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ANALYSIS OF TEST DATA FOR NO_x CONTROL IN COAL-FIRED UTILITY BOILERS



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ANALYSIS OF TEST DATA
FOR NO_x CONTROL
IN COAL-FIRED UTILITY BOILERS

by

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ABSTRACT

This report describes The Aerospace Corporation analyses of a large quantity of emissions, operating conditions, and boiler configuration data from full-scale, multiple-burner electric-generating boilers firing coal fuel. It is a companion publication to a previous Aerospace report on similar analyses of data from natural gas- and oil-fired utility boilers conducted for the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina ("Analysis of Test Data for NO_x Control in Gas- and Oil-Fired Utility Boilers," EPA-650/2-75-012, January 1975). Objectives of this study, as of the previous study, include (1) evaluation of the effects of combustion modifications on NO_x emissions, in fundamental combustion terms, and (2) evaluation of techniques for further reductions in NO_x emissions. The report includes the following results pertaining to coal-fired utility boilers: (1) discussion of the major sources of NO_x emissions; (2) parametric investigations of the effects on NO_x emissions of two-stage combustion, burners out of service, combustion air temperature, and excess air reduction; (3) discussion of probable short- and long-term hardware and operating condition modifications likely to yield further significant reductions in NO_x emission in coal-fired boilers; and (4) general comparisons of NO_x reduction techniques in utility boilers firing coal, oil, and natural gas fuels. A total of 186 tests conducted on eight utility boilers firing four significantly different coal types was used in the analysis. Boiler firing types included single-wall, opposed, and tangential configurations.

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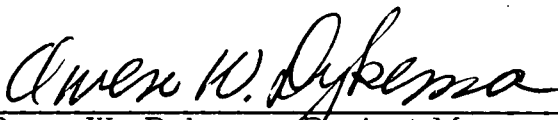
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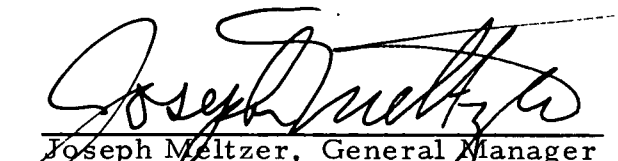
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FOREWORD

This study is a continuation of a previous Aerospace effort reported in "Analysis of Test Data for NO_x Control in Gas- and Oil-Fired Utility Boilers" (EPA-650/2-75-012, January 1975). The data analysis technique developed in that program is applied in this study, with some modification, to coal-fired utility boiler NO_x control test data.

The study reported herein was conducted for the U.S. Environmental Protection Agency, Combustion Research Branch, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, during the first year of a three-year continuing grant. (The previous study of gas- and oil-fired utility boiler test data was conducted under a separate EPA Grant No. R-802366 for this same EPA office.) The current study is primarily concerned with NO_x control methods and does not specifically address the possible limitations imposed on NO_x reduction by other undesirable side effects. However, the second year of the current grant includes analysis of combustion and flame instability mechanisms and the effects of combustion modifications, for the purpose of NO_x reduction, on plant efficiency. These are three side effects that can represent real, practical limitations on NO_x reduction.

A brief introduction and a summary of results of this study are contained in Section I. Section II describes the analysis of NO_x reduction techniques for coal-fired boilers, and includes a discussion of comparisons of NO_x control techniques for coal-, oil-, and natural gas-fired utility boilers. The appendixes include greater detail on some of the more important aspects of the study. More complete understanding of the analysis approach requires reference to the report on the previous study mentioned above. An overall view of the two years of study conducted by Aerospace on NO_x reduction in utility boilers may be found in a paper by O. W. Dykema and R. E. Hall in the proceedings of the EPA Symposium on Stationary Source Combustion, EPA-600/2-76-152c.

SECTION I

EXECUTIVE SUMMARY

1.1 CONCLUSIONS

Major conclusions from this study of oxides of nitrogen(NO_x) control data from coal-fired utility boilers, which appear well supported by the data shown and discussed in Section II of this report, are listed below.

- a. Test data available to this study show that NO_x emissions as low as 200 to 250 parts per million (ppm) have been reached in full-scale coal-fired utility boilers by using combustion modification techniques. Results of this study indicate the potential for significant reductions beyond this point by further application of simple combustion modifications. However, this further reduction can only be demonstrated through full-scale testing, during which any limiting side effects would be evaluated (see Section 1.2, Recommendations).
- b. Conversion of fuel-bound nitrogen to NO_x appears to be the dominant source of NO_x emissions in coal-fired utility boilers. In the normal firing configuration, with all burners active, this source appears to contribute 60 to 92 percent of the total measured NO_x emissions.
- c. Reduction of NO_x derived from the fuel-bound nitrogen, at least with the combustion modifications represented in the data of this study, can only be accomplished by providing a fuel-rich environment in the furnace regions where the initial

hydrocarbon reactions are taking place. As a minimum, this implies that some of the combustion air must be diverted away from the active burners, the fuel flow increased in the active burners, or both. The main unknown in this combustion modification, as well as an area where practical, effective solutions to NO_x from fuel-bound nitrogen conversion may be found, is in the definition of where in the furnace and where relative to the burning coal particles the appropriate initial hydrocarbon reactions are taking place. In this study, the assumption was made, and the data tend to indicate, that these appropriate reactions are occurring over the full distance from the burner exit to burnout of the coal particles and in the local product gases rather than exclusively in a stoichiometric flame surrounding the individual coal particles.

- d. Biased-firing burner array configurations with the air-only burners concentrated in the top levels, or elevations, of the burner array yield lower total NO_x emissions (with coal fuels) than configurations with the same number of air-only burners located elsewhere in the array. Although it is difficult to substantiate, with available data, the separate effects of these configurations on conversion of fuel-bound nitrogen and on thermally generated NO_x , it appears that the former configurations always yield lower conversion of fuel-bound nitrogen than the latter and probably yield equal or lower thermally generated NO_x .
- e. A substantial portion (8 to 20 percent) of the total NO_x emissions generated in boilers where fairly large numbers of air-only burners are concentrated in the top levels of the burner array appears to be thermally generated in the final mixing zone where the remaining excess air, from the air-only burners, is mixed with the gases resulting from fuel-rich combustion in

the active burner region. Reduction of NO_x from this final mixing zone requires reduction of the average temperature in the zone by reduction of combustion air (and fuel) temperature, by use of a coal with a low combustion temperature rise, or by increased cooling of the combustion gas enroute to this final mixing zone. (The remaining 0 to 20 percent of the total NO_x not discussed in conclusions b and e is thermally generated in the active burner region.)

- f. Reduction in the overall boiler excess air, with most burner array configurations, results in reduction of NO_x emissions. A significant reduction in NO_x with all burner array configurations, however, appears to result if the overall boiler excess air is reduced until carbon monoxide emissions become large. There appears to be a direct effect of carbon monoxide in the flue gases on NO_x .
- g. A general comparison of conclusions of this study of NO_x control data from coal-fired utility boilers with those reported in the previous study of data from oil- and natural gas-fired boilers indicates that the same general combustion modification techniques for NO_x reduction, involving the use of NO_x ports, burners-out-of-service and combustion air temperature control, apply with all three fuels. Specific hardware and operating conditions to achieve minimum NO_x emissions with each of these fuels depend primarily on the concentration of chemically bound nitrogen in the fuel and on the physical state of the fuel. These specific differences are discussed in Section 2.3.

RECOMMENDATIONS

Results of this study indicate that full-scale testing should be conducted, not only to verify the trends in NO_x reduction indicated by this study but also to evaluate any limiting side effects. Such testing should include the following combined combustion modifications:

- a. Reduce overall boiler excess air until carbon monoxide emissions become large and limits because of excessive carbon monoxide or smoke are encountered.
- b. Provide a separate path into the boiler for more than 25 percent of the combustion air, preferably through NO_x ports located as high in the boiler as possible, but alternatively through, or supplemented by, air-only burners concentrated in the top levels (one or more) of the burner array.
- c. Reduce the temperature in the final mixing zone. The only directly applicable method of reducing this temperature (in a given boiler firing a fixed coal type) within the data of this study is to reduce the combustion air temperature. Simply reducing the heat transfer efficiency of the air preheater, of course, can result in significant efficiency losses. Some means (such as an additional economizer stage) must be provided to transfer more heat from the flue gases to the steam cycle prior to entering the preheater.

The above recommendations for full-scale testing address what appear to be the major variables that affect NO_x emissions from coal-fired boilers in terms of the combustion modifications present in the data sample analyzed. To the degree that the effects of these combustion modifications are properly interpreted, other modifications can be postulated that would be expected to accomplish the same result but have not been demonstrated, at least within the data sample of this study.

Requirements for the reduction of NO_x emissions from large utility boilers were established at a time when only general guidelines concerning the desired combustion conditions for minimum NO_x generation were available from laboratory research. Methods of operating a boiler or necessary hardware modifications to provide those combustion conditions in a full-scale, multiple-burner boiler were not clearly established. Analytical and experimental research in this area continues today. As is often the case in rapid technology development, the hardware and operating sides of the industry were required to achieve certain goals using limited guidelines supplemented by the conventional, effective method of "cut-and-try." A vital part of the iterative research and development process is the feedback to research of the results of this full-scale testing, both to provide evaluation of the initial guidelines developed as well as to provide a new source of information to guide further research and development.

The problem of describing and controlling the combined aerodynamics, reaction, and heat transfer within the reaction section of a full-scale combustor is highly complex and involves a large number of independent variables. A reasonable analysis of full-scale test results, then, requires a fairly large number of tests in which all of the significant variables are varied, even though the significance of the variables cannot be easily assessed before the results are analyzed. The large number of variables and the resulting large number of tests required for analyses dictate the use of a computer, at least until the major variables can be identified and the analysis simplified.

A widely used method of analysis of large data samples is called multiple regression analysis. This is very similar to the least squares fit technique often used to develop simple relations between single dependent and independent variables from data except that in this case the computer program is used to least squares fit a single dependent variable simultaneously to a large number of independent variables.

A powerful and easily used form of this analytical tool for the study of NO_x control results if the independent variables that are thought to significantly affect NO_x emissions are grouped, in roughly quantitative ways, to define a new set of independent, composite variables each of which affect NO_x in a linear way. A single, linear equation for NO_x can then be written, and the simpler linear regression analysis technique can be used. This is particularly necessary in studying NO_x control because thermally generated NO_x is known to be a highly nonlinear function of local air-fuel ratios and is exponential in temperature. The advantage of such an approach to NO_x data analysis is that most of the unknown quantities in the relations of NO_x to the large number of fundamental variables can be lumped into the coefficients of these grouped, linear terms, and these coefficients then can be determined empirically in the linear regression analysis of the data.

This approach, then, was the one taken in this analysis of test data for NO_x control in utility boilers. A rough model of mixing in large, multiple-burner utility boilers was constructed to provide estimates of the air-fuel ratios and temperatures in a large number of mixing zones. NO_x emissions generated in each type of zone were then calculated, using a Zeldovich-type of NO_x formation rate equation for thermally generated NO_x and a unique model for conversion of fuel-bound nitrogen to NO_x . The resulting equation consisted of eight terms describing thermal NO_x generated in eight types of mixing zones in the boiler, one term to calculate the NO_x generated from conversion of fuel-bound nitrogen, and a constant (necessary for the linear regression analysis). The linear sum of these ten terms represents the NO_x emissions from the boiler.

The calculation of the values of each of these terms (except the constant) for each test condition is complex and requires a computer program. By means of input of relatively detailed information on boiler geometry, burner array configurations, and operating conditions, however, any number of fundamental variables, singly or in combination, can be investigated parametrically. In this manner, the entire approach can be evaluated (by comparison of data with the parametric calculations), the major variables

determined, and general approaches to NO_x reduction investigated. The most useful end results, then, are the general, major considerations, substantiated by data, which appear to lead to significant reduction of NO_x emissions. Such general conclusions can be used to guide development testing.

SUMMARY

Most of the construction of the rough mixing model, derivation of the terms representing thermally generated NO_x , and initial regression analyses and parametric analyses were conducted in a previous study of natural gas- and oil-fired utility boilers. This work and results related to these fuels are reported elsewhere.¹

In order to apply that same technique to coal-fired utility boilers in the subject study, it was necessary to (1) modify the mixing model to include tangentially configured boilers, (2) expand the model of the conversion of fuel-bound nitrogen to NO_x , and (3) expand the interpretation of NO_x thermally generated in a final mixing zone (for cases where the final excess air is added to the products of fuel-rich combustion in the active burner region through NO_x ports or air-only burners concentrated in the top levels of the burner array).

In general, results of this study indicate rather specific methods of reducing NO_x . Nothing in this study of NO_x reduction techniques alone indicates fundamental phenomena that would prevent reduction of NO_x emissions to zero. This latter conclusion in itself, however, is not sufficient to draw the broader conclusions that reduction of NO_x to zero is possible, practical, or even feasible. A number of other practical limits such as flame instability, boiler wall corrosion, boiler operational instability, plant efficiency losses, or excessive emission of other air pollutants can and probably will set limits on NO_x reduction.

As this study depends on empirical correlations, extrapolations beyond the existing data involve some degree of risk. In the practical sense, this means that other phenomena that affect NO_x emissions, but are currently unknown or are not taken into account in the model of this study, may become important in the hardware configurations and operating regimes beyond existing data and could also limit further NO_x reduction. Because all analyses of NO_x reduction methods depend on empiricism, however, a risk in extrapolation is always present in these analyses.

The advantages of this type of study, however, are that results are expressed directly in terms of real, full-scale, multiple-burner utility boilers and that these results are substantiated directly by data from these boilers. Thus, they can be used directly to guide full-scale developmental testing leading to maximum reduction of NO_x emissions and to evaluate results of such testing relative to previous full-scale test data. Limits uncovered by such full-scale testing can then be superimposed on the NO_x reduction data to identify rapidly the real, practical problems limiting NO_x and the real, practical NO_x minima.

It seems very important to establish where conversion of fuel-bound nitrogen occurs spatially in relation to the burning coal particles and clouds of particles and in relation to the burnout cycle of the particles and clouds. This information can be used to establish burner design and coal particle sizes and size distributions such that the initial portions of coal combustion involving fuel-bound nitrogen conversion occur in locally fuel-rich environments, with the remainder occurring under conditions designed to enhance complete hydrocarbon reactions.

Other modifications, which might substantially reduce thermal NO_x in the final mixing zone by reducing the temperature in this zone, could include water spray in the combustion air or recirculation of cooled flue gases in the combustion air. Because cooling or diluting the combustion air could have an adverse effect on stability of a very fuel-rich flame, it might be possible (and necessary) to introduce such cooling or dilution only in the combustion air introduced through the NO_x ports or the air-only burners. NO_x emissions generated in this final mixing zone might also be reduced by decreasing the mixing time through increasing the rate of mixing of the final-stage air with the products of combustion coming from the active burner region. Any or all of these additional combustion modifications may be necessary to achieve significant NO_x reductions in the light of practical limitations on the simpler approaches, discussed in Section 1.2.

This study of NO_x reduction in coal-fired utility boilers clearly indicates the significance of the fuel-bound nitrogen as a source of NO_x emissions. If the model for conversion of fuel-bound nitrogen developed in this study is reasonably accurate, however, then the total NO_x emission problem can be separated into that associated with this source and that associated with thermally generated NO_x . Results of both this study and the previous one indicate that the two mechanisms appear to be relatively independent (i. e., thermally generated NO_x does not appear to be a strong function of the NO_x generated from conversion of fuel-bound nitrogen and vice versa). Results of this study of coal-fired data, then, can be interpreted in terms of thermally generated NO_x alone (as with natural gas fuels) or in terms of fuels with much lower (than coal) concentrations of nitrogen chemically bound in the fuel (as with low nitrogen oil fuels). When the results of this study of coal-fired test data are viewed in this light, they substantiate the conclusions reached in the previous study of natural gas- and oil-fired utility boiler test data.

SECTION II

EFFECTS OF COMBUSTION MODIFICATIONS ON NO_x EMISSIONS

The purpose of conducting this study on large quantities of NO_x emissions data from operational, multiple-burner utility boilers is to gain some useful insight into the combustion processes occurring in boilers as they affect NO_x emissions. Although a single equation containing only ten apparently linear terms is developed and used in parametric calculations in this study, this equation is not a simple one and is not intended for ready use by any interested party. A relatively complex computer program is necessary to calculate the appropriate values of each of these ten terms, for each test condition and hardware configuration, from a number of independent variables, and through a number of highly nonlinear functions. The purpose of this study, instead, is to use this complex equation and the large sample of data to define the major variables and processes affecting NO_x emissions, evaluate the effects of these variables and processes on NO_x emissions, and use the insight gained in this manner to develop simpler rationale to explain existing data. This simpler rationale can then be used to guide developmental testing toward even further reduction of NO_x emissions.

Most of the major assumptions, approaches, and analyses used to develop the equation used in this study are discussed in the report on the previous analysis of natural gas- and oil-fired data.¹ Those major modifications and improvements necessary to apply that analysis technique to data from coal-fired utility boilers are discussed in this report. These two reports, then, are considered to contain sufficient information on the approach

used here that similar models and equations could be developed by any agency desiring to do so.

The coal-fired utility boiler data used in this study were selected to represent the major firing types (i. e. , single-wall, horizontally opposed, and tangential) and a range of coal types, including a nominal type and types representing the available extremes of high nitrogen, high ash, and high moisture content. Throughout this study, an attempt was made to develop an equation that would adequately correlate all of the coal-fired data in a single sample. With all of the diversity in firing and coal types represented in the sample, it was hoped that the resulting observations and conclusions might have broad applicability to other boilers and coal types not in the data sample. As a single verification case, data from one particularly complex boiler and coal configuration were held out of the data sample used to develop the parametric equation.

This section, therefore, contains discussion of (1) the modifications to the approach necessary to apply the previous analysis to coal-fired data, (2) observations from the correlations, (3) results of parametric studies of the data, (4) results of analysis of the boiler not in the data sample used to develop the equation, and (5) general conclusions.

The general approach taken in this and the previous study¹ was the following: (1) assemble a rough model of NO_x generation in a large multiple-burner utility boiler, using generally accepted principles; (2) use that model to generate a single equation, which, if all of our input knowledge were correct and accurate, would directly predict NO_x emissions; (3) use that equation to correlate the available data and correct for inadequacies in the input assumptions; and (4) analyze the resulting correlation equation and use that equation to parametrically analyze the data to gain such insight as is possible relative to control of NO_x emissions. This procedure is little different from that used in the analyses in the previous study.¹ Exceptions that required some modifications both to the model and to the approach resulted from (1) the strong dominance of NO_x generated from conversion of nitrogen chemically bound in coal fuels, (2) the wide range of peak combustion temperatures represented by the range of coal types and combustion air temperatures in the data sample, and (3) the explicit attempt to generate a single equation applicable to all of the coal data sample and with as broad applicability as possible. Two major modifications resulting from these three major differences are discussed in Sections 2.1.2 and 2.1.3 below.

2.1.1 NO_x Model

In the previous study,¹ all of the boilers in the data sample were of the face-fired type, both single-wall and horizontally opposed. The coal-fired data sample of this study includes both of these firing types as well as tangentially fired boilers. The tangentially fired configuration is particularly important because more pulverized coal is fired in tangential boilers than in any other utility boiler configuration.

Figures 1 and 2 show schematics of the mixing zones model constructed for the boilers of the earlier study¹ and used, without change, for the face-fired coal boiler types of this study. Figure 3 shows a horizontal section of the model tangential boiler used in this study. Basically, the

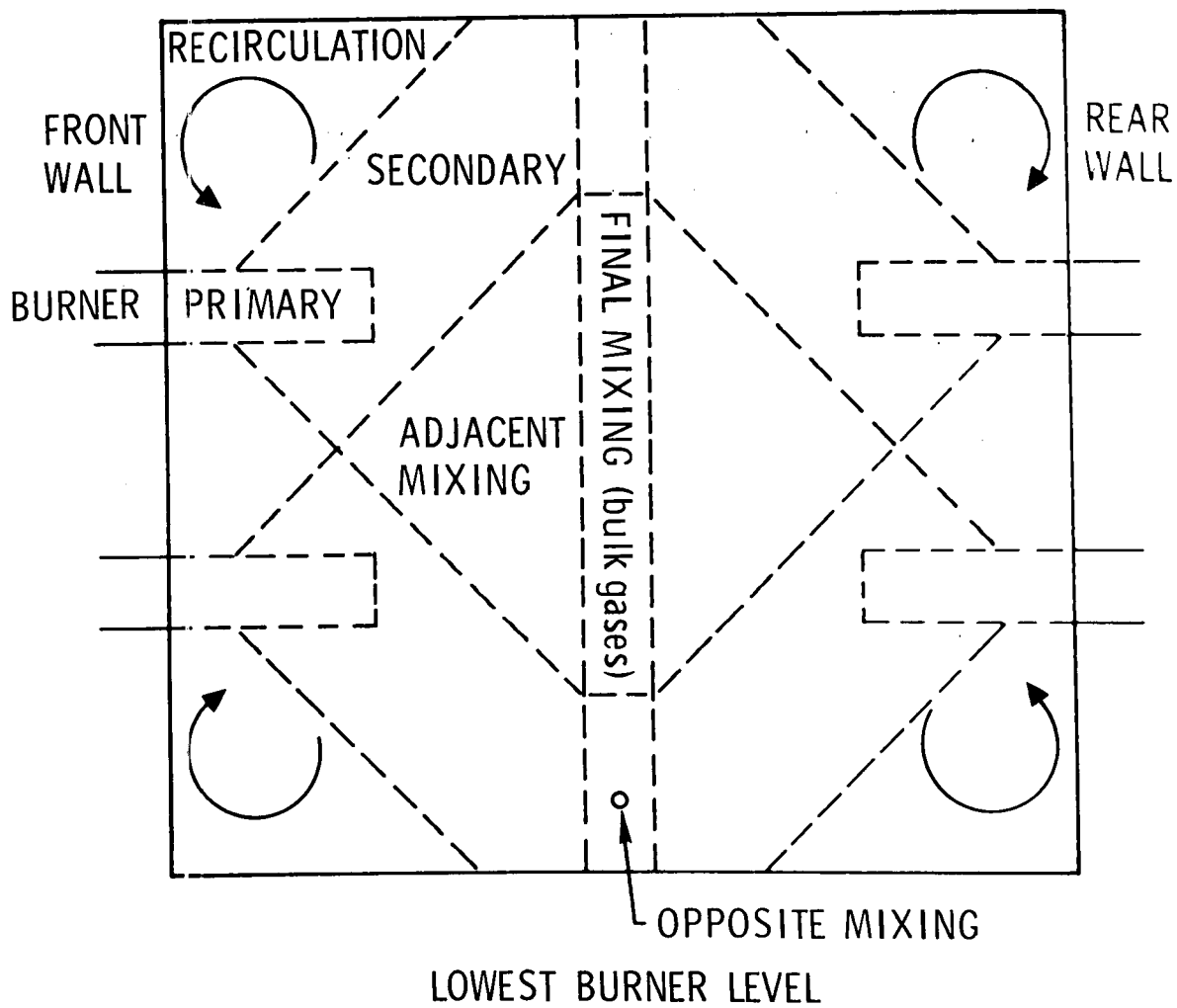


Figure 1. Mixing zone model – horizontal section at lowest burner level

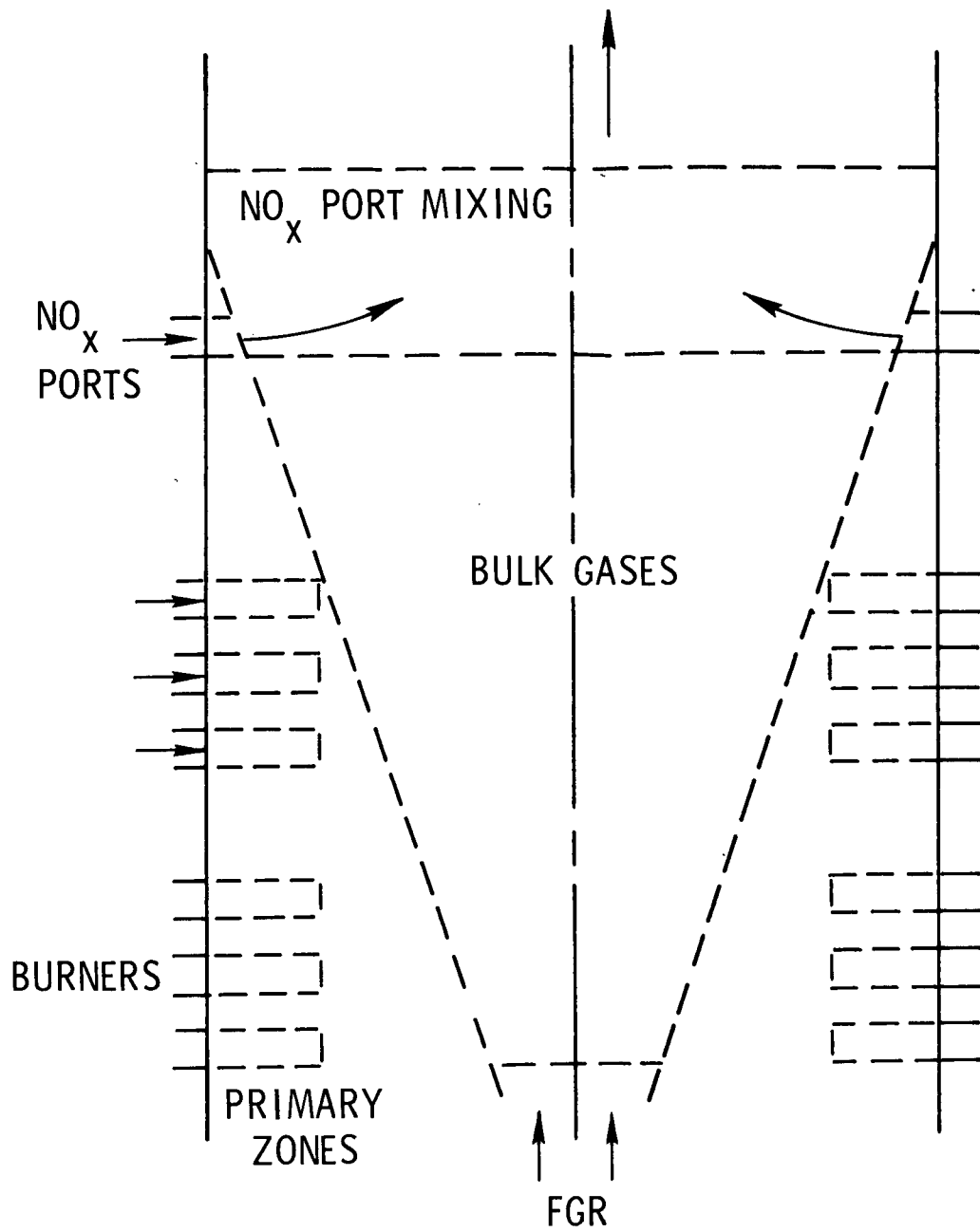


Figure 2. Mixing zone model – vertical section

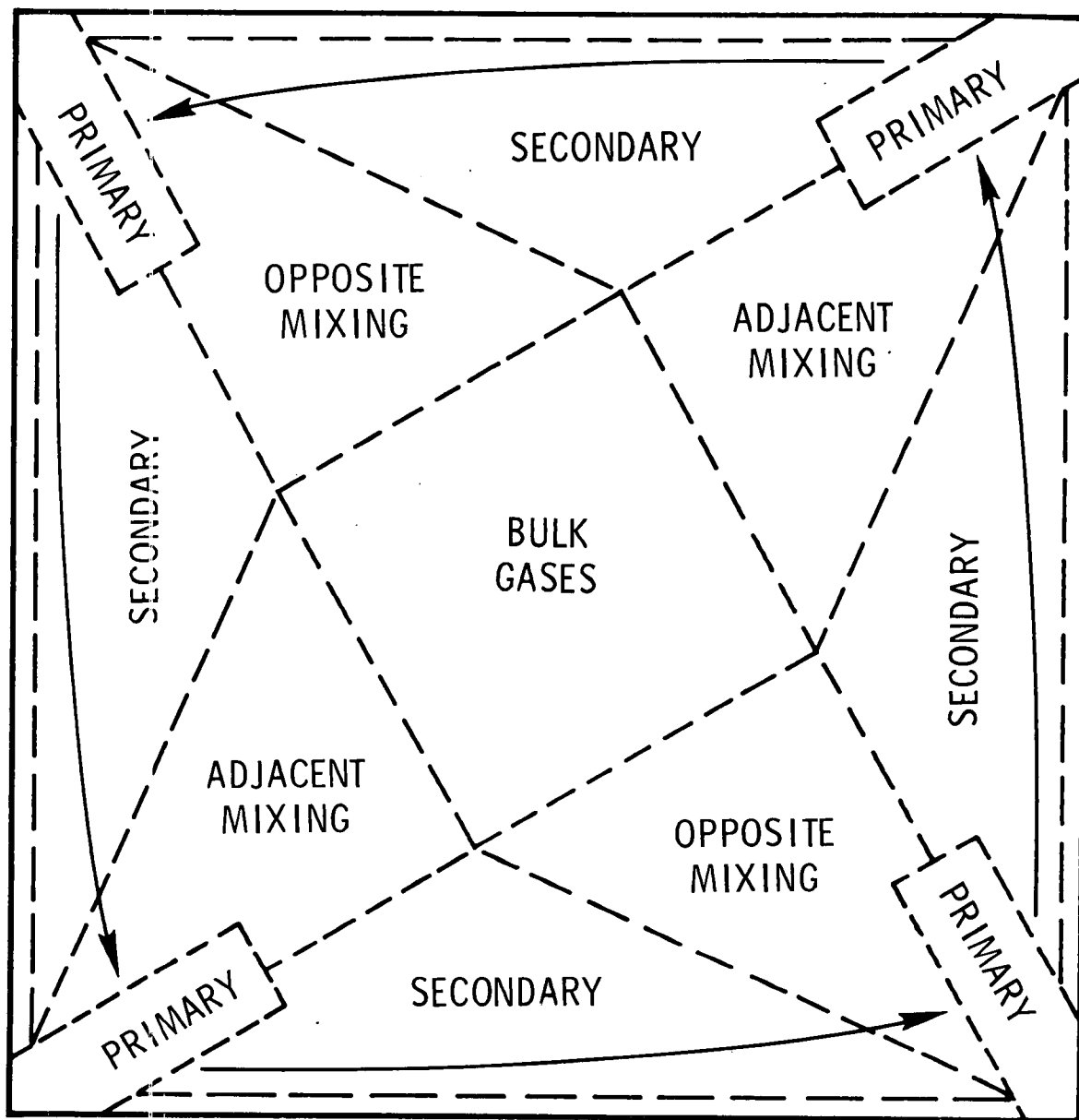


Figure 3. Mixing zone model for tangential boilers – horizontal section at lowest burner level

burners of the horizontally opposed model were simply moved into the corners, with their centerlines aligned slightly off center to induce the swirling bulk gas flow typical of a tangential boiler. With this swirling flow, it was assumed that the recirculation flow does not recirculate to the burner directly above but instead recirculates to mix with the flow from the burner that is located in the next highest level but in the corner that is next in the direction of swirl. Figure 4 shows the assumed recirculation paths of both the face-fired and tangential boilers. The most significant result of this change is the much longer cooling time for the recirculation gases in the tangential configuration.

The other significant change in the model considered necessary to adequately describe tangential boilers results from the vertical distribution of primary and secondary combustion air in each corner array of burners. In a face-fired boiler, each of the burners appear to be identical to every other burner, and each fuel-and-primary air port is surrounded by its proportionate share of secondary air. With all burners active, each burner unit, consisting of fuel plus primary air plus secondary air, is operating at the overall boiler air-fuel ratio. Similarly, all of the bulk gases are at the overall boiler air-fuel ratio. The vertical burner arrangement in a tangential boiler, however, appears to be such that if there are n fuel-plus-primary air burner levels, or vertical fuel levels, there are $n + 1$ secondary air port levels. Each active burner level, then, consists of a $1/n$ fraction of fuel plus primary air but only a $1/(n+1)$ fraction of secondary air. Thus, all of the burner units and all of the bulk gases in the region of the active burners would be operating at an air-fuel ratio less than that of the overall boiler until the final (top) secondary air port flow is added to the total. This operation is analogous to operation with NO_x ports in a face-fired unit. In this model, for tangential boilers, then, the top level of secondary air ports is treated as a fixed NO_x port level, admitting the remaining $1/(n+1)$ fraction of the secondary air. Details of the mixing zone lengths, cooling times, and NO_x port flows used in the model for tangential boilers are discussed in Appendix A.

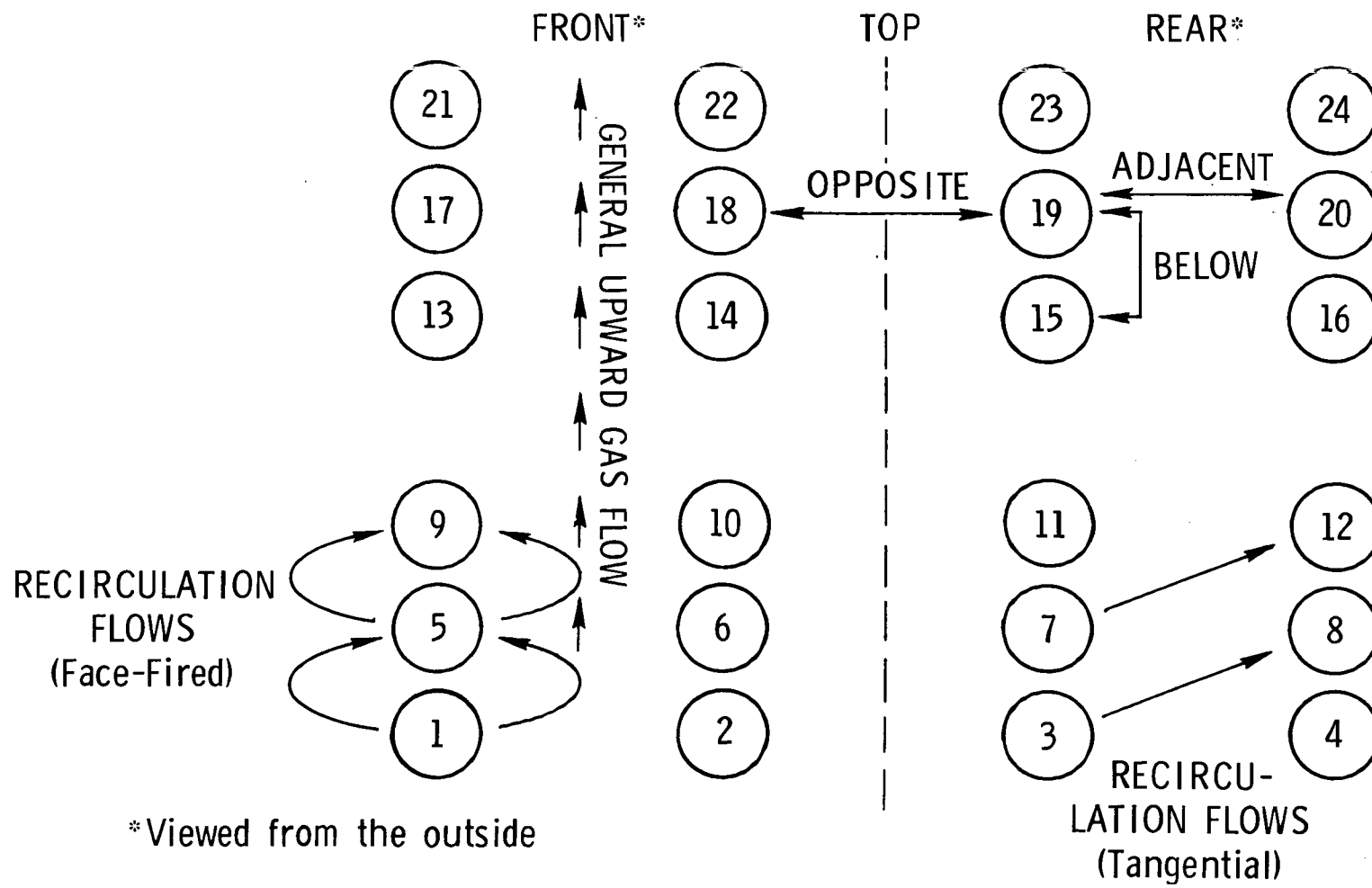


Figure 4. Mixing zone model – definition of burner configurations

The previous study¹ dealt with natural gas and low nitrogen oil fuels. The conversion of fuel-bound nitrogen was of no importance with the natural gas fuel and of little importance with the oil fuel. As a result, the majority of the modeling and analysis effort was devoted to the generation of NO_x by thermal mechanisms. Initially, the equation developed for the regression analyses contained as many as 22 terms describing thermal NO_x generation and only one term accounting for NO_x generated from conversion of fuel-bound nitrogen. The latter term represented a simple, constant fraction of conversion of the fuel-bound nitrogen, regardless of the burner operating conditions. Regression analyses of the oil-fired data, however, established a final equation that behaved as though the efficiency of conversion of the fuel-bound nitrogen was approximately a linear function of the burner air-fuel ratio, with the conversion efficiency ranging from about 63 percent at excess air levels represented by three percent oxygen approximately to zero under burner air-fuel ratio conditions involving about 70 percent of theoretical (stoichiometric) air. For the purposes of understanding the control of NO_x from low nitrogen oil-fired boilers, that representation of the conversion of fuel-bound nitrogen appeared adequate.

In coal-fired boilers, however, fuel-bound nitrogen concentrations are so much larger that NO_x derived from this source dominates the total NO_x emissions. It was necessary, therefore, to improve the description or model of fuel-bound nitrogen conversion. Observations from the analyses of the oil-fired data served as a starting point for this improvement, amplified by the research literature. Basically, many observers²⁻⁶ have noted that (1) the conversion efficiency of fuel-bound nitrogen to NO_x at a fixed fraction of excess air is some inverse function of the weight fraction of nitrogen chemically bound in the fuel, (2) the efficiency of this conversion with a given coal is directly proportional to the local air-fuel ratio, (3) the rate of conversion of this nitrogen is of the order of the hydrocarbon-air reactions themselves, and (4) the conversion efficiency appears to be a weak function (if at all) of local gas temperatures. These observations were used to

postulate a simple model of the conversion process in which (1) the conversion efficiency is inversely proportional (empirically to the two-thirds power) to the weight fraction of nitrogen in the fuel (ash-and-moisture-free); (2) the conversion efficiency is linearly proportional to the local air-fuel ratio, with zero NO_x occurring at an air-fuel ratio where there is just sufficient oxygen present in the air to oxidize the carbon to carbon monoxide and the hydrogen (other than that already bound to oxygen in the moisture) to water; (3) the appropriate local air-fuel ratio is the average of that in the regions where the initial hydrocarbon reactions are taking place; and (4) the conversion efficiency is independent of the local temperature.

Figure 5 shows a plot of data available to this study from full-scale tests and some laboratory experiments relating conversion efficiencies at three percent oxygen to weight fraction of nitrogen in the fuel. As the full-scale data may involve some thermally generated NO_x , the empirical curve shown in the figure was established to represent a lower bound of the full-scale data but represents the actual data in the case of the controlled tests conducted in the laboratory. Much more data of this type are available,² but not all of the appropriate test conditions were available to this study. In general, these additional data confirm a curve of the type shown.

As the mechanism(s) involved in the conversion of fuel-bound nitrogen is not well known, the functional relationship between conversion efficiency and local air-fuel is also not well known. It appears, however, that the conversion process represents some sort of exothermic oxidation reactions that occur at about the same time and at about the same rate as the normal hydrocarbon oxidation reactions. If such is the case, nitrogen oxidation must compete with carbon and hydrogen oxidation reactions for the available oxygen. Indications are that the conversion efficiency goes to zero approximately when the available oxygen is not sufficient to oxidize the carbon to carbon monoxide and the hydrogen (that which is not already bound to oxygen in the moisture in the coal) to water.^{1, 2, 3} In the simplest sense, this might be thought to imply that the nitrogen oxidation reactions can reasonably compete with carbon monoxide for the available oxygen but not at all with hydrogen and free carbon.

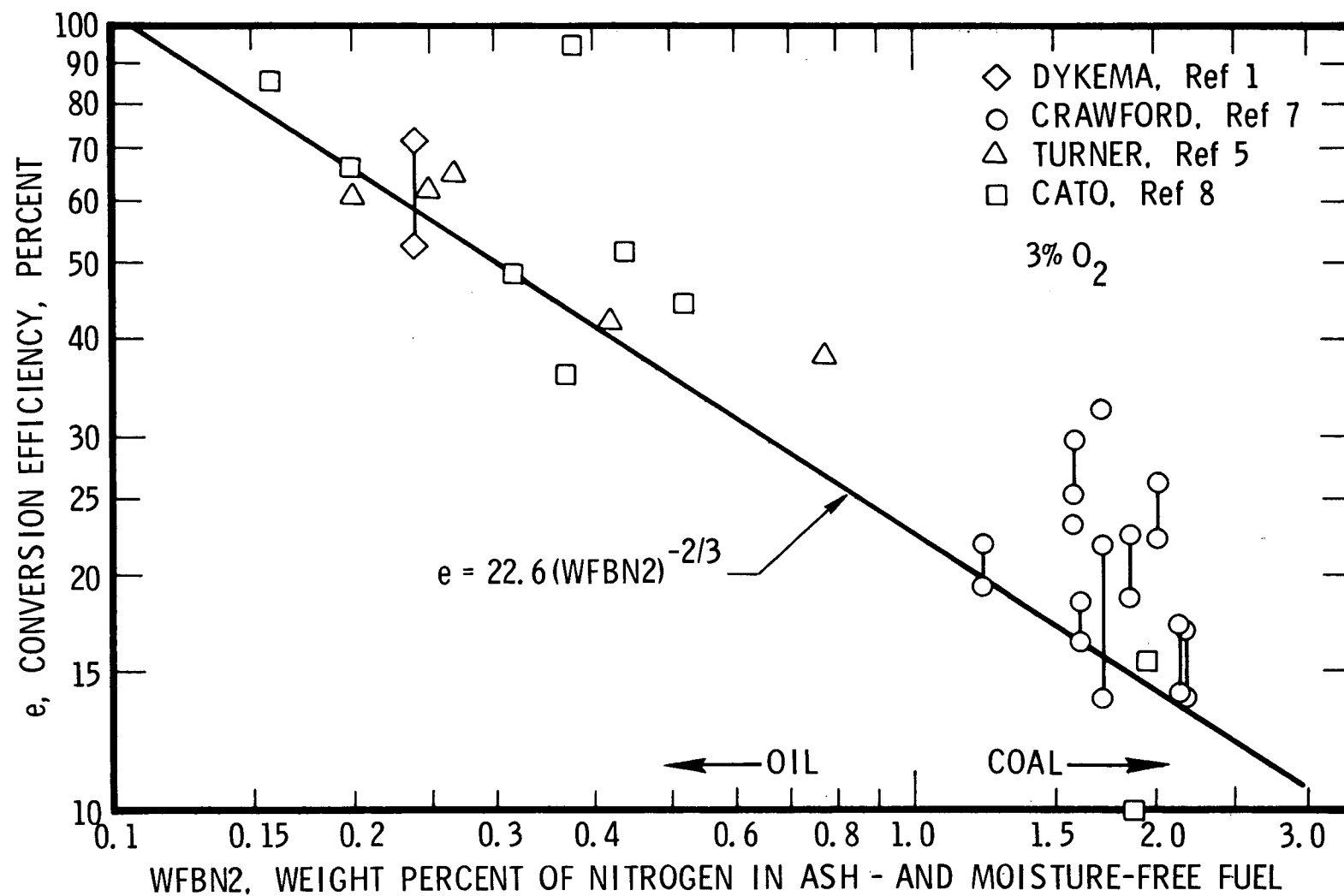


Figure 5. Variation of efficiency of conversion of fuel-bound nitrogen to NO_x with concentration of nitrogen in fuel

Lacking better definition, a simple conversion efficiency model was initially postulated in which the oxygen available for oxidation of fuel-bound nitrogen was that which is left over after all of the available hydrogen is oxidized to water and all of the carbon at least to carbon monoxide. It was further assumed that, for a given fuel, a fixed fraction of this remaining oxygen oxidized the fuel-bound nitrogen to NO, with the remainder further oxidizing the carbon monoxide to carbon dioxide. The fraction of oxygen involved in oxidizing the fuel-bound nitrogen to NO was established such that the conversion efficiency at three percent oxygen was that given by the empirical expression (and curve) of Figure 5 for the specific weight concentration of nitrogen in the ash- and moisture-free fuel.

The resulting model indicates a linear relation, for a given fuel, between fuel-bound nitrogen conversion efficiency and the local air-fuel ratio and, for excess air fixed at three percent oxygen, an inverse relation (to the two-thirds power) between conversion efficiency and the concentration of nitrogen chemically bound in the fuel. The conversion efficiency, in this model, is zero when the fraction of theoretical air is such that all of the oxygen in the air (or more) is necessary to oxidize the carbon to carbon monoxide and the available hydrogen to water. Figure 6 shows calculations from this model for the four coal types of this study and the low nitrogen oil of Reference 1. While the model is largely empirical and the theoretical considerations involved are sketchy, it will be seen later in this report that the available data tend to show good agreement. There has not appeared to be any significant reason to reexamine this model. The calculations involved in the model are described in more detail in Appendix B.

The problem of calculating the efficiency of conversion of fuel-bound nitrogen to NO_x from the above model, as used in this study, would now be quite simple and straightforward if the coal and oil gasification and the gas mixing rates in the active burner region were well known. In that case, the average local air-fuel ratio in the regions where the initial hydrocarbon reactions were taking place could be accurately determined and the average conversion efficiency calculated. As development of these rates was

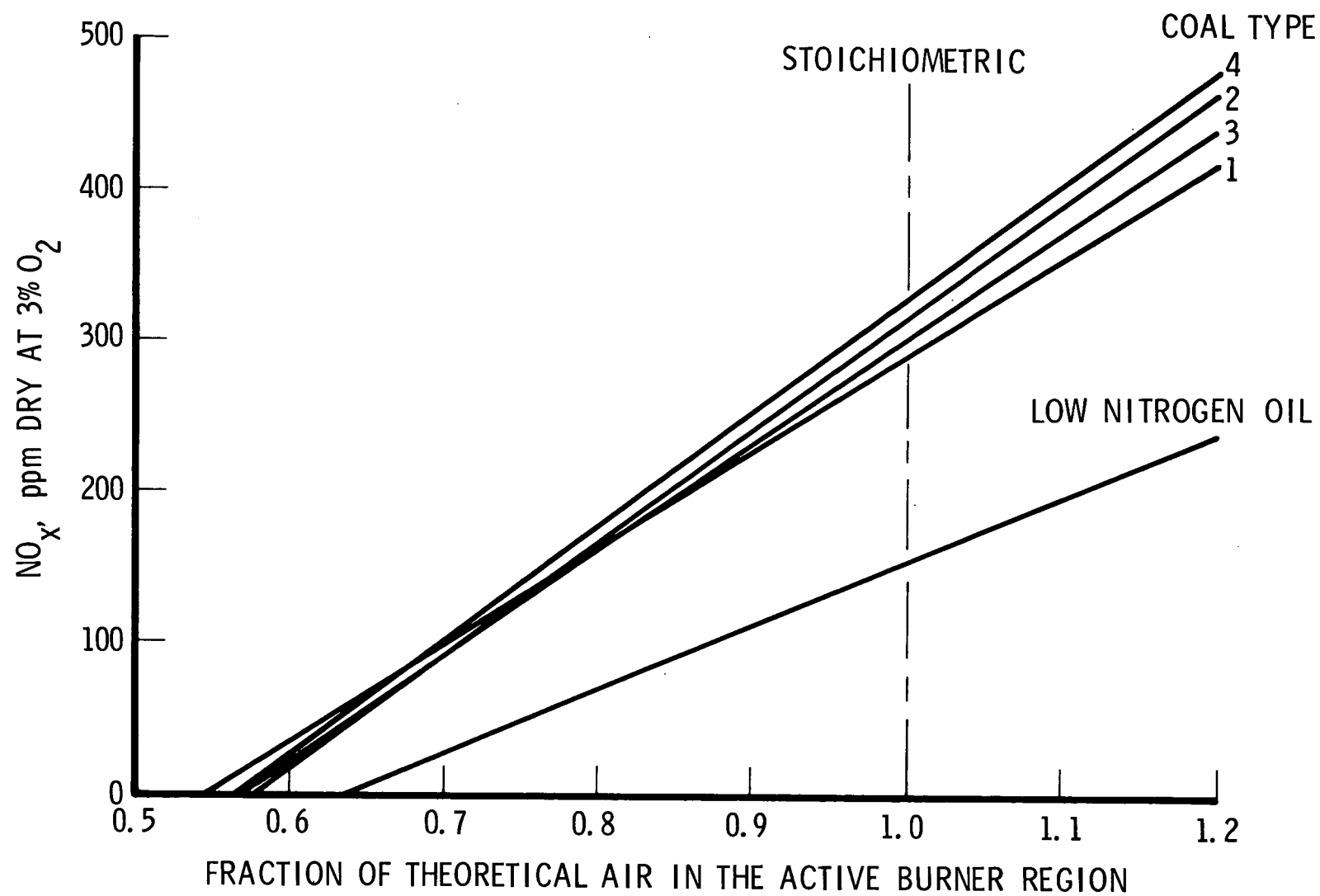


Figure 6. NO_x generated by conversion of fuel-bound nitrogen

not within the scope of this study, an approximate method was developed at least to take into account the effects of the slow gasification rates of coal particles on this conversion efficiency.

Observations on coal flames in boilers of various firing types indicate that luminous, reacting flames appear to extend 15 to 20 feet into the boiler from the burners. If the firing configuration is such that gross mixing between burner flows and bulk gases is forced to occur within that distance, then the average local air-fuel ratio in the region where the initial hydrocarbon reactions are taking place (including some further distance for gas mixing) would approximately be the average of all of the burner flows and the bulk gases at that level. If such mixing does not occur within that distance, then the appropriate average would be that of the burner flows alone. Both the opposed and tangential firing configurations are designed to force such mixing early. The opposed, coal-fired boiler in this study allows a maximum of about 14 feet for mixing within the burner flows before forced mixing with opposed burner flows begins. Certainly mixing with bulk gases begins well before that, at least in the higher burner levels. The tangential configuration is designed to induce swirling bulk gases and more direct and early mixing of bulk gases with burner flows and between the burner flows.

For the opposed and tangential boiler configurations, then, the appropriate average air-fuel ratio for calculation of the fuel-bound nitrogen conversion efficiency at a given burner vertical level was taken to be the average of all of the burner flows introduced into the boiler up to and including that burner vertical level. The appropriate air-fuel ratio for all of the coal introduced into the boiler (the average for the region of the active burners) was then taken to be the average of all of the levels where fuel is being introduced. This averaging process can be described as follows:

$$\frac{AFRP}{AFRB} = \sum_{i=1}^n \left[\frac{NBFA_i}{NBFA_T} \left(\frac{\sum_{i=1}^i NBT_i}{\sum_{i=1}^i NBFA_i} \right) \right] \quad (1)$$

where

AFRB = air-fuel ratio of the active burners

AFRP = average air-fuel ratio in the active burner region

NBFA_i = number of active burners in the i burner level

NBFAT = total number of active burners in the burner array

NBT_i = total number of burners in the i burner level

n = number of burner levels

If all of the active burners, and none of the air-only burners, are located below some vertical level (for example, all burners in the top row air-only and all burners below the top row active), then the average air-fuel ratio of the active burner region (AFRP) is equal to that of the active burners (AFRB). In the case where air-only burners are mixed with active burners, the average air-fuel ratio is always higher than that of the burners. As the efficiency of conversion of fuel-bound nitrogen has been observed to increase with the local, effective air-fuel ratio, these higher average air-fuel ratios always increase the NO_x generated from the fuel nitrogen. In general, this accounts for the fact that, when air-only burners are mixed (vertically, horizontally, or both) with active burners and gross forced mixing is early, some of the gasified fuel will initially react in local regions of high air-fuel ratio and generate higher levels of NO_x from fuel-bound nitrogen conversion. From the standpoint of NO_x generated from conversion of fuel-bound nitrogen alone, this latter case implies that minimum NO_x requires that air-only burners be located in the highest levels of the burner array.

Single wall-fired boilers, however, involve no direct mechanism for creating this gross mixing. In boilers with small numbers of burners and limited vertical distribution of the burner array, the array begins to resemble a single burner. In a single burner configuration, there is little or no mixing with bulk gases and, in fact, the transition from "burner flows" to "bulk gases" is even difficult to define. In the single wall-fired coal

boilers of this study, the burner flows at the lowest level can proceed, with little or no forced mixing with bulk gases, for 22 to 32 feet across the boiler. In this study, therefore, the average air-fuel ratio in the initial reaction period was taken as that of the active burners, regardless of the locations of air-only burners in the burner array. Treating the conversion of fuel-bound nitrogen in single-wall burners in this manner implies that any effect of the vertical location of air-only burners in these boilers must result from effects on thermally generated NO_x .

For purposes of regression analysis of the coal data sample, the NO_x contributed by conversion of fuel-bound nitrogen was calculated from the model and the mixing assumptions discussed above, and subtracted from the measured value of NO_x . The regression analysis, then, was conducted only on that portion of the NO_x assumed to be due to thermal mechanisms. Verification of this total approach will be discussed in Section 2.2.2.1.

2.1.3 Final Mixing Zone

Throughout the gas and oil fuel studies, it was evident that there was a source of thermally generated NO_x within the boiler which was essentially independent of variations in NO_x port air flow, burners out of service, and excess air. This source was represented, at least partially, by the constant in the equation resulting from the linear regression analyses.¹

In the previous study,¹ the two fuels were analyzed separately. Thus, in each data sample used in the regression analyses, the fuel combustion temperature rise and product species at given air-fuel ratios were constant. Also, the combustion air (reactant) temperatures measured at rated load in the boilers in those data samples were not greatly different (31 K, 56°R difference). As a result, peak combustion product temperatures at full rated load, in all of the data used for any regression analysis, were constant, within the scatter of measured combustion air temperatures. The linear regression analyses, then, were able to fit the data acceptably by assigning the NO_x generated in that zone to a single constant. Parametric analyses discussed elsewhere¹ concluded that the source of this thermal NO_x was in the NO_x port or final mixing zone but did not further identify other characteristics.

The coal data sample, however, includes coal types with widely varying combustion temperature rises and boilers involving widely different full-load combustion air temperatures, resulting in peak combustion temperatures varying over a range of more than 370 K (670°R). The linear regression analyses on the coal data sample still attempted to fit the effects of this temperature variation between coal and boiler types to a single constant applicable to all of the coal and boiler types. Comparison of parametric calculations for the individual boilers with the data from the boilers, using the equation developed from regression analysis of the entire coal sample, showed that the parametric calculation was clearly not accounting for variations in this constant with the individual coal and boiler types. Although this constant, amounting to 146 ppm of NO_x , was present in all of the parametric calculations, the constants represented in the data appeared to range from as low as 33 ppm to well over 200 ppm for the various coal and boiler types. It was concluded early in this study, then, that the zone where this NO_x is generated was not adequately represented by any of the terms in the regression analysis equation.

If the data from the individual boilers were analyzed separately, new constants would be obtained appropriate to those firing conditions. Unfortunately, most of the coal-fired boiler data samples are too small to obtain meaningful results. In any case, such an approach would limit the generality of the overall study results and limit the application of these results to those boilers in the data sample analyzed, at least to the extent that 100 to 150 ppm error could result from inadequate knowledge of this constant. It was also concluded, therefore, that further study was necessary to develop an additional thermal NO_x term, or an empirical correction term, to account for the variation of this constant for various coal and boiler types.

Details of the observations from available data, and the development of this new term, are described in Appendix C. This study concluded that this new term, independent of burner air-fuel ratio (constant), probably represents the NO_x generated during the final, large-scale mixing of any excess air not entering the boiler through the active burners (i.e., entering

through air-only burners, NO_x ports, or both) with the products of fuel-rich combustion in the active burner region. This is a transient mixing region that was not included in the original model and equation. It does not exist when the burner air-fuel ratio is greater than stoichiometric (as when all burners are active). The new term is a function only of the equilibrium combustion temperature rise and the nitrogen and oxygen concentrations in the product species at the stoichiometric air-fuel ratio, and the gas cooling enroute to the location in the furnace where this mixing takes place.

This new term is the primary one, in the model and in the equations used for parametric calculations, that shows the beneficial effects of NO_x ports over air-only burners located in the top row of the burner array. It also shows the beneficial effects of locating such NO_x ports high in the boiler to maximize the cooling time before introducing this final excess air. General confirmation of this term will be shown in Section 2.2, Results.

2.1.4 Coal-Fired Data Sample

Most of the data on coal-fired boilers used in this study were obtained from the field testing of the Exxon Research and Engineering Company.⁷ Some additional, unreported data were obtained from the Tennessee Valley Authority from tests on the Widows Creek No. 5 boiler. Instrumentation and gas sample analysis techniques used are discussed elsewhere.⁷

A major problem usually encountered in using any test data after the testing has been completed is that not all of the data necessary for a particular analysis technique or model were measured. In full-scale hardware testing, it is also often impractical to measure the desired primary data. As a result of these problems, much of the primary data necessary to this study had to be calculated from other, secondary data.

Data on coal feed rates were not available. As a result, coal feed rates were calculated from the measured boiler load, the lower heating value of the coal type, and an assumption of constant plant efficiency. This

is not a very accurate calculation, particularly at low boiler loads, but was considered adequate for this study for the following reasons:

- a. NO_x emissions do not appear to be a strong function of the total throughput flow. Although it is widely recognized that NO_x is, in many cases, a significant function of load, this effect appears to be primarily a result of variations in combustion air temperature with load rather than of the total flow rate. Combustion air temperatures were measured.
- b. Although the plant efficiency in some cases decreases significantly at low load, the primary emphasis of this study was on reduction of NO_x at full rated load. Data taken at low load were almost never used for any purpose in this study. In any case, low load testing often involved burner configurations where some of the air registers were fully or partially closed. These data were eliminated from the data sample for other reasons, as discussed below.

As in the previous study,¹ overall boiler excess air data were calculated from the ratio of the measured oxygen and carbon dioxide levels. Theoretical stoichiometry was used to relate the excess air level to this ratio. It is recognized that measured oxygen and carbon dioxide levels do not agree accurately with theoretical stoichiometry but, without measured flow rates, no method was available to calibrate this error. As this error tends to be constant for all of the data, trend results should be relatively accurate.

Combustion air temperatures are actually measured at the exit of the air preheater, as in the previous study.¹ These temperatures were used in that and the subject study to represent temperatures of the combustion air entering the burners from the windbox. No data were available in either study with which an estimate could be made of the combustion air temperature change occurring between these relatively widely separated locations.

Finally, a most important parameter to this study is the distribution of combustion air between separate windboxes (if more than one) and between the multiple active and air-only burners fed from a common windbox. In the previous study,¹ it was found that the presence of a significant fraction of combustion within a burner (such as a recirculation pilot zone anchored within the burner) can significantly change the resistance to air flow through the burner, particularly relative to this resistance in an air-only burner. Further, a typical windbox is not normally aerodynamically designed, and air flow maldistribution among the burners can be inherent. For lack of appropriate data, the combustion air flow distribution was assumed to be equal to multiple windboxes. It was also assumed equal to all burners (active and air-only) fed from a common windbox as long as all air registers were in approximately the same position. A great deal of effort was expended, particularly in the previous study,¹ to account for the changes in air flow distribution in configurations where some air registers were fully or partly closed. These efforts were finally abandoned in this study and all such data were deleted from the sample. It appears that air leakage even through a so-called closed air register can be appreciable and can lead to significant errors in calculated air flow distribution.

For comparison purposes, Table 1 shows the entire data sample used in this study of coal-fired boilers as well as that previously reported.¹ Data from a total of 186 tests in eight coal-fired boilers were used in this study. Boiler configurations represented single-wall, opposed, and tangential firing. In addition, data from 12 tests on a second opposed-fired boiler were held out of the data sample used for regression analysis for a later test of the generality of the resulting prediction equation.

Table 1 shows a total data sample of 575 test conditions with coal, oil, and natural gas fuels. An additional 70 test conditions were also reduced and entered into the program, which involved attempts to shut off the combustion air, or secondary air, to some burners by closing the air registers. As discussed above, these tests were later deleted from the sample.

Table 1. SUMMARY OF TOTAL DATA SAMPLE

FIRING TYPE	No. OF BOILERS	RATED LOAD, MW	No. OF BURNERS	NO _x PORTS	No. OF TESTS		
					COAL	OIL	NAT GAS
SINGLE- WALL	1	105	18	NO	3	-	-
	2	125	16	NO	72	-	-
	2	180	16	NO	-	29	27
	2	240	12	NO	-	43	31
	1	260	16	NO	18	-	-
	1	340	16	NO	14	-	-
OPPOSED	2	240	12	YES	-	6	47
	2	350	24	YES	-	61	145
	1	800	54	NO	17	-	-
TANGENTIAL	1	330	20	NO	22	-	-
	1	360	20	NO	40	-	-
TOTAL: 16				TOTALS:	186	139	250
				GRAND TOTAL:	575		

Overall, the effect of deleting these tests, representing only 11 percent of the total, was minor.

Analyses of the coals burned in the boilers of this study are reported elsewhere.⁷ In order to minimize the work load in calculating equilibrium combustion temperatures and product species, the seven coal types fired were reduced to four, more general coal types. The analyses of these synthesized coals are shown in Table 2.

Table 2. ANALYSES OF COAL TYPES

COAL TYPE	C	H	O	N	S	ASH	MOISTURE, % (Proximate)	HIGHER HEATING VALUE, Btu/lb
1-HIGH MOISTURE	63.6	4.5	19.2	0.90	0.70	11.1	32.0	7,200
2-HIGH ASH	58.8	4.7	9.3	1.3	0.90	25.0	10.5	8,900
3- NOMINAL	70.5	4.7	9.3	1.3	3.1	11.1	10.5	11,700
4-HIGH NITROGEN	72.3	4.7	9.3	1.7	1.7	11.1	10.5	11,700

The primary observation of all of the data analyses and parametric calculations involving coal-fired data is the predominance of the NO_x generated from conversion of the fuel-bound nitrogen. With the coals of this study, with all burners active and operating at excess air corresponding to three percent oxygen (116 percent of theoretical air), this source contributes 390 to 450 ppm of NO_x (see Figure 6), representing 60 to 92 percent of the total NO_x emissions measured under these operating conditions in the boilers of this study. Thus, the model derived for fuel-bound nitrogen conversion is the most significant part of this analysis of coal-fired data. The model indicates that NO_x from fuel-bound nitrogen conversion is a function of the weight fraction of nitrogen chemically bound in the ash- and moisture-free fuel, and the effective fraction of excess air. Therefore, that model can be confirmed by plotting the data for a given coal and boiler type as a function of the average effective fraction of excess air in the active burner region, as defined in Section 2.2.2 and Equation (1).

A second significant source of NO_x in coal-fired boilers appears to be that thermally generated in the final mixing zone, as defined and discussed in Section 2.1.3 and Appendix C. Calculations from Figure 16 (Appendix C) show that this zone can be the source of more than 170 ppm of NO_x , representing from eight to more than 20 percent of the total NO_x emissions, in the boilers of this study. (The remaining zero to 20 percent not resulting from conversion of fuel-bound nitrogen or from this final mixing zone represents NO_x thermally generated in the active burner region.) NO_x from this zone is independent of the fraction of theoretical air in the burners, and a function of peak combustion temperatures (at stoichiometric in the appropriate zone). It will appear as a relatively constant level of NO_x , at burner air-fuel ratios less than stoichiometric, for a given coal type and boiler, added to the NO_x derived from conversion of fuel-bound nitrogen. This final mixing zone exists only in boiler configurations in which relatively large fractions of air are added to the products of fuel-rich combustion in the

active burner region through air-only burners concentrated in the top levels of the burner array or through NO_x ports (or both). This zone will not exist in boiler configurations in which (1) all burners are active, (2) the air-fuel ratio in the active burners is greater than stoichiometric (regardless of the presence or location of air-only burners), and (3) air-only burners are located low in the active burner array. Data confirmation of the model of NO_x from this zone results from the variation of this relatively constant level of NO_x added to that of the bound nitrogen line.

Confirmation of the prediction of thermal NO_x generated in the complex gasification, mixing, and reaction region of the active burners, however, is not easy to show. The parametric equation requires eleven terms involving highly nonlinear Zeldovich NO_x formation rate terms that represent functions of as much as 11 different air-fuel ratios and as many more local temperatures to adequately describe the thermal NO_x generated in the zones in this region. These terms generally reflect the effects of burner air-fuel ratio and peak combustion temperatures but are also complex functions of a large number of other variables. It was for this reason that the data in the previous oil and gas study¹ were analyzed parametrically, as functions of a number of single variables, with no attempt to show all of the data as a function of just one or two variables.

In this study, the primary concern is with significant reduction of NO_x from coal-fired boilers, in which NO_x emissions are primarily functions of two major variables: the fraction of excess air in the active burner region and the peak combustion product temperature downstream (above) this region. Changes to these two variables to reduce NO_x from conversion of fuel-bound nitrogen and from the final mixing zone also tend to reduce thermal NO_x from the active burner region as well. As thermal NO_x from the active burner region already represents a relatively small fraction of the total in coal-fired boilers and should totally disappear if significant reductions are made in NO_x from the major sources, it will generally be neglected in the following data presentations. All of the data

from each significant coal and boiler type will be shown as a function of the average fraction of excess air in the active burner region. It must be kept in mind that, although thermal NO_x generated in the active burner region is some function of this single parameter, it is also a complex function of other parameters. As a result, that portion of the total NO_x thought to be generated in that source may require further observations with respect to the variation of other variables. A rough indication of the thermal NO_x generated in the active burner region will be shown by a parametric calculation for normal operation (all burners active).

2.2.1 Data Interpretation

Figure 7 shows the data from the sister boilers, Widows Creek Units No. 5 and 6 of the Tennessee Valley Authority, plotted against the single parameter, fraction of theoretical air in the active burner region (100 percent of theoretical air represents the stoichiometric air-fuel ratio for that coal). As these boilers are of the single-wall configuration, according to the discussion in Section 2.1.2 the fraction of theoretical air in the active burner region is the same as the fraction of theoretical air in the burners. Superimposed on this data are three schematic-like lines or curves showing the three major sources of NO_x discussed above. The line shown, describing NO_x from fuel-bound nitrogen conversion, is taken directly from Figure 6. For this particular boiler, because it is so nominal, the constant determined directly from regression analysis of the total data sample is appropriate. This constant, then, representing NO_x from the final mixing zone, is shown added to the fuel-bound nitrogen line. Finally, thermal NO_x generated in the active burner region is bounded by adding to the sum of the first two sources a typical Zeldovich curve, for an arbitrary constant time.

It can be seen that a schematic such as shown in Figure 7 is almost enough to explain the majority of the significant variations in NO_x emissions from coal-fired boilers. The lower limit of all of the data is

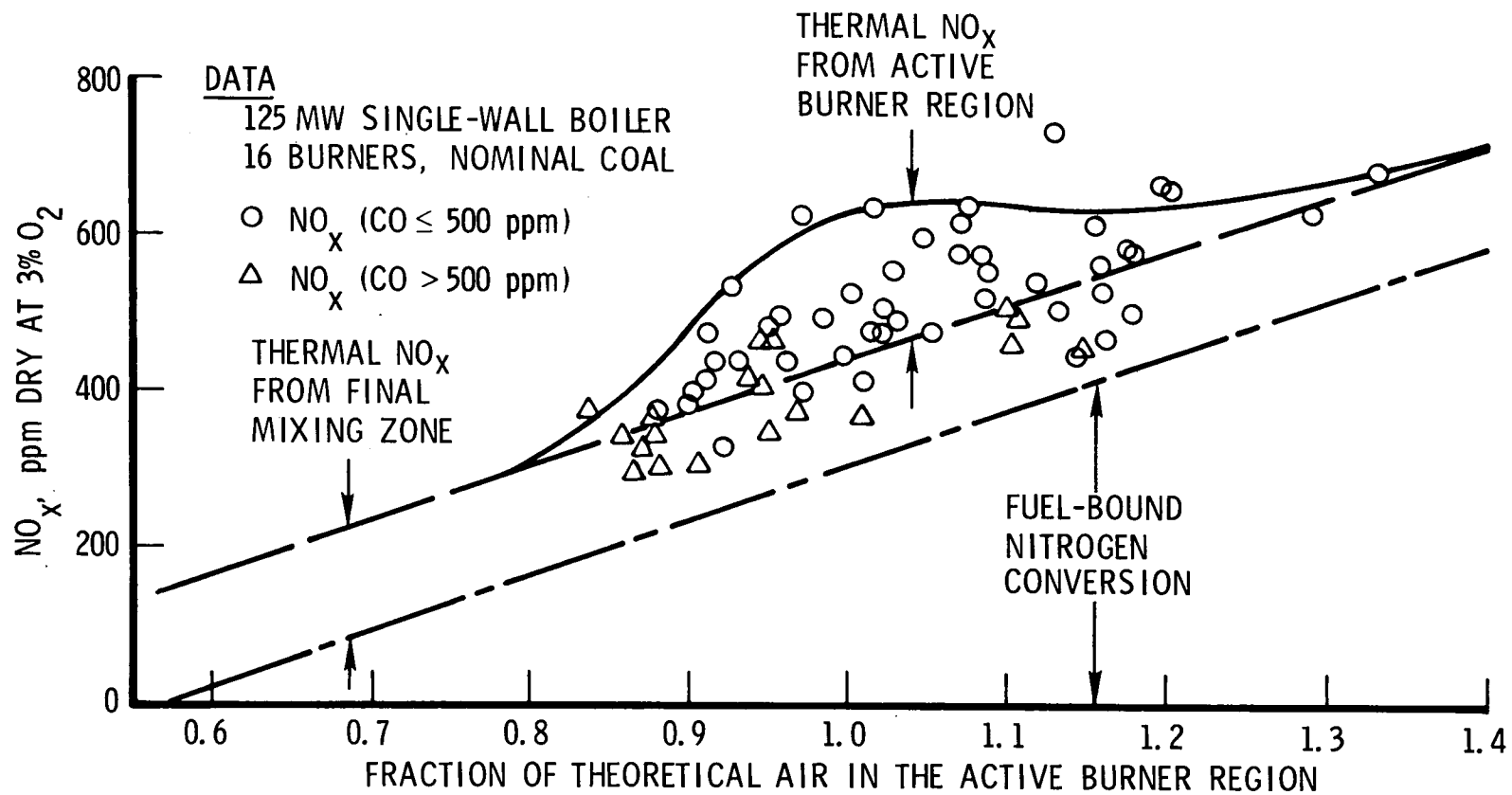


Figure 7. Major sources of total NO_x emissions

reasonably close to, but not below, the fuel-bound nitrogen conversion line. The slope of the lower limit of the data generally tends to confirm the slope of the bound nitrogen line.

The second, parallel line generally correlates the lower limit of NO_x under full-load and nominal excess air conditions and a variety of air-only burner configurations. Those configurations with the air-only burners in the top rows lie close to this line. Of the data below this line, 80 percent exhibited excessively high carbon monoxide emissions (greater than 500 ppm), represented tests at less than 80 percent of rated load, or both.

Finally, the data above the second line represent the thermal NO_x generated in the active burner region and are reasonably bounded by a Zeldovich curve, added to the sum of the first two lines. It can be seen that at least the upper bound of the data is related to the fraction of theoretical air in the burners but other variables are also effective. For example, all of the data points shown in Figure 7 above 600 ppm represent configurations either with all burners active (above 115 percent of theoretical air) or with two air-only burners located in the bottom row of the burner array.

In the case shown in Figure 7, because it is a single-wall configuration and the fraction of theoretical air in the active burner region is the same as that in the burners, the Zeldovich curve and the data describing thermal NO_x generated in the active burner region are roughly centered around the stoichiometric air-fuel ratio (100 percent theoretical air), as expected. If these boilers were of the opposed or tangentially fired configurations, however, the average fraction of theoretical air in the active burner region, in the cases where air-only burners were located in the bottom level of the burner array, would be higher than the fraction in the burners [see Equation (1)]. The data shown in Figure 7 representing thermal NO_x generated in the active burner region, and the bounding curve, would be skewed toward higher levels of the fraction of theoretical air in the active burner region, and the Zeldovich curve would not be centered

about stoichiometric. This illustrates the point that the average fraction of theoretical air in the active burner region is not the only relevant parameter with respect to NO_x thermally generated in the active burner region. NO_x data plotted against this parameter alone, particularly data from opposed and tangentially fired boilers, can be expected to show some high levels of thermal NO_x that require further study, if it is desirable to explain these high levels.

The data shown in Figure 8 indicate that total NO_x emissions are higher when air-only burners are located in the bottom level of the burner array than when they are located in the top level. Figure 8 shows the results of parametric calculations on the effects on NO_x of the vertical level of a full horizontal row of air-only burners, for all of the firing types. This figure confirms that, in all cases, NO_x emissions are lowest when the air-only burners are located in the top level. Also, the discussions in Section 2.1.2 as well as Equation (1) indicate that when the air-only burners are concentrated in the top rows there is no air introduced into the region of the active burners (below the top rows) other than that normally entering through the active burners. The average fraction of theoretical air in the active burner region, therefore, is equal to that in each active burner. Thus, because there is no apparent reason not to locate the air-only burners in the top row, it is assumed at this point that only that case is of interest. If this assumption is made early, most of the questions and complications involved in the thermal NO_x generated in the active burner region can be dismissed or avoided.

The remaining data and effects on NO_x of interest from coal-fired boilers, then, are those related to the two straight lines shown in Figure 7 and to the methods of reducing the NO_x from the final mixing zone and from conversion of bound nitrogen, all in boiler configurations in which air-only burners are located in the top levels of the burner array.

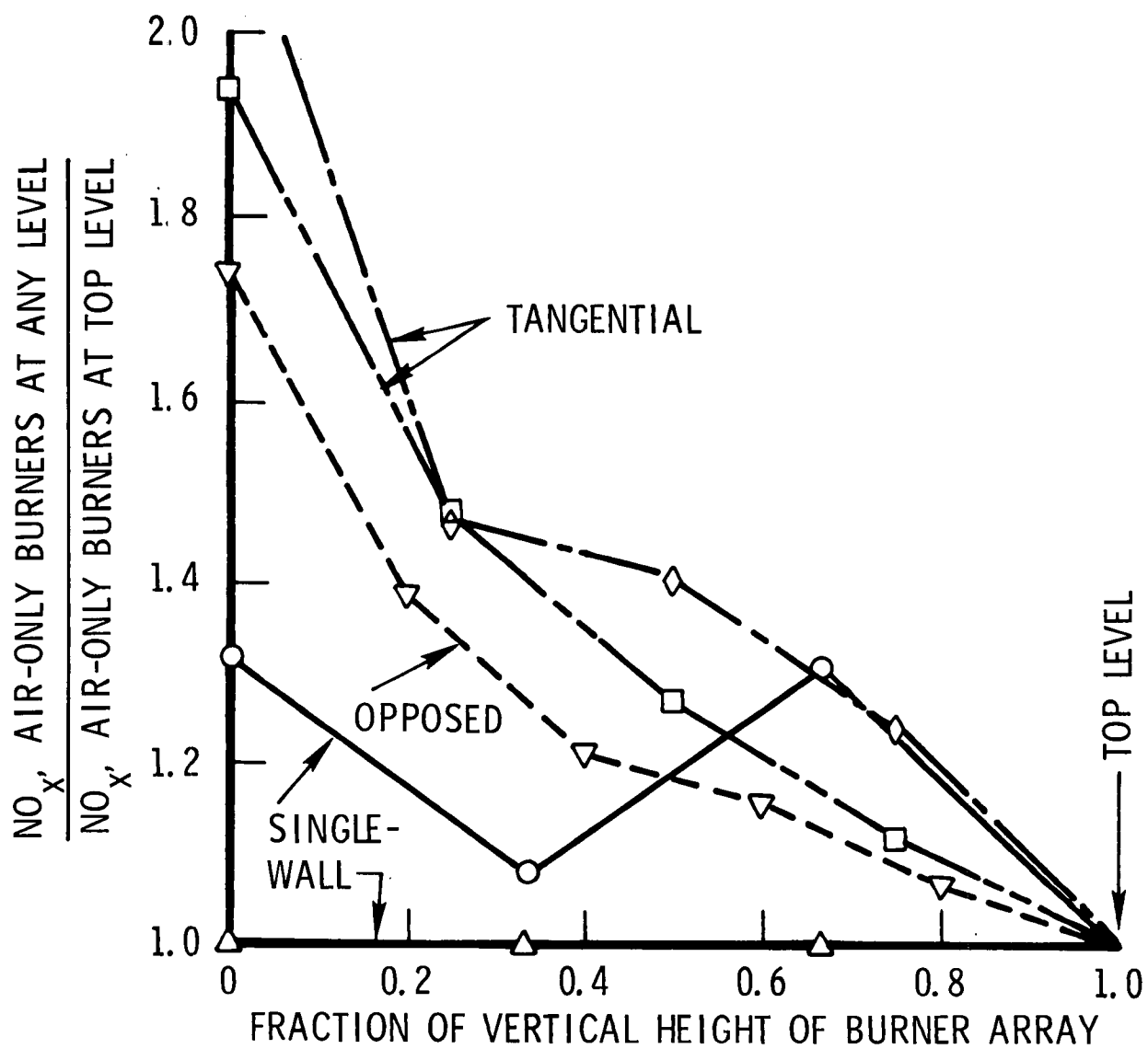


Figure 8. Results of parametric calculations on effect of locating air-only burners at various vertical levels in burner array

2.2.2

Parametric Calculations

In line with the discussion in Section 2.2.1, it is considered that only boiler configurations in which the air-only burners are located in the top levels of the burner arrays are of interest here. All other burner configurations in the same boiler will yield the same or higher NO_x levels. The effects of the number of air-only burners can be shown, and confirmed by data, directly on a plot of NO_x versus the fraction of theoretical air in the active burner region. The effects of peak combustion temperatures on the thermal NO_x generated in the final mixing zone can be shown by parametric variations in this parameter on a single boiler and verified by the data variations between boilers. Because NO_x reduction by load reduction is not an acceptable means of controlling NO_x from utility boilers, only NO_x emissions under full rated load conditions are of interest here.

Thus, the four parametric calculations of interest in each of the significant combinations of coal and boiler types, under full rated load conditions are (1) a reference or nominal calculation with all burners active and with variations in overall boiler excess air, (2) increasing numbers of air-only burners located in the top levels of the burner array, (3) the same calculation as in (2) but with the combustion air temperature reduced (arbitrarily to 422 K, 300°F), and (4) the line describing the NO_x generated from the conversion of fuel-bound nitrogen.

In all cases, the parametric calculations and all of the data available for each boiler are plotted against the fraction of theoretical air in the active burner region. This parameter is appropriate for all of the parametric calculations and most of the data because the fraction of theoretical air in the active burner region is the same as that in the burners (a uniform air-fuel ratio in the active burner region equal to that in the burners). All of the data are plotted because some verification can be obtained from most of the data. Finally, attempts to select only the data closely representing one of the parametric calculations can reduce the applicable data sample nearly to zero.

Figures 9 through 13 show such plots of parametric calculations and data for the significant combinations of coal and boiler types in the data sample used for regression analysis. Significant observations and confirmation by data will be discussed separately for (1) the conversion of fuel-bound nitrogen, (2) NO_x generated in the final mixing zone, and (3) other significant observations.

2.2.2.1 Fuel-Bound Nitrogen

According to the discussion in Section 2.1.2, the model developed to calculate NO_x generated from conversion of fuel-bound nitrogen should predict a lower limit of NO_x at any fraction of theoretical air for each of the coal types. This semiempirical model was not a part of the regression analyses because the NO_x calculated from this model was subtracted from the measured NO_x before the remainder was analyzed. The data can serve to verify the magnitude of the NO_x calculated from the model by closely approaching the calculated value but not going below it. The linearity, the slope, and (by extrapolation) the intercept of the calculated line as a function of the fraction of theoretical air in the active burner region can be verified by comparing the calculated line with the lower limit of the data.

With the exception of the data describing the tests with the high ash coal, Figure 13, the lower limit of all of the coal-fired data tends to closely approach the fuel-bound nitrogen conversion curve. In Figures 10 and 12, some data even lie right on or slightly below this line. Within the accuracy of the data it can be concluded that (1) no data are available that are significantly below the calculated fuel-bound nitrogen conversion line, and (2) the data are sufficiently close to the calculated line that no general change to the model (or the empirical curve of Figure 5) to increase the magnitude of the NO_x from this source is warranted.

Figure 13, showing the results from firings with the high ash coal (type 2), appears to show considerable deviation from the calculated fuel-bound nitrogen conversion line. None of this data come closer to this

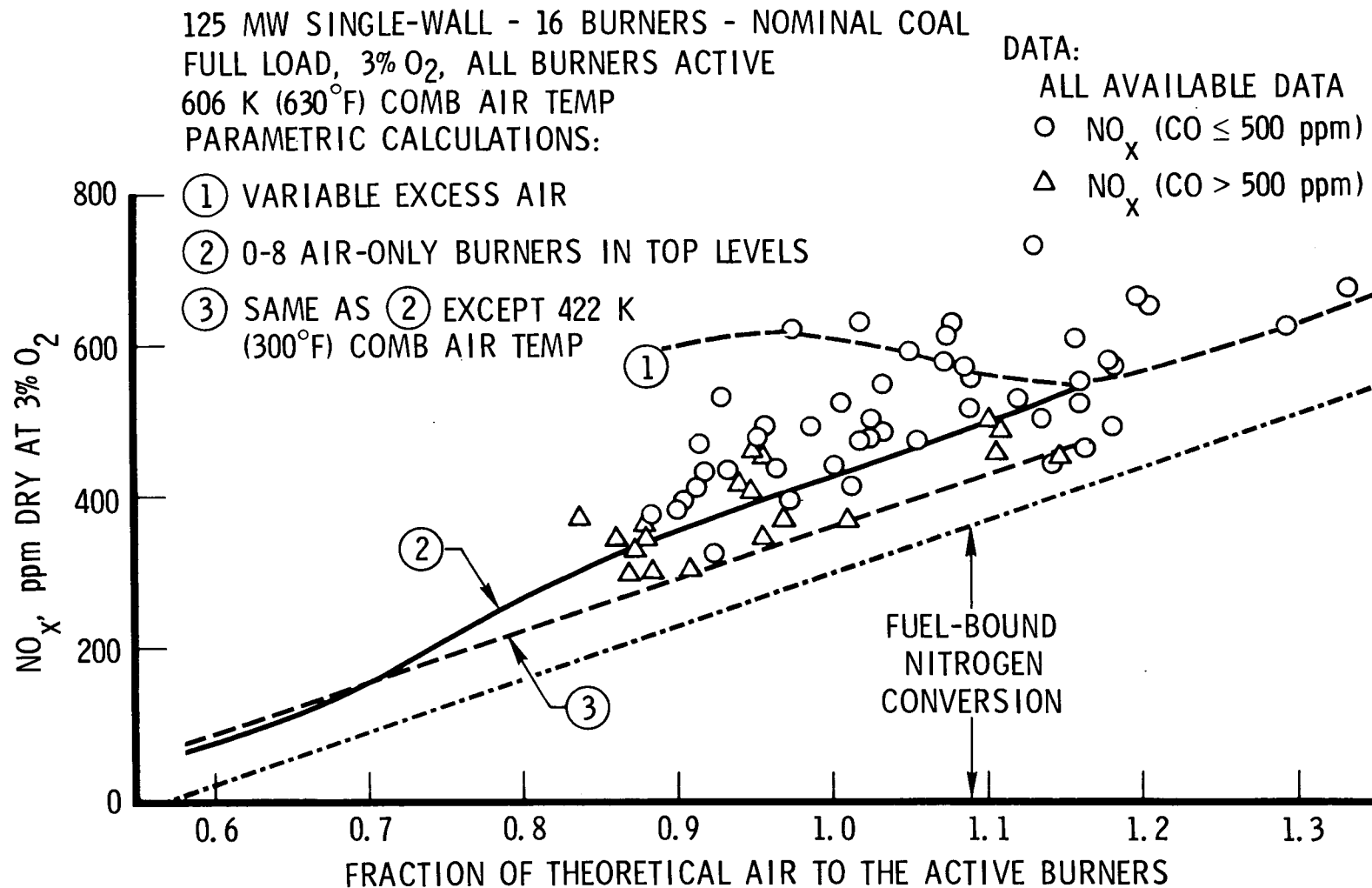


Figure 9. Typical single-wall boiler firing nominal coal type with typical combustion air temperature

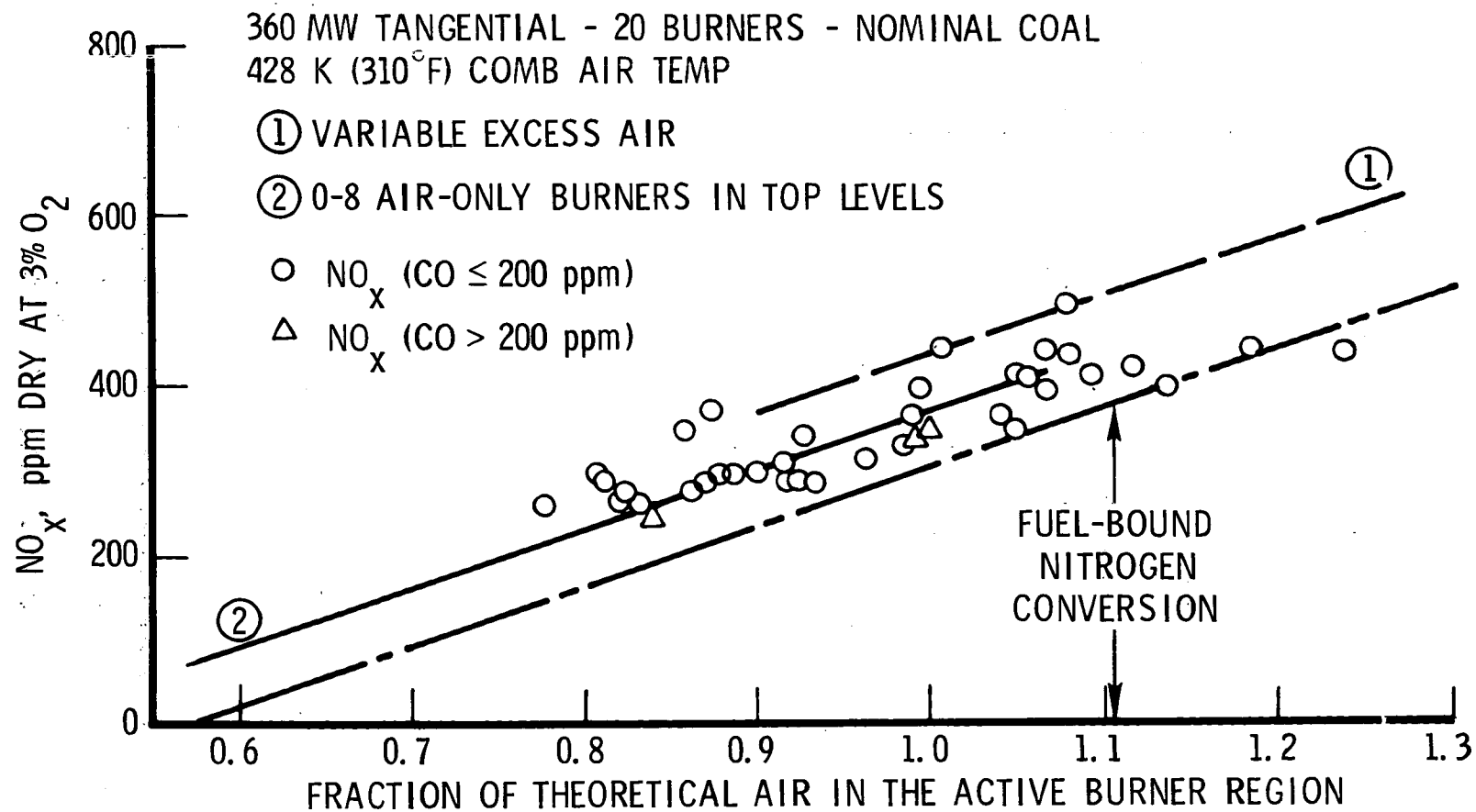


Figure 10. Effects of low combustion air temperature in boiler firing nominal coal

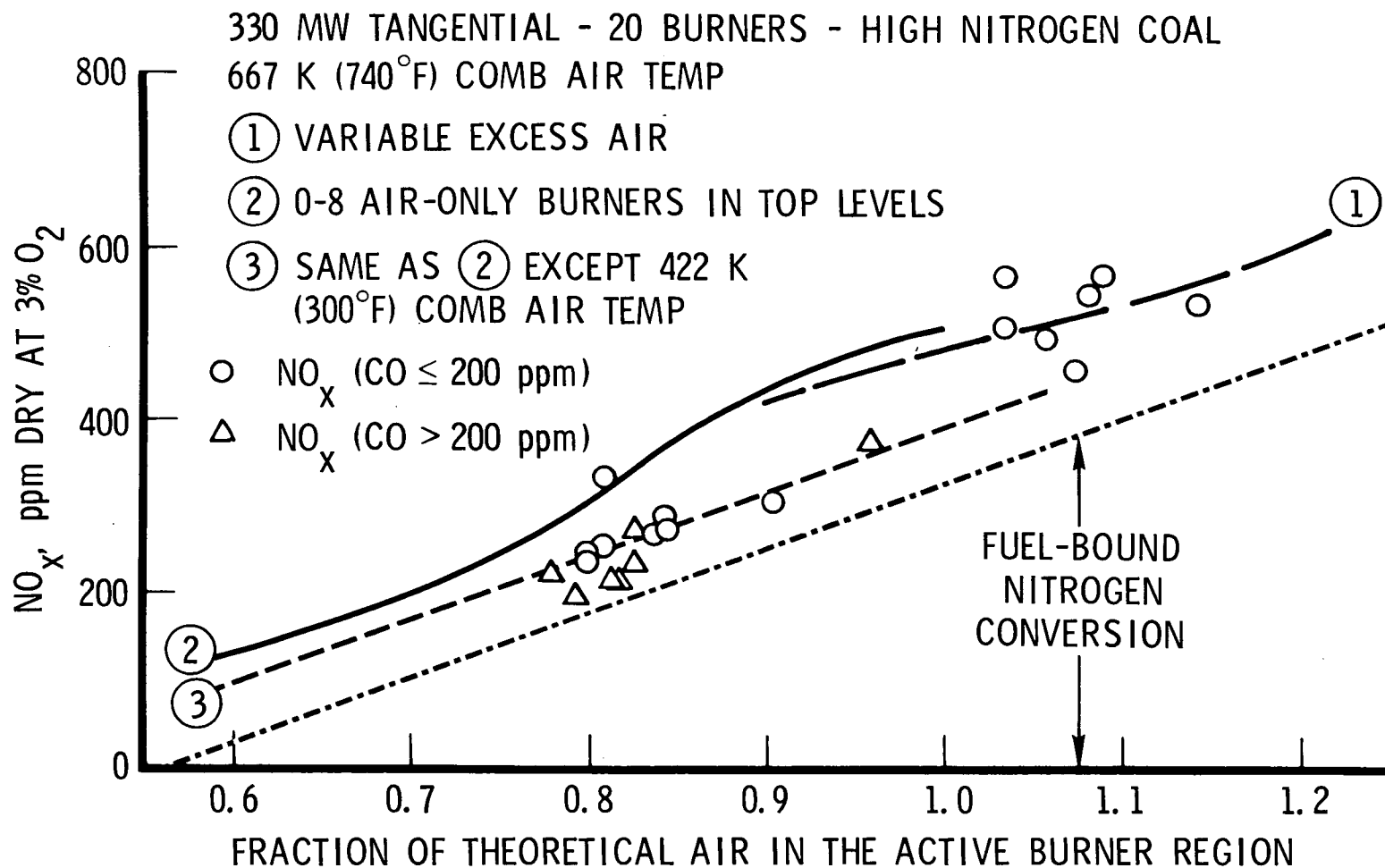


Figure 11. Effects of high combustion air temperature and high fuel nitrogen in tangential boiler

105 MW SINGLE-WALL - 18 BURNERS - HIGH MOISTURE COAL (Lignite)
 550 K (530°F) (est) COMB AIR TEMP

① VARIABLE EXCESS AIR

② 0-8 AIR-ONLY BURNERS IN TOP LEVELS

③ SAME AS ② EXCEPT 422 K
 (300°F) COMB AIR TEMP

○ NO_x ($\text{CO} \leq 200$ ppm)

△ NO_x ($\text{CO} > 200$ ppm)

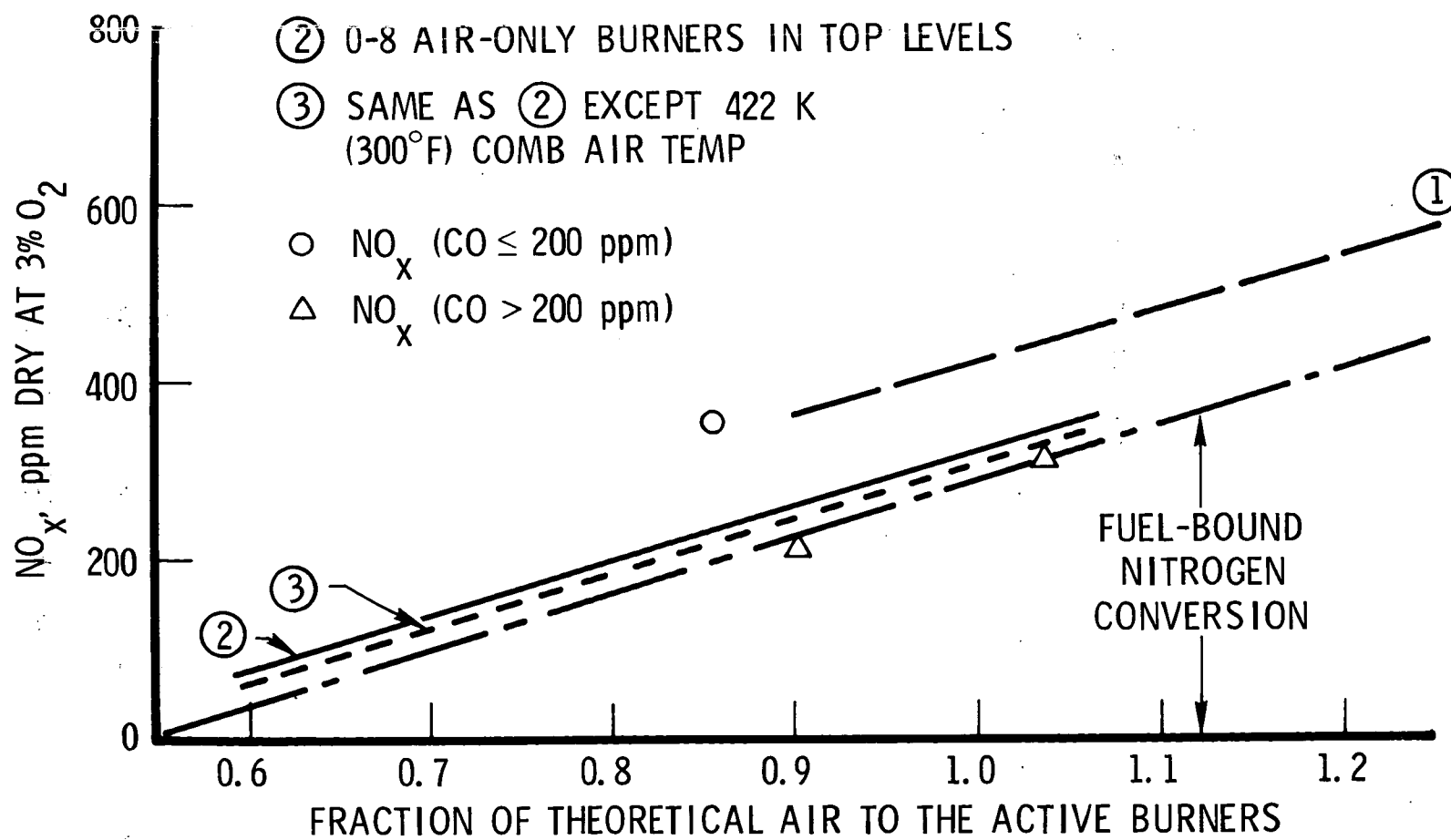


Figure 12. Effects of high moisture, low combustion temperature rise coal (lignite) with nominal combustion air temperature

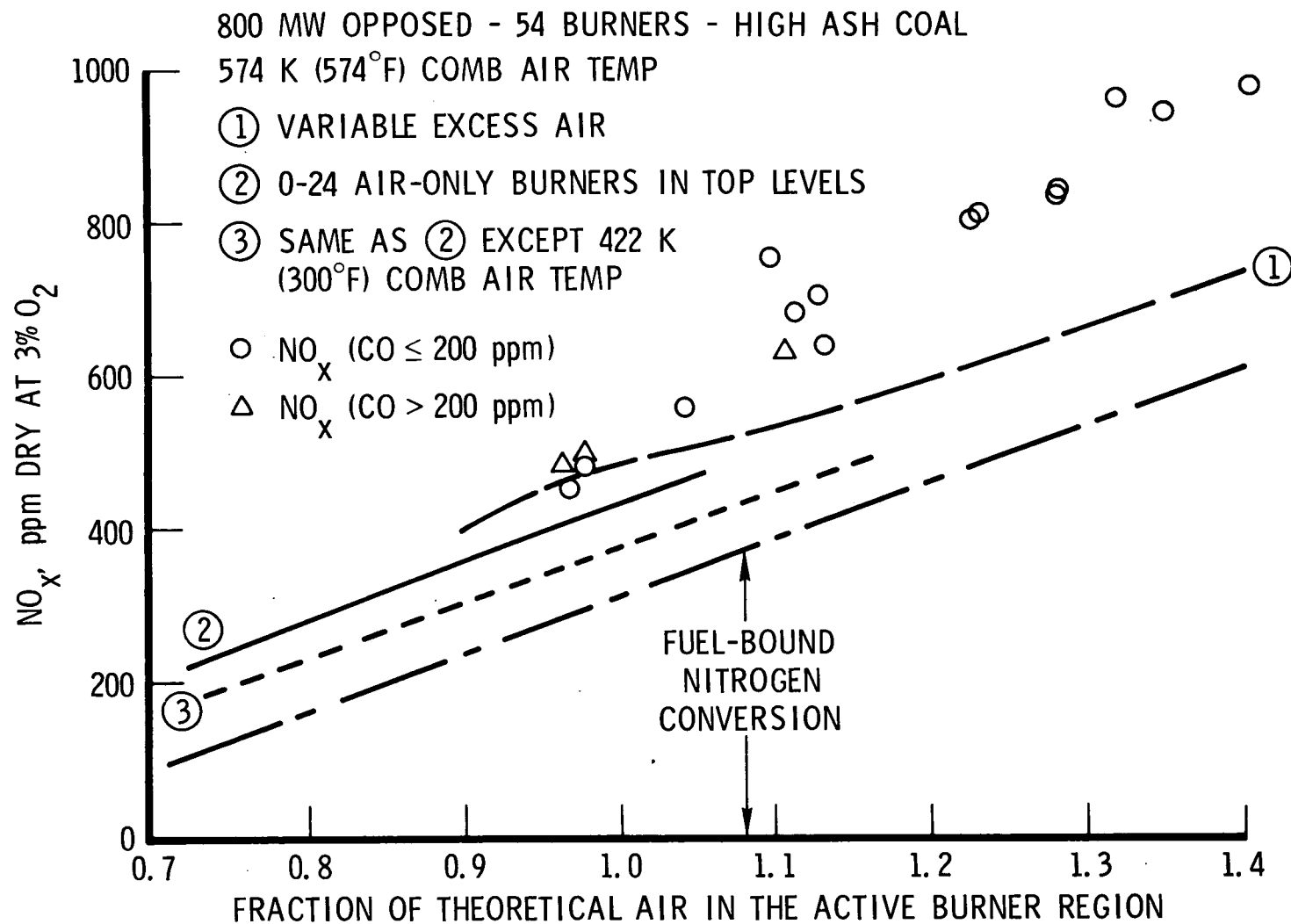


Figure 13. Effects of high ash coal with moderate combustion air temperature

line than about 160 ppm, even though high carbon monoxide levels are shown in some tests and some data represent operation at less than 75 percent of rated load. Unfortunately, data from other boilers firing this high ash coal were not available to this study. This boiler was also by far the largest in the data sample and involved the most complex and unsymmetrical burner array configuration, with a large number of burners (54) arranged such that some burners are opposed and some are not. Thus, there were insufficient data to determine if the apparent disagreement with the magnitude of fuel-bound nitrogen conversion calculation is real and, if so, whether the disagreement results from the coal type or the large and complex burner configuration.

In general, most of the data also tend to confirm the calculated slope of the fuel-bound nitrogen conversion line. The lower limit of the data shown in Figures 9 and 11 shows good agreement in slope. Figure 10 might be interpreted to indicate a somewhat shallower slope, but Figures 11 and 13 might indicate that a somewhat steeper slope is appropriate. Although not shown here, the lower limit of all of the oil-fired data from the previous study also tends to confirm the magnitude and slope of the fuel-bound nitrogen conversion line. There appears to be no reason, from the data of this study, then, to make any general, empirical change to the slope of the fuel-bound nitrogen conversion line calculated from the model.

To the extent that this linear relation can be assumed to hold in extrapolations to zero NO_x , the general agreement in both magnitude and slope tends also to verify this intercept. The model discussed in Section 2.1.2 and developed in Appendix B, then, appears to be rather well substantiated by the data.

2.2.2.2 Final Mixing Zone

Verification of the existence of the final mixing zone, as discussed in Section 2.1.3, and of the appropriate levels of NO_x generated

in the final mixing zone can be generally obtained from four main observations:

- a. This zone should exist only in firing configurations where air-only burners or NO_x ports (or both) are concentrated above the active burners.
- b. In firing configurations such as described in case a above, where there are few air-only burners, small NO_x ports, or overall boiler excess air is very high, the air-fuel ratio in the burners may be above stoichiometric. In this case, while a zone of final mixing of excess air with the products of combustion in the active burner region would physically exist, these combustion products would not be fuel-rich. As a result, the air-fuel ratio in this mixing zone would not pass through stoichiometric and the "final mixing zone," as defined in Section 2.1.3, would not exist. The thermal NO_x generated under such conditions could be higher or lower than that generated when the burner air-fuel ratios are less than stoichiometric, depending primarily on the temperature in this final mixing zone. With firing configurations such as described in case a, operated under conditions where the burner air-fuel ratios are below and above stoichiometric, the data may show a step change in thermal NO_x levels near stoichiometric. This step change, if it is observed in the data, may be the most direct evidence of the existence of this final mixing zone.
- c. Burner configurations without NO_x ports and with all burners active should show thermal NO_x levels higher or lower than those involving this final mixing zone,

depending on the temperature in this zone. Because the mixing patterns in the active burner region in this case are not the same as those of case b, thermal NO_x levels may not be the same as those in case b. In either case b or c, the parametric calculation for the appropriate configuration should account for these different thermal NO_x levels.

- d. Burner configurations with air-only burners distributed in the lower levels should show NO_x levels higher than those with the air-only burners in the top levels. It should be recalled, however, that none of the parametric calculations shown in the subsequent figures are intended to duplicate this case.

Figure 9 shows data from a boiler firing coal with a relatively nominal combustion temperature rise and involving a relatively nominal full-load combustion air temperature. This boiler has no NO_x ports. The parametric curve shown in the figure as no. 1 represents the firing configuration where all burners are active and only the overall boiler excess air was varied. It is recognized that in the actual boiler testing this excess air was never reduced below 105 percent of the theoretical (stoichiometric) air. The parametric calculation below this level of excess air is intended only to approximate some of the burner configurations with air-only burners located in lower levels of the burner array. The parametric calculations labeled nos. 2 and 3 represent the firing configuration with varying numbers of air-only burners located in the top levels of the burner array. These latter two calculations do involve a final mixing zone. The calculation labeled no. 3 represents the NO_x reduction that would be expected if the combustion air temperature were reduced to 422 K (300°F) in the firing configuration no. 2. As such a temperature reduction was not accomplished on any single boiler, confirmation of the effect of this change can only be estimated from the effects of different combustion air temperatures in different boilers.

The data shown in Figure 9 generally tend to confirm the parametric calculations. More detailed definition of the data (than shown in the figure) indicates that the measured NO_x levels with air-only burners concentrated in the top levels of the burner array tend to group around curve no. 2. All of the data grouped around curve no. 1 represent configurations either with air-only burners located in the lowest levels of the burner array (less than about 112 percent of theoretical air in the burners) or with all burners active. The difference between the constant amount of NO_x thermally generated in the final mixing zone and that thermally generated in the active burner region with all burners active (no final mixing zone) is small. (Curve no. 2 is about the same level above the fuel-bound nitrogen line as is curve no. 1 for excess air levels above about 115 percent of theoretical air.) Reduction in the combustion air temperature by 182 K (327°F) is predicted to result in reduction of thermal NO_x by about 70 ppm over the burner air-fuel ratio range between 85 and 115 percent of theoretical air. Actual full-load combustion air temperatures (604 K, 627°F) over this range show about 125 ppm of thermal NO_x .

Figure 10 shows the effect of reduction in combustion air temperature of 176 K (317°F) in a boiler firing the same coal type as that fired in the previous boiler (Figure 9). The relatively constant level of NO_x added to that from fuel-bound nitrogen conversion in firing configurations involving the final mixing zone is about 65 ppm, a reduction of about 60 ppm over the previous case.

The parametric calculations shown in Figure 10 indicate that curve no. 1, however, was not significantly affected by the combustion air temperature reduction. As discussed in Section 2.1.1, because of the way the secondary air is introduced in a tangential boiler, this firing type is treated, in this study, as a case effectively involving fixed NO_x ports. Also, in all of the burner configurations tested in the two tangential boilers of this study that involved air-only burners, the air-only burners were located only in the top level of the burner array. Thus, all of the data and

the parametric calculations shown in Figure 10, and later in Figure 11, represent configurations where air-only burners, NO_x ports, or both, are concentrated above the active burners. The final mixing zone, as defined in Section 2.1.3, however, would exist only in those cases where the fraction of the theoretical air in the active burner region (the same as in the burners, in all of these configurations) was less than stoichiometric. Thus, with these tangential boiler data, a step transition between curves nos. 1 and 2 could be expected to appear in the data around stoichiometric. Above this level, the agreement is poor. All of the data shown above stoichiometric excess air resulted from firing configurations with all burners active. As such, they should be grouped about parametric curve no. 1. A step change of about 70 ppm would be expected around stoichiometric excess air, in a transition from curves nos. 1 and 2. Instead, most of the data show no step and, in fact, indicate that the thermal NO_x drops off to zero at very high levels of excess air. This apparent trend in this boiler is unexplained. It will be seen, however, that this trend is not evidenced in the data from the other tangential boiler in this study.

Comparison of Figures 9 and 10 appears to indicate the reduction in the NO_x from the final mixing zone expected from the reduction in combustion air temperature. There is also a difference in firing type between these two boilers, however, which could have caused the observed reduction. This question can be reasonably resolved by comparison of Figures 10 and 11. These data both represent tangential boilers of approximately the same design and size. There is a small difference in the coal type. The boiler of Figure 10 was fired with the nominal coal type 3, which contained 1.3 percent by weight (of the total coal weight) chemically bound nitrogen, while the coal fired in the tangential boiler of Figure 11 contained 1.7 percent nitrogen (type 4). This difference should be accounted for by the calculation of NO_x generated from conversion of the fuel-bound nitrogen. The temperature rise due to combustion at stoichiometric conditions is very nearly the same for these two coal types (only 13 K, 23° F, difference).

Curve no. 2 shown in Figure 11 indicates that the thermal NO_x , in this case, is between about 150 to 190 ppm. This is commensurate with the higher combustion air temperature of this boiler compared to the other tangential configuration (240 K, 432°F, higher). Both of the parametric calculations shown in Figure 11 show considerably greater thermal NO_x generated in the active burner region over the air-fuel ratio range between about 85 and 105 percent of theoretical air. At the normal NO_x levels, it appears that incorporating just a few air-only burners, located in the top level, into the burner array actually increases the thermal NO_x and partially offsets the decrease in NO_x from fuel nitrogen. Incorporating four or more air-only burners in the top row, however, appears to reduce NO_x from both the thermal and fuel nitrogen sources, and rather steep reductions in overall NO_x emissions result.

The data shown in Figure 11 represent just two main firing configurations: (1) those representing four air-only burners concentrated in the top level of the burner array, shown grouped around 81 percent of theoretical air; and (2) those with all burners active, grouped around 107 percent of theoretical air. The first data group should be represented by curve no. 2 and the second by curve no. 1. The data around 81 percent of theoretical air show NO_x levels well (50 to 115 ppm) below curve no. 2 when excessive carbon monoxide levels are present, as expected, but the tests with acceptable carbon monoxide levels are also, on the average, lower than curve no. 2 by 64 ppm.

The data grouped around 107 percent of theoretical air show good agreement with parametric curve no. 1. Thus, this tangential boiler does not show the tendency for the thermal NO_x to approach zero at high levels of excess air that was indicated in Figure 10.

The data shown in Figure 11, although limited in range, appear to indicate that parametric curve no. 2 perhaps should be more like curve no. 3 and that a step transition from curve no. 2 to curve no. 1 may exist around stoichiometric excess air.

The effect of combustion air temperature on NO_x is postulated here to result from variations in the peak combustion temperature in the final mixing zone. These temperatures result from (1) an initial reactant temperature established primarily by the combustion air temperature; (2) a temperature rise from this level due to, and inherent in, the combustion of the coal; and (3) cooling of the combustion products enroute to the region of interest in the furnace. Thus far, the data shown have concentrated on the effect of combustion air temperature in boilers firing coals with essentially the same combustion temperature rise (at the same air-fuel ratio).

Coal type 1 (see Table 2) is a high moisture (lignite) coal. The high moisture content results in a lower heating value and a lower temperature rise due to combustion. The temperature rise due to combustion of coal type 1, at stoichiometric air-fuel ratio, is calculated to be 260 to 270 K (470 to 490° F) lower than those of the coal types fired in the boilers discussed thus far (coal types 3 and 4). Parametric calculations for a single-wall boiler firing this type of coal are shown in Figure 12. The parametric calculations show no indication of significant thermal NO_x generated in either the active burner region or the final mixing zone when any number of air-only burners are located in the top levels of the burner array (curves nos. 2 and 3). With all burners active, however, the parametric calculations (curve no. 1) indicate significant thermal NO_x (100 to 130 ppm)

The data available for verification of these calculations are very limited. Of 14 tests for which data were recorded,⁷ 11 tests were deleted from the data sample because some secondary air registers were fully or partially closed during these tests. As discussed in Section 2.1.4, it was considered impossible to determine the distribution of combustion air in these cases with accuracy sufficient for this study.

The two data points shown in Figure 12 on the line representing NO_x from conversion of fuel-bound nitrogen resulted from configurations with air-only burners concentrated above the active burners.

The appropriate parametric calculation shown in the figure is curve no. 2. These two firing configurations showed excessive carbon monoxide emissions (near 1000 ppm) and NO_x levels, as expected, slightly (30 to 45 ppm) below curve no. 2. The remaining useful test involved air-only burners located in the lowest levels of the burner array and, therefore, measured NO_x levels are not related to any parametric calculation shown in the figure. It is interesting to note, however, that, despite the very low combustion temperature rise of this coal, large increases in NO_x levels can result with air-only burners located low in the lower levels of the burner array. This may indicate greater mixing of the burner flows and bulk gases in the active burner region in this single-wall boiler than anticipated (and the resulting greater conversion of fuel-bound nitrogen).

Further confirmation of calculations for lignite coal will be shown later in this section in the analysis of a boiler not in the data sample used for regression analysis.

A further example of the effect of reduced combustion temperature rise because of the coal type could be obtained from the boiler in the data sample firing the high ash coal (coal type 2 of Table 2). The high weight fraction of inert ash in this coal limits the heat release per unit weight of this coal and absorbs some of the heat of combustion. Equilibrium combustion calculations indicate that the temperature rise due to combustion of this coal under a stoichiometric air-fuel ratio is 1697 K (3055°F), compared to 1566 K (2819°F) for the lignite coal (type 1) and 1836 to 1823 K (3305 to 3281°F) for coal types 3 and 4, respectively. Thus, the combustion temperature rise of this high ash coal is intermediate between the lignite coal and the nominal coal represented by coal type 3. The full-load combustion air temperature of this boiler was nominal (574 K, 574°F).

Figure 13 shows the calculations and available data for the boiler firing this high ash coal. The calculations, as expected, show a level of thermal NO_x generation (above the NO_x levels from fuel-bound nitrogen conversion) intermediate between that calculated for the coals with

low and high peak combustion temperatures. The data, however, deviate considerably from the calculations, particularly at high levels of overall boiler excess air.

As mentioned in the discussion with respect to Figure 13 in Section 2.2.2.1, the burner configuration in this boiler is so complex and unsymmetrical that it is difficult to estimate the appropriate effective fraction of theoretical air in the active burner region when air-only burners are located anywhere but in the top level of the burner array. Nearly half of the data represent tests with such mixed burner configurations. Of the remaining data only one test (that with the lowest level of excess air in the burners) was conducted with excess air in the burners less than stoichiometric. That test, although it showed excessive carbon monoxide emissions (260 ppm), still showed NO_x levels 78 ppm higher than the parametric calculation (curve no. 2). All of the data shown in Figure 13 at NO_x levels above 820 ppm resulted from testing with all burners active. The disagreement here with the appropriate parametric calculation (curve no. 1) is large, averaging more than 200 ppm.

At this writing, no satisfactory explanation of this disagreement has been discovered. The data appear to show a large (about 200 ppm) step change in NO_x levels when the excess air in the burners is about 105 to 110 percent of theoretical. This might imply that much more thermal NO_x is being generated than calculated. On the other hand, it is conceivable that the fuel-bound nitrogen conversion efficiency is higher with this high ash coal than with the others in the sample. It might be conjectured that a larger fraction of the nitrogen normally remaining in the char is converted to NO_x under the very high levels of excess air required in these boilers to burn out the carbon in the char. Unfortunately, no further data were available to this study involving these very high ash coals.

Although the disagreement between the calculations and the data shown in Figure 13 is large for test conditions where the excess air in the burners is high, the disagreement is much less at the lower levels of

excess air and appears to be decreasing further with excess air in the burners. From the standpoint of a NO_x reduction program, then, the parametric calculations (particularly curve no. 2) may still be useful. Perhaps the general conclusion from the data of Figure 13 should be that very strong reductions in NO_x levels can be achieved by reducing the excess air in the burners to less than about 105 percent of theoretical and that further reductions may be indicated by the parametric calculations.

2.2.2.3 Boiler Not in the Data Sample

If the entire data analysis approach taken in this study of coal-fired boilers is indeed general, and if the range of coal types and boiler configurations included in the data sample analyzed adequately represent the operational spectrum, then the resulting parametric equation should also be sufficiently general to predict NO_x emissions in other boilers not in the data sample.

Use of the parametric equation to accurately predict NO_x emissions, however, requires a great deal of information on boiler geometry, coal analysis, and operating conditions. It also requires a relatively complex computer program to calculate the values of the terms in the equation as the desired variables are parametrically varied. The results of this study would be much more widely useful if just a few simple calculations could be made at least to predict reasonably obtainable lower limits of NO_x and to provide direction on how to modify combustion to reach these lower limits. To some extent it is academic to explain why certain test conditions yield very high NO_x emissions if NO_x reduction is the purpose of the exercise.

In order to evaluate such an approach, the data from Leland Olds Boiler No. 1, of the Basin Electric Power Cooperative,⁷ were excluded from the sample used for the regression analyses. This boiler was thought to represent a complex test of the generality of the results of this study. A high moisture (lignite) coal (with the low combustion temperature rise) was fired in this boiler but full-load combustion air temperatures were very

high (783 K, 950°F). The burner configuration in this boiler is also very complex, consisting of two levels of horizontally opposed burners, four burners in each wall at each of these two levels, topped by four unopposed burners in a single level in only one wall.

Initial considerations regarding the boiler configurations of interest to a NO_x reduction program were the following:

- a. Only NO_x emissions under full rated load are of interest.
- b. A nominal, reference operating condition, with all burners active, is desirable.
- c. Most of the literature and the results of this study (see Figure 8) indicate that minimum NO_x emissions with air-only burners in the burner array result when these air-only burners are located in the top level of the array. Prediction of NO_x levels with other configurations is not of interest. This also simplifies prediction because, with all air-only burners located in the top level, the average, effective fraction of excess air in the active burner region is equal to the fraction of excess air in the active burners. [Equation (1) is equal to one.]
- d. Minimum NO_x levels are achieved when the overall boiler excess air is as low as possible, consistent with acceptable carbon monoxide emissions. For configurations involving air-only burners, then, the overall boiler excess air was set at a level that yields three percent excess oxygen (116 percent of theoretical air).
- e. An indication of the effect of reduction in combustion air temperature is desirable.

Under these considerations, the prediction of NO_x levels for this boiler, not in the data sample used for regression analyses, was accomplished as follows:

- a. NO_x emissions generated from conversion of fuel-bound nitrogen were estimated by selecting the appropriate curve from Figure 6 (in this case, coal type 1). This curve could also be calculated according to the procedure outlined in Appendix B.
- b. The thermal NO_x levels with all burners active were taken directly from the constant resulting from the regression analysis of the entire coal sample (i.e., 146 ppm).
- c. Thermal NO_x levels with air-only burners located in the top levels of the burner array, a constant resulting from the final mixing zone, were estimated from the curve shown in Figure 16 of Appendix C. The appropriate temperature for that figure was estimated from (1) the combustion temperature rise at stoichiometric air-fuel ratio, from equilibrium combustion calculations for coal type 1; (2) the measured full-load combustion air temperature or the arbitrarily chosen 422 K (300° F); and (3) a rough estimate of 110 K (200° F) cooling of the peak combustion temperature enroute to the final mixing zone.

Figure 14 shows the results of these simple parametric calculations for Leland Olds No. 1. The data show good agreement with the parametric calculations, both curves nos. 1 and 2, including the lower levels of NO_x consistently observed when carbon monoxide emissions are high. These data also show a distinct step transition between curves nos. 1 and 2 at a level of excess air in the burners of about 105 percent. This is consistent with

218 MW OPPOSED - 20 BURNERS - HIGH MOISTURE COAL (Lignite)

780 K (950°F) COMB AIR TEMP

① VARIABLE EXCESS AIR

② 0-8 AIR-ONLY BURNERS IN TOP LEVELS

③ SAME AS ② EXCEPT 422 K
(300°F) COMB AIR TEMP

○ NO_x (CO \leq 200 ppm)

△ NO_x (CO $>$ 200 ppm)

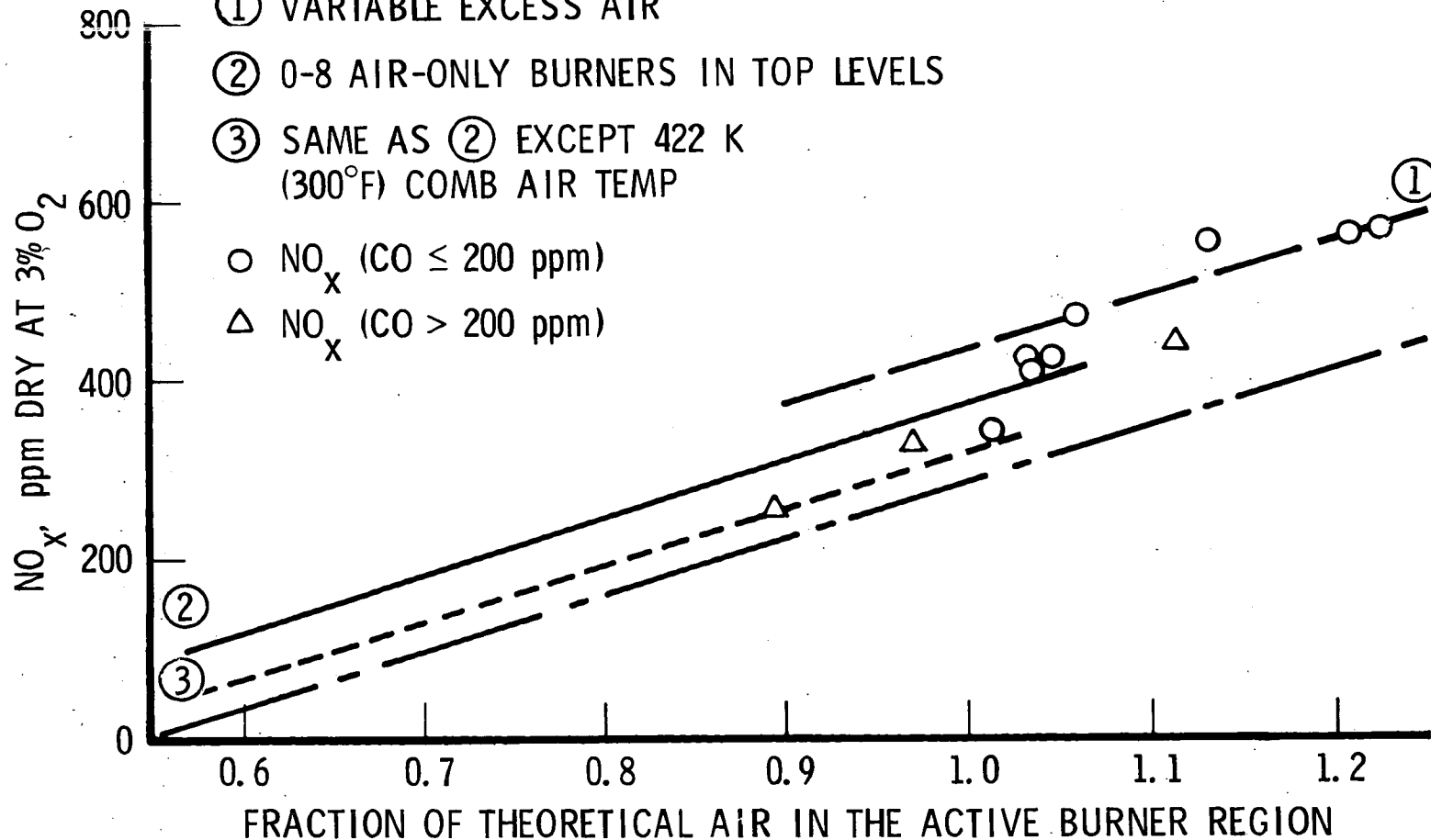


Figure 14. Parametric calculations for boiler not in data sample used to derive equation

the level of excess air above which the final mixing zone, as defined in Section 2.1.3, would cease to exist. This is because the final mixing would not force the air-fuel ratio of the products of combustion from the active burner region to pass through, or even approach, the region of high thermal NO_x generation near stoichiometric.

In general, then, the agreement between data and the simple parametric calculations are perhaps better in this case, of a boiler not in the data sample used for regression analysis, than it is with any of the others. As this boiler is largely a horizontally opposed configuration, the agreement here also tends to indicate that the disagreement observed with the high ash coal (Figure 13) is probably not due to the opposed-firing configuration, as such.

2.2.3 Boiler Excess Air

One other observation from the calculations and data of this study deserves some attention. In the comparison of data with the parametric calculations shown in Figures 9 through 14, it was consistently observed that NO_x levels measured during tests that also exhibited excessively high levels of carbon monoxide tended to be lower than the calculated curve. While not expressly stated, closer examination of the data also shows that NO_x levels measured during tests in which the overall boiler excess air was very high (and carbon monoxide levels very low) tended to be higher than the calculated curve. These observations appeared to be generally true regardless of the boiler or burner configuration represented by the test data.

It is well known that when the overall boiler excess air is reduced, some level is reached below which carbon monoxide emissions begin to rapidly increase. Thus, the above observations could simply be attributed to a strong effect of excess air on NO_x emissions. It seemed clear, however, that either the model used in this study or the regression analysis of the data, or both, failed to account for a very strong, step change

in NO_x when overall boiler excess air was in the range where carbon monoxide levels begin to become excessive (about two to three percent oxygen). This could imply a phenomenon that was not properly modeled.

A separate, more detailed study of the effect of overall boiler excess air alone on NO_x and carbon monoxide emissions with available data is usually difficult to interpret because either a number of other significant variables are also varying or there is too little data. By the time that all of the data with different boiler geometries, burner configurations, and significantly different load levels are eliminated, usually very little data are left to show this effect. One exception in the data sample of this study is the data from the sister boilers Widows Creek No. 5 and 6.

Data from these sister boilers represent the largest coal-fired data sample from a single coal and boiler type in this study. It was possible, then, to select only data from this sample where the firing configuration was held constant (all burners active) and the boiler was operated near rated load (greater than 80 percent of rated capacity), and still have enough data left to show meaningful results. These selected data were averaged over each 0.5 unit of excess oxygen and are shown in Figure 15.

This figure shows the usual trend for NO_x to decrease and carbon monoxide to increase as the overall excess air is decreased, but it also shows what might be interpreted as an independent effect of the presence of high concentrations of carbon monoxide on the NO_x levels. The effect of boiler excess oxygen (or air) appears relatively small at excess oxygen levels above about 3.5 percent and below about 2.7 percent. In between these excess oxygen levels, decreasing excess oxygen appears to result in a step-like change in NO_x levels amounting to about 150 ppm, accompanied by a strong increase in carbon monoxide emissions from negligible levels to over 1000 ppm. While this trend is not as clear in other data samples, it appears that the step reduction in NO_x with the appearance of high levels of carbon monoxide emissions as overall boiler excess air is reduced, in this excess oxygen range, occurs in other boilers fired in this same

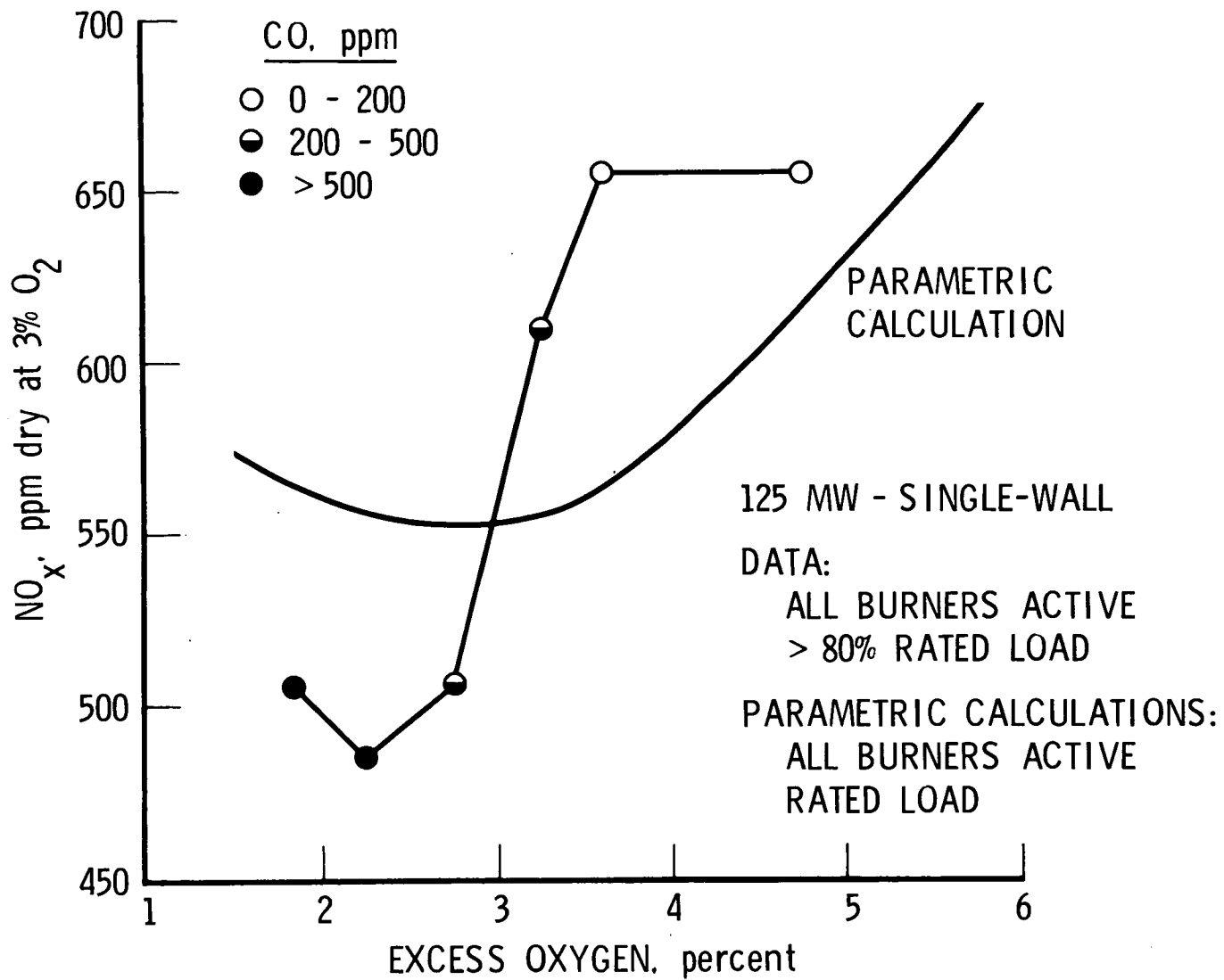


Figure 15. Effects of excess air and carbon monoxide levels on NO_x

configuration as well as in this same boiler fired with some burners out of service (air-only).

The possibility of some sort of competition between carbon monoxide and NO_x for the available oxygen (or reduction of NO_x by carbon monoxide) was implied in the assumptions in the fuel-bound nitrogen model, discussed in Section 2.1.2. It was assumed there that the oxygen remaining after all of the carbon had been oxidized to carbon monoxide and the free hydrogen to water was divided in some fixed proportions between oxidation of the carbon monoxide to carbon dioxide and the fuel-bound nitrogen to NO_x . Figure 15 indicates that, for levels of excess oxygen greater than about 3.25 percent, there is more than enough oxygen available to oxidize all of the carbon monoxide to carbon dioxide. The resulting NO_x levels, under these conditions, may be established by the availability of the fuel-bound nitrogen (for example, in the volatiles rather than in the ash). Reducing the excess oxygen from 3.25 to about 2.25 percent (only a one percent reduction) results in a strong increase in carbon monoxide emissions with measured values exceeding 1000 ppm. At 2.25 percent excess oxygen, then, the efficiency of conversion of the available fuel-bound nitrogen may now be at least partly established by the competition between the carbon monoxide and fuel-bound nitrogen for the remaining oxygen (oxygen limited).

Although much of the above paragraph is conjecture, Figure 15 does appear to indicate that such a step change in NO_x levels with overall boiler excess air exists. This observation is somewhat supported by the data shown in Figure 9 and to a more limited extent by that shown in Figures 10, 11, and 12. Closer examination of data in these figures shows that what appears to be unexplained data scatter around some of the parametric calculations is, to a large extent, a result of this strong but limited (step) decrease in NO_x with the appearance of excessive levels of carbon monoxide emissions.

It is not clear, at least from this study, what characteristics of the coal control the magnitude of this step or even if the coal characteristics alone are the determining factors. Perhaps it is not important

to answer this question in this NO_x reduction study since it is clear from any study of NO_x control in coal-fired boilers that maximum reduction of NO_x emissions requires that the overall boiler excess air be reduced to the point where carbon monoxide emissions begin to become unacceptable. In the light of the apparent significant effect of carbon monoxide emission levels on NO_x, however, it might be desirable to reevaluate those levels currently considered unacceptable as well as those operating practices that tend to maintain carbon monoxide emissions well below these levels.

GENERAL DISCUSSION OF THE STUDY OF COAL-, OIL, AND NATURAL GAS-FIRED DATA

Study of techniques for NO_x reduction in coal-fired boilers clearly indicates the significance of the fuel-bound nitrogen as a source of NO_x emissions. If the model for conversion of fuel-bound nitrogen developed in this study is reasonably accurate, however, then the total NO_x emissions problem can be separated into that associated with this source and that associated with thermally generated NO_x . Results from this study of coal-fired data and those from the previous study of oil- and natural gas-fired data indicate that the two mechanisms do not appear to be inherently related to each other (i.e., thermally generated NO_x does not appear to be a strong function of the NO_x generated from conversion of fuel-bound nitrogen, and vice versa). All of the results of this study, then, should serve to extend and corroborate the results of the previous study.

The observations on NO_x reduction from the study of oil- and natural gas-fired data are related to the more basic observation that thermal NO_x can be minimized by operating either on the fuel-rich or on the fuel-lean sides, well away from stoichiometric. Subtraction of the NO_x calculated for conversion of fuel-bound nitrogen from the test values shown and discussed in this report shows the same general conclusions of the previous report.¹ General observations of combustion modifications for minimum NO_x emissions, then, can be discussed for all three fuels and can be shown to depend on the amount of nitrogen chemically bound in the fuel.

The general technique for minimizing NO_x emissions from the conversion of fuel-bound nitrogen involves maximum reduction of the air available for combustion in the local regions of the boilers where the solid or liquid fuel is gasifying and where the initial hydrocarbon reactions are taking place. Without major modifications to existing boilers, this implies the operation of large numbers of burners on air-only, NO_x ports, or both, all located as high as possible in the boiler.

Techniques for minimizing thermally generated NO_x depend on the concentration of nitrogen in the fuel. In high nitrogen fuels such as coal, the air available for combustion in the active burner region must be maintained as low as possible, at least until the initial hydrocarbon reactions are completed. This will also minimize NO_x thermally generated in the active burner region. The remaining problem area, then, is in the boiler mixing zone where the remaining excess air must be added to the hot products of the earlier fuel-rich combustion to bring the total for the overall boiler up to about three percent excess oxygen. It is in this region that the local air-fuel ratio of the bulk gases must pass through the region of high thermal NO_x generation rates around stoichiometric as the remaining excess air is added. The data of this study indicate that techniques which reduce the gas temperature in this region (i.e., reduce combustion-air temperature or low temperature rise due to combustion) are quite effective in minimizing NO_x thermally generated in this region.

If there is no nitrogen chemically bound in the fuel, as with natural gas, it is not necessary to maintain fuel-rich conditions in the early combustion regions. In fact, in order to avoid establishing mixing zones anywhere in the boiler where the air-fuel ratio must pass through the regions of high thermal NO_x generation rates, it appears most desirable to maintain air-fuel ratio conditions in natural gas burners well above that of the overall boiler, finally approaching the boiler air-fuel ratio at the latest possible moment through the use of fuel-rich burners in the top level of the burner array, or through the use of fuel-rich NO_x ports. This optimized concept has not been tested in full-scale utility boilers. With more standard modifications, involving air-only burners, air-only NO_x ports, or both, the remaining active burners can only be fuel-rich. With gaseous fuels, where the intimate air-fuel mixing in the burner flows is rapid, minimum NO_x emissions normally result from the same burner and NO_x port configurations that minimize NO_x emissions in coal-fired boilers (i.e., large numbers of

air-only burners concentrated in the top levels of the burner array, open NO_x ports and reduced peak combustion temperatures).

Low nitrogen-bearing oil fuels (less than about 0.25 percent nitrogen, by weight) represent an intermediate case between that of coal and natural gas. Clearly, if very low NO_x emissions are required, the NO_x resulting from conversion of this low concentration of fuel-bound nitrogen must be eliminated. This means that the burner air-fuel ratio must be the same as for minimum NO_x in coal-fired boilers. If, however, the level of NO_x emissions resulting from conversion of the fuel-bound nitrogen at air-fuel ratios somewhat above that of the overall boiler is acceptable, then the optimum natural gas configuration might be appropriate. The natural gas configuration might at least minimize thermally generated NO_x , leaving only the NO_x resulting from the conversion of some fraction of the fuel-bound nitrogen. As liquid fuels require considerable time to vaporize and, therefore, intimate air-vapor fuel mixing is slow compared to that of natural gas, the average, local air-fuel ratio surrounding the burning oil vapor can approximately be maintained air-rich simply by locating air-only burners in the lower levels of the burner array (i. e., by maintaining air-rich bulk gases). All of the oil-fired boiler data analyzed previously¹ indicated that, within the range of the configurations tested, minimum NO_x emissions resulted from this latter case.

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APPENDIX A

MIXING ZONE LENGTHS IN TANGENTIAL BOILERS

In the mixing model for all boiler firing types, the mixing of various flows entering a zone is assumed to occur instantaneously at the beginning of the zone. The resulting mixture is then assumed to flow uniformly through the zone, cooling and generating NO_x . The average time for cooling enroute to a given zone is taken as the sum of the stay times in all of the zones upstream of the given zone plus one-half of the stay time in the given zone. The time for NO_x generation in that given zone is the stay time in that zone.

Stay times are all calculated from the length of the zones divided by the average flow velocity within the zones. Because of the significantly different flow and mixing patterns, it was necessary to modify some of the mixing zone definitions and lengths used with face-fired boilers to approximate the mixing in tangential boilers. Figures 1 and 3 of the main body of the text generally show the modifications in burner flow mixing. The resulting differences in zone lengths are discussed briefly here.

The primary zone lengths are considered to be approximately the same in face and tangentially fired configurations. These lengths are taken as twice the horizontal width (or diameter) of the burners. In the tangential configuration, the horizontal width of "a burner" was taken as that of the primary (carrier) air and fuel duct assuming a square geometry.

In the opposed-fired boilers, the sum of the lengths of the secondary and the opposite zones were taken to be the distance from the

firing wall to the center of the furnace (midway between the firing faces) minus the length of the primary zone. The length of the opposite (and adjacent) mixing zone was taken as twice that of the secondary zone. Thus, for opposed-fired boilers,

$$ZLAO = \frac{(HDF/2) - ZLP}{1.5} \quad (2)$$

and

$$ZLS = ZLAO/2 \quad (3)$$

These same assumptions were used for the tangential boilers except instead of the burner flow going from a firing wall to the center of the furnace (see Figure 1 of the main body of the report) the flow from a burner in the tangential furnace goes from a corner of the furnace to a point off the centerline of the furnace (see Figure 3). This total distance was taken as the average horizontal length of a side of the furnace times the cosine of 30 degrees. If the same proportions as in the opposed-fired boiler are used, the lengths of the opposite (and adjacent) and the secondary mixing zones can be calculated from

$$ZLAO = \frac{[0.866 (HWF + HDF)/2] - ZLP}{1.5} \quad (4)$$

and

$$ZLS = ZLAO/2 \quad (5)$$

The greatest difference between the wall-fired and the tangentially configured boiler flow patterns appears to be in the recirculation flow. The recirculation flow in a face-fired boiler was assumed to originate from one burner, recirculate in essentially a 360° circle and mix with the

flow from the burner in the next elevation above. This case was assumed because the flows from all other burners are either parallel or directly opposed to the flow from a given burner. In the tangential configuration, however, the flow from a given burner is not parallel to, nor does it directly oppose, the flow from other burners. Instead, a given burner flow is more or less directed at the next burner in the direction of the general rotation of the bulk gases. Low-pressure regions generated by entrainment of gases near a burner in one corner are much more likely to generate a recirculation flow from the burner in the adjacent corner.

In the wall-fired boilers, the recirculation flow was taken to travel a distance of π times the length of the primary zone at the velocity in the primary zone. In the tangential boilers, the same amount of recirculation flow was taken to travel a distance equal to the average horizontal length of the furnace walls at one-half of the velocity in the primary zone. Thus, the stay time of a given quantity of reactants in a recirculation zone in an opposed-fired furnace is given by

$$TUR_o = \frac{\pi ZLP}{VP} \quad (6)$$

while the equivalent stay time in a recirculation zone in a tangential furnace is

$$TUR_t = \frac{HWF}{2} \frac{HDF}{VP} \quad (7)$$

For typical opposed-fired and tangential boilers where the horizontal section might be a square 12.2 meters (40 feet) on a side and the horizontal width of the burners might be 0.914 meters (3 feet), the ratio of stay times in each of the mixing zones in a tangential boiler compared to these same zones in an opposed-fired boiler (in this study) are shown below:

<u>Mixing Zone</u>	<u>Ratio of Stay Time, Tangential/Opposed</u>
Primary	1.00
Recirculation	4.24
Secondary	2.04
Adjacent/Opposite	2.05

The stay time in the recirculation region in a tangential boiler, under the mixing assumptions of this study, is more than four times that in a face-fired boiler. (In all cases only about one-third of the flow from a given burner is assumed to pass through the recirculation zone.) This flow in a tangential boiler also passes very close to a water wall along the entire length of the recirculation zone. Unfortunately, no allowance could be made in this study for the possibly increased cooling rate in this zone caused by combined radiative and convective heat transfer.

In general, the total cooling time involved in burner flows in a tangential boiler, before they enter and mix with the bulk gases, is about twice that of face-fired boilers. The stay times in the bulk gas mixing zones, for the same vertical distance between burners, are taken as the same, in all cases, as are the NO_x port or final mixing zones. The effect of these longer cooling times is particularly strong in reducing the temperatures in the final mixing zone, equivalent to configurations with NO_x ports located very high in face-fired boilers.

APPENDIX B

MODEL FOR NO_x FROM CONVERSION OF FUEL-BOUND NITROGEN

The basic assumptions on which this largely empirical model of conversion of fuel-bound nitrogen to NO_x is based are discussed in Section 2.1.2 of this report. The data for oil fuels shown in Figure 5 of the main body of the report need no explanation other than the reference sources cited in the figure. Several attempts were made to include the coal data with the oil data such that the oil and coal data were internally consistent in the same fashion that the oil and coal data samples were consistent with each other (i.e., the curve that separately fit the oil data and the one that separately fit the coal data were the same curve). It was found that the measured efficiency of conversion of the nitrogen bound in the coal was always lower than that which would be predicted by extrapolating a reasonable fit of the oil conversion efficiency data unless the appropriate weight fraction of bound nitrogen in the coal was taken as that fraction of the coal weight with all of the inert diluents (ash and moisture) removed. This result seems reasonable because (1) this is essentially the same definition of weight fraction of bound nitrogen in the oil fuels (as they contain negligible ash and moisture), and (2) addition of any amount of inert solids containing no nitrogen to a coal (which would change the weight fraction of the overall fuel that is bound nitrogen) would not be expected to affect the amount of NO_x generated during the reaction.

For the data shown in Figure 5, the fraction of the coal weight that is ash was obtained directly from the ultimate analyses for the coal

fired.^{7,8} The moisture was obtained not from the proximate analyses but from an assumption that all of the oxygen reported in the ultimate analyses was bound with the appropriate weight of hydrogen in the form of water. On the average, this calculation results in a weight percent of moisture in the coal about 2.4 percent less than that cited in the proximate analysis. This difference is as large as ten percent (low) with the lignite coals. No attempt was made to correct for this difference.

The empirical curve shown in Figure 5 was established to fit the average of the oil data because these data resulted from testing either with large quantities of flue gas dilution⁵ or with very low combustion air temperatures.⁸ Nearly all of the NO_x measured in these tests should have resulted from conversion of fuel-bound nitrogen. The data for coal-firings, however,^{7,8} were obtained under test conditions where thermal NO_x could be appreciable. The curve was therefore fit to that data as a lower bound.

No serious attempt was made to generate any data, or to fit the curve, for fuels where the weight fraction of fuel-bound nitrogen was less than about 0.2 percent. It is meaningless that the curve fit to the data reaches 100 percent conversion for a fuel with a weight percent of bound nitrogen slightly greater than 0.1 percent.

The expression for NO_x emissions, in ppm (dry), can be written from stoichiometry. If the equivalent coal molecule is written



the NO_x emissions, expressed as nitric oxide (NO), ppm (dry), are

$$\text{NO} = \frac{(ec)10^6}{0.9996 K_1 (\text{AFRCL}) + (b/2) - (a/4)} \quad (9)$$

where

e = fraction of fuel-bound nitrogen converted to NO

AFRCL = air-fuel ratio of the overall boiler, by weight

$$K_1 = (1 + A)(\text{MW fuel})/(\text{MW air}) \quad (10)$$

The two main assumptions used in the further development of this model of fuel-bound nitrogen conversion, as discussed in Section 2.1.2 of the text, are (1) the conversion efficiency e is directly proportional to the availability of oxygen in the boiler region where the initial hydrocarbon reactions are taking place, and (2) only the oxygen remaining after all of the carbon in the fuel has been oxidized to carbon monoxide and all of the hydrogen (not already bound in moisture in the fuel) to water is available to form NO. The conversion efficiency e , according to these assumptions, can be written

$$e = K (\text{AFRP} - \text{AFRCOS}) \quad (11)$$

where

AFRCOS = air-fuel ratio, by weight, at which assumption (2) is exactly satisfied [here called "CO stoichiometric" (COS)]

AFRP = air-fuel ratio, by weight, in the effective local region, defined in assumption (1)

When AFRP is that value corresponding to three percent excess oxygen, then the conversion efficiency should be given by the curve or equation of Figure 5 of the main body of the report. Therefore,

$$e = e_3 \left(\frac{\text{AFRP} - \text{AFRCOS}}{\text{AFRP}_3 - \text{AFRCOS}} \right) \quad (12)$$

where e_3 and AFRP_3 are the values of e and AFRP when AFRP corresponds to three percent excess oxygen. In order to generalize Equation (12), all of the air-fuel ratios can be related to stoichiometric (reaction to carbon dioxide). If AFRS is defined as this stoichiometric air-fuel ratio, the

following ratios-of-ratios can be defined:

$$RAFRP = \frac{AFRP}{AFRS} \quad (13)$$

$$RCOS = \frac{AFRCOS}{AFRS} \quad (14)$$

$$RAFR3 = \frac{AFRP_3}{AFRS} \quad (15)$$

and Equation (12) can be written

$$e = e_3 \left(\frac{RAFRP - RCOS}{RAFR3 - RCOS} \right) \quad (16)$$

In order to use the equation describing the curve fit of Figure 5, it is convenient to write that equation in terms of fractions rather than percents:

$$e_3 = 0.01049 (WFBN2)^{-2/3} \quad (17)$$

where e_3 and WFBN2 are now the fraction of conversion of bound nitrogen and the fraction of the ash- and moisture-free fuel that is bound nitrogen, respectively. Substitution of Equation (17) into Equation (16) yields

$$e = 0.01049 (WFBN2)^{-2/3} \left(\frac{RAFRP - RCOS}{RAFR3 - RCOS} \right) \quad (18)$$

The constant c , defining the atoms of nitrogen in the equivalent coal molecule in Equations (8) and (9), can be written

$$c = 0.8574(WFBN2) \left(\frac{1 - f_{H2O} - f_A}{f_{Ca}} \right) \quad (19)$$

where f_{H2O} , f_A , and f_{Ca} are the fractions of the total weight of the fuel that are water, ash, and carbon, respectively; and WFBN2 is again the weight fraction of nitrogen in the ash- and moisture-free fuel.

For convenience, the denominator of Equation (9) can be rearranged such that

$$NO = \frac{(ec)10^6}{0.9996 K_1 (AFRCL - K_3)} \quad (20)$$

where

$$K_3 = \frac{(a/4) - (b/2)}{0.9996 K_1} \quad (21)$$

Finally, through substitution of Equations (18) and (19) into Equation (20) and grouping of terms into those which are functions of the fuel alone and those which are functions of the operating conditions, the NO_x generated by conversion of fuel-bound nitrogen, in ppm (dry), can be written

$$NO = FFUEL \left(\frac{RAFRP - RCOS}{AFRCL - K_3} \right) \quad (22)$$

where

$$FFUEL = 8,944 \left(\frac{1 - f_{H2O} - f_A}{f_{Ca}} \right) \left[\frac{(WFBN2)^{1/3}}{K_1 (RAFR3 - RCOS)} \right] \quad (23)$$

For purposes of calculation of the constant K_1 , according to Equation (10), a representative ash was assumed consisting of 50 percent by weight of SiO_2 , 20 percent each of Al_2O_3 and Fe_2O_3 , and percent CaO . The molecular weight of this ash is 75.09. The equivalent moles of ash in the equivalent fuel (8) is then given by

$$A = 0.16 \left(\frac{f_A}{f_{Ca}} \right) \quad (24)$$

Appropriate values of the fuel-related terms in Equation (22) for the four coal types listed in Table 2 of the main body of the report and for the oil and gas fuels used in the data of the previous study,¹ plus values for the stoichiometric air-fuel ratio, by weight, are listed below:

Fuel	AFRS	FFUEL	RCOS	K_3
Coal Type				
No. 1	8.048	5626	0.546	0.150
No. 2	8.001	6520	0.578	0.254
No. 3	9.437	7338	0.571	0.254
No. 4	9.548	7945	0.565	0.254
Oil*	13.84	5557	0.638	0.798
Natural Gas	15.88	0	0.738	1.586

In Equation (22), the constant FFUEL is a function only of the characteristics of fuel fired. It is a function of the one-third power of the weight fraction of nitrogen chemically bound in the ash- and moisture-free fuel. For all of the fuels listed above, the fraction of theoretical air corresponding to three percent excess oxygen (RAFR3) is about 1.16.

The numerator of Equation (22) essentially represents the oxygen available in the boiler region where the hydrocarbon reactions are

* A low sulfur, low nitrogen oil, with 0.24 percent nitrogen, by weight.

taking place after the oxygen necessary to oxidize the carbon to carbon monoxide and the hydrogen (not already bound in moisture in the fuel) to water has been removed. Because RAFP is linear, linear averages of varying conditions in this region are appropriate.

The denominator of Equation (22) essentially represents the total flue gas (the dilution factor), of which the NO is one specie. In order to calculate the NO, in ppm (dry), which would be measured if the overall boiler excess air were such that three percent oxygen were also measured, AFRCL must be set to approximately 1.16 times AFRS. The calculations of NO in ppm (dry), at three percent excess oxygen from Equation (22) for the fuels listed above, are plotted in Figure 6 of the main body of the report.

APPENDIX C

FINAL MIXING ZONE

It became apparent in the early regression analyses of samples of coal-fired data containing wide variations of combustion temperature rise and full-load combustion air temperatures that errors of as much as 120 ppm NO_x in the constant derived by the analyses could result when applying the results of analyses of the full data sample to a particular coal and boiler type. It was concluded that a new term should be developed to account for this apparent variation in the constant. Four main observations formed the basis for this new term:

- a. The correlation equation used in the early regression analyses appeared to contain no term or terms that could account for differences in the constant appropriate to the different coal and boiler types. Therefore, the related phenomena must not be described in the initial equation.
- b. The variation in the constant indicated by the individual boiler data samples, including all of the coal, oil, and natural gas samples, appeared to be some exponential function of the peak combustion temperature.
- c. Parametric calculations for all of the coal-, oil-, and natural gas-fired boilers indicated that the source of this constant NO_x is in the NO_x port or final mixing zone.
- d. There was some evidence that the appropriate value of this constant was different when all burners were active and no NO_x port flow was involved, as compared to tests where some burners were operated air-only.

As a result of these observations and further parametric calculations it was concluded that the most likely source of this NO_x is the region (and period of time) where the final excess air is mixed with the products of fuel-rich combustion coming from the active burner region. In this region, the fuel-rich gases are forced to shift relatively slowly through the air-fuel ratio region of high thermal NO_x generation rates near stoichiometric to the fuel-lean air-fuel ratio of the overall boiler. As long as a burner configuration is involved where the burner air-fuel ratio is less than stoichiometric, this region will exist somewhere in the boiler. It will be independent of the actual burner and overall boiler air-fuel ratios (constant with respect to these variables) and should be a function only of the combustion product temperature in that mixing zone. This assumption is supported by the main observations discussed above in the following ways:

- a. The "tank-and-tube" type of mixing assumed throughout the model, including this final mixing zone, assumes instantaneous mixing and, therefore, no term was present in the initial equation accounting for NO_x generated during any transient mixing. In this final zone, large fractions of the total boiler flow are involved in the mixing process and the assumption of instantaneous mixing is in the greatest error. This is also the most critical zone because the maximum thermal NO_x generation rates are represented in the mixing.
- b. The rate of thermal NO_x generation in this transient mixing zone, always at air-fuel ratios near stoichiometric, should be a function only of the combustion product temperatures in that zone.
- c. A significant transient mixing zone of this type, involving the mixing of relatively large fractions of the total flow, would exist only where large fractions of the combustion air are added to the total flow in some concentrated region of the

boiler. In the data samples of this and the previous study this case is represented almost totally by configurations where large numbers of air-only burners are concentrated in the top levels of the burner array, where NO_x port air flow is involved, or both.

- d. A concentrated region of mixing of large fractions of the total flow such that the air-fuel ratio passes through stoichiometric during the mixing would not exist if all of the burners were active and, therefore, already operating at air-fuel ratios above stoichiometric. Thus, NO_x data plotted as a function of the burner air-fuel ratio can, in some cases, exhibit some type of discontinuity near the stoichiometric air-fuel ratio.

As a result of the above assumptions, the data from each of the boilers in the entire 575-test coal, oil, and natural gas sample were examined to derive estimates of the value of this constant. NO_x levels measured under the following conditions were taken as the appropriate data: (1) full-load firing conditions, (2) air-only burners concentrated in the top levels of the burner array, (3) NO_x port flow involved, and (4) the active burner air-fuel ratio was calculated to be less than stoichiometric. For the natural gas fuel, these measured levels approximately represent the constant directly. For the coal and oil fuels, and NO_x generated from the conversion of fuel-bound nitrogen, calculated from the model described in the previous subsection, was subtracted from the measured NO_x levels to derive the estimate of the constant. In many cases involving air-only burners, the boiler was never tested under full load with the air-only burners concentrated in the top levels of the burner array. In such cases it could only be assumed that NO_x levels and the constant would be lower if such configurations had been tested.

For each of the boilers for which estimates of the appropriate constant could be derived, the equilibrium combustion product gas temperatures and the concentrations of N_2 and O_2 in the products in the appropriate zone in the boiler (SONST in Figure 16 is the product of these concentrations: $[N_2][O_2]^{1/2}$), under stoichiometric combustion conditions, were calculated from the flow and cooling model. Figure 16 shows a plot of the available data generated in the above manner and an approximate empirical fit to the data. Of the five coal-fired boilers where reasonable estimates could be derived, four provide a good empirical fit. The one that deviates considerably from the fit (82 ppm higher than the curve) is the high ash coal, which, as shown in the text of this report, also deviates from the other coal types and boilers in many other ways. Three of the four available estimates for oil- and natural gas-fired boilers indicate only that the constant should be lower than the plotted value while data from one gas-fired boiler indicates an appropriate constant about 34 ppm higher than the empirical curve. This latter error is small enough to be considered within the scatter of the primary data used to derive the data shown in the figure.

Thus, the available data, limited as it is, tend to show a reasonable fit to an equation of the appropriate form; i. e., an exponential in temperature. From the discussion thus far, one might expect that this empirical fit should represent some mixing time, Δt , times a Zelodvich-type equation for the rate of formation of NO_x . The constants in the empirical equation, however, would not be expected to be exactly those of a Zeldovich rate equation. The entire mixing process, during which the local air-fuel ratios pass through the entire range around stoichiometric and the NO_x formation rates are always less than or (briefly) equal to the maximum, was approximated in the empirical fit only by the maximum NO_x formation rate. Thus, the empirical equation would necessarily imply much shorter mixing times and much less sensitivity to the local temperature in order to correctly fit the actual, average process.

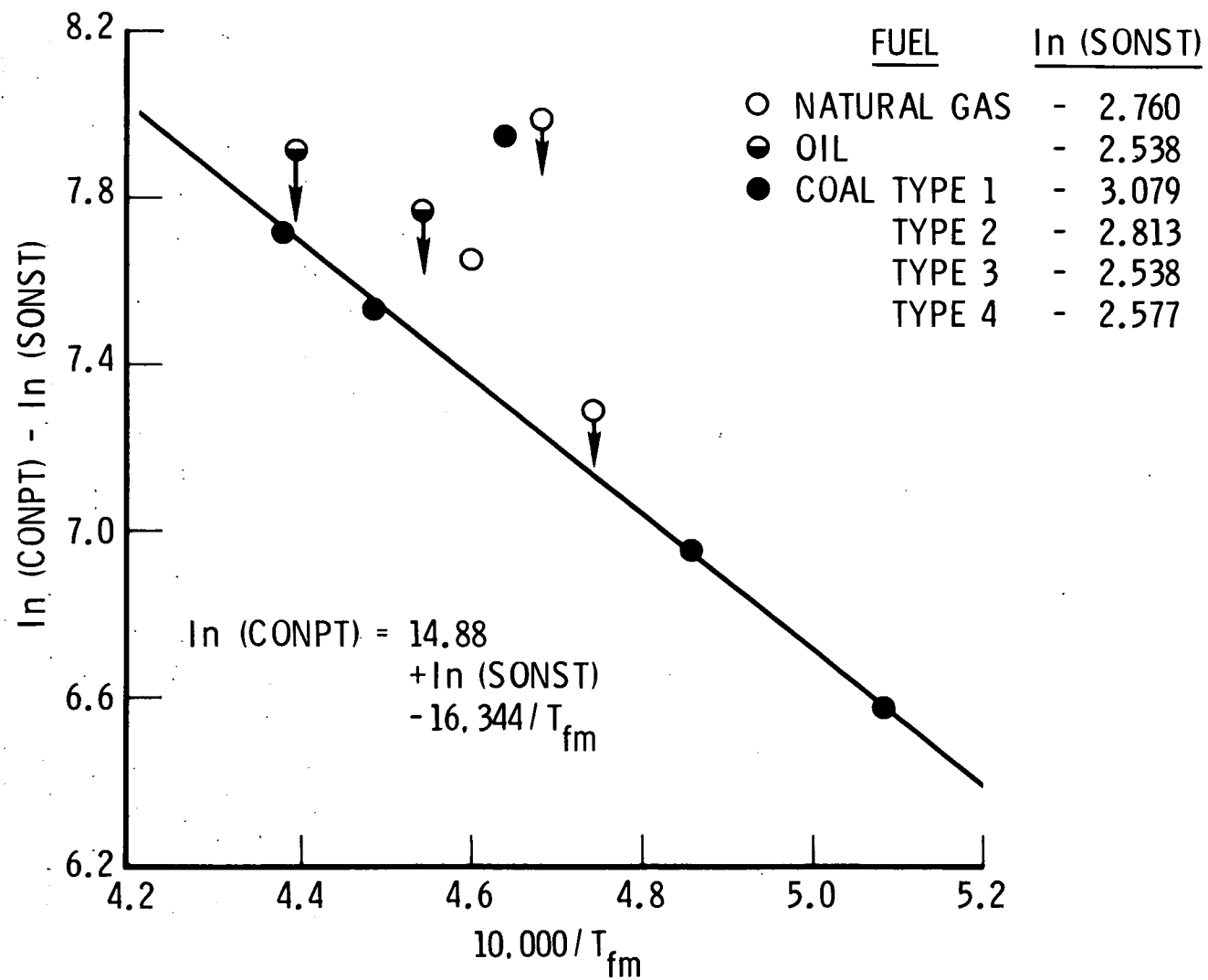


Figure 16. Empirical fit of NO_x generated in final mixing zone (CONPT) as a function of temperature in this zone (T_{fm})

The Zeldovich NO_x formation rate equation used throughout this and the previous study¹ was

$$\frac{d[\text{NO}]}{dt} = (2.4 \times 10^{18}) [\text{N}_2] [\text{O}_2]^{1/2} \exp\left(-\frac{6.79 \times 10^4}{T}\right) \quad (25)$$

The rate equation used to fit the data of Figure 16 was

$$\frac{d[\text{NO}]}{dt} = \left(\frac{2.9 \times 10^6}{\Delta t}\right) [\text{N}_2] [\text{O}_2]^{1/2} \exp\left(-\frac{1.63 \times 10^4}{T}\right) \quad (26)$$

where Δt is the mixing time, in seconds; $[\text{NO}]$ is in ppm; $[\text{N}_2]$ and $[\text{O}_2]$ are in mole fractions; and t and T are in seconds and degrees Kelvin, respectively. For peak local gas temperatures in the range of 2100 to 2500 K (3780 to 4500° R), these two equations yield the same NO_x formation rates if the equivalent mixing times Δt are in the range of 1 to 55 milliseconds. This is a reasonable range of mixing times considering that only the maximum formation rates were used to represent the average mixing process. Similarly, the derivatives of Equations (25) and (26) with respect to temperature show that, in the above temperature range, the empirical rate equation is two to four orders of magnitude less sensitive to gas temperature variations than is the theoretical. Again, this observation is a reasonable result of the approximation used in the empirical fit.

Thus, the general observations and the empirical fit to available data tend to confirm the existence of a zone of mixing, where the final excess air is added to the products of fuel-rich combustion in the active burner region, which is a significant contributor to the overall NO_x emissions. At the very least, an empirical correction was developed to account for potential errors of as much as 120 ppm in the constant derived from regression analyses of data samples containing wide variations in combustion temperature

rise and full-load combustion air temperatures. This new term was used to correct the constant obtained from regression analysis of the full data sample for parametric calculations involving a single coal and boiler type.

GLOSSARY

A	ash
AFRB	air-fuel ratio, by weight, of the active burners
AFRCOS	air-fuel ratio, by weight, of COS
AFCRL	air-fuel ratio, by weight, of the overall boiler
AFRP	air-fuel ratio, by weight, in the effective local region where the initial hydrocarbon reactions are taking place
AFRS	stoichiometric air-fuel ratio
AFR3	air-fuel ratio at three percent excess oxygen
c	atom of nitrogen in the equivalent coal molecule
CONPT	NO _x generated in the final mixing zone, ppm
COS	carbon monoxide stoichiometric
e	fraction of fuel-bound nitrogen converted to nitric oxide (conversion efficiency)
f	fraction of total weight of fuel
FFUEL	function of characteristics of fuel fired
HDF	horizontal depth of the furnace from front to back burner walls in the region of the active burners, meters (feet)
HWF	width between the side walls of the furnace in the region of the active burners, meters (feet)
K ₁	constant (Equation 10)
K ₃	constant (Equation 21)
NBFA	number of active burners
NBFAT	total number of active burners in the burner array
NBT	total number of burners

NO	nitric oxide
NO _x	oxides of nitrogen
n	number of burner levels
ppm	parts per million
R	ratio
SONST	product involving the mole fractions of nitrogen and oxygen; $[N_2] [O_2]^{1/2}$
T	temperature, kelvin
TUR	stay time in the recirculation zone, seconds
VP	average flow velocity in the primary zone, meters/second (feet/second)
WFBN2	weight fraction of bound nitrogen in ash- and moisture-free fuel
ZLAO	length in the direction of flow in the adjacent and opposite mixing zones, meters (feet)
ZLP	length in the direction of flow in the primary mixing zone, meters (feet)
ZLS	length in the direction of flow in the secondary mixing zone, meters (feet)
Δt	mixing time, seconds

Subscripts

fm	final mixing zone
i	burner levels
o	opposed fired boilers
t	tangentially fired boilers
3	three percent excess oxygen

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16. ABSTRACT The report describes the analyses of a large quantity of emissions, operating conditions, and boiler configuration data from full-scale, multiple-burner, electric-generating boilers firing coal fuel. Objectives of the study include: (1) evaluation of the effects of combustion modifications on NO_x emissions, in fundamental combustion terms; and (2) evaluation of techniques for further reductions in NO_x emissions. The report includes the following, pertaining to coal-fired utility boilers: (1) discussion of the major sources of NO_x emissions; (2) parametric investigations of the effects on NO_x emissions of two-stage combustion, burners out of service, combustion air temperature, and excess air reduction; (3) discussion of probable short- and long-term hardware and operating condition modifications likely to yield further significant reductions in NO_x emission in coal-fired boilers; and (4) general comparisons of NO_x reduction techniques in utility boilers firing coal, oil, and natural gas fuels. Boiler firing types included single-wall, opposed, and tangential configurations.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
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