AP-42
Section 1.3
Ref #57

SIXTEENTH SYMPOSIUM
(International)
ON
COMBUSTION

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At The Massachusetts Institute of Technology
Cambridge, Massachusetts
August 15-20, 1976

Organized by
THE COMBUSTION INSTITUTE
Pittsburgh, Pennsylvania
1976

DEVOLATILIZATION AND OXIDATION OF COAL NITROGEN

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The pyrolysis of the nitrogen content of coal was studied by rapidly heating dispersed pulverized particles of a lignite and a bituminous coal to temperatures of 1000 and 2100 K. Nitrogen evolution paralleled that of the total volatiles with the notable exception that little nitrogen was released until 10 to 15 percent of the coal had been devolatilized. A pseudo-first order rough fit of the nitrogen pyrolysis data yielded a rate constant of $9.3 \times 10^3 \exp(-22{,}700/RT)$ sec^{-1}.

Oxidation of the coal was studied in a laminar diffusion flame produced by injecting the coal particles into a flowing helium/oxygen mixture. At a furnace temperature of 1500 K, the conversion of the nitrogen in the coal to nitric oxide was found to decrease from about 60 percent at a fuel equivalence ratio of 0.2 to 10 percent at equivalence ratios above 1.5. At the higher equivalence ratios, however, 30 percent of the char remained unreacted and 45 percent of the original coal nitrogen was retained in the char. Similar oxidation experiments were conducted with char produced by devolatilizing coal at 1500 K under conditions at which the char retained about two-thirds of the original coal nitrogen. Conversion to nitric oxide of the nitrogen retained in the char was significantly lower, by factors of two to three, than conversion for coal nitrogen but showed a similar trend with fuel equivalence ratio. From the difference of the coal and char oxidation results it was inferred that, at a furnace temperature of 1500 K, sixty to eighty percent of the NO_x was contributed by the oxidation of nitrogen released with the volatiles and that the conversion efficiency of volatiles to NO_x and its dependence on fuel equivalence ratio were similar to data previously reported in the literature for the oxidation of model fuel nitrogen compounds burned in laboratory premixed and diffusion flames.

Introduction

Oxidation of nitrogen organically bound in coal contributes a major fraction of the emissions of nitrogen oxides (NO_x) from pulverized coal flames.[1,2] Partial control of this source of NO_x emissions can be achieved by the use of staged combustion[3,4] or delayed mixing burners.[5,6] However, further improvements in NO_x emission control are needed if coal is to supply a major fraction of the fuels burned in stationary combustors.

In a typical coal flame, part of the nitrogen is released with the volatiles in the early stages of combustion and the remainder is retained by the char residue. Nitric oxide is produced by the oxidation of the nitrogen in both volatiles and char but, at present, little information is available on the relative contributions of these two sources of NO_x emissions and on how the emissions can be modified by changes in combustor operating conditions. Several speculative models[7,8,9] describing the formation of nitric oxide from coal nitrogen have been proposed. However, in the absence of data on the high temperature pyrolysis of the nitrogen in coal, some of the parameters in the speculative models were derived from literature more pertinent to coke production than to pulverized coal flames. It is the purpose of the present study to supply data on the kinetics of coal-nitrogen pyrolysis at the higher temperatures of interest in coal flames and on the efficiencies with which the bound nitrogen in volatiles and char are converted to NO_x. These results are useful in determining

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the relative contribution of volatiles and char to NO_x emissions and in identifying potential strategies for the control of NO_x emissions.

Experimental

Two electrically heated resistance furnaces were used for the pyrolysis and oxidation studies. For short residence times (5 to 300 milliseconds), a system similar to that developed by Kimber and Gray[10] was employed. Coal suspended in argon was injected along the axis of a furnace through a narrow (1.2 mm I.D.) water-cooled tube. The coal stream was rapidly heated to the furnace temperature by conduction from a preheated surrounding argon stream augmented by radiation from the walls. The partially devolatilized coal was quenched by a water spray and collected in a water-cooled bronze filter that could be positioned at various distances along the axis of the furnace. Pyrolysis at longer times, of the order of a second, was studied by reducing the surrounding gas stream velocity and allowing the particles to fall into either a crucible maintained at furnace temperatures or to a water-cooled section at the bottom of the furnace. In addition, experiments were conducted in which the coal was heated slowly to furnace temperatures in a crucible. The above options permitted the examination of the effect of both times of heating and rates of heating on devolatilization. Details of the equipment, procedures, and methods for characterizing temperature and residence time are described elsewhere.[11,12,13]

Experiments under oxidizing conditions were performed in a simulated air stream consisting of 21 percent oxygen in helium. Approximately 15 percent of the stoichiometric oxygen requirements were fed with coal through a nozzle on the axis of the furnace. The overall stoichiometry was varied by varying the flow rate of the main helium/oxygen stream. The oxidation experiments, yielded diffusion flames attached to the injector nozzle. The conditions in the experiment differ from those in practical systems in temperature and rate of mixing of fuel and oxidant so that the results, although pertinent to coal combustors in general, do not simulate in detail any practical system.

The furnace temperature could be varied up to a maximum of 1740 K for the experiments in oxidizing atmospheres, and up to 2200 K for those in inert atmospheres. The heating rate ranged from 1 K/sec in the crucible experiments to estimated values ranging from 2×10^4 K/sec to 6×10^5 K/sec in the free fall and short residence time experiments. The experimental conditions were selected to include those expected in pulverized coal flames; namely, peak temperatures of 1500-2100 K, particle heating rates of 10^4 to 10^5 K/sec, and residence times in the combustion zone of 200 to 1000 milliseconds.

A Montana lignite-A from the Savage Mine and a Pittsburgh Seam #8 hvA bituminous coal from the Ireland Mine were used as examples of Western and Eastern coals. Size-graded, nominal 38-45 micron fractions were studied. These coals have been used in several complementary studies in this laboratory and their characteristics and pyrolysis behavior are described elsewhere.[11,12,13] The nitrogen content of the coals as determined by the Kjehdahl method was 0.88 percent for the lignite and 1.20 percent for the bituminous coal. All nitrogen measurements on the char and coals in this study were performed by the Galbraith Laboratories, Knoxville, Tennessee. The conversion of nitrogen to nitric oxide in the oxidation runs was determined from measurements of the nitric oxide concentration in the effluent from the furnace using a chemiluminescent analyzer (Thermo-electron Model 10A).

Results

Measurements were made of the nitrogen retained in char produced by heating samples of coal in crucibles until the weight approached a constant value. Heating times varied from 20 minutes at 2100 K to 12 hours at 600 K. The results on nitrogen retention and dry weight loss are summarized in Fig. 1. Most of the nitrogen evolution occurred at temperatures above that of the ASTM proximate analysis procedure (1223 K) even though most of the total weight loss occurred at temperatures below that of the ASTM test.

Time resolved measurements of the nitrogen retention are presented in Fig. 2. The data at times up to 300 milliseconds were obtained using the fast flow furnace and the data at one second were obtained in the drop tube furnace.

The results for the oxidation runs are summarized in Fig. 3. The fraction of the nitrogen in coal that is converted to nitric oxide, the carbon burnout, and the fraction of the nitrogen in the original coal retained in the char are reported as a function of fuel equivalence ratio for a furnace temperature of 1500 K. At very fuel-rich conditions the fuel nitrogen oxidation to nitric oxide fell to levels below

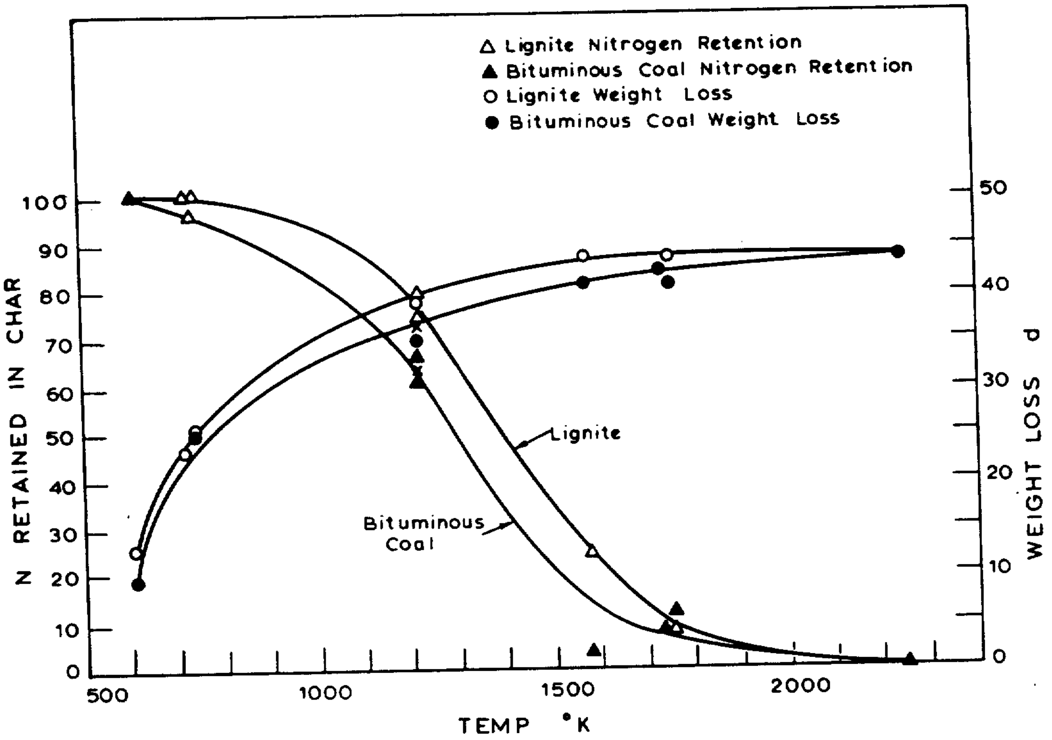


FIG. 1. Nitrogen retention in char and weight loss (dry) for coal heated in crucibles

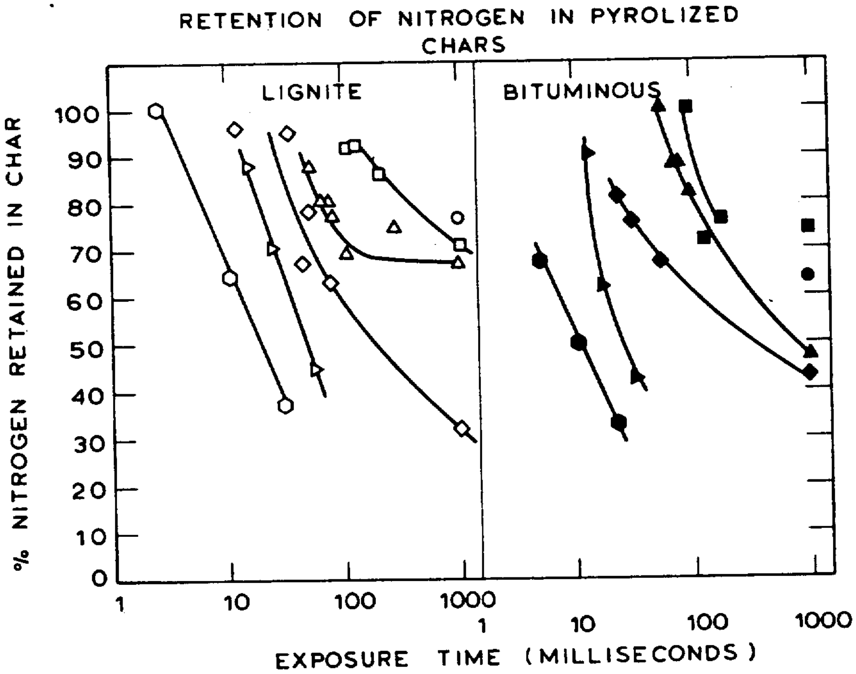

RETENTION OF NITROGEN IN PYROLIZED CHARS

FIG. 2. Retention of nitrogen in char versus time Furnace temperatures: ○—1000°K, □—1260°K, △—1510°K, ◇—1740°K, ▷—1960°K, ⬡—2100°K

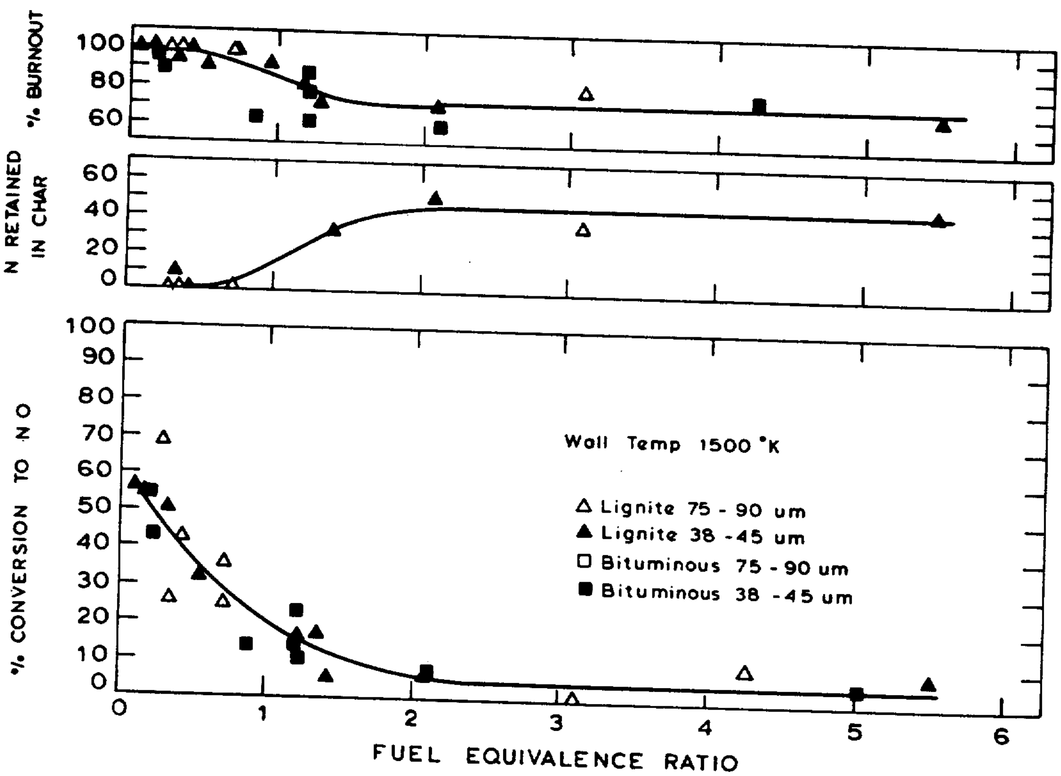


FIG. 3. Conversion of coal nitrogen to nitric oxide, percent carbon burnout, and percent of coal nitrogen retained in char. Furnace temperature 1500°K.

10 percent, the carbon burnout decreased to a value of about 70 percent (i.e. 30 percent of the original carbon persisted as char), and the fraction of the coal nitrogen retained by the char increased to 46 percent. The fate of the coal nitrogen in the oxidation experiments did not vary significantly with coal type or particle size over the limited range investigated in this study, but is expected to be a function of furnace temperature.

In an attempt to separate the contributions of volatiles and char to nitric oxide emissions from coal combustors, a series of oxidation experiments were performed on chars produced by heating lignite in argon at 1500 K for one second. About two-thirds of the nitrogen in coal is retained by the chars produced in this manner (see Fig. 2). The percentage of the nitrogen in the char that is oxidized to nitric oxide is shown as a function of equivalence ratio for the char in Fig. 4. The percent conversions to nitric oxide are lower than the corresponding values for coal nitrogen but show a similar trend with changes in equivalence ratio. As in the case of coal, the carbon burnout decreased and the nitrogen retained in the char increased as the equivalence ratio increased.

Discussion of Results

Pyrolysis

An important parameter in models for estimating the conversion of coal nitrogen to nitric oxide is the distribution of nitrogen between volatiles and char in the early stages of combustion. The data in Fig. 1 show that the nitrogen retained in the char, produced by heating coal in crucibles, falls to negligible values at the temperatures to be expected in flames. The present results are consistent with the early data obtained under the relatively low temperature conditions pertinent to coking operation,[14-17] and extend the available data to higher temperatures. However, these results on the nitrogen retention in char at long times do not provide a valid measure of the distribution of nitrogen between char and volatiles in a pulverized coal flame, as will be shown below.

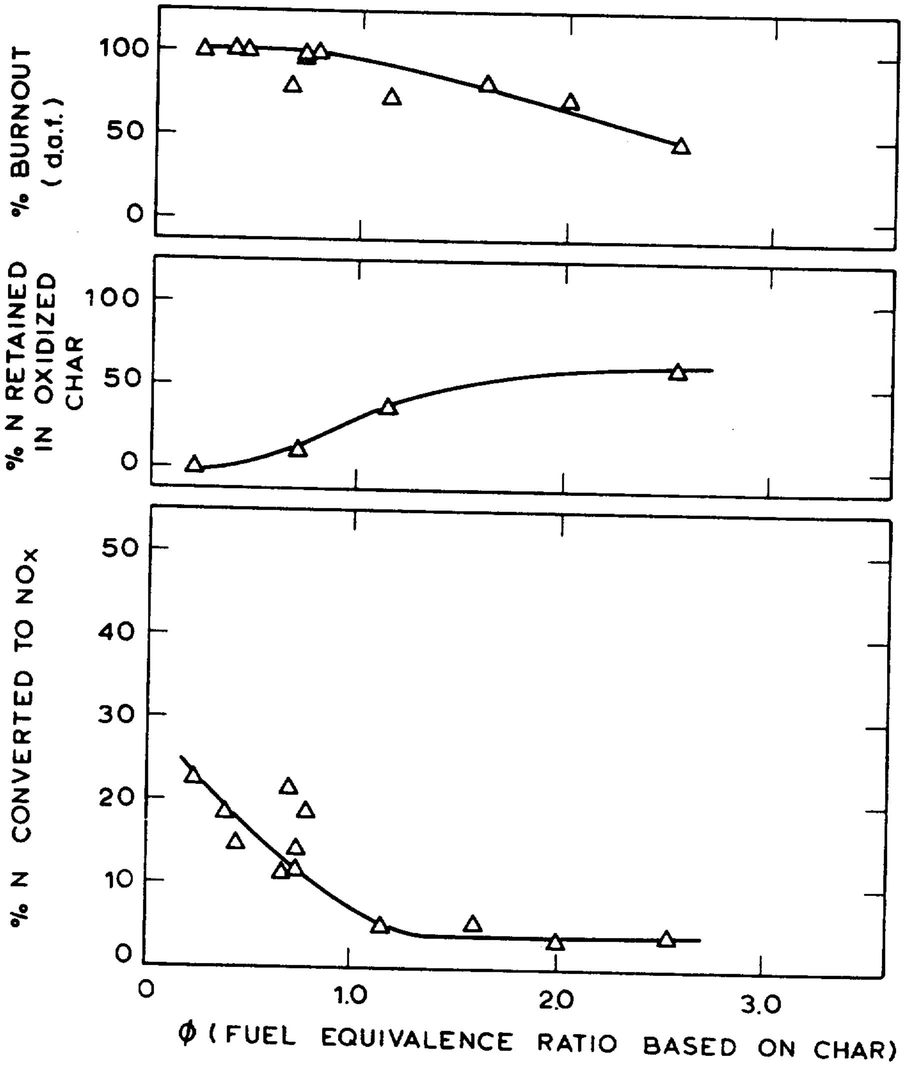


FIG. 4. Conversion of char nitrogen to nitric oxide, percent char burnout, and percent of char nitrogen retained in unburned char. Char was produced at 1500°K.

The data in Fig. 2 show that the release of nitrogen for the temperatures and times of interest to combustors is kinetically controlled. In order to interpret the kinetics of pyrolysis it is desirable to first discuss, qualitatively, the structure of the nitrogen in coal and the mechanisms that determine the release of nitrogen from coal. Functional form analysis suggests that coal consists of condensed aromatic rings, linked primarily by methylene bridges. Substitutions on the aromatic rings include aliphatic, hydroxyl, and carbonyl groups. The number of rings in a basic aromatic unit is found to increase with increases in rank of the coal and ranges from two in lignites to about eight in a high rank bituminous coal.[18] It is generally believed that most of the nitrogen in coal is incorporated in the ring structure in resonance stabilized heterocyclic rings,[16,19-26] with possibly small amounts of nitrogen contained in side chains,[27-30] but this view is not universally accepted. Evidence of the structure of nitrogen in coal is derived from destructive pyrolysis or oxidation, and suggests that the primary N-containing rings are built around pyridine and pyrrole.[16,19-29] Studies of pyrolysis of simple heterocyclic molecules such as picoline[31,32,33] have been used to develop mechanisms for pyrolysis. The experiments on model compounds indicate that the nitrogen is evolved primarily as nitriles, a result that is consistent with the identification of HCN as a principle product of the pyrolysis of coal.[33,34]

The above descriptions of coal structure and pyrolysis of model nitrogen compounds provide a basis for proposing the following speculative model for the behavior of coal nitrogen during pyrolysis. In the early stages of coal pyrolysis the volatiles generated are expected to be dominated by the release of side chains and aliphatic links. Subsequently, the aromatic rings will decompose, releasing some nitrogen. Secondary condensation reactions, leading to char formation, will compete with the decomposition reactions leading to volatile evolution. Condensation reactions are thought to be of the Diels-Alder type and can lead to the formation of multiple rings with internal carbon atoms. Nitrogen, if incorporated in the products of condensation reactions, will be either in a side chain or a peripheral atom in a multi-ring structure. Thus it is expected that condensation reactions will lead to the formation of relatively nitrogen-free chars.

The above speculative scheme is qualitatively supported by the present pyrolysis results. The data on nitrogen retention by the char versus weight loss of the coal (on a dry-ash-free basis) for both the flow (open points) and crucible (closed points) experiments are shown in Fig. 5. (The half-shaded points correspond to data collected by allowing coal to fall into a crucible maintained at furnace temperature.) About ten percent of the coal weight is lost before any nitrogen is evolved, consistent with the postulate that most of the nitrogen evolution is delayed until ring rupture occurs. Beyond this point the nitrogen loss in the flow experiments is proportional to the incremental weight loss. The rate of fractional evolution of nitrogen is, however, higher than the rate of fractional weight loss since the slopes in Fig. 5 are 1.25 for the lignite and 1.50 for the bituminous coal. The curve for the crucible experiments lies below that for the flow experiments, consistent with the postulate that the condensed carbon ring structure once formed cannot be destroyed by prolonged heating at high temperatures under conditions at which nitrogen atoms bonded in the peripheries of the rings are driven off. Several points of the above discussion merit emphasis (1) with the exception of an induction period for nitrogen release (speculatively attributed to a period in which the composition of the volatiles is dominated by the release of essentially nitrogen-free side chains), the kinetics of nitrogen release parallel that of total volatile release as supported by

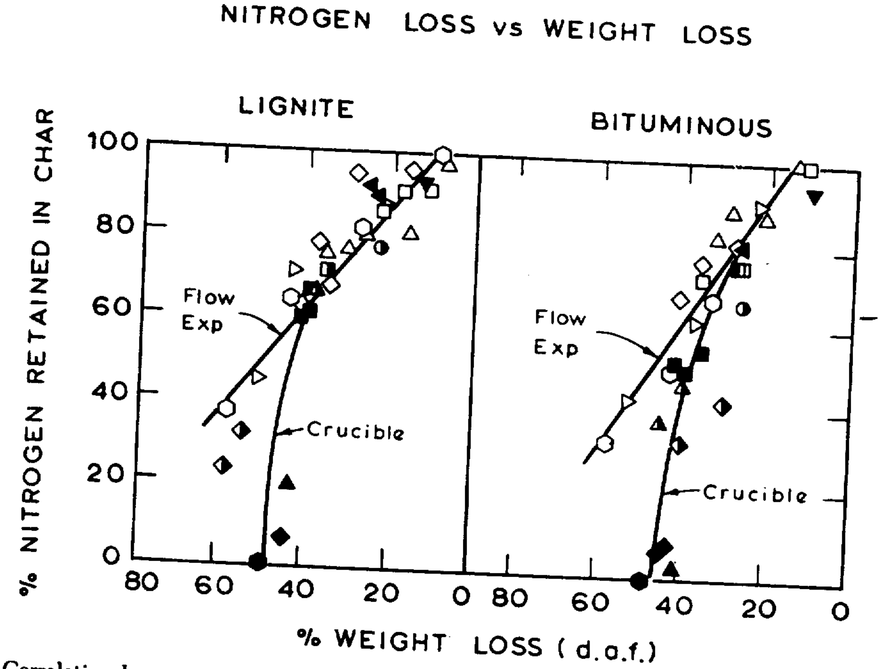


FIG. 5. Correlation between nitrogen retention and weight loss (dry-ash-free). Furnace temperatures: O—1000°K, □—1260°K, Δ—1510°K, ◇—1740°K, ▷1940°K, ○ —2100°K

the linearity of the nitrogen retention versus weight loss correlation for the flow experiments (2) condensation reactions leading to stable carbonaceous matrices do not have their counterpart for nitrogen reactions as supported by the fact that all the nitrogen in the char is released by prolonged heating at high temperatures. It is interesting to note that the relative rates of release of nitrogen and carbon during hydrogasification follows a trend similar to that reported above.[35]

Kinetic data on pyrolysis are often correlated by use of a first order rate expression, with the reactant sometimes defined as the residual starting compound or, for complex materials such as coal, the residual weight of volatile matter. The rate constant fitted in such a manner is a composite of the constants of the competing parallel and sequential elementary reactions that determine the decomposition rate, and usually yield an activation energy and frequency factors that are considerably lower than those of the elementary reaction steps.[13,36,37] The apparent first order rate constant fitted to the early portions of the nitrogen release data of Fig. 3 is compared with the rate constants for the pyrolysis of model nitrogen compounds and elementary first order reactions in Fig. 6. For elementary reactions (of the simple fission type) the activation energy is expected to be approximately equal to the bond energy, of the order of 70 to 100 kcal/mole, and the frequency factor to be of the order of 10^{15} sec.$^{-1}$ The constants for the elementary reactions in Fig. 6 are those recommended by Benson and O'Neal[38] based on reliable experimental data adjusted to agree with values predicted by absolute reaction rate theory. As expected, the empirical rates for the composite reactions governing the pyrolysis of the model nitrogen compounds[32,33] and coal yield activation energies and preexponential factors that are considerably lower than those for the elementary reactions. The first order pyrolysis rate constant for the two coals studied is found to be $9.3 \times 10^3 \exp(-22{,}700/RT)$ sec.$^{-1}$

In order to obtain rate parameters more

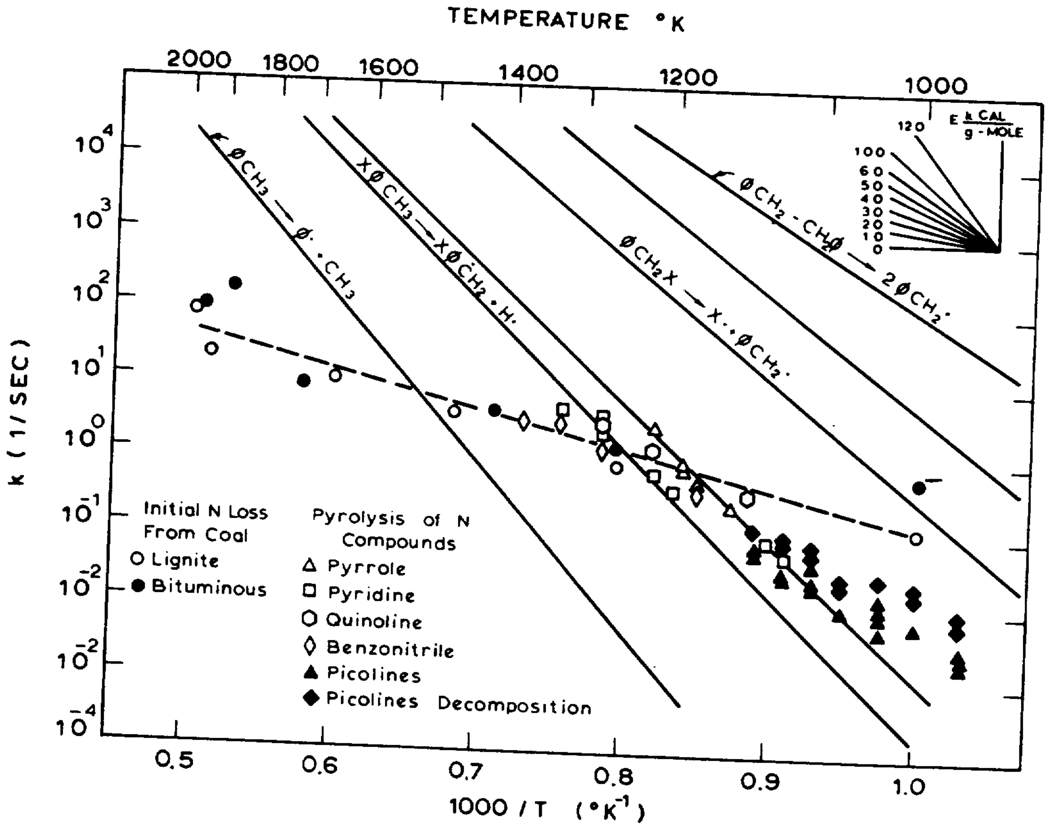


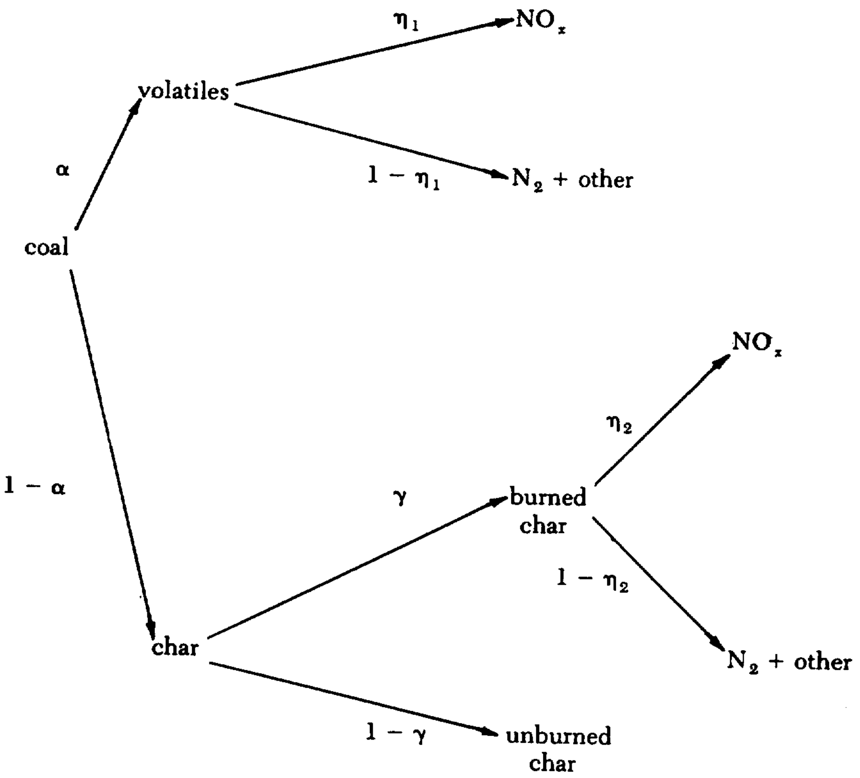
FIG. 6. Pseudo-first order rate constants for coal nitrogen pyrolysis compared with rates of pyrolysis of model compounds,[32,33] and rates of elementary pyrolysis reactions.[38]

representative of the primary reactions several refined methods for interpreting pyrolysis data have been proposed.[12,35,36,39,40] Although such methods of interpreting kinetic data yield constants closer to those expected for elementary reaction steps, the fitted parameters are still gross averages and cannot be related to the fundamental reactions occurring during coal pyrolysis. Fundamental rate parameters will probably emerge from mechanistic interpretation of coal reactions[41] rather than from the fitting of global pyrolysis data.

Oxidation

The conversion efficiency of the coal nitrogen to nitric oxide reported in Fig. 3 is specific to the mixing patterns and scale of the equipment of this study. Never-the-less the percent conversion of coal nitrogen to nitric oxide at equivalence ratios typical of commercial units (0.7 to 0.8) is in the range of the values estimated from field and pilot scale studies.[1-3,14] As the equivalence ratio is increased the conversion efficiency decreases, as expected, but a significant fraction of the nitrogen is retained by the unburned char. This retention of nitrogen in the char differentiates coal from light distillate oils and affects the reduction in NO_x emission achievable by use of staged combustion in coal-fired furnaces inasmuch as the nitrogen in any unburned char from the first stage may be subsequently oxidized to nitric oxide in the second stage. The amount of nitrogen that will be retained by the char leaving the first stage will be a function of the temperature-time history of the char, and can obviously be reduced by increasing either the temperature or the residence time in the first stage. The data in Fig. 4 shows that the conversion to nitric oxide of the nitrogen retained by the char, although lower than the corresponding values for coal, cannot be neglected. The data from Figures 3 and 4 can be used to obtain preliminary estimates of the fractions of the NO_x formed in pulverized coal flames that are contributed by the volatiles and char. As a first approximation it will be assumed that the conversion efficiencies to nitric oxide of the nitrogen in the char and volatiles are independent.

The fate of the fuel nitrogen during combustion of coal can be represented by the following simplified scheme



where α is the fraction of the coal nitrogen that is released as volatiles, η_1 the fraction of the volatile nitrogen that is converted to NO_x, γ is the fraction of the char nitrogen that is consumed, and $\gamma\eta_2$ is the fraction converted to NO_x. The overall conversion η^* of coal nitrogen to NO_x is then given by

$$\underset{\substack{\text{Overall}\\ \text{Conversion}\\ \text{to NO}_x}}{\eta^*} = \underset{\substack{\text{Volatile}\\ \text{Contribution}}}{\alpha\eta_1} + \underset{\substack{\text{Char}\\ \text{Contribution}}}{(1-\alpha)\gamma\eta_2} \quad (1)$$

For a furnace temperature of 1500 K, the value of α as determined from Fig. 2 is 0.67. The values η^* and $\gamma\eta_2$ are reported as functions of fuel equivalence ratio in Figures 3 and 4. From this information it is possible to derive values of both the efficiency of conversion, η_1, of the volatile nitrogen to NO_x and the fraction of the total NO_x contributed by the volatiles ($\eta_1 \alpha/\eta^*$). The values thus derived are shown as a function of equivalence ratio in Fig. 7.

At a furnace temperature of 1500 K, 60 to 80 percent of the NO_x is contributed by the volatiles. Results from batch experiments in laboratory-scale fluidized beds[42] indicate that oxidation of the bound nitrogen compounds released during devolatilization of the coals studied yielded nitrogen oxides in amounts that increased with temperature from negligible values below 1000 K to about two-thirds of the total at the maximum temperature studied (ca. 1200 K). This is qualitatively in agreement with the present pyrolysis data which show little devolatilization of coal nitrogen at temperatures below 1000 K and a major contribution by volatiles to the NO_x emissions at a furnace temperature of 1500 K.

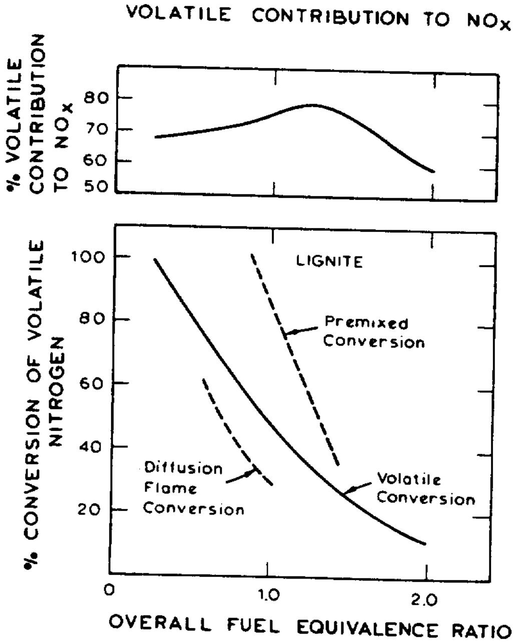


Fig. 7. Conversion of volatile nitrogen to nitric oxide and the contribution of volatile nitrogen to total nitrogen oxide emissions.

The fractional conversion η_1 of the volatiles to NO_x is found to decrease with increasing fuel equivalence ratio in a manner similar to previously reported data on premixed[43,44] and laminar diffusion flames[44] (see Fig. 7).

During the combustion of the residual char, the equivalence ratios governing the fuel nitrogen oxidation will be determined by the oxygen concentrations external to and within the pores of a char particle. The relatively low efficiencies of conversion to NO_x of the nitrogen retained in char is believed to be a consequence of the local depletion of oxygen at the particle surface or within the pores. The problem is further complicated by the possibility that part of the nitrogen oxides produced at the char surface may be subsequently reduced, either homogeneously or heterogeneously. Reduction of nitric oxide by char has been shown to be important in fluidized-bed coal combustors[42] and may also be significant in pulverized coal flames as any nitric oxide produced on the large internal surface area of coal must diffuse through the fine pores (mostly below 12 Å[45]) to the particle surface. Homogeneous reactions may also be important[46] although the mechanism is not well established.

Practical Implications

There are subtle interactions between the devolatilization and oxidation steps in pulverized coal combustion which complicate the development of NO_x control strategy. Low temperature operation favors retention of the nitrogen by the char; inasmuch as the conversion efficiency of the nitrogen in the char to nitrogen oxides is lower than that of the volatiles at a given fuel equivalence ratio, low temperature operation should favor low NO_x emissions for a single-stage combustor. As the temperature is raised, however, increases in the devolatilization kinetics increase the local fuel equivalence ratio tending to offset the effect of having a larger fraction of the fuel nitrogen burned in the volatiles. Available data suggest that changing temperature alone does not have a significant effect on fuel nitrogen conversion in coal-fired combustors, possibly as a consequence of compensation by the two opposing effects described above.

The present results on fuel-rich oxidation indicate that significant amounts of the original nitrogen in coal may be retained by unburned char from the first stage of a staged combustor, which can be subsequently partially converted to NO_x in the second stage. This potential problem can be eliminated by operating the first stage of a staged combustor at high enough temperatures to complete the devolatilization of the bound nitrogen in a fuel-rich regime.

Acknowledgments

The authors gratefully acknowledge Hisashi Kobayashi who designed and built most of the equipment and helped take the pyrolysis data. Yip-Hong Song is acknowledged for his help with some of the experiments. Mr. G. Blair Martin, of EPA, has contributed useful suggestions and offered encouragement throughout this project which was supported by the EPA under grant number R-803242-01-0.

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