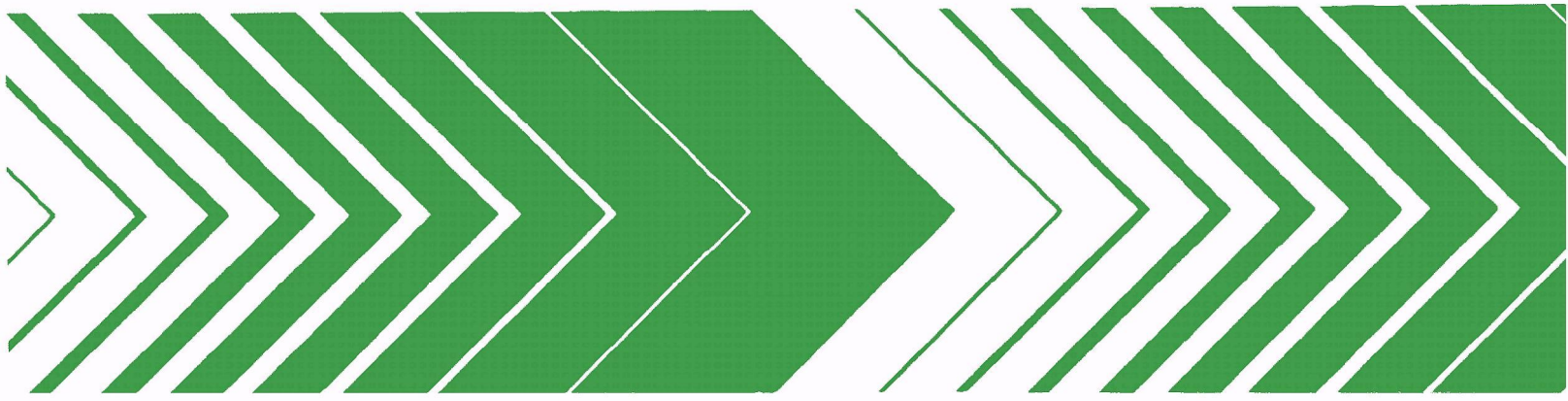

Research and Development



Combustion Modification Effects on NO_x Emissions from Gas-, Oil-, and Coal-Fired Utility Boilers



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Combustion Modification Effects on NO_x Emissions from Gas-, Oil-, and Coal-Fired Utility Boilers

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ABSTRACT

The report represents the conclusion of 4 years of analysis of large quantities of emissions, operating conditions, and boiler configuration data from full-scale multiple-burner, electric generating boilers firing natural gas, oil, and coal fuels. The overall objective of the study was to develop from this data: (1) further understanding of the effects of combustion modifications on combustion, and the resulting effects on NO_x emissions; and (2) directly applicable guidelines for the application of combustion modification techniques for the control of NO_x emissions in full-scale operating utility boilers. The report includes: (1) discussion of modeling techniques used to analyze the data; (2) conclusions relative to the sources of NO_x within the furnace; (3) guidelines for NO_x reduction; and (4) an example application of the guidelines. Boiler firing types include single-wall, opposed and tangential configurations.

The report concludes that NO_x emissions are generated, in varying degrees, from conversion of fuel-bound nitrogen (the predominant source), heterogeneous combustion and mixing zone, second-stage mixing zone, and active burner region. Maintaining very fuel-rich initial combustion conditions, holding the initial peak combustion to <2050 K, and delaying fuel gasification and mixing until the gas has been cooled somewhat should reduce NO_x emissions from all four main sources.

PREFACE

This study represents the conclusion of four years of study of modification of combustion in full-scale, multiburner utility boilers for the purpose of NO_x reduction and of some of the associated side effects. Previous work is reported in: (1) Analysis of Test Data for NO_x Control in Gas- and Oil-Fired Utility Boilers (EPA-650/2-75-012, January 1975); (2) Analysis of Test Data for NO_x Control in Coal-Fired Boilers (EPA-600/2-76-274, October 1976); (3) Effects of Combustion Modifications for NO_x Control on Utility Boiler Efficiency and Combustion Stability (EPA-600/2-77-190, September 1977); and (4) in papers presented at the first and second EPA Stationary Source Combustion symposia (EPA-600/2-76-152c, June 1976) and (EPA-600/7-77-073b, July 1977), respectively. The data and the analytical techniques reported in the earlier reports were used as the basis for, and were extended in, the work reported herein.

This study, as well as the three previous studies, was conducted for the U. S. Environmental Protection Agency, Combustion Research Branch, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, during the third year of a three-year continuing grant. (The first study was conducted under a separate EPA Grant No. R-802366 for this same EPA office.) The first study concerned the effects of combustion modifications of NO_x emissions in natural gas- and oil-fired boilers. The second study extended the analysis to coal-fired boilers. The third study evaluated the effects of combustion modifications (necessary for NO_x control) on two possible limiting side effects: (1) excessive loss of plant efficiency; and (2) combustion instability.

This final study report contains: (1) a consolidation and summary of the previous work, as modified by certain simplifications and extensions resulting from improved understanding gained in this work; and (2) a simple example calculation of the developed guidelines, to minimize NO_x emissions in an oil-fired tangential boiler.

A brief introduction is contained in Section I. Conclusions and recommendations are contained in Section II, and a brief summary of this final study is contained in Section III. Modifications made during this study to the analytical technique developed in the previous studies are discussed in Section IV. Results of the data analyses, using this modified NO_x calculation technique, are presented in Section V. Finally, the example application of the developed guidelines, to minimize NO_x emissions in an oil-fired tangential boiler, is shown in Section VI.

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NOMENCLATURE

FORTTRAN Notation

DCG = distance into the furnace, from the burner exit, for complete gasification and mixing

FSS = fraction of the vaporized fuel involved in combustion under stoichiometric conditions

SON = product of the oxygen and nitrogen concentrations, in the combustion products, appropriate to the Zeldovich NO_x formation rate equation

$$[\text{N}_2] [\text{O}_2]^{1/2}$$

Arabic Notation

A, B = arbitrary intermediate constants, equation (1)

$d\text{NO}_x$ = the increment NO_x formed in a given stream tube, ppm

K_r = a proportionality constant relating radiant heat flux, to a water wall, to the fourth power of the combustion gas temperature,
 $\text{J/cm}^2 \cdot \text{sec} - \text{K}^4$ ($\text{Btu/ft}^2 \cdot \text{hr} - {}^\circ\text{R}^4$)

\dot{Q} = the heat flux to the water walls,
 $\text{J/cm}^2 \cdot \text{sec}$ ($\text{Btu/ft}^2 \cdot \text{hr}$)

R_{sv} = the surface-to-volume (circumference-to-flow area) ratio of the radiant section of furnace,
 cm^{-1} (ft^2)

T = temperature, K (${}^\circ\text{R}$)

Z = an arbitrary variable defined by equation (7)

t = time, seconds

Greek Notation

ϵ_g = the effective emissivity of the combustion products,
dimensionless

σ = the Stephan-Boltzmann constant,
 $5.77 \times 10^{-12} \text{ J/cm}^2 \cdot \text{sec-K}^4$ ($1.74 \times 10^{-9} \text{ Btu/ft}^2 \cdot \text{hr-}^\circ\text{R}^4$)

Subscripts

f refers to the final conditions at the end of a stream tube

g refers to the combustion gases

i refers to the initial conditions at the beginning of a stream tube

w refers to the water wall

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A special acknowledgment is also due, once again, to the Los Angeles Department of Water and Power for its continued cooperation, over the years of this study, in making available its data from full-scale operating utility boilers firing natural gas and oil fuels.

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SECTION I

INTRODUCTION

This report contains the results of a four-year combustion modification study. The purpose of the study was to reduce NO_x emissions from utility boilers. In general, this work was neither a detailed analytical study from first principles (of some aspects of the NO_x control problem) nor a full-scale, cut-and-try experimental program. Rather, it represents an effort to bridge the gap between these two extremes. Detailed information developed from first principles, where available, was supplemented by empiricism, using laboratory and full-scale boiler data, to develop an engineering calculation for nitrogen oxide (NO_x) emissions from full-scale, multiburner utility boilers firing natural gas, oil, and coal fuels.

Initially, the NO_x calculation was relatively uncertain. Therefore, by means of regression analysis techniques, a large amount of data (about 600 tests) were used to quantify the NO_x calculation coefficients. The data was obtained from special NO_x testing in full-scale, operating utility boilers. Guidelines for NO_x reduction were then developed by conducting parametric calculations with the quantified NO_x calculation expression.

Simplifications and improvements made in the current study resulted in a direct, sufficiently accurate calculation. The analytically developed expression could be used directly to calculate the NO_x emissions, without the need to quantify via regression analysis. The large data sample was then used only to assess and verify the calculation.

The resulting NO_x calculation is not a simple equation, in terms of the significant independent variables, which can be written down here. The final equation used in the regression analyses consisted of only three terms (NO₁, NO₂, and NO₃) each with a constant coefficient, plus a regression analysis constant. Each term represents the result of a complex computer calculation of the NO_x contribution from a major source within the furnace (i. e., the active burner region, the second-stage mixing zone, and the conversion of fuel-bound nitrogen to NO_x). Since the objectives of this study were primarily to analyze

data and to develop further understanding and guidelines for the control of NO_x , the computer program listing and user manual are not included in this report.

In general, the direct calculation is adequate for natural gas- and oil-fired boilers. It was necessary, however, to empirically establish the coefficient of one of the three terms to obtain satisfactory agreement with data from the coal-fired boilers. Guidelines for NO_x reduction in full-scale, multiburner boilers were then reevaluated in the current study.

Early in the previous studies, it appeared that strongly staged combustion, necessary as a prime combustion modification to minimize NO_x , might result in significant losses in plant efficiency and/or flame and combustion instability. Later in those studies, a separate analysis was conducted to evaluate these possibilities. It was concluded that there is no evidence, at least within the range of the available data, that staged combustion significantly affects plant efficiency; however, flame and combustion instability could be more of a problem under these conditions. An analytical method was developed to guide modifications to assure stable combustion.

This report is based on the previous work but largely reports the results of this final study, which was conducted over the period July 1976 through December 1977.

SECTION II

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations result from the entire four-year effort to develop guidelines for nitrogen oxide (NO_x) emission control in utility boilers. These guidelines are within the constraints of high plant efficiency, stable combustion, and low emissions of other air pollutants. Many conclusions and recommendations developed in the previous studies (referred to in Section I) are confirmed or modified in the current study; others have been developed in this study. Conclusions largely concern the sources of NO_x within a full-scale, multiburner boiler, as indicated by this analysis, while recommendations largely concern guidelines to reduce total NO_x emissions from the boilers by reducing the contributions from the various boiler sources.

All conclusions and recommendations are based on the overall conclusion that total NO_x emissions are lower when two distinct and separate stages of combustion are involved (staged combustion) than when air-only burners are distributed among the active burners in the burner array (off-stoichiometric combustion). This is especially true when fuels containing significant amounts of bound nitrogen are used.

2.1 CONCLUSIONS

NO_x emissions appear to be generated, in varying degrees, from four main sources in full-scale, multiburner boilers:

- a. Conversion of Fuel-Bound Nitrogen. By far the predominant source (nearly 100 percent) of NO_x emissions in tangential coal-fired boilers is the conversion of fuel bound nitrogen. The same is true, to a lesser degree, in other coal-fired boilers, depending on the degree of combustion staging. Somewhat less than half of the NO_x from low-nitrogen oil-fired boilers (and, of course, none from natural gas-fired boilers) is from fuel-bound nitrogen.

- b. Heterogeneous Combustion and Mixing Zone. Significant contributions to the overall NO_x emissions can be thermally generated in the heterogeneous combustion and mixing region just off the active burners. This contribution is largely independent of the degree of combustion staging (the overall active burner air-fuel ratio). This is because air-fuel ratios in this region range from zero (in the fuel) to infinity (in the as-yet unmixed combustion air), and some combustion is always occurring under stoichiometric conditions at the highest combustion product temperatures anywhere in the boiler (a combination of the stoichiometric combustion temperature rise and the absence of significant heat loss). The same is true with gaseous fuels because the gaseous fuel and combustion air mixing is not instantaneous. NO_x contributions from this region can be reduced only by controlling the temperature-time history of reactants in these near-stoichiometric flames.
- c. Second-Stage Mixing Zone. Calculations indicate that a significant amount of NO_x can be formed during the mixing of the second stage combustion air with the products of fuel-rich combustion in the first stage. As in the heterogeneous combustion region, this mixing is not instantaneous, and all of the products from the first stage must shift from fuel-rich through stoichiometric to fuel-lean conditions as this mixing occurs, over a finite time period. Unlike the heterogeneous region, however, considerable cooling has already taken place in the first stage before the second stage air is introduced. Calculations indicate that less than about 80 ppm of the total NO_x are contributed by this final mixing zone.
- d. The Active Burner Region. If the peak temperatures in the heterogeneous combustion region are very high (of the order of 2200 K (3500°F)), significant NO_x can be generated in the remaining completely gasified and mixed regions of the active burner region where there has not yet been sufficient cooling to reduce the thermal NO_x formation rate. Normally, however, modifications necessary to control NO_x from the major sources discussed in (a) and (b) will also reduce NO_x formed in the remaining parts of the active burner region to negligible levels.

Overall conclusions regarding the potential for NO_x reduction by combustion modifications are dependent on the guidelines discussed in the following paragraphs.

2.2 RECOMMENDATIONS

The following recommendations concern guidelines for combustion modifications most effective in minimizing NO_x formed from the various sources discussed in Section 2.1. They are based on observations from the final direct NO_x calculation program and not from parametric calculations involving a NO_x data correlation equation quantified by regression analyses, as in the previous studies. As a result, extrapolations beyond existing data are somewhat more dependable. In addition, further analytical and experimental studies are recommended.

2.2.1 Guidelines

The guidelines developed during the course of this study for the most effective control of NO_x are as follows:

- a. Conversion of Fuel-Bound Nitrogen. With fuels containing significant bound nitrogen, minimum conversion can be obtained by maintaining very fuel-rich initial combustion conditions until all of the fuel has gasified, mixed with combustion air, and the products have shifted to equilibrium under the fuel-rich conditions. This can be accomplished under staged combustion conditions with the burners operated at overall burner air-fuel equivalence ratios of less than about 0.7. Such fuel-rich burner operation may create greater problems of combustion instability and/or flame liftoff; however, analytical and engineering design techniques have been developed in the previous studies to control these potential problems.
- b. Heterogeneous Combustion and Mixing Zone. NO_x thermally generated in the heterogeneous combustion region of the active burner can best be minimized by controlling the initial peak (near stoichiometric) combustion temperatures to less than about 2050 K (3230°F) and, to some extent, by delaying fuel gasification and mixing until some gas cooling has transpired. Combustion temperatures can be minimized, while maintaining high plant efficiency, by transferring more heat to the steam cycle, prior to entering the air preheater, and less to the combustion air and/or by recirculating flue gases into the combustion air in the windbox or in the burners, prior to combustion. While both of these approaches

would involve considerable retrofit construction, both have been applied, with success, in existing boilers.

- c. Second-Stage Mixing Zone. Reductions in the initial peak combustion temperature necessary to minimize NO_x thermally formed in the heterogeneous combustion region should effectively prevent significant thermal NO_x in the second stage of combustion. Care must be taken, however, to avoid cooling the gases from the active burner region to such low values that carbon monoxide and any unburned hydrocarbons in the products of fuel-rich combustion in the first stage cannot be burned out to acceptable levels of emissions of these pollutants. This optimum compromise can only be determined in the specific boiler. As initial peak temperatures are reduced, under the very fuel-rich staging, the primary source of NO_x emissions may shift from the heterogeneous combustion region to this final mixing zone.
- d. The Active Burner Region. The very fuel-rich combustion staging discussed in recommendation (a), coupled with the reduced initial peak combustion temperatures discussed in recommendation (b), should be adequate to prevent significant NO_x formation in the remainder of the active burner region.

2.2.2 Application of Guidelines

Some expected results and further implications in application of these guidelines are as follows:

- a. Potential NO_x Reduction. Full application of the above guidelines, according to the calculations of this study, should reduce NO_x emissions in levels less than 100 ppm with natural gas, oil or coal fuels. These calculations are supported by data from full-scale operating utility boilers, in (only) one case, with natural gas fuel, to NO_x levels well below 100 ppm. With oil and coal fuels, however, the calculations are similarly supported only to about 200 ppm. With the latter fuels, then, the predicted further reductions, to less than 100 ppm, represent extrapolations from existing data.
- b. Uncertainties and Further Study. The remaining uncertainties in these extrapolations include the following:

1. Effectiveness of modifications necessary to maintain combustion stability and to avoid flame liftoff
2. Possible overall incomplete burnout of carbon monoxide and/or hydrocarbons
3. Further hydrocarbon combustion in the second stage, with attendant increases in NO_x from that source.
4. Effects of very fuel-rich first stage combustion on water-wall tube life.

All of these uncertainties should be evaluated experimentally in full-scale operating utility boilers. So that boiler safety can be ensured, modifications designed to avoid flame liftoff should first be evaluated with a full-scale burner firing into a laboratory furnace.

Much analytical work remains to be done to improve understanding of the fundamental, coupled physical and chemical processes involved in the generation and control of NO_x emission from full-scale, operating utility boilers. Such work would not only increase the accuracy of current NO_x control guidelines but would develop greater confidence in the resulting extrapolations from existing data. The subject studies have indicated that the most significant of these areas is the probable role of NO_x destruction mechanisms in the net conversion of fuel-bound nitrogen to NO_x in the regions of heterogeneous combustion of coal and oil.

SECTION III

SUMMARY

3.1 BACKGROUND

This report contains the results of a four-year combustion modification study. The purpose of the study was to reduce NO_x emissions from utility boilers. The general approach was to derive an analytical calculation technique based, where possible, on what appear to be well-established mechanisms for controlling NO_x formation in heterogeneous flames. Remaining gaps in knowledge were bridged with empiricism, by use of laboratory data on the particular process where available. Large samples of data from NO_x testing in full-scale operating boilers were then used either to quantify the resulting calculations through regression analyses or to verify and evaluate the calculations.

The calculation technique was developed in a study reported in Reference 1, specifically for natural gas- and oil-fired boilers. The model of combustion and NO_x formation developed as the basis for the calculation divided the radiant section of the boiler into 104 series and parallel tank-and-tube type of mixing and reaction zones. In each of these zones, the mixing between the separate flow streams entering the zone and the resulting hydrocarbon-air reactions (shifting equilibrium) were assumed to take place instantaneously (in the tank). Thermal NO_x formation occurred when the tank products (slug flow) flowed to the next serial mixing zone. Thermal NO_x formation was calculated by means of a simple rate equation based on the Zeldovich mechanism. NO_x concentrations were always assumed to be low enough (below equilibrium) that homogeneous gaseous NO_x destruction mechanisms, at least those resulting from the Zeldovich mechanism, could be neglected. In the initial study, NO_x formation from conversion of fuel-bound nitrogen was approximated as a simple constant fraction of the concentration of nitrogen in the fuel. This latter approximation was used primarily because: (1) very little was known, at the time, either about the magnitude of NO_x emissions which might be generated from this source or about the conversion mechanism; and (2) natural gas contains no fuel-bound nitrogen and the oil fuel involved in the related data sample contained little nitrogen. Other approximations necessary to provide a manageable calculation and that were appropriate to the engineering nature of the overall calculation included: (1) the use of a constant

(linear) combustion gas cooling rate (with time); and (2) the assumption of instantaneous gasification and mixing of the fuel with the combustion air at the exit of the active burners.

Application to coal-fired boilers of the model developed in previous studies required a more accurate and variable calculation of the NO_x formed from conversion of the fuel-bound nitrogen. There is still no recognized mechanism for this conversion, particularly in heterogeneous flames. A semiempirical calculation, based on a simple, global model and using available laboratory and some full-scale utility and industrial boiler data (oil and coal), was developed. This calculation was subsequently shown to agree quite well with estimates of the NO_x resulting from conversion of fuel-bound nitrogen in the coal data sample of this study. Results of the application to coal-fired boilers are reported in Reference 2 and general results from the studies of gas-, oil-, and coal-fired utility boilers were presented at the EPA First Symposium on Stationary Source Combustion [3].

In general, the results of the studies of NO_x control in natural gas-, oil-, and coal-fired utility boilers indicated no limit to NO_x reduction by combustion modification that is inherent in that NO_x control technique. The developed NO_x calculation does have zero NO_x as a solution within what are thought to be reasonable hardware and operating conditions. NO_x limits, then, were thought to lie in some undesirable side effects which might appear during attempts to reach those hardware and operating conditions. One possible effect is the increased potential for corrosion from the very fuel-rich operation of the active burners (necessary to minimize conversion of fuel-bound nitrogen). This area must be investigated experimentally and is being pursued by other agencies. Two other possible limiting side effects are significant reductions in plant efficiency and combustion and flame instability. These effects were studied in the third year. Results of that study are reported in Reference 4 and were summarized in a paper presented at the EPA Second Stationary Source Combustion Symposium [5]. In general, results of that study indicated that (1) no significant effect of staged combustion on plant efficiency could be observed within the scatter of the data and (2) a potential exists for increased problems with flame liftoff and combustion instability under the very fuel-rich burner operation necessary to control NO_x emissions from conversion of fuel-bound nitrogen. The available data sample was not adequate to verify the effects of reduced combustion air temperature and flue gas recirculation in the active burners on either plant efficiency or combustion stability. An analytical technique was developed to assure combustion stability even under the very fuel-rich operating conditions.

During the study of coal-fired utility boilers [2], an ancillary effort was made to develop a reasonable approximation of finite rate gasification and mixing, particularly with coal fuels. Such a calculation was developed, but it was beyond the scope of that study to incorporate this calculation in the overall NO_x model.

The current study, the last in this long-term effort, consisted of three tasks: (1) modification of the NO_x calculation technique to incorporate results of insight and knowledge gained in the earlier studies; (2) evaluation and assessment of the validity of the new NO_x calculation; and (3) demonstration of the application of the resulting guidelines by suggesting modifications to an example boiler to minimize NO_x emissions within the constraints of high plant efficiency, stable combustion, and low emissions of other air pollutants.

One result of the earlier studies of natural gas-, oil-, and coal-fired utility boilers was a conclusion that NO_x emissions are as low or, in most cases, lower when the boiler is operated with staged combustion than with off-stoichiometric combustion. The two firing configurations are defined as follows: (1) in staged combustion, all of the combustion air not entering the furnace through the active burners is introduced downstream of all the active burners (two distinct and separate stages of combustion); and (2) in off-stoichiometric configurations, air-only burners can be distributed anywhere in the active burner matrix. In staged combustion, the air-fuel ratio is uniform throughout the entire active burner region. With off-stoichiometric configurations, the combustion products from an active burner can immediately mix with the air from an adjacent air-only burner. These products can subsequently mix with the products from another active burner, and so on. The mixed air-fuel ratio can cross back and forth across stoichiometric, repeatedly, while still in the active burner region.

It was decided, therefore, that off-stoichiometric configurations were no longer of interest in this NO_x reduction program. Not only were all of the tests involving off-stoichiometric configurations eliminated from the data sample, but the capability to calculate NO_x emissions in these very complex mixing cases was deleted from the computer program. This action greatly simplified the computer program and allowed incorporation of more detailed (and, therefore, more complicated) and improved calculations in (1) calculating overall boiler air-fuel ratios from measured O_2 and CO_2 data, allowing for carbon losses; (2) finite rate mixing of the second stage combustion air with the products of combustion in the active burner region; (3) radiation cooling of the combustion products proportional to the fourth power of the product temperature; and (4) finite rate gasification and mixing of the fuel and combustion air from the active burners. Some effort was also spent in an (unsuccessful) attempt to improve the calculation of NO_x generated from conversion of the fuel-bound nitrogen. Although the above improvements were incorporated into the overall NO_x emissions calculation, it is still an engineering analysis, and these improvements were incorporated as first-order approximations commensurate with the engineering nature of the remaining program.

Perhaps the most significant result of limiting the program to staged combustion configurations was that the number of terms required to calculate the NO_x emissions were greatly reduced and the remaining terms have more direct and clear physical significance. This allowed greater confidence in the direct calculation of NO_x emissions, without the use of regression analyses to quantify the coefficients of the remaining terms. In this study, then, the regression analyses were used primarily as one means with which to evaluate the validity of the NO_x calculations. More insight and information could be developed from direct comparison, on a point-by-point basis, of the NO_x calculations with the measured data. In these comparisons, the NO_x emissions were calculated directly, with little dependence on the results of the regression analyses. The calculation consisted of summing the NO_x contributions from just three sources within the furnace: (1) NO_x thermally generated in the active burner region (including that generated in the heterogeneous combustion region where finite rate gasification and mixing occur); (2) NO_x generated in the active burner region from conversion of the fuel-bound nitrogen; and (3) NO_x thermally generated in the region of finite rate mixing of the second-stage air with the products of combustion in the active burner region (the final mixing zone). In this calculation, where possible, the coefficients of these terms were taken to be equal to 1.0 (the theoretical value), and the constant in the regression analysis was taken to be equal to zero.

3.2.2 Assessment of the Validity of the Calculation

The validity of the final, modified NO_x emissions calculation was assessed in two ways: (1) by examination of the results of regression analyses; and (2) by direct comparison, on a point-by-point basis, of the calculated and measured data.

In general, the results of these assessments showed that the NO_x calculations were in good agreement with the available measured data except that: (1) agreement with the data from the single-wall boilers firing natural gas or oil fuels was very poor; and (2) with coal fuels the calculation indicated that considerable NO_x is thermally generated in the active burner region, while the measured data, particularly for tangential boilers, indicate negligible amounts.

Direct calculations, using just these three terms, all with term coefficients of 1.0, and no constant showed good agreement with the measured data from the opposed-fired boilers firing natural gas and oil fuels. On the average, the NO_x levels calculated for 92 tests with natural gas in the opposed fired boilers were higher than the measured levels by only 7 ppm, but an average deviation of just under 100 ppm remained. Calculations for 30 tests in these same boilers with the oil fuel were high by 50 ppm, but the average deviation was only 44 ppm. Direct calculations for coal-fired tangential boilers, neglecting all NO_x calculated to be thermally generated in the active burner region (a term coefficient of zero), also showed good agreement

with that data. The data calculated in this manner for 62 tests in two tangential boilers, firing somewhat different types of coal, were higher than the measured, by only 26 ppm with an average deviation of 43 ppm. This same type of calculation for the single-wall, coal-fired boilers, however, showed that the calculation was low by a constant 127 ppm.

The direct calculation is considered adequate for boilers firing natural gas and oil fuels. The poor data agreement with data from single-wall boilers firing these fuels is considered a result of inadequate input data (combustion air temperatures in the burners) rather than of error in the subsequent calculation. Calculation of NO_x thermally generated in the active burner region needs further work.

A summary of the final appropriate term coefficients and empirical constants are shown in the following table:

Firing Type	Fuel	No. of Tests	Term Coefficients ^a			ppm	
			ABR	FMZ	FBN	Empirical Const.	Avg Deviation
Opposed	Gas	92	1.0	1.0	NA	0.0	100
Opposed	Oil	30	1.0	1.0	1.0	-50	44
Single-wall	Coal	34	0.0	1.0	1.0	+127	46
Tangential	Coal	62	0.0	1.0	1.0	0.0	43

a. Active burner region ABR, final mixing zone FMZ, and fuel-bound nitrogen FBN.

3.2.3 General Guidelines

The primary objective of this and the preceding studies of NO_x control in utility boilers was to develop and verify simple guidelines which can be used, along with a judicious testing program, to minimize NO_x emissions within the bounds of high plant efficiency, stable combustion, and acceptable levels of emission of other air pollutants. The very fuel-rich burner operation necessary to achieve very low levels of NO_x emissions can result in an increased tendency for combustion instability and flame liftoff. An analytical technique was developed to provide stable combustion. Care would have to be taken in burner design so that the flames in the burner exit are soundly anchored. (See, also, Recommendations, Section 2.2.2.)

The primary effects of staged combustion, with a very fuel-rich first stage, are to minimize NO_x from conversion of fuel-bound nitrogen and thermal NO_x generated in the mixing and combustion

of product gases in the active burner region. Active burner air-fuel equivalence ratios of less than about 0.7 may be necessary to achieve very low NO_x contributions from these sources.

With such fuel-rich operation of the active burners and the entire first stage of combustion, significant NO_x may still be thermally generated in two other regions of the furnace: (1) the subregion of the active burner region where the fuel gasifies and the resulting gases mix with the combustion air (heterogeneous combustion); and (2) the region where the second-stage air is mixed with the products of fuel-rich combustion coming from the active burner region (the first stage). Calculations in this study consistently indicated that NO_x from the second source is usually quite small but cannot be neglected if very low total NO_x levels are sought.

NO_x generated in the region of heterogeneous combustion appears to be relatively independent of the burner air-fuel ratio because the local air-fuel ratios are largely controlled by the relative rates of gasification and mixing. Burner design changes which tend to slow the rate of fuel gasification and decrease the rate of mixing of these gases with the combustion air can substantially reduce the NO_x generated in the heterogeneous combustion region. A more direct approach, however, (which also reduces NO_x formed in the second stage) is to reduce the peak combustion temperature in the heterogeneous combustion region. This can be done by techniques such as (1) reduction of the combustion air temperature, (2) dilution of the combustion air with flue gas recirculated into the windbox or burners, and (3) water sprayed into the combustion air. The objective of all of these is to reduce the maximum (near stoichiometric) flame temperature in the earliest regions of combustion, before appreciable gas cooling has occurred. Calculations in this program indicate that maximum initial flame temperatures (which occur at the burner exit) less than about 2050 K (3230°F) minimize NO_x formation in the heterogeneous combustion region and virtually eliminate any from the second-stage mixing region.

The data available to this study show trends which verify the guidelines presented herein. Estimates of very low NO_x levels achievable with these guidelines are largely based on the calculation developed in this and the previous study. The calculation was improved in this study to the point where the empiricism involved is greatly reduced. For example, regression analyses of large data samples are no longer used to quantify the NO_x calculation. Thus, conclusions relative to minimum NO_x levels achievable by combustion modifications represent relatively small analytical extrapolations from existing data.

The NO_x calculation shows zero NO_x as a solution within the range of what are thought to be acceptable utility boiler operating conditions. Limits on NO_x reduction may arise as a result of undesirable side effects such as combustion instability, flame liftoff, excessive water-wall erosion/corrosion, or from unknown effects

which are currently not a part of the NO_x calculation. An example of the latter might be incomplete hydrocarbon combustion in the very fuel-rich first stage, followed by combustion in the oxidizing atmosphere of the second stage. These guidelines, however, are intended to guide the way to minimum NO_x , in conjunction with testing to reveal these other possible limiting factors. Full-scale boiler testing and long-term operation with natural gas and oil fuels have rather closely approached the desired operation, with no significant evidence of undesirable operation.

3.2.4 Example Application of Guidelines

As an analytical example of the application of the guidelines discussed in Section 3.2.3, an existing 320 MW natural gas-fired tangential boiler was selected for modification to oil-firing. The guidelines were applied to achieve minimum NO_x emissions.

Staged combustion was (analytically) achieved by using the existing NO_x ports and by operating the top two rows of burners (8 of the 24) air-only. A burner air-fuel equivalence ratio of 0.638 was selected as a design point to minimize (theoretically to zero) conversion of the fuel-bound nitrogen to NO_x . The oil fuel used contained 0.24 percent nitrogen, by weight.

The combustion air temperatures, at full load, were reduced by about 39 K (70°F) to account for the higher oil combustion temperature. The combustion air and flue gas recirculation temperatures were controlled, respectively, to 478 K (400°F) and 542 K (515°F).

In addition, flue gases were (analytically) recirculated and mixed with the combustion air prior to mixing with the fuel. The amount of recirculated flue gas was treated as a variable, and the resulting NO_x emissions were then calculated. This calculation showed that, such recirculation of flue gas in amounts corresponding to more than 15 percent of the total burner air (all combustion air except NO_x port air), in combination with the staged combustion and combustion air temperature control, resulted in predicted total NO_x emissions of less than 20 ppm.

SECTION IV

MODIFICATIONS TO THE ANALYSIS

4.1 BACKGROUND

This section contains the results of a four-year combustion modification study. The purpose of the study was to reduce NO_x emissions from utility boilers. Earlier reports on the study are listed as References 1 through 5. The first year of the study analyzed these effects in natural gas- and oil-fired utility boilers [1]. The second year extended that approach to coal-fired boilers [2, 3]. The third year examined the implications of these combustion modifications on overall plant efficiency (electrical output per unit of heat input with the fuel) and on combustion and flame stability [4, 5] since these requirements might represent limitations on reduction of NO_x by combustion modifications.

The entire study made use of a large amount of data from special tests of the effects of certain combustion modifications on NO_x emissions from full-scale operating utility boilers. A total of 575 tests involving combustion of natural gas, oil, and four types of coal fuels in single-wall, opposed, and tangential firing configurations were included in the sample. Distribution of the data among the fuels and firing configurations is shown in References 1 and 2.

It was recognized from the outset that little of the necessary basic phenomena involved in the formation and destruction of NO_x in diffusion flames was well understood. Application of existing understanding to the simultaneous and coupled gasification, mixing, reaction, and heat transfer processes occurring in a full-scale multi-burner utility boiler is still an extremely complex problem. Many researchers were and are studying certain aspects of this problem, but none are capable of integrating all aspects into a single analysis capable of direct and accurate prediction of NO_x emissions from full-scale utility boilers starting from first principles. It is highly unlikely that such a solution will ever be achieved (nor is it necessary that it be achieved). Understanding of all applications of combustion can be thought of as islands of fundamental understanding connected by empirical bridges into satisfactory, workable design analyses. For example, the basic chemical kinetics of combustion are thought to be well

understood only in the case of hydrogen-bromine and, perhaps, hydrogen-oxygen flames. The kinetics of hydrocarbon-air flames, the case of interest in fossil-fuel-fired boilers, are very poorly understood. Thus, with fossil fuels, the process of empirical bridging and global approximation begins even at the most fundamental level.

The approach taken throughout this study was to start with what is known about some of the individual processes, develop some simple models or estimates of some of the more poorly known or complex phenomena, and form them into a single expression which should at least include most of the known, significant phenomena and have the proper analytical form. The large samples of full-scale boiler data were then used, via regression analyses, to fill in some of the remaining gaps and to quantify the analytical expression. Results of the regression analyses could be used to comment on the accuracy of some of the assumptions incorporated in the analytical expression and to provide a semiempirical, quantitative expression. This expression could be exercised, in a parametric fashion, to further elucidate the effects of some of the design parameters on NO_x emissions. This whole process represents an orderly, engineering approach to the development of useful guidelines to minimize NO_x emissions in full-scale utility boilers. It can also provide other information, substantiated by data, for feedback to fundamental and applied research programs.

The first attempt at this process (1) involved a simple Arrhenius-type rate equation for the formation of NO_x (zero destruction rate), based on the Zeldovich mechanism, to account for thermally generated NO_x . The question of the appropriate rate coefficient was bypassed by setting up the final expression so that the rate coefficient was part of the coefficient of most of the terms. The rate coefficient was thus lumped in with many other unknowns, and the total was quantified by subsequent regression analyses of the large data samples. Considering the other unknowns represented in the coefficients of the terms in the final expression and the current state of understanding of these rate coefficients, this step was considered justified. Since the fuels involved in this first study (natural gas and low nitrogen oil) contained little bound nitrogen, the amount of fuel-bound nitrogen converted to NO_x was approximated by a simple, constant fraction of the nitrogen in the oil (and none in the natural gas).

The available data from full-scale, operating utility boilers included relatively accurate measures of fuel flow rates, but combustion air flow rates either were not measured or were measured by devices calibrated against calculations based on the measured fuel flow rates and the air-fuel ratio as indicated by flue gas chemical compositions. Total combustion air flow rates, then, were calculated in this initial study directly from the measured oxygen and carbon dioxide concentrations in the flue gas. Simple stoichiometry was used, involving the assumptions of negligible carbon loss and negligible carbon monoxide in the flue gases.

The mixing, reaction, cooling, and NO_x formation in the radiant section of the boiler (the furnace) was approximated by dividing the major flow and mixing paths into 109 zones and modeling each of these zones by the so-called tank-and-tube approximation. At the beginning of each zone (the tank) mixing of the different streams entering the zone, with perhaps different chemical compositions and temperatures, was assumed to be instantaneous. The resulting mixed gases, at uniform chemical composition and initial temperature, were then assumed to flow through the zone (the tube), forming NO_x and cooling. The total NO_x emissions were then calculated by summing the contributions from each of these zones. Because the natural gas and oil fuels in the available data sample were fired only in single-wall or opposed configurations, a general model of this tank-and-tube scheme was set up for those configurations. The complexity of such a model, of course, dictated a computer solution.

The resulting analytical expression used in the regression analyses contained seven linear terms to describe the formation of thermal NO_x , plus a single term for fuel-bound nitrogen conversion and a constant. Of the seven thermal NO_x terms, five described similar zones in the active burner region, one concerned the zone where NO_x port flow (if any) is added and one described the NO_x generated in the final zone after all fuel and air have mixed and reacted but the product gases are still sufficiently hot to form significant NO_x .

While the final expression consisted only of the linear sum of these nine terms, each term required a more or less complex computer calculation. A great deal of this complexity resulted from the need to calculate the NO_x for test cases where air-only burners were intermixed with active burners (fuel plus air). Such configurations result in what is usually called "off-stoichiometric combustion". This term is often used to differentiate from "staged combustion", wherein all combustion air not entering the furnace through active burners enters through air-only burners and/or NO_x ports located above (downstream of) the active burners. Besides the mechanical problem of identifying air-only and active burners on either side of (adjacent to), opposite, and below a given burner, this intermixing of air-only and active burners often resulted in huge shifts in local air-fuel ratios (sometimes between very fuel-rich and very fuel-lean) in the lower parts of the furnace as flows from active burners mixed directly with flows from air-only burners. In addition, cases where the average bulk gas air-fuel ratio starts fuel-lean (air-only burners located low in the burner array) and approaches the overall boiler air-fuel ratio from the fuel-lean side of stoichiometric had to be accounted for as well as the more conventional staged combustion case where the bulk gas air-fuel ratio starts fuel-rich and approaches the overall boiler air-fuel ratio from below (and crosses) stoichiometric.

As a result of these complexities and the large number of terms required to describe the mixing processes for all cases, the

the coefficients in the final expression were difficult to calculate directly. It was largely left to the subsequent regression analyses to quantify these coefficients. Further, since a data sample can be fit in many ways by an expression containing a large number of terms, it was also difficult to interpret the resulting coefficients of an individual term with regard to the accuracy of the assumptions and the calculation technique involved in that term. The resulting expression, however, quantified by the regression analyses, did relatively accurately fit the available data and was successfully used in parametric calculations to evaluate the effects of single and multiple independent variables (modifications) on NO_x emissions.

Another effect of the complexity of those NO_x calculations was to allow (and justify) only very simple expressions for some of the other phenomena such as the gas cooling rates, the vaporization rates of the oil, and the mixing of gaseous and vaporized fuel with the combustion air. Combustion product cooling was simply taken as linear with time, and the vaporization and mixing rates were taken as infinite (instantaneous vaporization and mixing at the burner exit). Any further complexity introduced in that program might have created a totally computer-oriented study and obscured the engineering objectives of this study, i. e., to develop useful guidelines for combustion modifications to reduce NO_x emissions.

Application of this technique to coal-fired utility boilers required (1) development of a more detailed calculation of the NO_x generated by conversion of fuel-bound nitrogen, (2) modification of the tank-and-tube mixing and flow scheme to accommodate tangentially fired boiler configurations, and (3) improvement in calculation of the thermal NO_x generated in the second stage in two-stage combustion configurations. Each of these necessary modifications were again complicated by the need to describe or calculate NO_x formation in the off-stoichiometric firing configurations (air-only burners mixed in with active burners in the burner array).

The final effort in studying the effects of combustion modifications for NO_x control was to evaluate the possible effects of these modifications on overall plant efficiency and on flame and combustion stability [4].

In each of the earlier studies, new phenomena were investigated, and techniques of analysis were developed, extended, evaluated, and improved. This study was intended to incorporate all improvements developed in the first three years of study, to improve, where possible, those areas shown to be most uncertain and to draw final guidelines for the control of NO_x within the constraints of high plant efficiency, low emissions of other air pollutants, and stable flames and combustion. The question of whether tube wall corrosion is affected by staged combustion operation was not addressed in this study. This subject is being investigated in other EPA-sponsored work.

The major single objective of this study was to simplify the calculation of NO_x within the furnace of utility boilers so that certain desirable improvements (and recomplikations) could be accomplished within the scope of this final, limited study. The only significant simplification which appeared reasonable was to eliminate the enormous complexity created by the initially presumed need to provide the capability to calculate and correlate NO_x emissions in boilers modified for off-stoichiometric combustion. These are configurations where air-only burners are mixed in with active burners in the burner array. Some of the resulting analytical complications are discussed in Section 4.1.

Nearly all of the results and data from the studies of the effects of the locations of air-only burners in natural gas-, oil-, and (particularly) coal-fired boiler burner arrays showed that NO_x emissions are always lowest when all of the combustion air not entering the furnace through the active burners is introduced above, or downstream of, all of the active burner flows (two-stage combustion). This appears to result from the need to hold the local air-fuel ratio low, while the fuels gasify and the initial hydrocarbon reactions and the simultaneous fuel-bound nitrogen conversion reactions are completed. Particularly with coal fuels, which gasify more slowly and contain significant concentrations of fuel-bound nitrogen, early mixing of air flows from adjacent air-only burners with the still gasifying and reacting flow from an active burner can increase the overall conversion of fuel-bound nitrogen to NO_x . The same is true, but to a lesser extent, with oil fuels. There are some indications that two-stage combustion of gaseous fuels (containing no hydrocarbon-bound nitrogen) with a fuel-lean first stage may produce NO_x emissions at least as low as conventional two-stage combustion. Even in this case, however, off-stoichiometric configurations still appear to generate more (thermal) NO_x than either two-stage configuration.

Thus, while off-stoichiometric combustion configurations are academically interesting and certainly represent an interesting analytical challenge, such configurations do not appear to represent useful approaches to maximum NO_x reduction. Therefore, all off-stoichiometric configurations were eliminated from the draft sample, and the NO_x calculation program was restricted to two-stage configurations with a fuel-rich first stage.

The direct result of this simplification was to reduce the entire active burner region (burner flows as well as bulk gases flow) to a single, constant air-fuel ratio. This eliminated the need to describe the relative burner locations in detail; to calculate the various combinations and locations of active and air-only burners adjacent to, opposite of, and above and below each other; to track the subsequent

mixing in the active burner region from these various combinations of air-fuel ratios; and to estimate the average, effective air-fuel ratios in the region where the fuels are gasifying and mixing and the fuel-bound nitrogen conversion is occurring. The minimum of five terms, previously required, to adequately calculate and correlate thermal NO_x formation in the active burner region could be reduced to a single term, covering the NO_x generated in the active burner region.

The NO_x calculation and correlation equation was reduced to only three terms, plus the necessary constant. One term describes the NO_x formed in the first stage. A second term describes the NO_x formed in the final mixing zone (or second stage), where all combustion air not entering the furnace through the active burners enters through air-only burners in the top rows of the burner array or through NO_x ports above the burner array and mixes with the products of combustion in the first stage. The third term accounted for conversion of fuel-bound nitrogen.

A major advantage of this simplification is that the first two terms represent the thermal NO_x formed under distinctly different operating conditions (the first and second stages of combustion), while the third term represents the NO_x independently formed in the first stage via the conversion of fuel-bound nitrogen. By observing NO_x data variations resulting from major variations in combustion staging or operating conditions, it appeared more feasible to attempt direct calculation of thermal NO_x in the two major regions and the fuel-bound nitrogen conversion and to compare these calculations with the measured data. Certainly, the coefficients developed from the multiple regression analyses of the data can be more meaningful with regard to evaluating the accuracy of assumption and estimates involved in calculation of the NO_x terms in the correlation equation.

In the initial studies [1, 2], for example, the calculated value of a given term might represent the NO_x generated in all of the secondary mixing zones immediately downstream of active burners located immediately above air-only burners. No NO_x data are available for direct comparison with the calculated values for such terms. When off-stoichiometric burner configurations are in the data sample, it is necessary to account for these and other complicated mixing zones. The regression analysis is capable of quantifying the appropriate coefficients, but it is only the sum of these quantified terms which can be directly compared to measured NO_x data.

The first major improvement effected in this study, then, was the decision to make every effort to calculate NO_x directly with the three variable terms and to use the measured data as well as the coefficients of these terms (resulting from regression analyses) to evaluate the calculations and to develop further insight into the effects of certain hardware and operating conditions on NO_x formation in utility boilers.

One problem introduced by the simplification of the NO_x calculation was that a great deal of data in some of the samples used in the previous studies [1, 2] resulted from tests of off-stoichiometric firing configurations, and these data were deleted from the sample used in this study. Table 1 identifies the boiler types used in this study, and Table 2 shows the remaining data sample. In a previous study [1], 250 and 139 tests on natural gas- and oil-fired boilers, respectively, were available. Thus, the decision to exclude off-stoichiometric firing configurations reduced the available natural gas-fired data sample by more than half but reduced the oil-fired data sample by only about 29 percent. While the data sample available for the single-wall, coal-fired boiler type (Table 1, boiler reference no. 5) was reduced by about half, the data samples for the two tangential boilers (nos. 6 and 7) were not affected at all. In addition, 52 tests on four other coal-fired boilers were not studied because of the limited and somewhat questionable data.

4.3 IMPROVEMENTS

Major improvements which, within the scope of this study, could be incorporated in the analysis as a result of the simplification of the NO_x calculation and correlation equation included: (1) more accurate calculation of the overall boiler air-fuel ratio from measured flue gas compositions; (2) more detailed calculation of the NO_x formed in the final mixing zone, where all of the combustion air not entering the furnace through the active burners is mixed (at some finite rate) with the products of combustion in the active burner region; (3) more realistic product gas cooling rates; and (4) allowance for finite rate fuel gasification and mixing. Some consideration was also given to some additional effects of the combustion process in turbulent, heterogeneous diffusion flames on the NO_x emissions. Each of these improvements is briefly discussed in the following paragraphs.

4.3.1 Boiler Air-Fuel Ratios

In the study of the effects of combustion modifications, for NO_x reduction, on plant efficiency [4], considerably more attention was paid to carbon losses. In the current study, carbon losses are defined as that carbon in the fuel which cannot be accounted for in the sum of the measured CO and CO_2 in the flue gases.

In the plant efficiency study, these losses represented direct combustion efficiency losses. Relatively accurate fuel flow rate measurements were available only for the natural gas- and oil-fired data. Therefore, plant efficiency was studied only with respect to the boilers firing these fuels. Carbon losses were not excessively large, and no significant effects of staged or off-stoichiometric firing configurations on these losses could be determined. A great deal of scatter in the measured values of CO_2 and, where data was available, in CO was observed. This included a significant number of cases where the measured CO_2 levels were higher than theoretically possible for any level of O_2 .

TABLE 1. BOILERS IN THE DATA SAMPLE

Boiler Ref. No.	Firing Type	Rated Load, MW	No. of Burners	NO _x Ports	Fuels Used
1	Single wall	180	16	No	Natural gas, oil
2	Single wall	240	12	No	Natural gas, oil
3	Opposed	240	12	Yes	Natural gas, oil
4	Opposed	350	24	Yes	Natural gas, oil
5	Single wall	125	16	No	Nominal coal
6	Tangential	330	20	a	High nitrogen coal
7	Tangential	360	20	a	Nominal coal

a. Secondary air port design gives some degree of fixed, effective NO_x port air flow.

TABLE 2. SUMMARY OF THE TOTAL DATA SAMPLE

Boiler Ref. No.	No. of Tests								
	Total	NO _x Ports Closed				NO _x Ports Open			
		0	2	4	8	0	2	4	8 ^c
Natural Gas (total tests = 107)									
1	8	7	0	1	0	a	a	a	a
2	7	6	1	0	0	a	a	a	a
3	36	6	1	2	0	15	8	4	0
4	56	21	0	0	1	32	1	0	1
Oil (total tests = 49)									
1	7	6	0	1	0	a	a	a	a
2	12	10	2	0	0	a	a	a	a
3	6	3	0	0	0	3	0	0	0
4	24	11	0	0	0	13	0	0	0
Coal (total tests = 99)									
5	37	17	11	9	0	a	a	a	a
6	22	b	b	b	b	8	0	14	0
7	40	b	b	b	b	19	0	21	0

a. No NO_x ports installed.b. Some degree of effective NO_x port flow.

c. Number of burners operated air-only.

The measured levels of O_2 and CO_2 were used in all of the previous studies to calculate combustion air flow rates from measured (or estimated, in the case of coal) fuel flow rates through a calculation of the overall boiler air-fuel ratio. Simple stoichiometry was used to derive an expression for the air-fuel ratio which was predominantly a function of the measured O_2 levels. This was certainly adequate for natural gas- and oil-fired boilers because the carbon losses, except, perhaps, for O_2 levels less than about three percent, were negligibly small. Such is not always the case with coal fuels.

Figures 1(a) through (e) show plots of the measured CO_2 and O_2 data (volume percent, dry) of this study from the tests of the boilers fired with natural gas, oil, and two types of coal. The two lines shown on the figures represent the theoretical CO_2/O_2 relations for complete combustion of the carbon in the fuel to CO_2 and for a 20 percent carbon loss. The related air-fuel equivalence ratio for complete combustion of all of the carbon to CO_2 is shown across the top of the figures. The data from boilers firing the nominal coal (type no. 3) is shown separately for the single-wall boilers (Figure 1(c)) and the tangential type (Figure 1(d)) because the CO_2/O_2 data are significantly different between the two firing types.

Figure 1(a) shows an example of the large scatter in the data, with 18 data points appearing well above the theoretical for complete combustion of all carbon to CO_2 . Although some of that scatter could be due to scatter in the O_2 measurements, at least four cases show higher levels of CO_2 than would be possible with any level of O_2 . The majority of the data, however, show a rather regular trend from complete combustion of all of the carbon to CO_2 at O_2 levels above about 4 percent to what would appear to represent as much as a 10 percent loss with O_2 levels around 1 percent.

This trend is in the right direction since problems with excessive CO and smoke begin to appear with O_2 levels of less than about 3 percent. In all cases, measured CO levels were low enough that the carbon involved would be negligible compared to that in the CO_2 . It is usually normal policy, in fact, for the boiler operator to adjust operating conditions if measured CO exceeds some fixed (low) measured level. A similar adjustment is usually made, however, only to avoid clearly visible smoke from the stack.

Figure 1(b) also shows some measured data above the theoretical line for complete combustion of the oil fuel carbon to CO_2 . In general, however, the data appear to follow a line which would again appear to represent about a 10 percent carbon loss. A trend to zero carbon loss with increasing excess air (O_2) is not apparent.

If the data shown in Figures 1(a) and (b) truly represented carbon losses, one would expect that such losses with coal fuels would be much higher because of the large ash content of the fuel, the

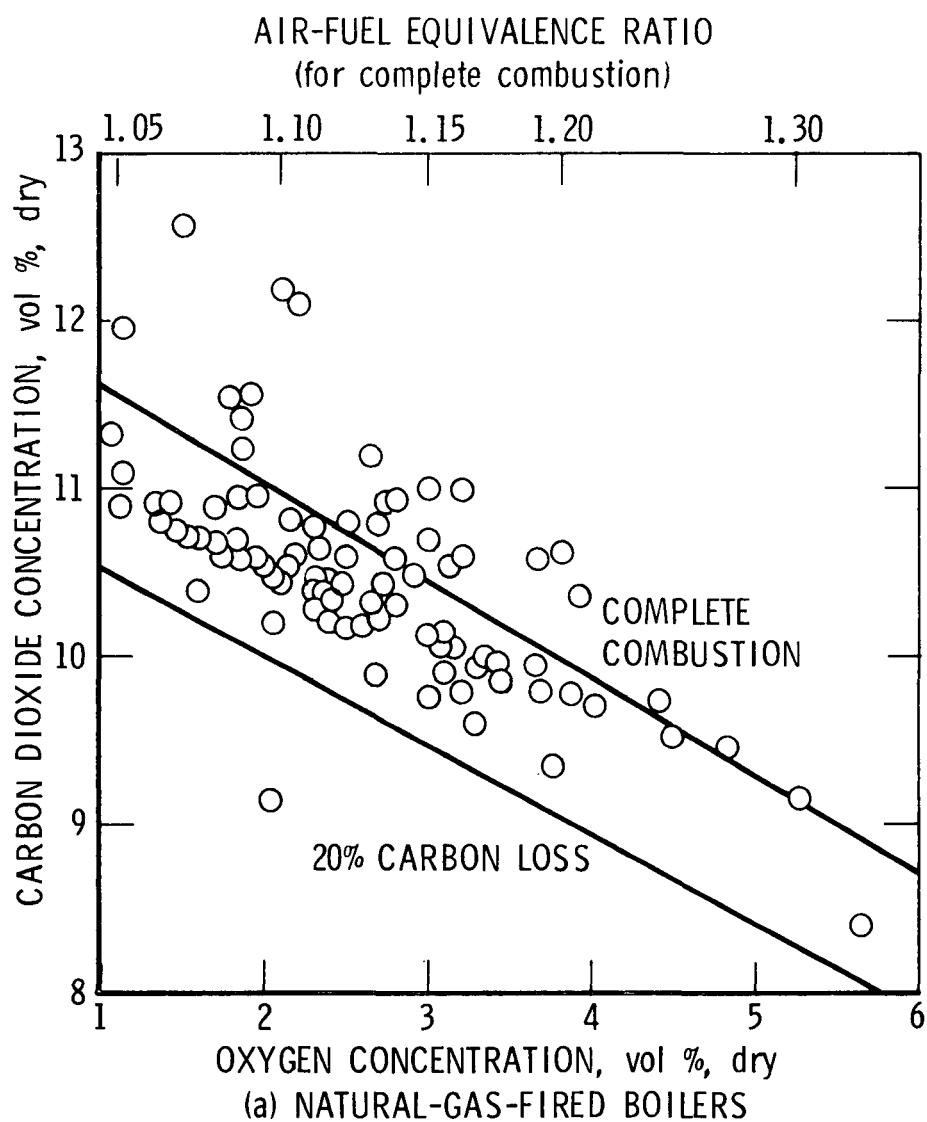


Figure 1. Carbon dioxide and oxygen concentrations measured in the flue gases. (Sheet 1 of 5.)

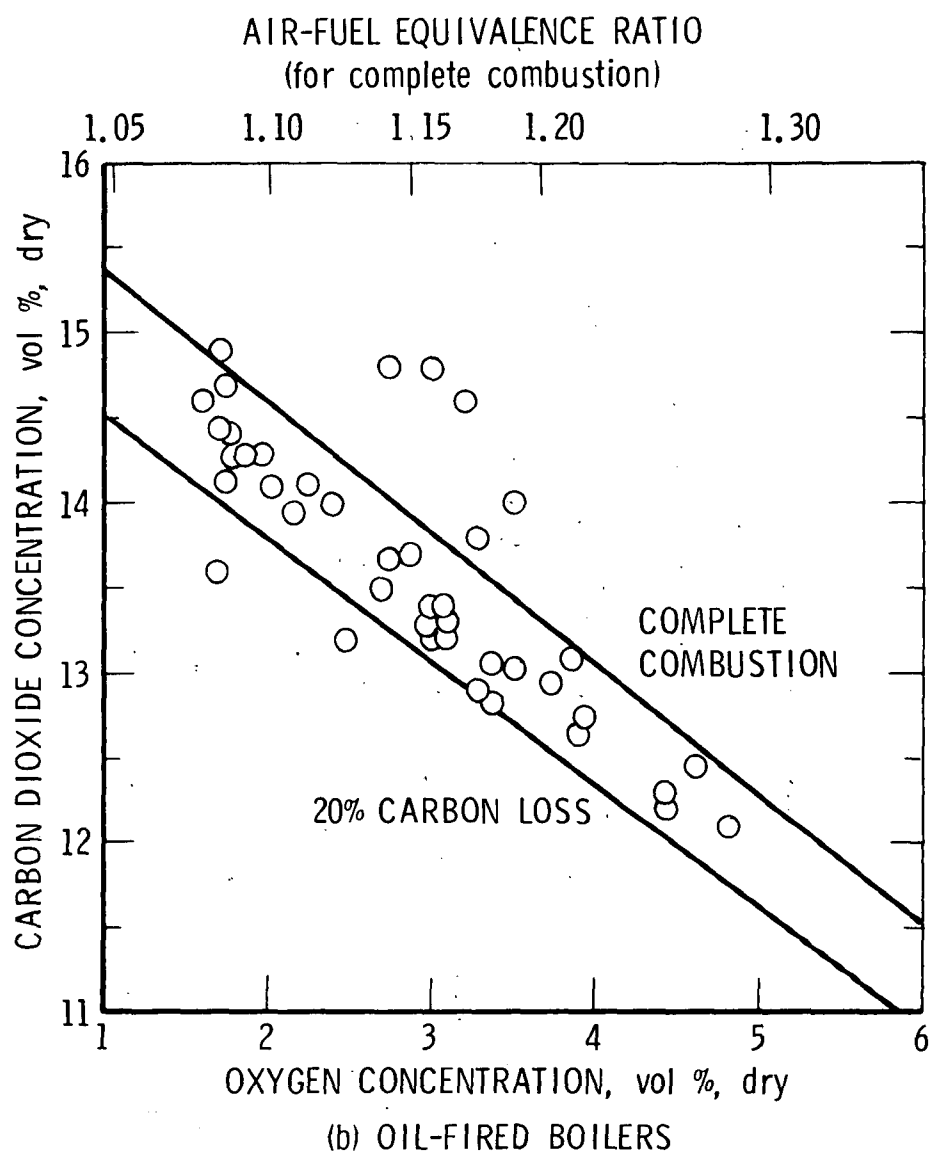


Figure 1. Carbon dioxide and oxygen concentrations measured in the flue gases. (Sheet 2 of 5.)

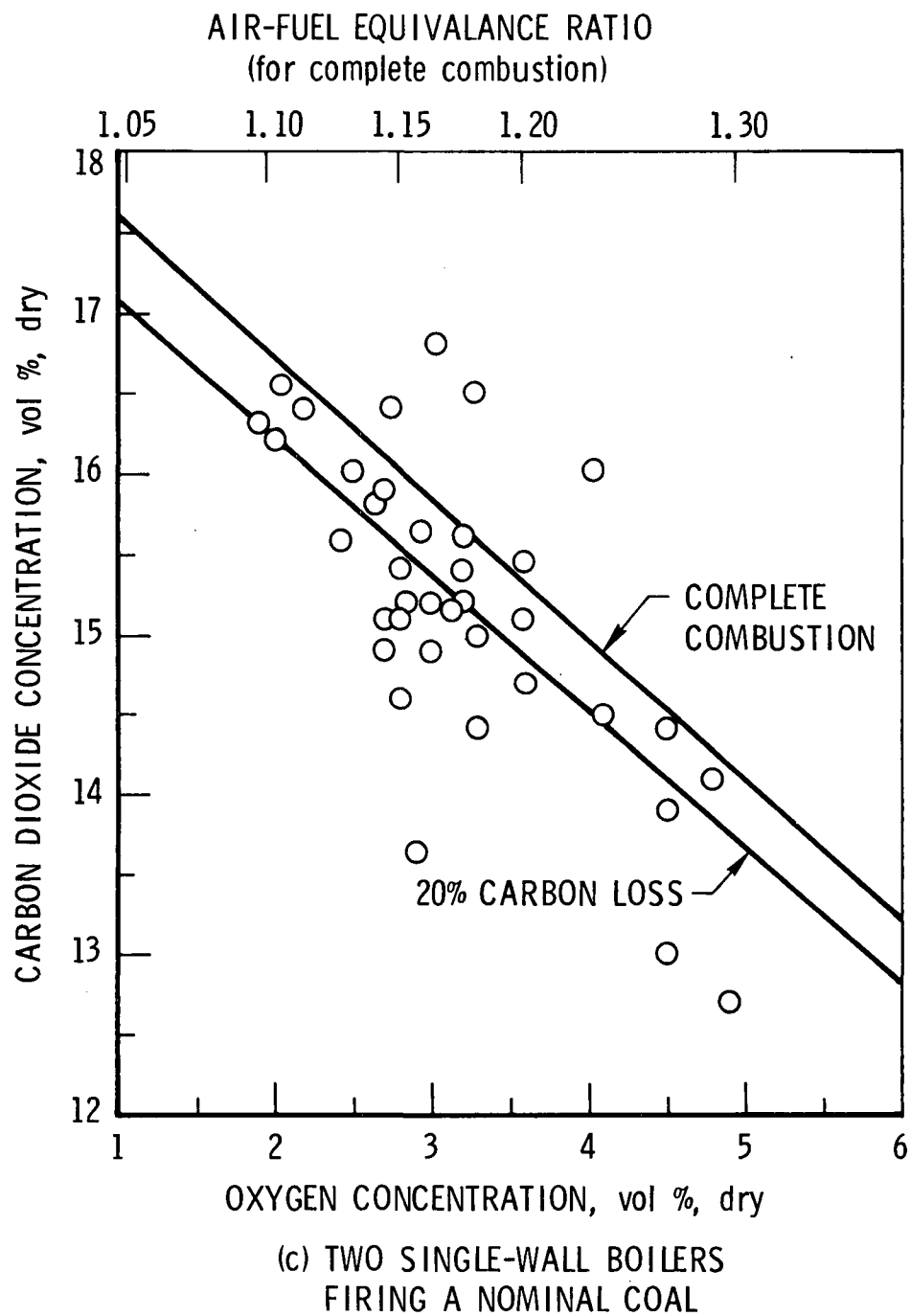
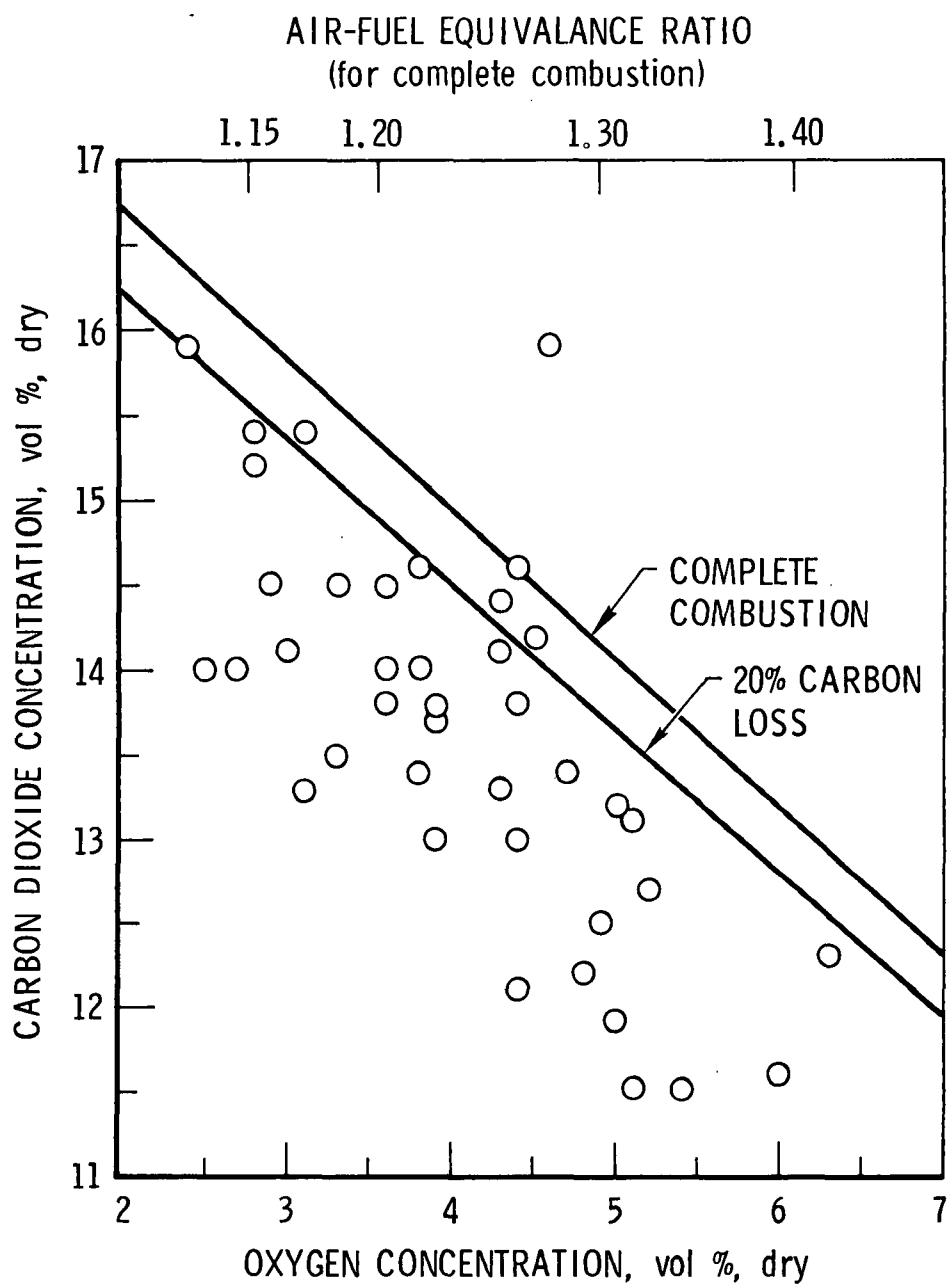


Figure 1. Carbon dioxide and oxygen concentrations measured in the flue gases. (Sheet 3 of 5.)



(d) 360-MW TANGENTIAL BOILER
FIRING A NOMINAL COAL

Figure 1. Carbon dioxide and oxygen concentrations measured in the flue gases. (Sheet 4 of 5.)

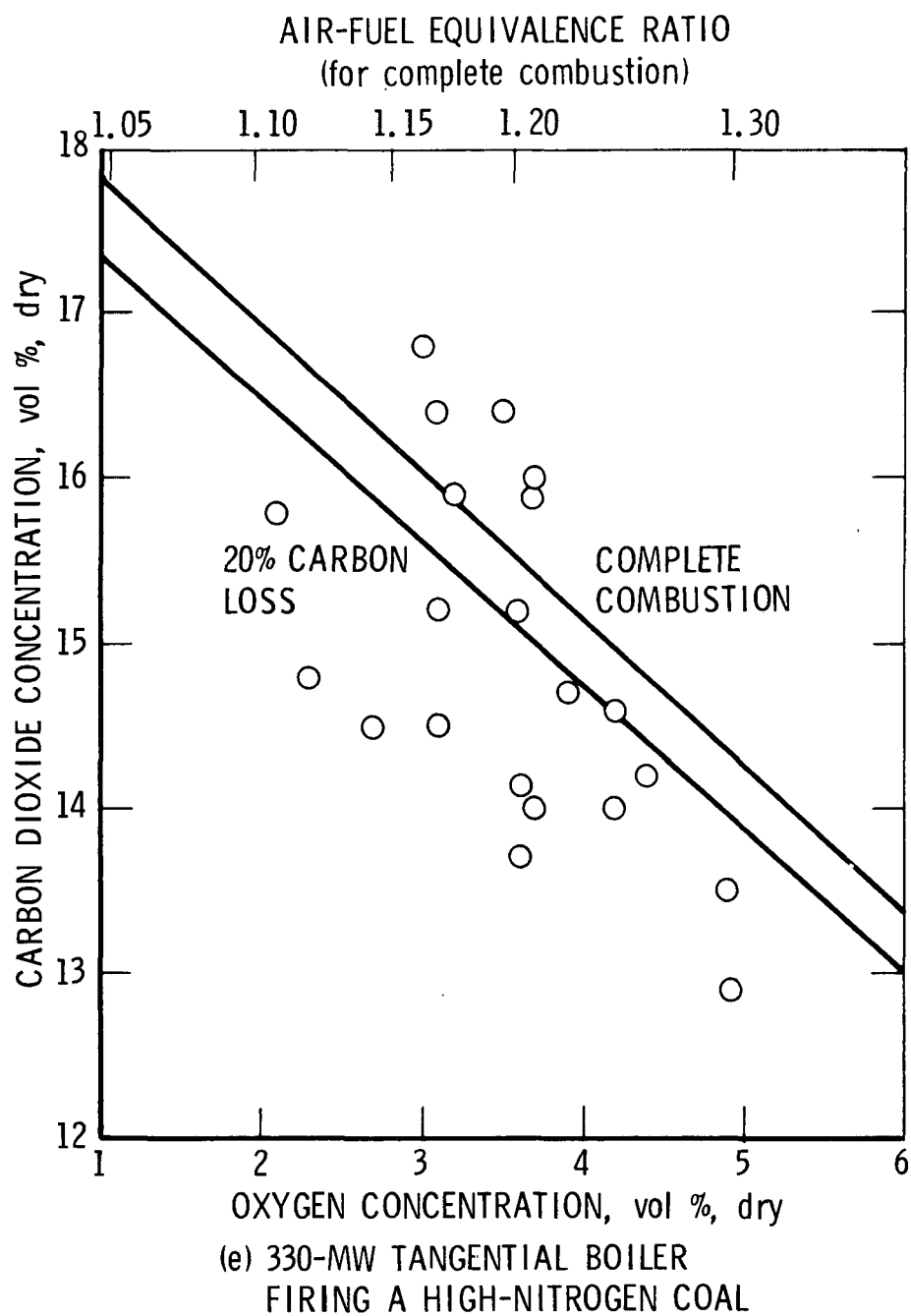


Figure 1. Carbon dioxide and oxygen concentrations measured in the flue gases. (Sheet 5 of 5.)

slagging, and the high particulate emissions associated with coal burning. Figure 1(c) shows the CO_2/O_2 data from two boilers with single firing walls firing a nominal type of coal containing 11 percent ash. These data also show a considerable amount of scatter, but the general trend could again be interpreted to indicate 10 to 15 percent carbon loss.

Figure 1(d) shows data from a tangential boiler firing the same type of coal fired in the single-wall boilers. Here the data are widely scattered and well below the 20 percent carbon loss line. Figure 1(e) shows data from a similar tangential boiler firing a coal type containing higher concentrations of fuel-bound nitrogen but the same fractions of ash and moisture. Again the data are widely scattered, but in this case the data are about as much above the zero to 20 percent carbon loss lines as below.

The causes of the large data scatter observed in Figures 1(a) through 1(e) are not known. Carbon losses of as much as 10 percent seem possible in coal-fired boilers but do not seem likely with natural gas and oil fuels. It may be possible that operation at very low levels of excess air, for special, short-term NO_x emissions testing, could produce higher carbon losses and CO than is considered normal. The calculated CO_2/O_2 relation for complete combustion shown in Figure 1(c) duplicates that indicated by Crawford [6] for this fuel.

It seems most likely, therefore, that the data scatter and the very low CO_2 levels measured with the coal fuels are due to some kind of stratification of the flue gases, relative to the sampling devices, yielding lower than the actual average levels of one or all of the CO_2 , O_2 , or CO. Some cases were actually noted in the data where different sampling points yielded CO measurements differing by 1000 to 2000 ppm. This, then, was the general assumption made for this study.

If carbon losses were significant in some tests, the major effect on the calculations of this study would be in the total air flow rate through the boiler. A measured level of O_2 in the flue gases, with some of the carbon lost to the combustion process, would indicate a lower input air-fuel ratio than if the carbon combustion were complete.

With regard to calculation of the combustion temperature rise, however, if the unburned carbon were assumed to pass through the combustion process like inert ash, being heated in initial combustion but then giving up this heat as the particles cool, then the carbon loss could essentially be neglected. Most combustion calculations neglect these effects. In any case, more detailed accounting of carbon losses in the local combustion processes would require knowledge of the carbon losses (or unburned carbon) at all points in the boiler.

Therefore, for these calculations, carbon losses as indicated by the CO_2/O_2 data were taken into account only in the calculation

of the overall boiler air-fuel ratio and, hence, in the total combustion air flow rate. Even here, the measured CO_2 data were bounded. The measured CO_2 data were tested against upper and lower limits corresponding to complete combustion and 10 percent carbon loss, for the measured O_2 level. If the measured CO_2 was higher or lower than these limits they were assigned values equal to the nearest limit level. For calculation of the air-fuel equivalence ratio and hence the equilibrium temperature rise, complete combustion of all carbon in the fuel to CO_2 was assumed (only the measured O_2 level was used).

Although the data scatter in all samples is large, accounting for possible carbon losses as high as 10 percent, at least in determining the total boiler air flow rate, is considered an improvement over the usual process of neglecting carbon losses altogether. This makes little difference in the natural gas- and oil-fired data, but the coal data show much stronger evidence of carbon losses. Of course, the large scatter attributed to the CO_2 data could also represent equally large scatter in the O_2 measurements, possibly because of the same stratification problems, but no independent check on O_2 measurements was available. Obviously, large scatter in the O_2 data will reflect directly in large scatter in calculated NO_x levels.

4.3.2 The Final Mixing Zone

In the study of NO_x emissions from coal-fired boilers [2], it was observed that nearly all of the NO_x emissions from coal-fired boilers resulted from the conversion of fuel-bound nitrogen and from thermal NO_x generated in the final mixing zone. The final mixing zone was defined as that region in the furnace where all of the combustion air not entering the furnace through the active burners was mixed with the products of (in some cases, fuel-rich) combustion in the active burner region. This was particularly true if the data from off-stoichiometric configurations were excluded. In that study, the calculation of NO_x from the final mixing zone was taken as a simple constant for a given boiler and fuel. That constant was an empirical function only of the peak temperature of the product gases entering that zone.

The data indicated that in staged combustion configurations, where the first stage (active burner region) air-fuel ratio was below stoichiometric, mixing of the remaining combustion air with the products of fuel-rich combustion from the active burner region was a relatively slow process; during this process the average air-fuel ratio in the zone passed through stoichiometric. Modeling of the entire final mixing zone as a single tank (instantaneous mixing)-and-tube missed the significant quantities of NO_x which could be generated while the air-fuel ratio was in the region of stoichiometric, where temperatures and the NO_x formation rate (exponential in temperature) are highest.

Of course, there is considerable cooling of the combustion gases within the active burner region before these gases reach

the final mixing zone. These first stage product gases, in all cases, represent more than about three-quarters of the total flow through the boiler and contain all of the fuel. Even though there is further re-action between the first stage products and the remaining excess air in the final mixing zone, the first stage gases could have cooled sufficiently that negligible NO_x would be formed in this final mixing zone. Thus the initial combustion air temperature, the temperature rise due to combustion in the first stage, and the degree of cooling of the first stage product gases enroute to the final mixing zone critically determine the amount of NO_x formed in the final mixing zone. Because the NO_x formation rate is exponential in temperature, accurate calculation of the gas temperature up to the final mixing zone is important.

In the study of coal-fired boilers [2], the limited scope allowed only an empirical estimate of the effects of finite rate mixing in this zone to be developed. This provided at least a first-order correction for the single tank-and-tube model of this zone. In this study, the final mixing zone was divided into ten tank-and-tube subzones, in each of which one-tenth of the excess air was mixed with the products of the previous zone. In each of these subzones, the increment of air was mixed instantaneously with the products of the previous subzone, and a finite time was allowed for flow to the next subzone and for NO_x generation. The total time for this mixing was taken as the time required for flow of the combustion gases: (1) from the top level of the active burners to the top level of air-only burners (if any); (2) from the top level of air-only burners to the level of the open NO_x ports (if any); and (3) one-quarter of the furnace hydraulic diameter beyond the NO_x ports. In addition, the NO_x subsequently formed in the fully mixed product gases was included, to the point where the gases had cooled sufficiently that the NO_x formation rate became negligible.

Preliminary parametric calculations with this improved description of the final mixing zone showed, as expected, that, with constant overall boiler operating conditions, the NO_x formed in the final mixing zone increases to a maximum as the air-fuel ratio of the first stage is decreased. This is because significant NO_x is formed only during the time period when the effective air-fuel ratio of the product gases is near stoichiometric. With a very fuel-rich first stage, negligible NO_x is formed in the final mixing zone until sufficient additional air has been mixed with these fuel-rich products to bring the effective air-fuel ratio near stoichiometric. The highest first stage air-fuel ratio where maximum NO_x is formed in the final mixing zone, and the subsequent total NO_x formed in the whole final mixing zone, are strongly dependent on the temperature of the fuel-rich products coming from the first stage. Given sufficient time for cooling and/or a sufficiently high rate of cooling, the thermal NO_x formed when the final excess air is mixed with the products of first stage combustion can be reduced to negligible levels.

There is some conjecture among researchers that, with very fuel-rich first stage combustion of a fuel containing significant concentrations of chemically bound nitrogen, some of the fuel, still containing some of the fuel-bound nitrogen, may remain unburned through the first stage. The fuel-bound nitrogen in this unburned fuel, then, could be converted to NO_x in the final mixing zone (during second stage combustion). It is clear that, if the first stage were operated so fuel-rich that no combustion could take place, the second stage would become the first stage of combustion and all fuel-bound nitrogen conversion would take place there. With stable combustion occurring in the first stage, however, it is not clear just how fuel-rich the first stage would have to be before significant fuel-bound nitrogen conversion begins to occur in the second stage. Such conversion, however, if it does take place in the second stage, might generate considerably more NO_x because of the greater availability of oxygen in the second stage of combustion.

Evidence of this phenomenon might be indicated by overall NO_x emission data which decrease monotonically with the first stage air-fuel ratio until a minimum is reached. Further reduction in the first stage air-fuel ratio, then, would show a rather rapid rise in total NO_x emissions. Some data (unpublished) exhibiting these characteristics have been derived in laboratory experiments. It is not yet clear, however, whether the rise in NO_x levels at very low first stage air-fuel ratios is due to conversion of fuel-bound nitrogen in the second stage or to the increased formation of thermal NO_x in the final mixing zone, as discussed in this section. The data from full-scale boilers used in this study do not indicate this phenomenon. Whether this is because these boilers were never operated sufficiently fuel-rich in the first stage or because the phenomena cannot exist in full-scale, operating boilers is not known. In any case, no attempt was made in this study to allow for any conversion of fuel-bound nitrogen in the final mixing zone.

4.3.3 Gas Cooling Rates

In the previous studies of NO_x formation in utility boilers [1, 2], uncertainties in the complex flow, mixing and reaction processes occurring in full-scale, multiburner boilers, particularly when operated in off-stoichiometric configurations, indicated that nothing more complex than a constant time-rate of cooling of the combustion products could be justified. As a result of the large simplification afforded by eliminating off-stoichiometric configurations from the analysis and the data sample, it was considered that the next more accurate step could be taken in the description of combustion product gas cooling. Since the great majority of the heat transferred to the water walls in a typical utility boiler is transferred by radiation, a cooling rate in some way proportional to the fourth power of the local gas temperature seemed appropriate.

Again, the limited scope of this study and the remaining degree (or lack) of sophistication in the rest of the analysis did not allow

development of a comprehensive radiation cooling calculation or subroutine for these complex, full-scale boilers. A limited amount of measured data on heat fluxes to the water walls of an opposed, natural gas-fired boiler were available [1]. These data showed measured heat fluxes at six vertical locations in the boiler and measured gas temperatures at one location, with the boiler operated at three load conditions. From radiation heat transfer theory, variations in this heat flux data should follow an expression in the fourth power of temperature, such as

$$\dot{Q} = K_r (AT_g^4 - BT_w^4) \quad (1)$$

Plots of the heat flux data \dot{Q} against the measured gas temperatures T_g did indeed indicate an approximate fourth-power dependence. Several attempts to fit the data directly with equation (1), using reasonable estimates for the water-wall temperatures, resulted in the conclusion that BT_w^4 , must be negligibly small compared to AT_g^4 . Therefore, all of the heat flux data was adjusted by adding a small, constant heat flux (of 2 to 12 percent of the measured heat flux data) such that a fit of the data with equation (1) yielded a value for this second term which was exactly zero. This left the expression

$$\dot{Q} = K_r T_g^4 \quad (2)$$

where \dot{Q} is the heat/area-time, T_g is the temperature, and K_r was empirically determined as

$$\dot{Q} = K_r = \epsilon_g \sigma = .374 \sigma \quad (3)$$

where σ is the Stephan-Boltzmann constant and ϵ_g is the effective emissivity of the combustion products.

Although equation (2) neglects convective heat transfer to, and reradiation from, the water walls, as well as any external losses, the empirically derived value for the effective emissivity of the combustion gases is quite reasonable for gases composed largely of nitrogen, carbon dioxide, and water vapor. It was not within the scope of this study to describe radiant and convective heat transfer in greater detail. No allowance was made for increased gas emissivity with oil and coal fuels or with the air-fuel ratio, which generate greater luminosity. Therefore, gas cooling rates under conditions yielding higher luminosity should be higher than the rate derived here. Therefore, this change to a gas cooling rate proportional to the fourth power of the local gas temperature represents only a first-order correction to the constant rate used in the previous studies.

Equation (2) was not used, directly, in this study. The total heat flux entering the water walls over an increment of vertical

height, equation (2), was equated to a uniform heat loss from the combustion gases as they crossed that increment of height. This yielded a time rate of cooling given by the expression

$$\frac{dT_g}{dt} = -0.04 R_{sv} K_r T_g^5 \quad (4)$$

where R_{sv} is the surface-to-volume (circumference to flow area) ratio of the furnace.

In each stream tube of the tank-and-tube mixing scheme, the final temperature T_f was calculated from the initial temperature T_i from equation (5)

$$\left(\frac{T_i}{T_f}\right)^4 = 1 + 0.08 R_{sv} K_r T_i^4 t_f \quad (5)$$

where t_f is the time required for flow through the stream tube.

Similarly, in each stream tube (at a constant air-fuel ratio), equation (4) can be used to convert the Arrhenius rate expression for the formation of thermal NO_x (based on the Zeldovich mechanism) from a function of time to a function of temperature, and integrated over the stream tube from the initial to the final temperature. The resulting expression for the increment of NO_x (dNO_x) formed in a given stream tube is

$$dNO_x = 5.645 \frac{(SON)}{R_{sv} K_r} \left[e^{-Z} (Z^3 + 3Z^2 + 6Z + 6) \right]_{Z_i}^{Z_f} \quad (6)$$

where $Z = 67,900/T_g$ (7)

and the term SON represents a product of the nitrogen/oxygen concentrations appropriate to the Zeldovich NO_x formation rate equation, i. e., $[N_2] [O_2]^{1/2}$.

Equations (5) and (6) combine the effects of time and temperature on thermal NO_x formation. If gas temperatures are very high, the rate of cooling, equation (5), is very rapid, and the final temperature can be much lower than the initial temperature, even if the time required to flow through the stream tube is short. Large differences in initial and final temperatures yield, equation (6), large increments of NO_x formed in the tube. The same amount of NO_x could be formed in the tube with a much lower initial gas temperature if the time to flow through the tube is sufficiently long.

Equation (6) also shows the direct effect of the boiler surface-to-volume ratio R_{sv} and the rate of radiant heat transfer K_r on thermal NO_x formation. Small boilers, with larger surface-to-volume

ratios, should generate less NO_x emissions than the larger boilers. Similarly, increasing the rate of radiant heat transfer (the effective, net emissivity) will also reduce NO_x emissions.

In the active burner region (because the large local mixture ratio variations resulting from off-stoichiometric firing configurations have been deleted), the mixing in the tank at the beginning of each tank-and-tube section is between streams of similar composition; however, the stream temperatures may be different. Once the initial, mixed temperature is established, the temperature at the end of the tube can be calculated from equation (5), and these two temperatures can be used in equations (6) and (7) to calculate the increment of NO_x generated in that stream tube. The total NO_x formed in the first stage, then, is the sum of these increments along each flow path through the active burner region.

4.3.4 Finite Rate Gasification and Mixing

In the previous studies [1, 2] it was necessary to neglect the effects on NO_x formation of finite rate gasification of the oil and coal fuels and of the mixing of natural gas and the gasified oil and coal with combustion air. A preliminary model of such gasification and mixing was developed during the course of those studies, the latter based on a relaxation technique analogous to transient conductive heat transfer analyses. The resulting calculation was too detailed and complex for the NO_x emissions analysis used at that time and, despite the simplifications in this study, it is still too complex to be directly incorporated. There are no inherent limitations to incorporation, but it was beyond the scope of both the previous and this study.

That peripheral analysis was used generally, however, to investigate the effects of finite rate gasification and mixing on local air-fuel ratios and temperatures. The analysis was also used to develop a simpler (again first order) means of accounting for these rates, compatible with the scope of this study as well as with the degree of sophistication of the rest of the NO_x emissions analysis.

Results of these peripheral investigations, as well as other considerations of heterogeneous diffusion flames, indicate a combustion process wherein essentially pure fuel or fuel vapor is mixed with essentially pure combustion air, with the local air-fuel ratios ranging from zero to infinity. Initially, a very steep air-fuel ratio gradient exists between the sources of unmixed, gaseous fuel and the surrounding combustion air. As gasification and mixing proceeds, all of the fuel passes first through a stoichiometric air-fuel ratio region (the so-called wrinkled flame front); the products of stoichiometric reactions are then diluted with additional combustion air.

In cases where the total amount of combustion air available in the active burner region exceeds the stoichiometric air, the

mixing process proceeds until all of the fuel is gasified. The region of stoichiometric combustion products then approaches the fuel source more closely and finally disappears as the entire mixture approaches the products of combustion at the overall (excess air) air-fuel ratio. In cases where the overall average air-fuel ratio in the first stage is less than stoichiometric, a point is reached where the amount of fuel gasified exceeds the stoichiometric fuel for the available combustion air. At this point, the region of stoichiometric combustion (the flame front) expands away from the fuel source as the as yet unmixed air is over-diluted with products of fuel-rich combustion. Again, the stoichiometric region finally disappears as the entire mixture approaches the products of combustion at the overall (excess fuel) air-fuel ratio.

Results of the preliminary mixing studies indicated that a first order approximation of this finite rate gasification and mixing process, for the purpose of NO_x formation, could be developed by defining three parallel and simultaneous zones within the flows from the active burners: (1) a zone where the fuel either has not gasified or the air-fuel ratio is so fuel-rich that no NO_x could be formed; (2) a zone where the average air-fuel ratio is near stoichiometric (the flame front); and (3) the rest of the products not included in the first two zones.

A relatively simple calculation was set up, therefore, composed of these three zones. The rate of gasification and mixing was arbitrarily taken as a linear function of distance into the furnace. With natural gas fuel, the distance for final, complete mixing is that required for mixing only. The probable distance for complete mixing of gaseous fuel with the combustion air was selected from considerations of the analytical mixing results and empirical observations of flames in full-scale utility boilers. With natural gas fuel, the mixing calculations indicated that mixing should be complete within the core flow from the active burner (less than two diameters from the burner exit). Observations of flames in coal-fired boilers indicate that the sum of the distance required to gasify and mix these fuels is nearly the total distance from the burner to the opposite wall of the furnace in single-wall boilers, or to the centerline in opposed-fired boilers. Since impingement of reacting coal particles or partially mixed gases on a water wall can have very corrosive effects, it was finally assumed that both gasification and mixing of the coal particles and the derived fuel vapors are (just) complete at the opposite wall (or centerline). The appropriate distance for complete vaporization and mixing of oil droplets and derived fuel vapors lies between the distances established for the natural gas and coal cases. Some further parametric variations were conducted with oil fuels to better establish the appropriate distance.

In addition, because some fuel vapor must be available and mixed with some air right at the burner exit to provide continuous ignition and flame-holding, it was assumed that 20 percent of all fuels was already gasified and mixed, in stoichiometric proportions, at the

burner exit. In the cases of oil and coal fuels, this initial combustion could be provided by the very fine oil droplets and coal particles in the initial size distribution.

In each of the tank-and-tube zones describing the burner flows in the overall NO_x model, then, the quantity of fuel and air and the average air-fuel ratio in the three subzones was determined by calculating: (1) the amount of the fuel as yet ungasified (zero air-fuel ratio); (2) a fixed fraction of the gasified fuel plus the related stoichiometric proportion of combustion air (stoichiometric air-fuel ratio); and (3) all of the rest of the combustion air and gasified fuel, in whatever air-fuel ratio results.

The effective fraction of the gasified fuel in the subzone at stoichiometric air-fuel ratio, of course, is not a commonly used or well-established quantity. If mixing rates are very rapid compared to gasification rates, the flame fronts might be expected to be very thin and close to the gasifying fuel sources. Since natural gas is already gasified, the flame fronts might be expected to be more wrinkled, broader, and more diffuse. For this study, from considerations such as this, the fraction of the gasified fuel which, at any instant in time, is involved in reactions (including NO_x formation) typical of stoichiometric combustion was taken as 20 percent for all coal fuels and 30 percent for natural gas. Again, this fraction for oil fuels should be intermediate between those for gas and coal. Parametric calculations appeared to indicate that 24.5 percent was appropriate for oil.

The simple, finite rate gasification and mixing rate calculation described in this section is capable of approximately modeling the progress of gasification, stoichiometric combustion, and subsequent dilution of gaseous, liquid and solid fuels to completion. Initially, 80 percent of the fuel is not yet gasified (or is not yet mixed with any air, in the case of natural gas), 20 percent of the gasified fuel is mixed with a stoichiometric proportion of air, and the rest of the air is unmixed with any fuel. As the element of fuel and air proceeds into the furnace, more fuel is gasified; more fuel is involved in stoichiometric combustion (up to the limiting fractions discussed above); some products of stoichiometric combustion begin to be mixed with the remaining air; and the air-fuel ratio in the latter zone begins to decrease.

In the case where the available combustion air is in excess of the stoichiometric air, this process of gasification and mixing continues until all of the fuel is gasified. Subsequent mixing then increases the air-fuel ratio in the subzone, formerly at stoichiometric, and continues to decrease that in the remaining zone until they both become equal to the overall air-fuel ratio, at the (specified) end of the gasification and mixing distance. In the case where the available combustion air is less than the stoichiometric ratio to the fuel, this process of gasification and mixing proceeds as in the previous case until the air-fuel ratio in the third subzone decreases to stoichiometric. At that point, there is not

sufficient air remaining to sustain a region of stoichiometric combustion, and the air-fuel ratios in both zones decrease to the final, fuel-rich ratio at the end of the gasification and mixing distance.

The continuous gasification and mixing approximation described above was converted into finite steps and averaged over the length of each of the stream tubes in the overall tank-and-tube model of the burner flows. In effect, the series primary, secondary, adjacent, and opposite tank-and-tube mixing zones [1] were each further subdivided into these three effectively parallel tank-and-tube mixing sections. At the beginning of each of the series mixing zones, the gasification and thermal and composition mixing appropriate to the three parallel subzones were accomplished (instantaneously, in the tank) to establish the initial conditions for flow through the three parallel subzones in the next mixing zone in the series. Cooling and NO_x formation were calculated in each of these parallel subzones by the technique discussed in Section 4.3.3.

The somewhat complicated parallel-series gasification and mixing scheme discussed in this section is important only in the active burner flow streams in the lower part of the active burner region of the furnace. Since little bulk gas flow has yet been generated, these processes can proceed largely as idealized. In the upper parts of the active burner region, the gas flow and mixing picture becomes increasingly dominated by the bulk gas flow coming from the completed reactions in the lower parts. Not only is the composition of this bulk gas flow that of complete gasification, mixing, and combustion at the overall air-fuel ratio of the first stage of combustion (in some cases quite fuel-rich), but these gases have been in the furnace for some time and have cooled considerably. Some cool, recirculated flue gases may even be mixed in with these bulk gases. In this study, no attempt was made to further model finite rate gasification and mixing of any of the fuels in the presence of a significant cross-flow of bulk gases. Instead, as in the previous studies, the fraction of the vertical flow area of the furnace occupied by bulk gas flow at any burner level was linearly proportioned to the amount of active burner flow already in the furnace. In the upper burner levels, when the flow from an active burner intersects the bulk gas flow, all gasification and mixing of the fuel and air within the burner flow was assumed complete and mixed with the bulk gas flow. At all burner levels, the finite rate gasification and mixing scheme discussed in this section is carried out at least within the region of core flow (the primary mixing zone) at the exit of the burner.

Although the finite gasification and mixing rate approximation discussed in this section (and used in all NO_x emissions analyses performed in this study) appears somewhat complicated and contains two somewhat arbitrary constants, it does provide further insight into the NO_x formation process in full-scale, multiburner utility boilers. Furthermore, no other technique appropriate to the scope of this study is available. The two constants can be related to droplet and particle

size distributions in the initial oil sprays and pulverized coal streams. Large average droplet and particle sizes will extend the gasification distance further into the furnace and may also decrease the thickness of the stoichiometric flames surrounding the particles. Thus, incorporating this gasification and mixing calculation into the overall analysis of NO_x formation provides a qualitative means of investigating the effects of initial particle size distributions on NO_x emissions. Parametric variations of these constants, discussed in the Results, Section V, of this report, show that increased particle sizes can reduce NO_x formation in the early regions of the burner flows but also can decrease the cooling rate in these early regions, resulting in greater NO_x formation further downstream.

As often happens, however, improvements in accuracy or detail in the description of one phenomenon open the door to questions in others. In this case, the improvements in the description of finite rate gasification and mixing introduce further questions concerning the conversion of fuel-bound nitrogen to NO_x in the stoichiometric flame and the possible oxidation or reduction of this initial NO_x in the subsequent mixing of the products of stoichiometric combustion with the remaining excess air or fuel. This question is discussed further in Section 4.3.5. From the standpoint of the calculation used in this study, finite rate gasification and mixing in no way affects the efficiency of conversion of fuel-bound nitrogen to NO_x as calculated with the model developed and used in the previous studies [2].

4.3.5 Some Considerations Relative to Heterogeneous Flames

The more detailed modeling of heterogeneous diffusion flame processes discussed in the previous section opens the door to further questions regarding: (1) the mechanism of the initial conversion of fuel-bound nitrogen to NO_x ; and (2) the possible subsequent effects of excess carbon, unburned fuel, and CO on this initially formed NO_x . The three-step process of combustion discussed in Section 4.3.4 relative to finite rate gasification, mixing, and combustion in turbulent homogeneous (natural gas) and heterogeneous (oil and coal) diffusion flames emphasizes that all of the fuel originates from a very fuel-rich source (concentrated gaseous natural gas, liquid oil, or solid coal) and that, over much of the gasification and mixing time, initial, local combustion of the gasified and/or mixed fuel is under high-temperature, near-stoichiometric conditions. The products of this stoichiometric combustion are then mixed with the remaining air. Only after most or all of the fuel has been gasified and/or mixed is there insufficient air or fuel (overall fuel-rich or fuel-lean, respectively) to sustain this initial, local stoichiometric combustion. The two questions raised when turbulent heterogeneous diffusion flames are viewed in this manner involve: (1) the air-fuel ratio conditions under which the fuel-bound nitrogen is converted to NO_x (not a question with natural gas fuels, which contain no fuel-bound nitrogen); and (2) what happens to the very high levels of

NO_x formed in this stoichiometric region upon subsequent dilution by the remaining fuel or air (overall fuel-rich or fuel-lean respectively).

Many laboratory studies of the global effects of the overall air-fuel ratio on the efficiency of conversion of fuel-bound nitrogen to NO_x , using homogeneous, premixed flames, show a clear decrease in this conversion efficiency as the air-fuel ratio is decreased. Detailed probing of this type of flame appears to indicate that reactions which convert the fuel-bound nitrogen to NO_x occur as fast and in approximately the same physical location in the flame as those which consume the hydrocarbons in the fuel. One might assume, then, that in a heterogeneous diffusion flame, where the initial hydrocarbon reactions generally occur under fuel-rich, near-stoichiometric conditions, the efficiency of conversion of fuel-bound nitrogen to NO_x would always be similar in magnitude to conversion in a premixed gaseous flame under near-stoichiometric conditions. Further, one might also expect that the fuel-bound nitrogen conversion efficiency in a heterogeneous diffusion flame should be largely independent of the overall air-fuel ratio. Instead, the fuel-bound nitrogen conversion efficiency observed in laboratory heterogeneous diffusion flames and in full-scale, multiburner boilers appears to duplicate, in both magnitude and in variation with the overall air-fuel ratio, that observed in laboratory premixed gaseous flames.

It is not reasonable to postulate, for example, that combustion of pulverized coal in a full-scale boiler proceeds like a premixed gaseous flame. In the slow gasification and mixing processes surrounding heterogeneous combustion, it seems much more reasonable to assume that the chemical reactions are much faster than these physical processes and that the resulting combustion products subsequently maintain a reasonable shifting equilibrium as mixing proceeds.

Any view of the conversion of fuel-bound nitrogen in a heterogeneous flame must recognize that, in the very fuel-rich region between the fuel source (for example, a coal particle) and the surrounding flame, nitrogen can be present, both chemically bound in the gaseous hydrocarbon fuel and as molecular nitrogen from the surrounding air. Experimental evidence clearly shows, however, that oxidation of at least some significant fraction of fuel-bound nitrogen is rapid in this region, while oxidation of the nitrogen from the air is negligible. This implies that, in the mechanism through which at least a portion of the fuel-bound nitrogen is eventually oxidized to NO , the fuel-bound nitrogen may pass through a series of C-H-N-O intermediates (such as HCN and NCO) but may never appear as atomic or molecular nitrogen. In the latter form, it would be indistinguishable from the nitrogen in the air. In fact, that portion of the fuel-bound nitrogen which does not eventually appear as NO_x must have appeared very early as some stable nitrogen compound, such as molecular nitrogen, because it was subsequently able to survive passage through the surrounding hot, stoichiometric

flame and, in some cases, even a hot oxygen-rich environment, without appreciable oxidation to NO. The question, of course, concerns why some of the fuel-bound nitrogen appears to follow the chain to NO, while the rest does not.

The chemical form of the C-H-N-O compounds in the fuel appears to have little effect on the fraction of nitrogen converted to NO. In addition, in heterogeneous combustion, the initial oxidation of the carbon and hydrogen in the C-H-N molecules must be largely completed in the region between the fuel source and the surrounding stoichiometric flame; therefore, any oxidation of the fuel-bound nitrogen must also be completed in this region. These two observations suggest that: (1) initially all of the fuel-bound nitrogen is oxidized to NO, during the oxidation of carbon and hydrogen; and (2) some fraction of this NO is subsequently reduced to other, stable forms of nitrogen (such as N₂). This latter step would result because the initial oxidation reactions always occur in a fuel-rich (oxygen-limited) mixture, in a heterogeneous flame.

Following this simple view of the process of conversion of fuel-bound nitrogen, close to the fuel source (where little oxygen is available), little of the C-H-N oxidation reactions could occur, and little NO would be formed. As more oxygen is mixed with the fuel, closer to the stoichiometric flame, more NO would be formed, during the fast, highly exothermic hydrocarbon reactions, until a local air-fuel ratio is reached where there is just sufficient oxygen available to oxidize all of the fuel to CO, H₂O, and NO (called here the CO-stoichiometric air-fuel ratio).

If no further oxygen were supplied, the slower shift reaction



would begin shifting toward the water-gas equilibrium. This reaction requires no further oxygen (nor frees any) and is very nearly thermodynamically balanced. Essentially, all of the free oxygen is locked up in the water-gas equilibrium and in the NO and SO₂.

The mechanism by which the water-gas equilibrium is achieved can essentially be described in two steps



These are a pair of radical-shuttling reactions (H and OH). Reaction (9) is fast, and its rate constant is quite insensitive to temperature. However, at the relatively low temperatures of the very fuel-rich mixtures being discussed here, reaction (10) may be quite sluggish.

During the shift from the initially high concentrations of CO and H₂O to the equilibrium mixtures (involving higher CO₂ and H₂ concentrations), OH concentrations may be depleted and H concentrations increased by reaction (10). This may result in very low, nonequilibrium levels of OH and correspondingly high levels of H during the period when the water-gas reaction is shifting to equilibrium.

One of the four reactions basic to the extended Zeldovich (thermal) mechanism for NO_x formation and destruction that is particularly important in fuel-rich mixtures is



Clearly, if the OH levels are reduced and the H levels increased by the dominant water-gas shift reaction, then reaction (11) will be forced to the right, resulting in destruction of the NO.

In effect, the initially high CO concentrations require oxygen in order to reach equilibrium CO₂ levels; at the lower temperatures where reaction (10) is sluggish, it may be easier to obtain the oxygen from the NO via the forward reaction (11) rather than from the water via reaction (10). The competition for oxygen, then, in an oxygen-limited mixture, is one between the forward reactions represented in reactions (10) and (11) (both endothermic) when reaction (8) is seeking the water-gas equilibrium. This competition would ensure that, as long as the combustion is locally oxygen-limited, only a fraction of the available fuel-bound nitrogen would end up as NO, while the remaining fraction would be converted back to some other nitrogen compound such as molecular nitrogen. The latter might be thought of essentially as running the Zeldovich mechanism in reverse. Once this fractional conversion of the fuel-bound nitrogen is accomplished, the NO could be further reduced, but the fraction of the fuel-bound nitrogen already converted to other stable nitrogen compounds could not be easily oxidized to form more NO, except via the kinetically slow thermal mechanism.

In overall air-fuel mixtures containing excess air, however, the more volatile compounds will eventually be driven off, and the gasification rate will become slow compared to the local gas mixing rates. The char particle temperature may then rise, and further gasification and direct char combustion could occur, in the more highly oxidizing local conditions of excess air. Thus, under conditions of excess air, additional fuel-bound nitrogen, otherwise trapped in the char, could be converted to NO.

In overall air-fuel mixtures containing excess fuel, the products of stoichiometric combustion (including the fraction of fuel-bound nitrogen converted to NO but no C-H-N species) would at first be diluted with excess air, but then, eventually, as gasification and mixing near completion, they would be diluted with the products of fuel-rich

combustion. At no time in the life of a fuel particle would the air-fuel ratio at or very near the particle surface be higher than stoichiometric, and the latter stages of char particle combustion would be under fuel-rich conditions. Further, assuming that the water-gas equilibrium is maintained as the mixture becomes more fuel-rich, more hydrogen would be generated and the NO formed in the earlier stoichiometric combustion could be further reduced, perhaps to other nitrogen compounds such as molecular nitrogen.

In the case of staged combustion, with a fuel-rich first stage, the processes described in the preceding paragraph would finally again be reversed as the second-stage excess air is mixed into the products of the fuel-rich first stage. The first-stage products would contain: (1) the NO resulting from the initial conversion of the fuel-bound nitrogen to NO and the subsequent partial reduction of that NO; (2) no additional gas-phase fuel-bound nitrogen; and (3) some nitrogen still chemically bound in the char (neglecting, for the moment, any NO thermally formed in the first stage). Therefore, any additional fuel-bound nitrogen conversion which might occur in the second stage would have to come from further gasification and/or direct oxidation of the remaining char particles.

Much of the discussion in this section has been speculative. Alternative mechanisms concerning fuel-bound nitrogen conversion in heterogeneous flames, however, are not only lacking but those available are also largely speculative. The vast majority of the pertinent experiments and proposed mechanisms reported in the literature concern homogeneous, premixed flames. Similar pertinent experiments with heterogeneous flames usually describe only the effects of certain combustion conditions on the resulting overall fuel-bound nitrogen conversion efficiencies. Some recent work, however, can be interpreted as supporting the mechanism described in this section.

Aronowitz and Glassman [7], in studying the oxidation of methanol, report that carbon dioxide does not begin to form substantially until the methanol is depleted. They suggest two reaction steps, a first in which methanol forms carbon monoxide and a second in which the carbon monoxide is subsequently oxidized to carbon dioxide. Lewis 8 , in developing a model for entrained flow (particle) gasifiers, assumed that the heterogeneous reactions generate carbon monoxide, which is subsequently converted to carbon dioxide in the homogeneous chemistry via the OH radical originating from water.

Song, Beer, and Sarofim [9] used a simplified scheme for the conversion of nitrogen chemically bound in coal in which the conversion to NO_x of nitrogen in the volatiles and in the char are separate and independent processes. Their results show that the conversion efficiency of both are functions of the fuel/oxygen equivalence ratio and that both approach zero (for the volatiles) or become asymptotic

to very low values (less than 15 percent) for the char nitrogen at fuel-air equivalence ratios of about 1.7 to 2.0. This is the approximate ratio where just enough oxygen is available to initially oxidize all of the carbon and hydrogen to carbon monoxide and water, with little remaining for oxidation of the fuel-bound nitrogen.

Some effort was made during this study (unsuccessfully) to further develop and quantify the serial process for heterogeneous combustion and fuel bound-nitrogen conversion discussed in this section (involving: (1) oxidation of carbon, hydrogen, and nitrogen to carbon monoxide, water, and NO under fuel-rich to stoichiometric conditions; (2) water-gas shift reactions and partial reduction of the NO in overall fuel-rich mixtures; and (3) further oxidation of the nitrogen in the remaining char particles). Unfortunately, the considerable effort required to develop and incorporate this mechanism was not within the scope of this study. As a result, the model of bound nitrogen conversion first proposed and used in earlier studies in this program [2] has been little improved. It was used, essentially unchanged, throughout this study.

SECTION V

RESULTS OF DATA ANALYSES

In the previous studies [1,2], regression analyses were used to quantify the coefficients of the terms in a semiempirically derived equation for the total NO_x emissions (concentrations) from full-scale utility boilers. Because of the complexity and the large number of terms (nine) in the developed equation, it was difficult to interpret the resulting coefficients of each term with regard to the accuracy of the assumptions and the calculation technique involved in each term. The greatest benefit was derived from the parametric calculations concerning the effects of the broader combustion modifications on the overall boiler NO_x emissions; the entire nine-term expression as quantified by the regression analyses was used.

In this study, as a result of the simplifications and improvements, the NO_x calculation expression was reduced to three terms, plus the constant necessary for the regression analyses. Each of these terms was intended to represent a major source of NO_x in the furnace: (1) thermal NO_x generated in the active burner region (the first stage, in staged combustion); (2) thermal NO_x formed in the final mixing zone (the second stage, in staged combustion); and (3) fuel-bound nitrogen conversion (assumed to occur entirely in the active burner region). An attempt was made to directly calculate the NO_x contribution from each of these three sources, so that direct comparisons with available measured data could be made, where possible.

Significant barriers to direct correlation and comparison of all available data, in one large sample, were expected because of (1) unknown changes in effective gas emissivities between the three fuels (natural gas, oil and coal) and (2) uncertainties in the gasification and mixing rates appropriate to the three fuel states (gas, liquid and solid). As a result, correlations and analyses were made separately and will be discussed separately in this section for the three fuel types.

5.1

RESULTS OF REGRESSION ANALYSES

Table 3 shows the results of regression analyses of several samples of the available, appropriate NO_x emission data. In all cases, the data samples were small enough (Table 2) that direct comparison of the calculated NO_x levels with the measured NO_x were not only possible but more instructive (Section 5.2). The results of the regression analyses, therefore, were used more as an additional indication of the validity and accuracy of the NO_x calculations. Unlike the previous studies, parametric calculations with the quantified correlation equation were not conducted.

Significant observations from the results of the regression analyses fall into two categories: (1) the significance of the correlation coefficients and (2) the significance of the empirically-derived coefficients of the terms in the correlation equation.

5.1.1

Correlation Coefficients

Table 3 shows that the correlation coefficients for a given fuel and boiler type were adequate to good, ranging from 0.826 to 0.915, but that attempts to correlate data from several types of boilers, even involving the same fuel type, resulted in rather poor correlation coefficients (0.681 to 0.786). This same result was observed in the previous studies, as shown in the last column of Table 3. For the natural gas- and oil-fired boilers, the difficulty in correlating data from all boiler types together in a single sample appears to be related more to possible inaccuracies in some of the data obtained from the tests of the single-wall boilers. This problem will be discussed further in Section 5.2.

Difficulties were also encountered in correlating single-wall and tangential coal-fired boilers together in a single sample. As shown in Table 3, separate correlations of the two coal-firing boiler types are good, but when the data samples are combined the resulting correlation coefficient is rather poor. There is no apparent trend in the empirical values of the coefficients of the terms for the single-wall and tangential configurations when correlated separately or as a total coal-fired data sample.

5.1.2

Coefficients of the Terms

The best possible results of the regression analyses would be for the empirical coefficients of all terms in the correlation equations to be 1.0 and the constant to be zero. This result would imply that the calculated levels of NO_x from the three sources (terms) were exactly correct, both in slope (the sign of the coefficient) and in magnitude. Such a result, of course, would require that the measured data be exactly accurate as well. Large data scatter tends to reduce the magnitude of the constant (leading eventually to a case where any coherent variations are lost in the data scatter).

TABLE 3. RESULTS OF REGRESSION ANALYSES
OF NO_x EMISSIONS DATA

Sample Boilers	Empirical Coefficients for the Terms Representing the NO _x Sources					
	Correlation Coefficient	Thermal NO _x		Fuel-Bound Nitrogen Conversion	Constant	Correlation Coefficients, Previous Study
		Active Burner Region	Final Mixing Zone			
Natural Gas						
All boilers	0.786	0.289	8.43	NA	162	0.837
Opposed-fired only	0.826	0.564	4.10	NA	114	0.844
Oil						
All boilers	0.762	0.097	7.53	0.174	213	0.734
Opposed-fired only	0.875	-0.419	12.6	0.160	302	0.849
Coal						
All boilers	0.681	0.006	1.64	0.335	268	--
Single-wall	0.894	-0.054	5.74	0.802	254	--
Tangential	0.915	0.001	2.17	0.843	2	--

The coefficients for the two sources of thermal NO_x for natural gas-fired boilers are both positive, indicating that the calculated trends are correct. The magnitude of the coefficients for the term describing the active burner region and the magnitude of the constants are reasonable. This is not too unexpected because the combustion gas cooling rate was determined from data obtained with natural gas fired in the largest of the four pairs of sister boilers in the natural gas data sample. In addition, there are no problems associated with fuel gasification rates or with fuel-bound nitrogen or sulfur. The coefficients for the term describing NO_x formed in the final mixing zone, however, are much larger than one. This implies that either the gas cooling rate used in the calculation is too large or the time spent by the gas enroute to this final mixing zone is too large.

Study of the details of the NO_x calculations in several of the subzones within the active burner region shows that, with natural gas fuels, the total NO_x formed in the boiler is dominated by that formed in the very early combustion zones, just off the burner exits and in the lower burner levels, before appreciable mixing with bulk gases. These are the regions of maximum combustion product temperatures. Because of the exponential effect of temperature on thermal NO_x formation, the overall NO_x calculation is very sensitive to the combustion air temperature and to the burner air-fuel ratio. Unfortunately, as discussed in more detail in Section 5.2, the actual combustion air temperatures at the burner inlets were not directly measured but could only be inferred, for this data sample, from rather limited measurements at a distant location (at the exit of the preheater). This undoubtedly is a major cause of the rather large scatter in the calculated NO_x levels relative to the measured NO_x levels.

Similarly, NO_x formed in the final mixing zone is again exponentially sensitive to the combustion product temperature entering that zone. In this case, accuracy of the initial gas temperature is dependent on accurate measurement of the combustion air temperature and on accurate calculation of the burner air-fuel ratios, the gas cooling rates throughout the active burner region, and the quantity and temperature of any flue gas recirculation (from the furnace bottom). Calculated contributions of NO_x from the final mixing zone range over six orders of magnitude for the various operating conditions in the data sample but never exceed about 40 ppm. Because the NO_x calculation is exponentially related to the initial gas temperatures in that zone, small errors in any of the input data or the subsequent calculation can cause large variations in the calculated contribution of NO_x from that region.

As indicated by the appropriate coefficients in Table 3, for all fuels and boiler data samples, the regression analyses repeatedly indicate that the calculated NO_x formed in the final mixing zone, for one or more of the possible reasons discussed above, is low by factors ranging from 1.6 to 12.6. While this seems like a large error in the

calculation, it is not large compared to the six orders of magnitude of the range of the calculated contributions from this zone. The error merely tends to highlight the problem of trying to accurately calculate NO_x formation at relatively high temperatures in the light of the fact that that rate is exponentially related to temperature. No effort was made to further refine the cooling rate or any other part of the flow and mixing calculations to reduce this error.

Another interesting observation from the empirically determined term coefficients shown in Table 3 is that the coefficients for the term describing NO_x formed in the active burner region decrease to essentially negligible levels while those related to the NO_x formed from fuel-bound nitrogen increase to acceptably high levels in the fuel progression from natural gas, through oil, to coal. At the very least, this variation, within the scatter of the data, reflects the increasing significance in that progression of the fuel-bound nitrogen. These results indicate that, with significant concentrations of elemental nitrogen chemically bound in the fuel, variations in the measured data within the data scatter can best be explained by looking primarily at the conversion of this fuel nitrogen and neglecting variations in the thermal NO_x formed in the active burner region. This does not necessarily imply that thermal NO_x formed in the active burner region is negligible with oil and coal fuels; it does imply that the amount of NO_x formed in this region is relatively independent of variations in operating conditions (constant). In such a case, the regression analysis of the data could eliminate the thermal NO_x calculated to be formed in the active burner region (by developing a very small coefficient for that term) and instead account for that relatively constant NO_x in the derived constant. This appears to be the case with oil fuels and with coal fuels fired in the single-wall boilers.

The term coefficients and the constant shown in Table 3 for the tangential boilers, however, indicate that the thermal NO_x formed in the active burner region should not only be considered constant but also negligible. The derived coefficient for the term representing that region is essentially zero (0.001) and so is the derived constant (2 ppm). In addition, the coefficients for the NO_x from the final mixing zone (2.17) and from the conversion of fuel-bound nitrogen (0.843) are close enough to the expected 1.0 that the resulting corrections, in terms of ppm of NO_x , are quite small (+13 ppm and -51 ppm, respectively).

Comparing the term coefficients derived for the single-wall and the tangential boilers, then, seems to indicate that a significant, approximately constant amount of NO_x is generated in the active burner region and in the burner flow and mixing region upstream of the bulk gases in single-wall boilers; however, little NO_x is generated in this same region in tangential boilers. This result is qualitatively reasonable because (1) the active burner flow streams travel into the furnace much closer to the water walls and can take better advantage of direct

radiative and convective heat transfer to quickly cool the products of reaction and (2) the design of the burner arrays in a tangential boiler inherently provides effective combustion staging and even with all burners active the air-fuel ratio in the majority of the active burner region in the furnace is significantly lower than that of the overall boiler. These same characteristics may also account for the large scatter in the measured CO_2/O_2 data discussed in Section 4.3.1.

The agreement between the total calculated and measured NO_x data for the coal-fired boilers, particularly the tangential boilers, is considered excellent if the NO_x calculated for the initial combustion region is taken as a constant (zero in tangential boilers). A level of NO_x formed in this region that is relatively independent of the operating conditions is reasonable because of the slow rate of gasification of the solid fuel. Over most of the total coal gasification and mixing time (and distance into the furnace) the local air-fuel ratios are much more dependent on the rate of gasification rather than on the overall average burner air-fuel ratio. Only when gasification is nearly complete, and the mixing with bulk gases may already have begun, does the overall burner air-fuel ratio have an effect on NO_x formation. Thus, the negligible variation of the NO_x formed in the active burner region with variations in burner operating conditions appears reasonable with coal fuels and, to some extent, with oil fuels. The calculated magnitude of that constant level of NO_x formation with coal fuels, however, is still much too high. Despite the extensive efforts, described in Section 4.3.4, to allow for very slow gasification and mixing rates, particularly with the coal fuels, the calculation of the NO_x formed in the early regions of combustion of coal fuels results in NO_x contributions which are high. In single-wall boilers, this contribution is high by as much as an order of magnitude. If this were a problem of inaccurate combustion air temperature data (temperatures too high), as suspected from other observations, one might expect the coefficients of the term for the final mixing zone to be similarly low. In this case, however, as discussed in Section 4.3.3, it is likely that the actual gas cooling rate is much higher than that used in the calculation (derived from natural gas-fired heat flux data), thereby compensating for erroneously high initial temperatures. On the other hand, the very high calculated levels for the NO_x formed in the active burner region could also be an indication that high levels of NO_x are actually formed in the early combustion of liquid and solid fuels, as calculated, but are subsequently reduced by some NO_x destruction mechanism not incorporated in the calculation. Such a mechanism might be related to the mechanism of fuel-bound nitrogen conversion, as discussed in Section 4.3.5, or it could be an indication of the effect of fuel-bound sulfur (highest in coal) on NO_x formation, as postulated by Wendt [10] and others. There was not sufficient time in this study to further investigate some of these latter possibilities.

Results of the regression analyses, then, shed some light on calculation problems and general trends of NO_x emissions with the various fuels. More detailed results can be seen by direct comparison of the calculated and measured NO_x levels.

5.2 DIRECT DATA ANALYSES

While the observations from the correlations and the empirically derived coefficients of the terms (and the constant) in the NO_x equation are instructive relative to the accuracy of the calculations of NO_x formed in the various regions of the furnace, the fact that the contributions from each region to the final NO_x levels are calculated directly makes direct comparisons of calculated and measured NO_x levels perhaps even more instructive. Such direct comparisons were not feasible in the earlier studies because (1) it was not considered possible to express the contributions from each region in terms of NO_x in the flue gases, and (2) the larger number of terms (degrees of freedom) used in the earlier correlating equation made interpretation of any differences difficult.

The correlation equation used in this study consists of only three variable terms, representing the contribution of NO_x (expressed as ppm in the flue gases) thermally generated in the active burner region and in the final mixing zone and from the conversion of fuel-bound nitrogen, plus the constant necessary for regression analyses. With natural gas fuels, the fuel-bound nitrogen term is always equal to zero. The three variable terms represent real sources of NO_x, but the constant does not.

There is always a question concerning what NO_x source is represented in the constant or if the constant is merely an expression of the data scatter. Following the discussion in Section 4.3.4, concerning the finite rate gasification and mixing processes in the active burner region, it is clear that the NO_x generated in the active burner region logically could consist of two parts: (1) one in which the combustion conditions are largely controlled by the local gasification and mixing rates, relatively independently of the overall burner operating conditions; and (2) one in which the initial gasification and mixing processes are essentially complete, and the combustion conditions are directly dependent on the overall burner operating conditions. Since there is no gasification and only a short mixing region with gaseous fuels, the NO_x contribution from the active burner region should be largely variable and dependent on burner operating conditions. With solid fuels, however, the gasification rate may be small compared to the cooling rate, and by the time gasification is complete the product gas temperatures may be sufficiently low that further NO_x formation is small. In the latter case, the NO_x generated in the active burner region should be relatively independent of the burner operating conditions. The case with liquid fuels should lie somewhere between those of gaseous and solid fuels.

All of these effects are included in the computer calculation but are necessary to keep in mind when comparing the calculated NO_x data with the measured and in interpreting any significant differences.

5.2.1 Natural Gas Fuel

As mentioned, the NO_x contributions from the active burner region with gaseous fuels should be variable. Thus, despite the term coefficients and the constant shown by the regression analyses, the NO_x calculated directly from the active burner region and the final mixing zone, using coefficients of 1.0, should compare directly with the measured data (i.e., the constants derived by the regression analyses have no physical meaning).

Figure 2(a) shows a comparison of the measured and calculated NO_x data from 92 tests in two sizes (four boilers) of opposed-fired boilers with natural gas fuels (boiler nos. 3 and 4 in Table 2). Perfect agreement would be represented by all data lying exactly on the 45-degree line shown in the figure. The data show considerable scatter, but the agreement is generally good. On the average, the calculated NO_x levels are higher than the measured, but by only 6.6 ppm. The average difference (deviation) between the measured and calculated data, however, is just under 100 ppm.

A large part of the data scatter is due to the seven tests shown in Figure 2(a) where the calculated NO_x level is above about 810 ppm. These seven points have an average error of 227 ppm, with an average deviation of 267 ppm. Without them, the rest of the data shows an average error of -11.5 ppm and an average deviation of 86 ppm.

Some of the data scatter could be just that, random errors in either or both the measured NO_x levels or in the input data (particularly the combustion air temperature and the CO_2/O_2 data) from which the calculated NO_x levels were derived. The scatter could also be due to the inability of the calculation to take into account some subtle changes in operating conditions which have strong effects on the actual NO_x levels. Table 4 shows the data on operating conditions input to the NO_x calculation for the five tests for which NO_x levels between 917 and 984 ppm were calculated. All of these data were from the same boiler, with the same natural gas fuel and the same burner and NO_x port configurations, and none involve flue gas recirculation. None of the input operating conditions are significantly different among these five tests except the measured O_2 levels, and even these variations show no regular trend which could explain the observed variations in the measured NO_x levels. As a result, the NO_x levels calculated from these input data must be, and are, very nearly the same. These are all high load (even above rated) tests, and the combustion air temperatures are all

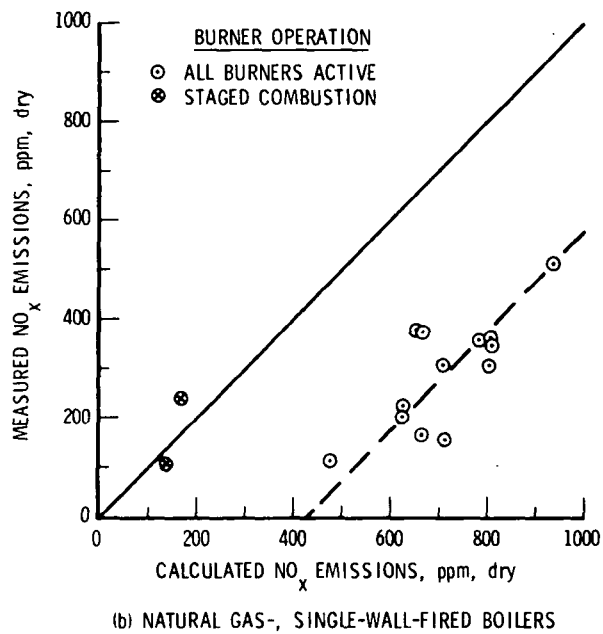
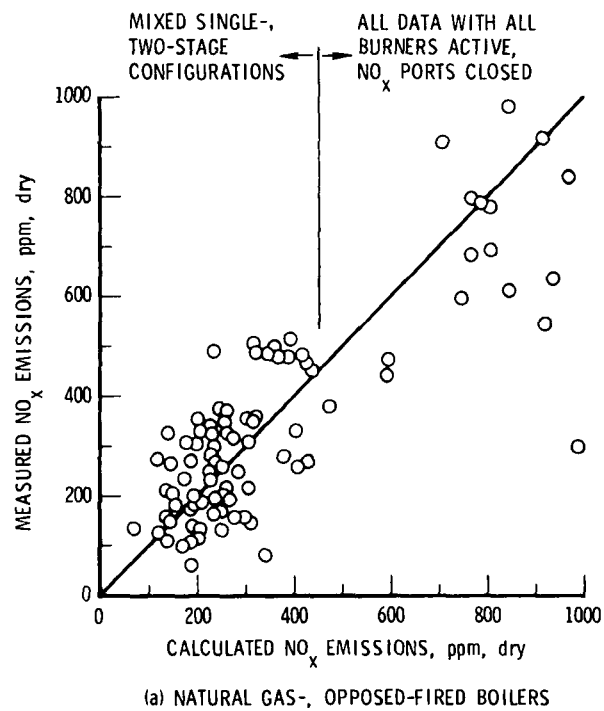


Figure 2. Comparison of calculated and measured NO_x emissions.

TABLE 4. EXAMPLE OF THE POSSIBLE WIDE VARIATION IN MEASURED
NO_x UNDER ESSENTIALLY THE SAME OPERATING CONDITIONS

Identical Conditions:					
350 MW, opposed-fired boiler					
Natural gas fuel					
All burners active, NO _x ports closed					
No flue gas recirculation					
Operating Conditions:					
Measured NO _x , ppm	O ₂ , %	CO ₂ , %	Load, MW	Fuel Flow, lb/sec	Combustion Air Temperature, °F
919	2.30	10.45	350	37.8	585
840	1.35	10.80	354	38.7	580
632	1.11	10.90	352	36.3	577
543	2.01	10.52	352	36.7	580
298	1.58	10.70	351	36.8	585
Average	1.670	10.674	351.8	37.260	581.4
Average Deviation, %	23.2	1.4	0.3	2.1	0.5
Unit Conversion:					
kg/sec = 0.435 (lb/sec)					
°K = 5 (°F + 460)/9					

very high. In addition, the O_2 levels are all relatively low, yielding very high values for the combustion temperature rise. The combination of these maximum temperatures yields maximum combustion product temperatures. At these very high temperatures, the NO_x formation rates (being exponential in temperature) are not only very high but are also extremely sensitive to small errors in those measurements which lead to the combustion product temperatures (i. e., combustion air temperature, CO_2/O_2 levels, and the equilibrium combustion temperature calculation). Small errors in these measured values could be responsible for the observed large errors in the calculated NO_x levels under these test conditions. Similarly, control of actual NO_x levels under these operating conditions is also difficult because of the large sensitivity of NO_x to small (but real) variations in these operating conditions.

Figure 2(b) shows a similar comparison of measured and calculated NO_x data, from 15 additional tests with natural gas, in this case, from two sizes (three boilers) of single-wall-fired boilers. Here the agreement between calculated and measured data is very poor for all but the two tests involving staged combustion. Of the data from tests with all burners active, on the average the calculated NO_x levels are higher than the measured levels by about 430 ppm. As in the previous study [1], concerning these particular boilers, the measured combustion air temperatures could be in error (too high). This is partially substantiated by the fact that the two cases of staged combustion (involving low combustion temperature rise resulting from the rich air-fuel mixture) show good agreement between calculated and measured NO_x levels. Also, it will subsequently be seen that this error is almost identical in the data from these same boilers when fired with oil fuels. Attempts in this and the previous study to correlate data from these boilers with that from the opposed-fired boilers have never been successful. Once again, no explanation other than the possibility of input data error could be found.

5.2.2 Oil Fuel

As mentioned in Section 4.3.4, NO_x generated in the active burner region with oil fuels could be partly generated in the sub-region dominated by the slow gasification of the liquid fuel or in the subregion more controlled by the burner operating conditions. Figure 3(a) shows a comparison of the measured NO_x levels with those calculated from the sum of the thermal NO_x contributions, from the active burner region and the final mixing zone, and the conversion of the fuel-bound nitrogen (with all term coefficients equal to one and with no additional constant) from the 30 (appropriate) tests in the opposed-, oil-fired boilers. Much of the data is in good agreement but there is a tendency to calculate excessively high NO_x levels at the lower end of the range. On the average, the calculation is about 50 ppm too high. The average deviation of the data about that corrected calculation (+50 ppm) is 44 ppm.

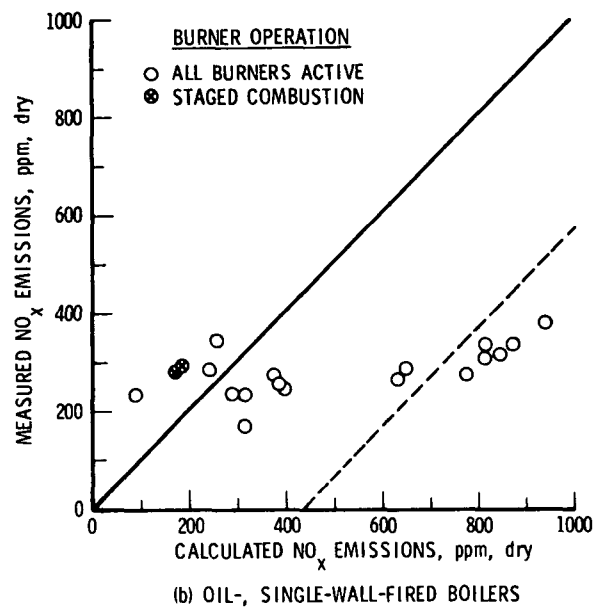
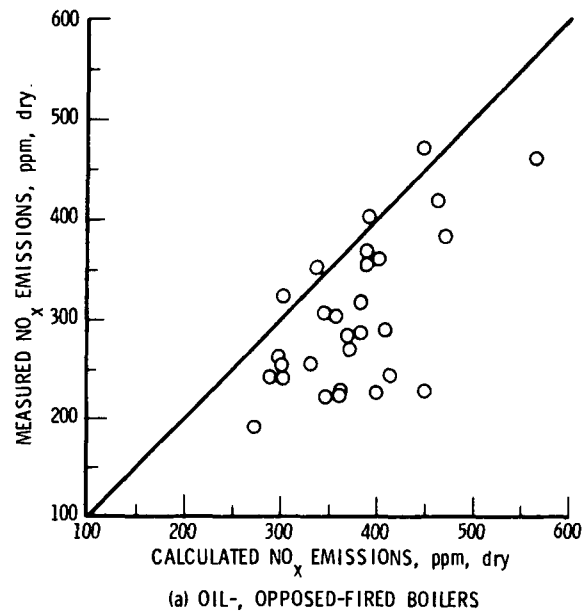


Figure 3. Comparison of calculated and measured NO_x emissions.

The apparent error in the calculation is not considered significant at this point because the NO_x contribution from the active burner region is rather strongly affected by the relatively unknown liquid vaporization rate and the assumption of the fraction of the vaporized fuel burning under stoichiometric conditions during the vaporization period. As discussed later in this report (Section 5.3), the thermal NO_x calculated to be formed in the active burner region could be reduced 50 ppm by, for example, increasing the distance for complete vaporization by about 5 percent. No effort was made to further tune the calculation.

Figure 3(b) again shows data from the two sizes (four boilers) of the single-wall configuration, analogous to Figure 2(b) but in this case firing oil fuel. Again, some of the calculated data agrees rather well with the measured, but with another group of data the calculation is high by about the same amount as with the natural gas fuel (430 ppm). Again, these data showing the large error involve the higher combustion air temperatures and lower air-fuel ratios, leading to maximum combustion product temperatures. The two tests involving staged combustion also both involve high combustion air temperatures, but the calculation shows a low NO_x level because of the fuel-rich combustion.

The cause of the large calculation error in some oil-fired, single-wall boiler data, then, as in the case of natural gas fired in these same boilers, could be errors in the measured combustion air temperatures. These temperatures were actually measured at the outlet of the air preheater, not in the burners, and were measured in only a small fraction of the tests. If the actual combustion air temperatures in the burners during these tests were lower by 5 to 30 K (10 to 60 °F), the calculated NO_x would also show good agreement with the measured NO_x .

5.2.3 Coal Fuels

Comparison of measured NO_x data from the coal-fired boilers with the calculated values, using term coefficients of 1.0 and no constant, immediately shows the problem with the calculated contribution of NO_x from the active burner region. While the total measured NO_x in the flue gases range from 200 to 600 ppm and the contributions from the final mixing zone and from the conversion of fuel-bound nitrogen appear quite reasonable and normal, the calculated NO_x contributions from the active burner region range vary widely, from as low as about 200 to more than 8000 ppm.

It seems quite possible, as with the oil fuel, that varying the constants describing the distance into the furnace for complete gasification and the fraction of the gasified fuel in a stoichiometric flame could reduce these calculated contributions to acceptable levels. However, the regression analysis (Table 3) consistently indicated that the

contributions from the variable portion of the active burner region should be neglected (a derived coefficient for the active burner region term essentially equal to zero) for all coal-fired boilers and, in the case of the tangential boilers, that the contributions from the constant portion of the active burner region should also be zero. The constant portion in coal-fired, single-wall boilers appeared to be significant. In the interest of time (in the study), therefore, no effort was made to empirically adjust the finite rate gasification and mixing constants for the coal fuels. Instead, the coefficient of the active burner region term was simply taken to be equal to zero for all coal-fired boilers of all configurations. The constant portion was also taken to be equal to zero for the tangential boiler. The constant portion appropriate to the single-wall-fired boilers was established directly from the resulting calculated and measured data comparison.

This conclusion implies that: (1) in single-wall, coal-fired boilers, essentially all of the thermal NO_x generated in the active burner region is generated, while the coal is gasifying, in a region where the combustion and thermal NO_x formation conditions are largely controlled by the transient gasification and mixing processes rather than by the active burner operating conditions (a not too surprising conclusion); and (2) in tangential boilers, the thermal NO_x generated in any portion of the active burner region is negligible compared to NO_x generated by conversion of fuel-bound nitrogen (a somewhat surprising result).

The conclusion relative to the single-wall boilers is somewhat different from that reached in the previous study [2]. Although both studies identified a relatively constant level of thermal NO_x , independent of burner operating conditions, and this constant level was almost exactly the same (125 ppm in the previous study and 127 ppm here), the previous study indicated that this NO_x was thought to be generated in the final mixing zone.

Figure 4(a) shows a comparison of the measured and calculated NO_x data for the two coal-fired single-wall boilers. A constant level of 127 ppm as the total NO_x contribution from the active burner region best fits the data comparison (the constant of 260 ppm determined by the regression analysis for these boilers undoubtedly partially accounts for random data scatter). The figure again shows reasonable agreement between measured NO_x levels and those calculated using a coefficient of zero for the active burner region term, 1.0 for the final mixing zone and fuel-bound nitrogen terms, and a constant level (ascribed to the active burner region) of 127 ppm. There appears to be a tendency for the calculation to be low at the low and high ends of the NO_x range. The average deviation for all of the data is 45.6 ppm. Neglecting the three tests at the very low calculated level, the average deviation would be 43.8 ppm.

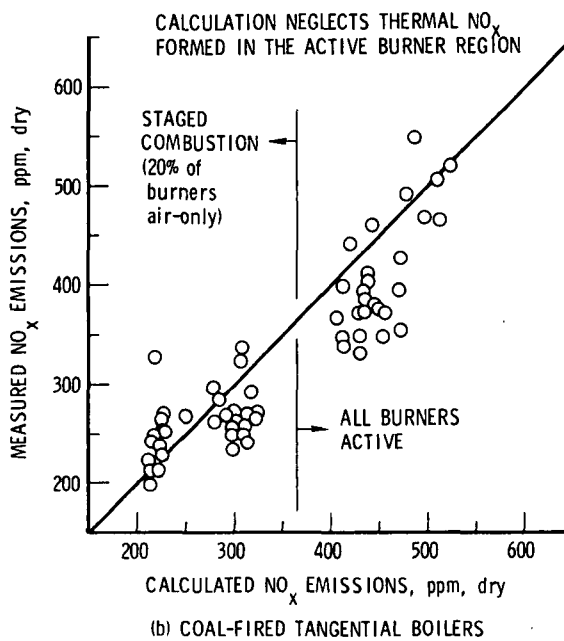
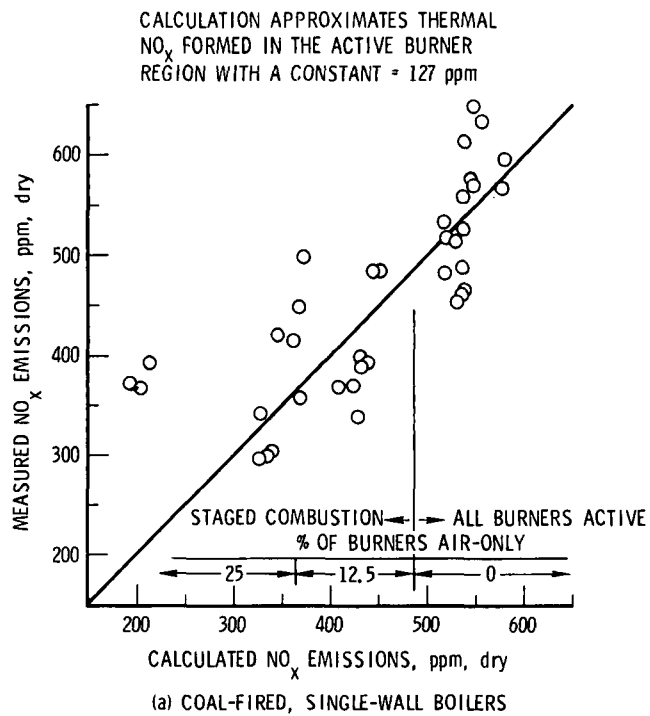


Figure 4. Comparison of calculated and measured NO_x emissions.

Figure 4(b) shows a comparison of the measured and calculated NO_x data for the two tangential boilers firing two types of coal (nominal and high nitrogen, 1.3 and 1.7 percent nitrogen, and 3.1 and 1.7 percent sulfur, respectively). This calculation neglects all NO_x formed in the active burner region and considers only that NO_x from the conversion of fuel-bound nitrogen and the thermal NO_x formed in the final mixing zone. However, that formed by conversion of the fuel-bound nitrogen represents about 95 percent of the calculated NO_x .

Agreement between the measured and calculated data from the 330 MW boiler is excellent. On the average, the calculated values are lower than the measured by only 9 ppm, with an average deviation of 30 ppm. The calculated data for the 360 MW boiler, however, is higher than the measured data by 44 ppm. For all tests, in both boilers (62 tests), the calculated levels are higher than the measured by 26 ppm, and the average deviation is 43 ppm.

Since the calculated NO_x levels are largely due to conversion of fuel-bound nitrogen and this source varies only with the burner air-fuel ratio for a given coal, the two groups of data shown in Figure 4(b) represent: (1) those tests with all burners active (the higher group); and (2) those operating with staged combustion (20 percent, the top row, of the burners operated air-only).

5.3

EFFECTS OF GASIFICATION AND MIXING RATES

As discussed in Section 4.3.4, the finite rate processes of gasification of a liquid (vaporization) or solid fuel have been approximated, in this study, by three parallel regions in the flow from an active burner. These regions (not necessarily physically contiguous) are assumed to contain the following: Region 1, all unvaporized fuel (and no air); Region 2, the fraction FSS^* of the total fuel vaporized up to that point, plus a stoichiometric equivalent proportion of air; and Region 3, all of the rest of the fuel and air coming from the active burner not in the first two regions. The gasification and mixing rate is estimated by selecting the distance DCG^* from the burner exit to some point in the furnace, over which the gasification and mixing is essentially completed.

The fuel and air specie concentrations in each of these three regions are related only to the fuel and air entering the furnace from a particular burner. Therefore, if these gasification and mixing processes are not complete before significant mixing with bulk gases (products of complete combustion from burner levels below the particular burner) begins, then Region 3 cannot exist beyond this point, and

*FORTRAN notation used in the calculation of this study to describe these terms.

it is likely that the stoichiometric flame (Region 2) will be greatly reduced in magnitude. As a result, the three-region gasification and mixing process approximation is carried out only until this bulk gas mixing begins.

With natural gas fuels, the burner flows are already gasified, and mixing is always assumed to be complete, at any burner level, within the burner core flow, before any significant mixing with bulk gases begins. With coal fuels, however, the gasification process takes so long that only at the lowest burner level, where no bulk gases have been generated in a lower burner level, is gasification and mixing complete before mixing with bulk gases begins. Therefore, with coal fuels, attempts to control NO_x by modifying coal particle sizes or gaseous mixing rates (i. e., burner design) will be most effective in burners located low in the burner array. Attempts to carefully control the gasification and mixing rates in the flow field from an active burner located high in the burner array will tend to be disrupted by the gross flow of bulk gases past the burner. On the other hand, burner design changes can be effective at all burner levels with gaseous fuels because the mixing is complete only a short distance into the furnace.

Of the two constants controlling the gasification and mixing approximation in this calculation, the distance DCG can be reasonably estimated from observations of full-scale flames in full-scale boilers. Clearly, maximum liquid droplet or coal particle sizes largely control DCG. The amount of combustion involved in a stoichiometric flame (FSS), however, is not easily estimated. It depends on the dispersion of the particles in the burner flow and the large- and small-scale turbulence in this flow, which, in turn, control the local gaseous mixing rate relative to the gasification rate. If the particles are widely dispersed and the local gaseous mixing rates are high compared to the gasification rates, the stoichiometric flame will be thin and close to the particles and the appropriate FSS will be small. If the particles are closely grouped (in particular clouds) and the local turbulence level and the gaseous mixing rates are low compared to the gasification rates, the region of stoichiometric combustion may be broad and may exist within and outside of the particle cloud. In such cases, the appropriate FSS will be large.

The effects of varying DCG and FSS values on thermal NO_x generated in this region of gasification and mixing are not obvious. By studying the effects of their variation on the various intermediate steps in the NO_x calculation, it appears that the primary effect of distributed gasification and mixing is to provide more time at temperatures where heat transfer (cooling) is appreciable but the NO_x formation is still low. While the temperatures and NO_x formation rates in Region 2, the stoichiometric flame, are always high, the existence of this and Region 1 limits the amount of fuel species in Region 3. The effective air-fuel ratio in Region 3 starts at infinity (no fuel) and slowly

decreases as gasification and mixing proceed. Thus, although oxidizer-rich, the temperature in this region rises relatively slowly. Over a considerable fraction of the particle lifetime, the temperatures in Region 3 are high enough to affect considerable cooling without generating appreciable NO_x (cooling is proportional to the fourth power, while NO_x formation is an exponential function, of the combustion product temperature). With fuel-rich burner operation (staged combustion), the effective air-fuel ratio in Region 3 must eventually pass through stoichiometric, but by this time there usually has been sufficient cooling to significantly reduce the peak NO_x formation rate.

Some parametric calculations were made to investigate the overall effect of variations in DCG and FSS. The opposed-, oil-fired boilers were used for the calculation. Table 5 shows these results. Thermal NO_x contributions from the active burner region are tabulated, with DCG and FSS as parameters. Calculations for two typical full-load tests, with all burners active, are shown in the table.

Clearly, increasing the maximum oil droplet sizes increases DCG, and the table shows that this results in minimum NO_x . Decreasing the gaseous mixing rate (relative to the gasification rate) should increase FSS. The table shows that increasing FSS also minimizes NO_x . Both of these effects, however, are reduced under conditions of staged combustion. The fact that the NO_x shown in Table 5 is sometimes higher with NO_x ports open than closed, for the same DCG and FSS, is correct but would be offset by a lower conversion of fuel-bound nitrogen with NO_x ports open. At least within the range of the variations in DCG and FSS tested, minimum NO_x with oil fuels is achieved with poor atomization (large droplets poorly distributed) in a burner air flow of low turbulence.

Although not specifically run parametrically, the case with coal fuels appears similar. Again, minimum NO_x should result, at least in single-wall-fired boilers, from operating conditions which reduce the coal particle gasification rate and decrease the local gaseous mixing rate. Study of NO_x data from tangential boilers, however, indicates that thermal NO_x formed in the active burner region is usually small. Variations in the gasification and mixing rates, therefore, should have little effect on NO_x in these boiler types.

Apparently, the general principles for NO_x reduction in the active burner region is simply to lengthen the total time to complete gasification and mixing.

5.4 GUIDELINES

The primary objective of this and the preceding studies of NO_x control by combustion modification was to develop guidelines which can be used to guide design and design modifications to minimize

TABLE 5. EFFECTS OF OIL VAPORIZATION AND MIXING
PARAMETERS ON THE THERMAL NO_x GENERATED
IN THE ACTIVE BURNER REGION

Example Cases			
350 MW opposed-fired boiler			
Horizontal depth of furnace = 30 feet			
Full-load operation, all burners active			
		Case 1	Case 2
NO _x Ports		Closed	Open
O ₂ , %		2.98	3.05
CO ₂ , %		13.28	13.40
		NO _x , ppm (dry)	
DCG, ft	FSS, %	Case 1	Case 2
5.5	0.25	450	328
6.5	0.25	219	253
7.5	0.25	95	160
7.5	0.20	159	209
7.5	0.15	258	243

- a. DCG = the distance into the furnace for complete vaporization and mixing
- b. FSS = the fraction of the vaporized fuel involved in stoichiometric combustion over the majority of DCG

NO_x emissions from utility boilers, within the bounds of high plant efficiency, stable combustion, and acceptable levels of emission of other air pollutants. This and the previous studies made use of a complex computer program and engineering model of NO_x formation in, and large samples of data from, full-scale, multiburner utility boilers to develop understanding of the major sources of NO_x in such boilers and to investigate the effects of variations in some of the major hardware and operating conditions on this NO_x. It is not the intent of this or the previous studies simply to provide the final computer program. Rather, the intent is and has been to glean from all of these studies useful information or guidelines on appropriate modifications in hardware and operating conditions which can be directly applied to full-scale, multiburner boilers.

This and the previous studies concluded that staged combustion can effect significant NO_x reductions while maintaining high plant efficiency and acceptable levels of emission of other air pollutants. Staged combustion is defined as fuel-rich operation of the active burners with the remaining combustion air introduced downstream of the active burner region. Analytical techniques were developed to assure stable combustion even with very fuel-rich operation of the active burners. Although staged combustion can affect major reductions in NO_x emissions, in most cases other techniques are necessary to further reduce the remaining thermally generated NO_x emissions.

Although there is little substantiating data in the data sample available to these studies, it appears that reduction of the combustion air temperatures can also be very effective in reducing NO_x emissions. This effect is clearly shown by the analytical calculation. Unless this temperature reduction is achieved by transferring more heat to the steam cycle (reduced flue gas temperature into the air preheater), however, significant plant efficiency losses can result (higher sensible heat losses up the stack).

The data sample available to these studies also did not include data on the effects of flue gas recirculation through the active burners. Analytically, however, these studies indicate that such flue gas recirculation could substantially reduce NO_x with fuels and in boilers where substantial fractions of the total NO_x result from thermal formation in the active burner region (i. e., natural gas fuels, most low nitrogen liquid fuels, and to some extent coal-fired, single-wall boilers). Such flue gas recirculation also should not affect plant efficiency or emissions of other air pollutants but could affect combustion stability. It should have little effect on NO_x from coal-fired or, perhaps, on some oil-fired tangential boilers.

In the previous studies [1, 2], parametric calculations were conducted and reported to show the effects of wide variations of some of the major boiler hardware and operating conditions on the total

NO_x, using term coefficients and constants derived empirically from regression analyses of all of the data. The data used in this study are a subset of those used in the previous study in that all of the so-called off-stoichiometric tests were eliminated. However, since both this and the previous NO_x calculations fit the same data, no specific parametric calculations were conducted in this study. Rather, this study attempts to explain more accurately why certain NO_x variations occur when one or more of the hardware or operating conditions are varied. This also gives more credence to interpolations and extrapolations within and beyond the available data because of the lesser degree of empiricism involved in this study.

The two major differences from the previous study (in the guidelines for reducing NO_x discussed here) result primarily from (1) the observation from the previous study (accepted at the outset of this study) that NO_x levels with staged combustion are equal to or less than those achievable with off-stoichiometric configurations and (2) the observation from this study that a relatively constant level of NO_x (relatively independent of variations in the degree of combustion staging) is apparently thermally generated in that part of the active burner region where the gasification and mixing rates rather than the burner operating conditions control the local air-fuel ratio.

The latter conclusion is different from that reached in the previous studies. This conclusion became apparent with the incorporation of an approximation of the finite rate gasification and mixing processes during this study. Previously this constant level was ascribed to the final mixing zone. This study indicates that the amount of NO_x generated in the final mixing zone in staged combustion is small compared to that generated in the region controlled by the gasification and mixing processes.

5.4.1 Natural Gas Fuel

Figure 2(a) compares NO_x emissions levels measured in the natural gas-, opposed-fired boiler data sample of this study against those calculated by the technique of this study. The calculation involved minimal empiricism (i. e., although the NO_x calculation equation was that set up for data correlation, the term coefficients were taken to be equal to 1.0 and the correlation constant was taken to be zero). Therefore, extrapolation outside of the range of the available data has more meaning and involves less risk than the parametric calculation of the previous studies, which used term coefficients and a constant derived from empirical regression analysis.

With natural gas fuel, the analytical calculation shows that NO_x thermally generated in the active burner region dominates the total NO_x. No NO_x is generated from conversion of fuel-bound nitrogen. In all of the calculations with natural gas fuels, the NO_x thermally generated in the final mixing zone was calculated to be less than 85 ppm, normally between zero and about 35 ppm. NO_x from

the final mixing zone was very sensitive to the combustion air temperature and only reached appreciable levels under full-load conditions. Examination of the calculation for NO_x from the final mixing zone shows that a relatively small reduction in peak temperatures entering this zone should effectively eliminate NO_x from this zone. This could be accomplished by (1) a small reduction in the peak combustion air temperature, (2) use of some flue gas recirculation (entering from any point(s) in the active burner region), or (3) delaying the introduction of the second-stage air as long as possible. More rapid mixing of the second-stage air could also reduce the NO_x from this zone.

Despite the rapid mixing of the natural gas with the combustion air near the burner exit, the calculation indicates that a small region of combustion under stoichiometric conditions will still exist in this mixing region under all overall burner air-fuel ratio operating conditions. Operating the burner very fuel-rich will effectively eliminate thermal NO_x formation in all other subregions of the active burner region. Using the staged-combustion technique alone, then, the calculation indicates that as the burners are operated increasingly fuel-rich the total NO_x levels should decrease to about 180 to 200 ppm (150 to 170 ppm from the active burner region and 30 to 40 ppm from the final mixing zone, with about half of the combustion air diverted to the second stage; the NO_x levels then remain relatively constant for even richer mixtures.

Figure 5 shows a plot of the NO_x data measured in tests of the four opposed-, natural gas-fired boilers (240 and 350 MW) under full-load conditions. The NO_x levels do indeed decrease with decreasing burner air-fuel equivalence ratios, to a level of about 150 to 180 ppm, with about half of the stoichiometric air passing through the active burners. The calculation also indicates that NO_x levels under conditions of overall boiler excess air greater than shown by the data (with all burners active) are also greatly reduced from the peak levels; however, this is not a solution of interest at this point.

It is unlikely that the burners could be operated with much richer mixtures than those shown. It is of interest, however, that these boilers were successfully operated at air-fuel equivalence ratios as low as those shown. Furthermore, they have been continuously operated, with natural gas, for several years at ratios of 0.55 to 0.67, with no detrimental effects on the boilers and with high plant efficiency and negligible emissions of hydrocarbon, smoke, or carbon monoxide.

Also, the possibility of flame liftoff and/or combustion instability with very fuel-rich burner operation is significant. Since most of the remaining NO_x under such fuel-rich burner operation is generated in the very early mixing and combustion region, just downstream of the burner exit, where stoichiometric combustion temperatures are maximum, various methods of reducing this peak temperature

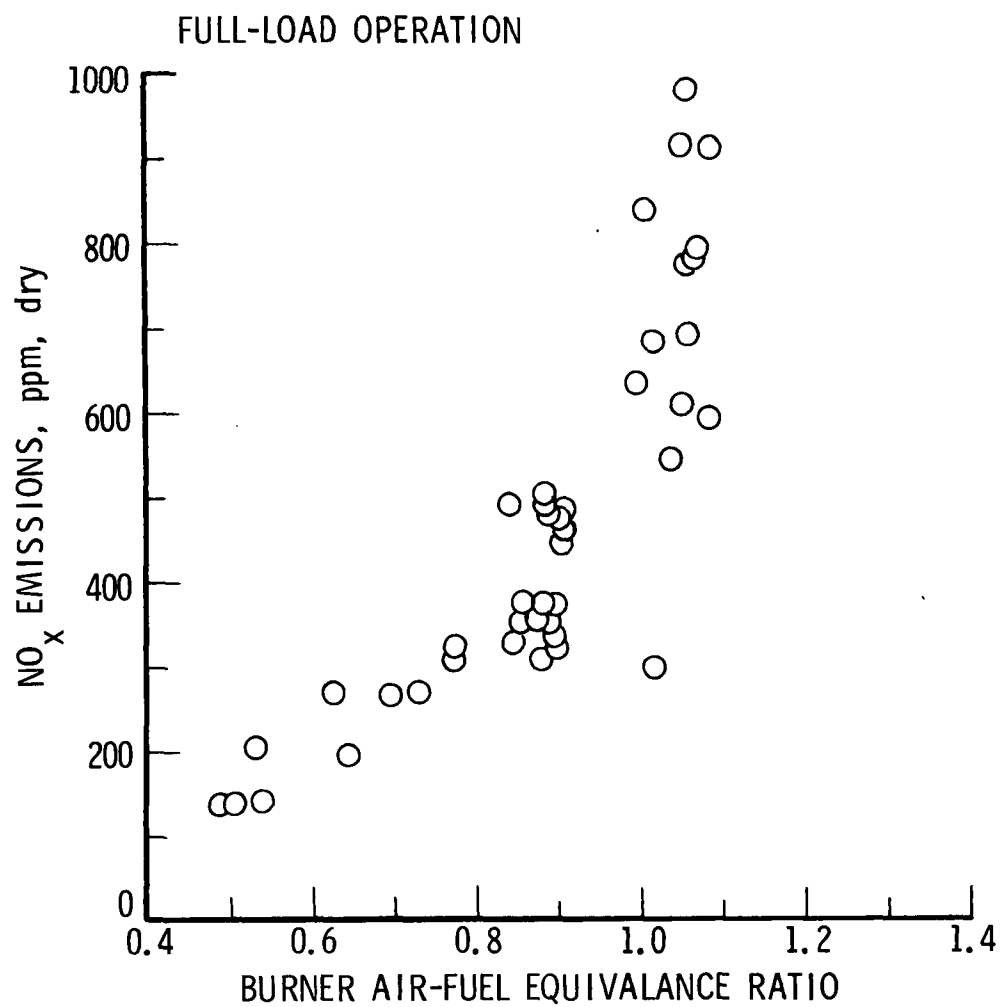


Figure 5. Effects of combustion staging on NO_x emissions: natural gas-, opposed-fired boilers.

are very effective in further reducing this residual NO_x . As in controlling NO_x from the final mixing zone, small reductions in the maximum full-load combustion air temperatures, using water sprays, or flue gas recirculation (in this case directly into the burners or the windbox) can significantly reduce this remaining NO_x . More rapid mixing of the gas with the combustion air should also be effective. Introducing water vapor or recirculated flue gases into an already very fuel-rich burner, however, could increase problems with flame liftoff and/or combustion instability. The use of water sprays would result in increased sensible heat losses up the stack, but the resulting efficiency losses should be small.

5.4.2 Oil Fuel

With oil-fired boilers, the calculation indicates that NO_x generated from conversion of fuel-bound nitrogen is an appreciable fraction of the total emissions levels, ranging from 22 to as high as about 60 percent in the burner air-fuel ratio range near stoichiometric. At this time, there is no known way to minimize NO_x from this source other than to operate with fuel-rich mixtures in the active burner region. Fortunately, this will also reduce much of the thermal NO_x formed in the active burner region.

All of the remarks concerning NO_x levels and reduction techniques in the final mixing zone with natural gas fuels apply to oil fuels as well. In the case of NO_x thermally generated in the active burner region with oil fuels, the problem is again similar to that with natural gas. With burners operated very fuel-rich, to minimize conversion of fuel-bound nitrogen to NO_x , an appreciable concentration of NO_x can be thermally formed in the stoichiometric flames surrounding the vaporizing fuel droplets. With the atomizers, oil fuel, and burners used in the boilers of this study, the calculation indicates that about 200 ppm of NO_x can be generated in this zone (depending on other boiler operating conditions).

Thus, it is anticipated that as increasing fractions of the combustion air are diverted to the second stage, the overall full-load NO_x levels should remain at least 200 ppm above NO_x levels generated from conversion of fuel-bound nitrogen until very fuel-rich mixtures are reached. Figure 6 shows a plot of the NO_x data available to this study from full-load staged combustion tests of the four opposed-fired boilers using oil fuel. As with the natural gas test data, the oil data show the large quantities of NO_x thermally formed throughout the active burner region when its air-fuel equivalence ratio is near stoichiometric. For richer mixtures, the data appear to show a trend to decrease to the expected 200 ppm (at full load), but the data does not extend to sufficiently rich mixtures to verify this lower limit. The dashed line shown in the figure is estimated from the previous parametric calculations (i. e., the calculation does show this limit).

FULL-LOAD OPERATION

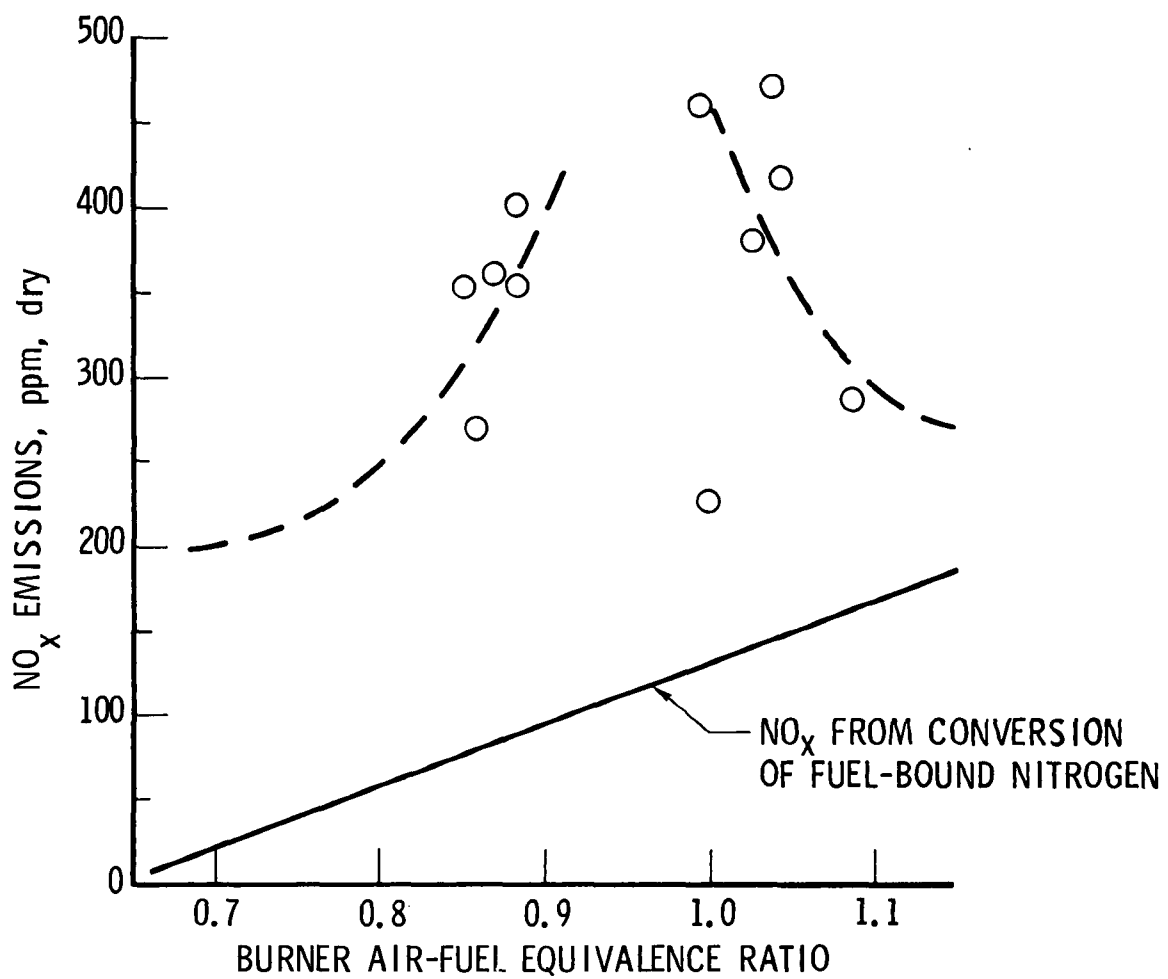


Figure 6. Effects of combustion staging on NO_x emissions: oil, opposed-fired boilers.

Table 5 shows that some reduction of this residual NO_x level could be achieved by reducing the degree of oil atomization and the spray distribution. This will increase the distance DCG, at least, and very likely increase the fraction FSS as well. Both of these trends should reduce the residual NO_x formed in the active burner region. The table indicates that increasing DCG by about 15 percent could reduce the residual NO_x by nearly 40 percent. This could reduce the residual NO_x formed in the active burner region under very fuel-rich burner operation to levels of the order of 120 ppm. Few data, other than the effects shown by parametric variations of DCG and FSS in the calculation of this study, are available to verify this trend.

As with the natural gas firings, the residual NO_x is formed in stoichiometric combustion in the vaporization and mixing region, and it is very sensitive to the peak combustion temperatures. Again, the use of combustion air temperature reduction, water sprays, and/or flue gas recirculation (directly into this flame zone) should reduce this residual NO_x level.

Although the data shown in Figure 6 indicates no staged combustion testing at air-fuel equivalence ratios less than 0.85, these boilers have now been operated for several years with (low sulfur) oil fuels at ratios of 0.55 to 0.7, with off-stoichiometric burner configurations, again with no significant detrimental side effects.

5.4.3 Coal Fuels

General guidelines for maximum reduction of NO_x from coal-fired boilers are in some ways simpler than for the other fuel types. NO_x emissions are usually strongly dominated by conversion of the fuel-bound nitrogen. Presently, no method of reduction of NO_x from this source other than staged combustion is apparent. For both oil and coal, the gasification process is sufficiently slow that some of this nitrogen conversion undoubtedly occurs well out into the furnace. In order to assure minimum conversion of the fuel-bound nitrogen, then, it appears highly desirable that the gasification and mixing processes be completed under the minimum (overall burner) air-fuel ratio conditions. This strongly suggests a staged combustion burner configuration rather than off-stoichiometric configurations. In the latter case, early mixing between adjacent active and air-only burners can raise the local air-fuel ratios and allow some gasification and mixing under hot, oxidizing conditions.

In the case of the coal-fired boilers, the related calculations are somewhat more empirical in that the NO_x levels calculated to be generated in the active burner region are all much too high. Although the calculations used in the data comparisons shown in Figures 4(a) and (b) involve the direct calculation (term coefficients of 1.0) of NO_x from fuel-bound nitrogen and the final mixing zone, the results of

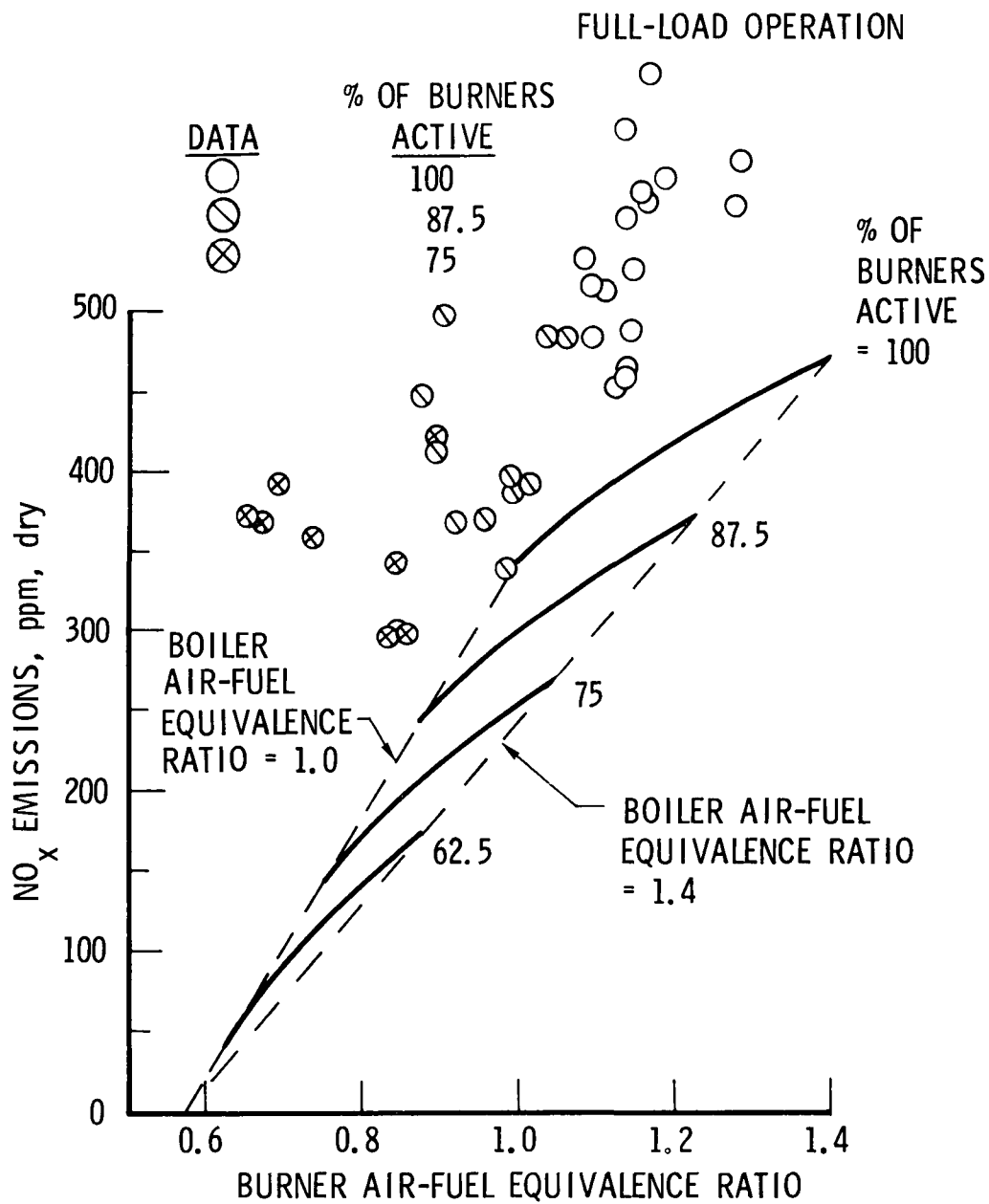
the regression analyses and the direct comparisons with measured data were used to conclude that the coefficients applicable to the term describing NO_x thermally generated in the active burner region should be set equal to zero. Also, with the single-wall boilers (only), the NO_x in the active burner region should be approximated by a constant level (equal to 127 ppm).

The major source of NO_x emissions from coal-fired boilers is from conversion of the fuel-bound nitrogen, and the major combustion modification technique for control is combustion staging. Therefore, the effect of combustion staging on NO_x from conversion of fuel-bound nitrogen is of greatest interest in developing guidelines for total NO_x control. Figure 7(a) shows a typical plot of measured data on overall NO_x emissions, and calculated curves on the NO_x emissions derived from conversion of the fuel-bound nitrogen in the single-wall-fired boilers. Both are shown plotted against the burner air-fuel equivalence ratio.

Combustion staging is accomplished in all of the coal-fired boilers in the available data sample by cutting off the fuel flow to some of the burners in the top burner level(s). Such combustion staging has a different effect on NO_x emissions than does varying the burner air-fuel equivalence ratio by varying the overall boiler ratio with a fixed burner configuration. Therefore, Figure 7(a) shows the calculated NO_x levels with four possible levels of combustion staging (62.5 to 100 percent of the burners active) and the variation of these NO_x levels within each of these four staged combustion configurations resulting from variations of the overall boiler air-fuel equivalence ratio between 1.0 and 1.4. The measured data points (total NO_x emissions) are coded to correspond to the NO_x levels calculated to result from conversion of fuel-bound nitrogen with the same staged combustion configuration. The difference between the data and the related calculated curve is a measure of the amount of thermally generated NO_x .

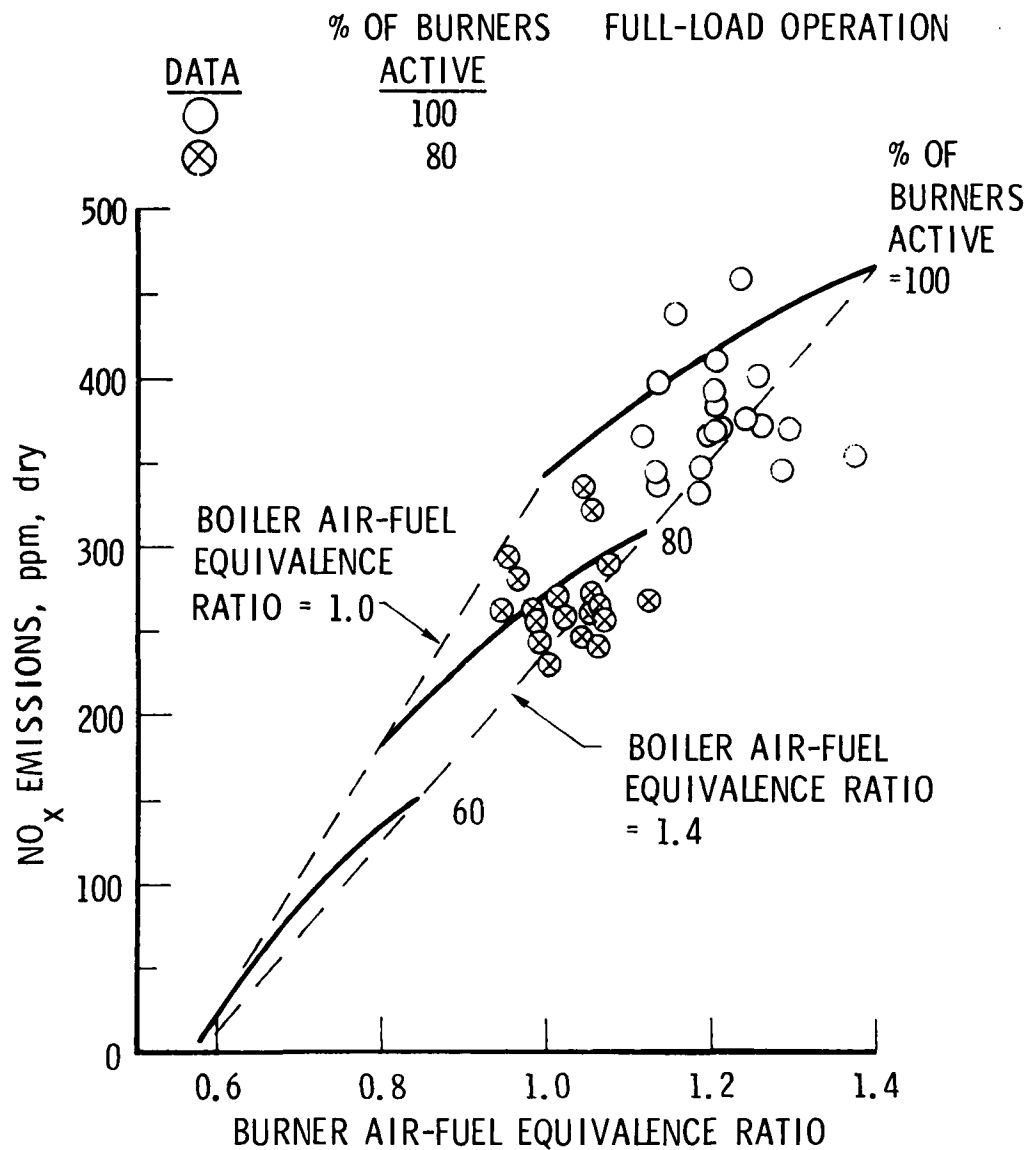
The measured data show a general trend corresponding to that shown by the calculation but are higher than the calculated levels by about the constant 127 ppm discussed in Section 5.2.3. These data are considered to verify the effects of staged combustion on NO_x formed from conversion of fuel-bound nitrogen but do not adequately explain the high levels of thermal NO_x apparently formed in these coal-fired boilers. The trend for the thermally generated NO_x to approach a very low (about 127 ppm) level with very fuel-rich burner operation seems to be reasonably established by most of the data, but the four data points at burner equivalence ratios between 0.6 and 0.8 are in sharp disagreement. While some reasonable conjectures concerning these four tests are possible, none can be verified at this time.

Figure 7(b) shows a similar plot for the 360 MW tangential boiler in the data sample firing the same coal type as was fired in



(a) TWO SINGLE-WALL BOILERS FIRING A NOMINAL COAL

Figure 7. Effects of combustion staging on NO_x emissions.
(Sheet 1 of 3.)



(b) 360 MW TANGENTIAL BOILER FIRING A NOMINAL COAL

Figure 7. Effects of combustion staging on NO_x emissions.
(Sheet 2 of 3.)

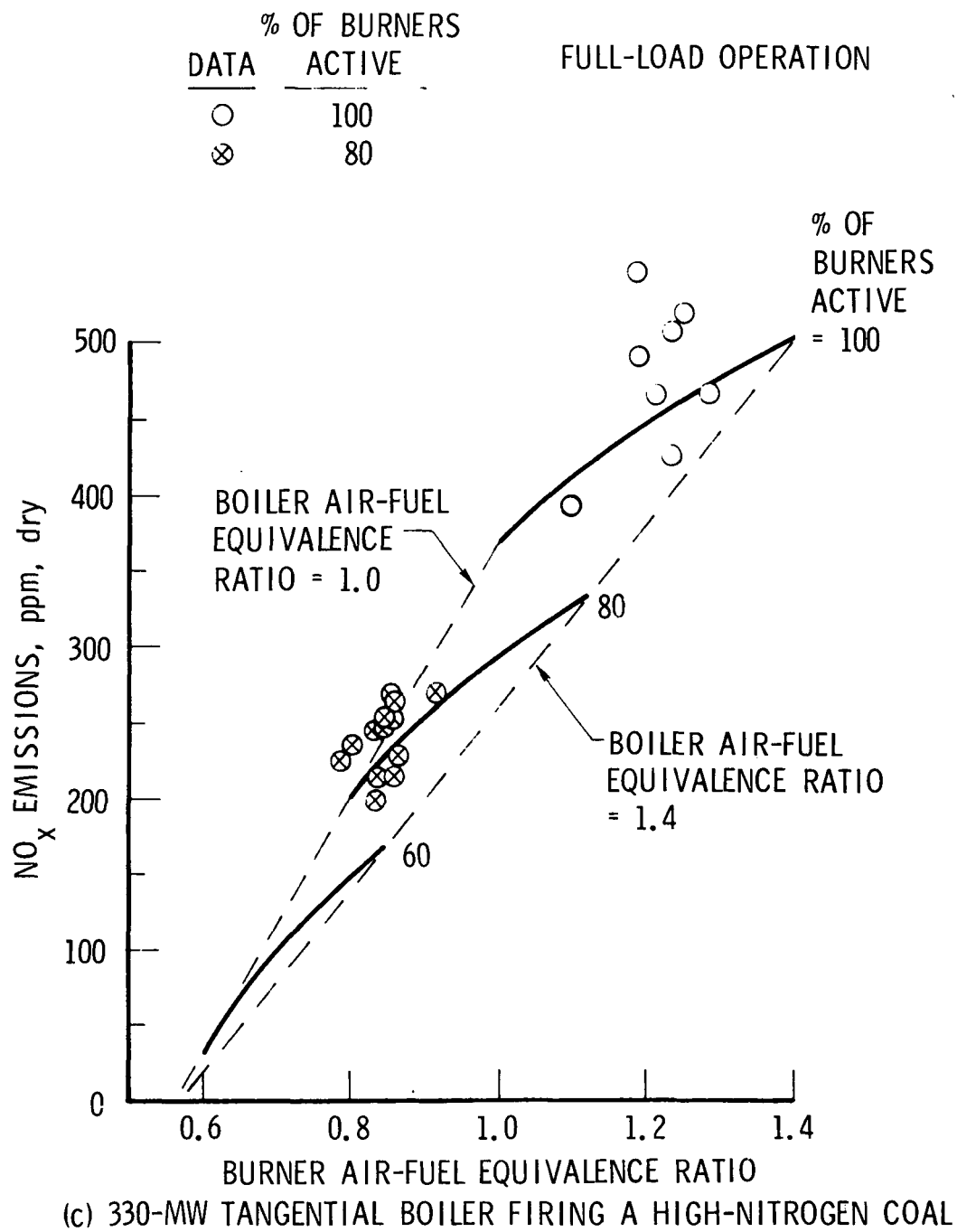


Figure 7. Effects of combustion staging on NO_x emissions.
(Sheet 3 of 3.)

the single-wall boilers. As discussed in Section 5.1, the tangential boiler configuration appears to almost totally eliminate thermally generated NO_x throughout the boiler. The data shown in Figure 7(b) tend to rather closely verify this, grouping about the appropriate calculated staged combustion configuration curves. By extrapolating these effects of staged combustion to a configuration in which only 60 percent of the burners are active, the calculation indicates that NO_x levels ranging from about zero to about 150 ppm could be achieved in this boiler.

Figure 7(c) shows a similar plot of the measured data and the calculated levels with staged combustion in the 330 MW tangential boiler in the data sample. Here, the data is even more directly in agreement with the calculations. Again, the calculated extrapolation indicates that NO_x levels between zero and about 160 ppm (depending on overall boiler excess air) should be possible with 40 percent staging of the combustion air (60 percent of the burners active).

Figures 7(a) through (c) show that staging about 40 percent of the combustion air should reduce NO_x emissions from conversion of fuel-bound nitrogen to very low levels, particularly if the boiler can be operated with low levels of excess air without generating excessive emissions of carbon monoxides, unburned hydrocarbons, and smoke. In tangential boilers, total NO_x emissions should also be very low with any level of combustion staging.

Single-wall, coal-fired boilers apparently thermally generate considerable NO_x emissions as well, possibly despite the degree of combustion staging. This thermally generated NO_x is thought to originate in the subregion of the active burner region where the coal gasification is taking place. Therefore, modifications to reduce the combustion air temperature or the temperature rise due to combustion (by dilution with recirculated flue gases, in the combustion air) may be necessary, in conjunction with the combustion staging, to achieve very low levels of total NO_x emissions in face-fired boilers firing coal fuels.

No data are available on long-term operation of coal-fired boilers with as much as 40 percent of the combustion air diverted to a second stage. Combustion instability may be a problem under such operation but analytical techniques to provide stable combustion are available [4]. The effects of such fuel-rich, reducing atmospheres in the active burner region on the water walls (possible erosion/corrosion) are not well-known but are being investigated in other research programs.

SECTION VI

EXAMPLE APPLICATION OF NO_x REDUCTION GUIDELINES

The reasoning behind the data support and the probable effects of the NO_x reduction guidelines developed in this and the previous studies [1, 2] are discussed in length in Section IV. An example application is shown in this section simply to pull together the various observations and results into a practical demonstration. The example chosen concerns modification of an existing boiler rather than the design of a new boiler.

Only those modifications necessary to minimize NO_x will be discussed. It is clear that some of these modifications will upset, to some degree (believed small), other aspects of boiler operation. These would have to be considered in the final, detailed boiler modification. Nothing in this or the previous study justifies any attempt here to comment on these other aspects of boiler design modifications and operation.

No justification for the boiler chosen is offered. It is simply considered a boiler, currently operated on natural gas fuel, which might one day be converted to oil firing. It has not been fired with oil fuel.

6.1 PRELIMINARY CALCULATIONS

Hardware dimensions and certain operating condition variables pertinent to this study are listed in Table 6. The table shows data both as they exist when firing natural gas fuel and as they might be modified for firing an oil fuel. The boiler NO_x port and burner hardware are essentially unchanged whether firing gas or oil except that a smaller number of oil guns (24) than gas ports (48) are used. This single change affects the (effective) vertical distance between the burners and between the top row of burners and the NO_x ports, the combustion air flow area assigned to each burner (to each oil gun), and the derived values for the furnace mixing zones and the combustion air flow admittances.

Like all tangential boilers, even those without NO_x ports, the design of the burner stack, in each corner of the furnace,

TABLE 6. VALUES OF EXAMPLE BOILER-SPECIFIC INPUT VARIABLES

Variable	Value	
	Gas	Oil
Boiler Geometry		
Horizontal width, ft	39	39
Horizontal depth, ft	34	34
Number of firing walls	4 ^a	4 ^a
Burner Array		
Total number of burners	48	24
Number of burners on a given level	4	4
Vertical distance between burners, ft	1.51	2.81
Horizontal width of a burner, ft	2.50	2.50
Burner air flow area, ft ²	3.78	7.03
NO _x Ports		
Number of ports	4	4
Vertical distance, top burner row to ports, ft	12.2	10.2
Derived Mixing Zone Dimensions, ft		
Primary and recirculation	4.39	5.98
Secondary	9.07	8.54
Adjacent/opposite	18.15	17.09
Air Flow Admittances, lb _f ^{1/2} -ft/sec		
Air-only burner	6.58	12.22
Active burners	6.58	12.22
NO _x ports	10.86	16.50

a. Four corners of a tangentially fired boiler

Units Conversion

meters = 0.3048 x (feet)

Kilograms = 0.4535 x (pounds)

effectively yields some builtin overfire air, or equivalent NO_x ports. This is because each fuel port is bracketed, above and below, by approximately equal combustion air ports. For a vertical stacking containing n fuel ports, therefore, there are $n+1$ combustion air ports. The main effect of this is to reduce the amount of combustion air associated with each fuel port to an $n/(n+1)$ fraction of the total. Thus, the air-fuel ratio existing throughout the active burner region, even with all burners active and no NO_x ports, is $1/(n+1)$ lower than the overall boiler air-fuel ratio. The remaining $1/(n+1)$ of the combustion air is then admitted through the top combustion air port in an effective second stage. In this example study, this effective overfire air is lumped with the air admitted through the NO_x ports. With the gaseous fuel (12 fuel ports in a vertical stack), this additional overfire air would represent $1/13$ of the total burner air. With oil, the additional overfire air would be $1/7$ of the burner air. This is the reason that the admittance to air flow through the effective, lumped NO_x ports listed in Table 6 is considerably larger with the oil fuel than with the gas. The vertical distance between the top row of burners and the effective NO_x ports is different for this same reason.

There was insufficient data available for this study to accurately calculate actual air flow admittances either for the NO_x ports or the burner air. The admittances listed in Table 6 are estimates. Their ratios, however, were established to correspond to the estimated air flow distribution between burners and NO_x ports. The air flow through all air ports in the burner stack was taken to be equal for all ports, whether or not the associated fuel port was active, and the air flow through the actual, designated NO_x ports was taken to be 5 percent of the total boiler air.

Not shown in Table 6, but necessary to the subsequent NO_x calculations, were data on the performance of the air-preheater. These data showed that, at the 320 MW level used for this example calculation, the temperature of the flue gases entering the air preheater when firing natural gas fuel, is 636K (685°F) and that of the combustion air leaving the preheater is 572K (570°F). No data were available with which to estimate the changes in the temperatures of the combustion air between the air preheater exit and the burners. It was estimated that a 28 to 56K (50 to 100°F) drop could occur.

6.2 MODIFICATION FOR MINIMUM NO_x

When firing this boiler with nitrogen-bearing oil fuels, a significant amount of NO_x emissions could be expected from conversion of the fuel-bound nitrogen. All of the studies to date, however, indicate that if the boiler is modified to operate with staged combustion such that the air-fuel equivalence ratio in the active burners is of the order of 0.6 to 0.7, NO_x from this source should be virtually eliminated, regardless of the nitrogen concentration in the fuel. Using the calculations

of this study (a relatively small extrapolation from available data), a design burner air-fuel equivalence ratio of 0.638 was chosen. Considering the burner and NO_x port admittances listed for oil in Table 6, this burner air-fuel equivalence ratio could be achieved, with the boiler operating with excess air equivalent to 3 percent oxygen, by operating the top two levels of burners (8 burners) air-only (16 active burners) and by restricting the NO_x ports such that the admittance of an equivalent NO_x port (in one stack) is 15.33, rather than the 16.50 listed in Table 6.

This low burner air-fuel ratio not only will minimize NO_x from conversion of fuel-bound nitrogen but will also virtually eliminate any thermal NO_x formation in the active burner region except that which might be formed in the subregion where fuel vaporization takes place. In the equilibrium products of combustion from air-oil mixtures with air-oil equivalence ratios less than about 0.7, both the very low oxygen concentrations and the very low combustion temperatures result in extremely low NO_x formation rates by the thermal mechanism.

This leaves the final mixing zone and the subregion of fuel vaporization and mixing as the only remaining sources of significant (thermal) NO_x . Flue gas recirculation (into the combustion air) and/or reduction in the combustion air temperature should minimize NO_x from both of these regions. The data from coal-fired tangential boilers indicate that thermally generated NO_x in any part of the active burner region should be negligible. No similar data are available from oil-fired tangential boilers, however, and, therefore, to be conservative, the calculation appropriate to face-fired boilers was used in this example.

The question of the actual temperatures of the flue gases and the combustion air in the burners of this example boiler is not resolved. For this example calculation, it was simply assumed that the temperatures of both the flue gases and the combustion air at the burners will be reduced by 94K (170°F). This temperature reduction was selected on the assumption that (1) up to 56K (100°F) reduction could already be occurring as a result of heat losses in the ducting between the air preheater and the burners and (2) an additional 39K (70°F) reduction is necessary to reduce the stoichiometric combustion temperature of the oil fuel to that of natural gas. That part of the 94K (170°F) temperature reduction which is not accounted for in the ducting losses should be accomplished by transferring more heat to the steam cycle (perhaps in the economizer section) to avoid increasing sensible heat losses up the stack. Suitable modifications in the preheater operation and performance may be necessary. The resulting temperatures of these gases at the burners, then, were taken to be 478K (400°F) for the combustion air and the recirculated flue gases, respectively.

With these temperatures, and the other burner, NO_x port and boiler operation modifications, the necessary amount of flue gas recirculation was treated as a parameter to calculate the remaining total NO_x emissions. The temperature reduction and the introduction of even small amounts of recirculated flue gases virtually eliminate any NO_x which might be thermally generated in the final mixing zone. The very fuel-rich operation of the burners virtually eliminates NO_x generated from conversion of fuel-bound nitrogen or thermally generated in any part of the active burner region, except in the subregion involving vaporization and mixing. The entire parametric calculation involving the amount of flue gas recirculation, is reduced to a calculation of the NO_x thermally generated in the subregion of vaporization and mixing.

Results of this calculation are shown in Figure 8. Also shown are results of similar calculations for the existing configuration firing natural gas fuel. The natural gas calculations are included to show the strong effect of a reduction of 56K (100°F) in the gas temperatures, as well as to provide a reference with which existing data can be compared.

Figure 8 shows a strong reduction of the NO_x emissions with increasing flue gas recirculation. In the most stringent case, involving a new oil-fired boiler located in the Los Angeles area, NO_x regulations for a 320 MW boiler require that NO_x emissions be less than about 37 ppm. To achieve this level with the oil-fired boiler configuration and operating conditions described would require flue gas recirculation into the burner air equal to 11.8 percent of the burner air (no flue gas recirculation into the NO_x port air is required). This would amount to about 11.2 percent of the total combustion air. The same NO_x level could be reached with natural gas fuel using flue gas recirculation equal to 10 to 14 percent of the burner air. While data on the NO_x emissions from this boiler when fired with natural gas are not currently available to this study, it appears that levels of the order of 35 ppm have been reached, but about 30 percent flue gas recirculation was required.

6.3

SIDE EFFECTS

The example case of modification of an existing boiler design for the purpose of NO_x reduction results in operation with (1) NO_x ports open, (2) one-third (the top two levels) of the burners operated air-only, (3) about 70 to 120°F reduction in combustion air and recirculated flue gas temperatures, and (4) recirculation of flue gases into the burner air in amounts equal to about 12 percent of the burner air.

From the standpoint of plant efficiency, face-fired boilers have been operated with oil fuel under such fuel-rich burner conditions

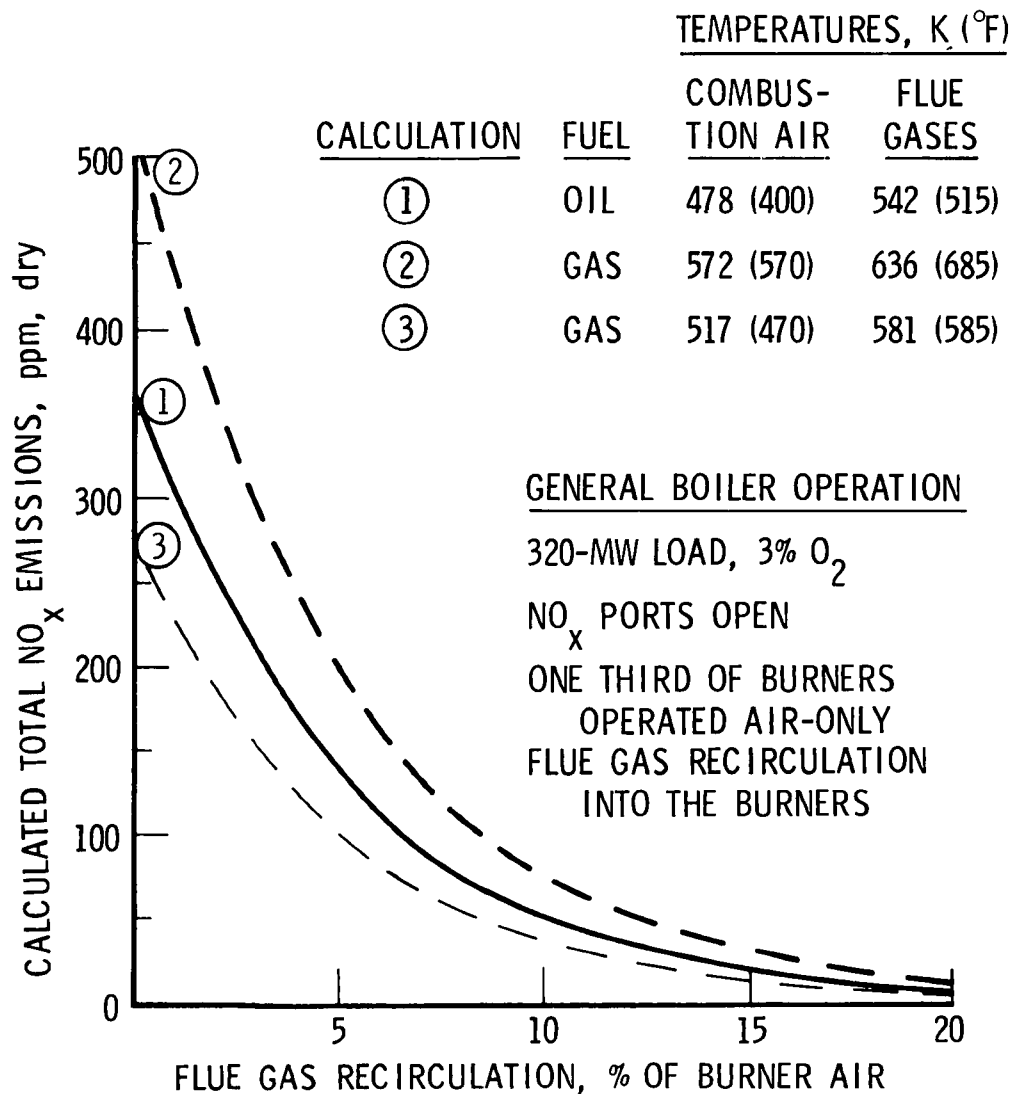


Figure 8. Parametric calculations to determine the necessary flue gas recirculation in the example boiler.

with no observable reduction in overall plant efficiency. Some evidence of combustion instability has been observed under such fuel-rich burner conditions, but analytical techniques are available [4] to provide stable combustion. Similarly, with adequate excess air in the second stage (3 percent O_2 or greater), no problems with excessive emissions of carbon monoxide, unburned hydrocarbons, or smoke are apparent. Face-fired boilers have been operated for some time with very fuel-rich first stage combustion of oil and natural gas fuels, with no apparent detrimental effects to the water walls. Thus, the modification for the very fuel-rich burner operation does not appear to create any new and undesirable side effects.

The reduction in combustion air temperatures would cause a small loss in plant efficiency if it were accomplished simply by transferring less heat in the preheater and allowing hotter gases to escape up the stack. If it is accomplished by transferring more heat to the steam cycle as recommended, however, no efficiency losses are expected.

The combination of very fuel-rich burner operation, reduction in combustion air and recirculated flue gas temperatures at the burners, and the introduction of recirculated flue gases into the combustion air, together, could cause some flame liftoff and/or combustion instability problems. There is little experience with this kind of fuel-rich, lower combustion temperature burner operation. In theory, the very fuel-rich operation should increase the tendency for combustion instability, but the lower reactant temperatures and the dilution of the heat release rate per unit volume flow should decrease this tendency. All three of these modifications should make flame-holding more difficult. Thus, possible problems in both combustion instability and flame liftoff should be anticipated, at least until tests indicate no problem.

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16. ABSTRACT The report represents the conclusion of 4 years of analysis of large quantities of emissions, operating conditions, and boiler configuration data from full-scale multiple-burner, electric-generating boilers firing natural gas, oil, and coal fuels. The overall objective of the study was to develop from this data: (1) further understanding of the effects of combustion modifications on combustion, and the resulting effects on NO _x emissions; and (2) directly applicable guidelines for the application of combustion modification techniques for the control of NO _x emissions in full-scale operating utility boilers. The report includes: (1) discussion of modeling techniques used to analyze the data; (2) conclusions relative to the sources of NO _x within the furnace; (3) guidelines for NO _x reduction; and (4) an example application of the guidelines. Boiler firing types include single-wall, opposed and tangential configurations. The report concludes that NO _x emissions are generated, in varying degrees, from conversion of fuel-bound nitrogen (the predominant source), heterogeneous combustion and mixing zone, second-stage mixing zone, and active burner region. Maintaining very fuel-rich initial combustion conditions, holding the initial peak combustion temperature to <2050 K, and delaying fuel gasification and mixing until the gas has been cooled somewhat should reduce NO _x emissions from all four main sources.			
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Emission	Plants	Utility Boilers	10B
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