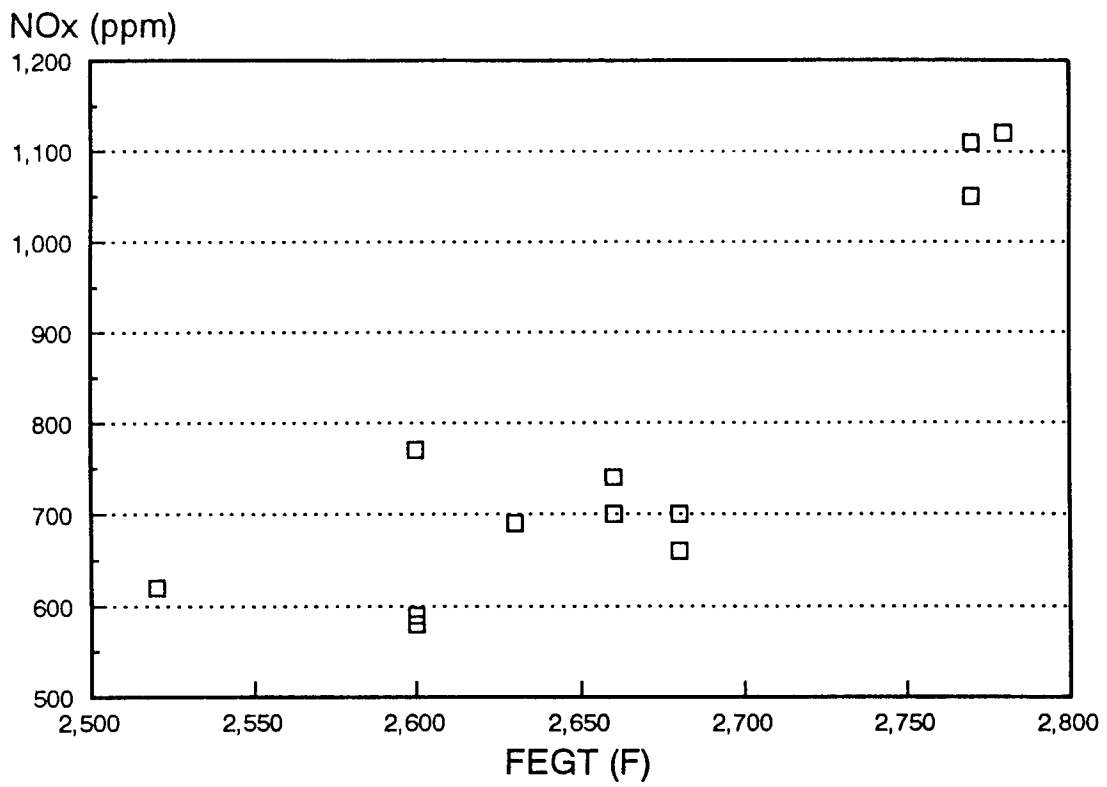


Figure 3
Comparison of NO_x and Furnace Exit Gas Temperature

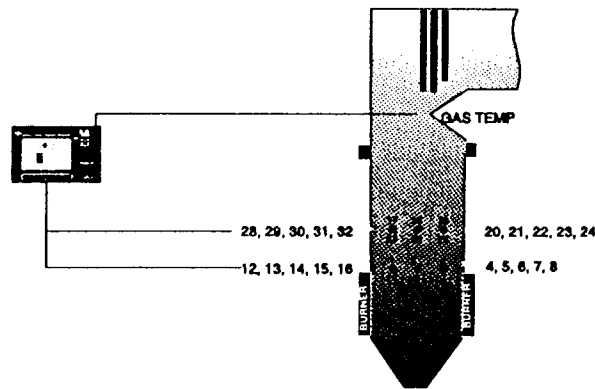


Figure 4
Integrated Cleaning Management System

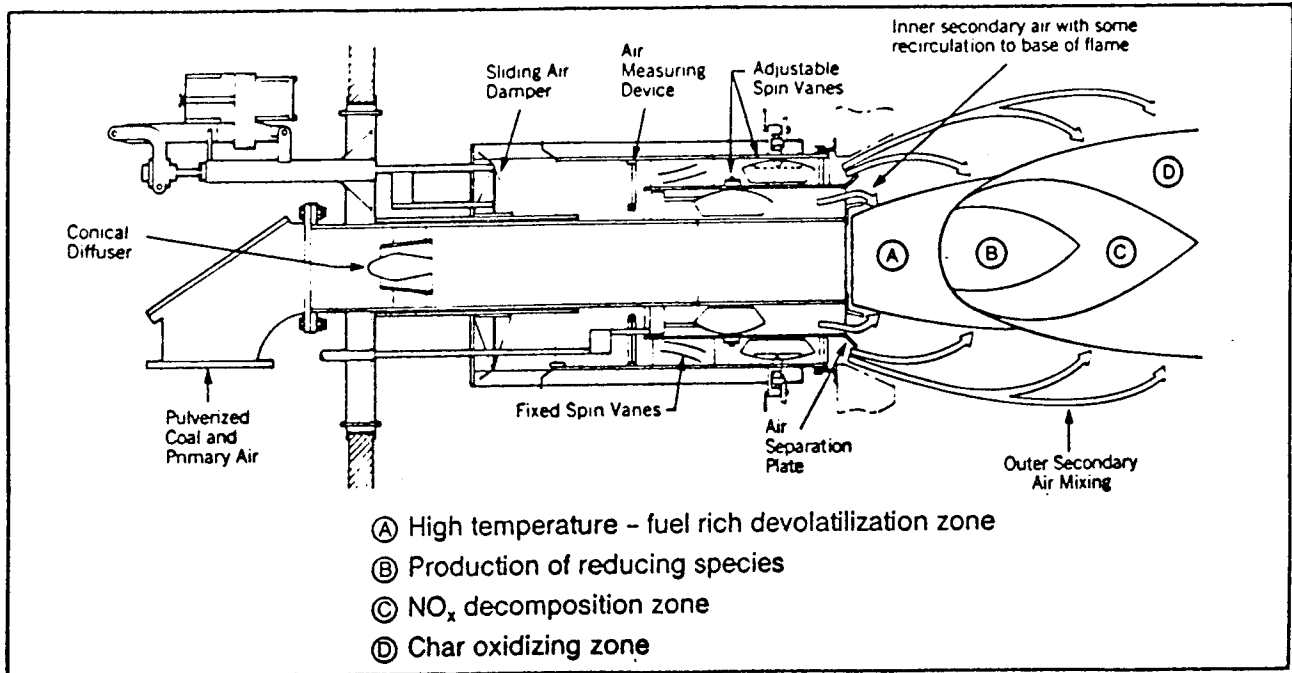


Figure 5
Test Burner Used for Laboratory Testing

Inner vane position: 2
Outer vane position: 4
NO_x: 1.0 (Reference)

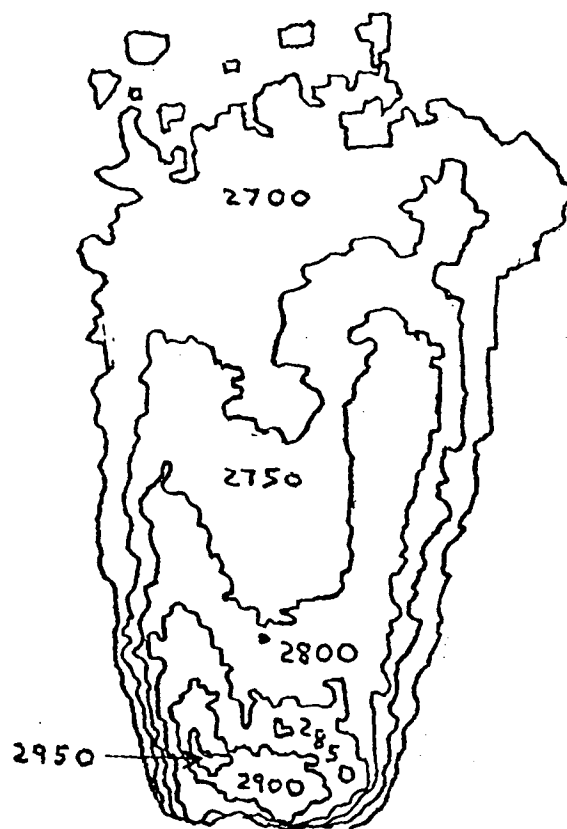


Figure 6
Burner Test Case 1

Inner vane position:
Outer vane position:

2
3

NO_x:

1.04 (Test Case 2/Test Case 1)

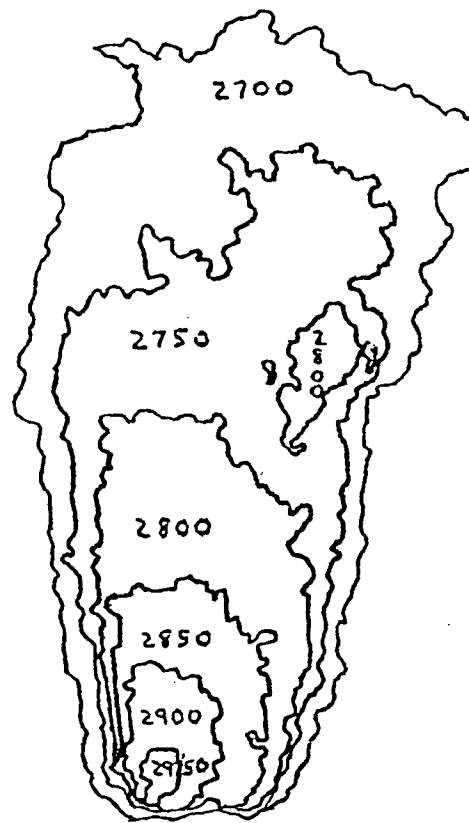


Figure 7
Burner Test Case 2

Inner vane position: 4
Outer vane position: 4
NO_x: 1.81 (Test Case 3/Test Case 1)

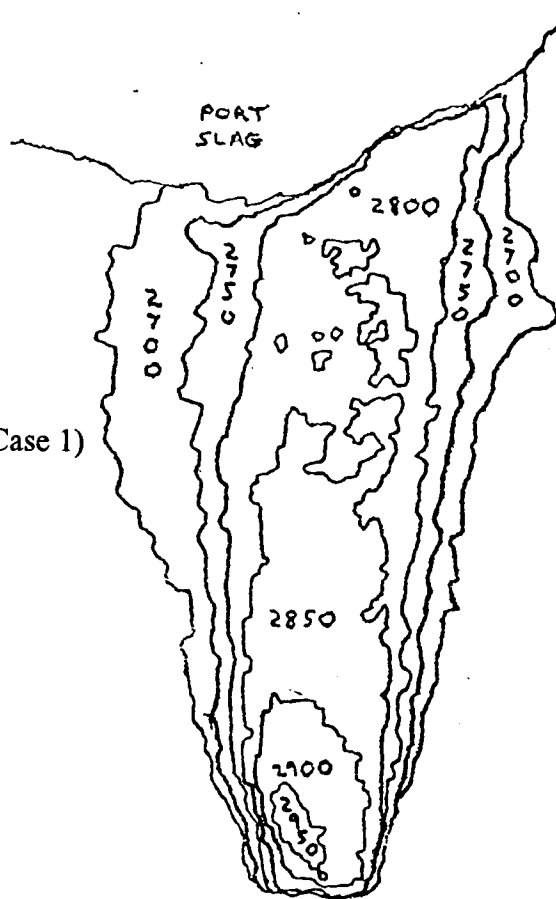


Figure 8
Burner Test Case 3