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On the Oxidation of Fuel Nitrogen in a Diffusion Flame

The kinetic mechanisms of fuel nitrogen conversion to NO and N_2 in a diffusion flame were investigated. A simple model of a diffusion flame in which the reaction zone has a finite thickness was developed. The purpose of this model was to allow the testing of complex kinetic mechanisms of pollutant formation under conditions where the fuel and oxidant feed rates are controlled by diffusion. A simple kinetic mechanism in which fuel nitrogen was simulated by nitrogen atoms showed the correct functional dependence of nitric oxide emissions on fuel nitrogen content. The model also predicts a significant effect of combustion intensity and temperature on fuel nitrogen conversion. For the hydrogen air diffusion flame the Zeldovich reaction mechanism could account for the production of N_2 as well as NO.

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SCOPE

When a fuel containing chemically bound nitrogen is burned, the fuel nitrogen is converted partially to NO and partially to N_2. An understanding of the kinetic mechanisms of this process is important since it will hopefully lead to progress in NO_x abatement by combustion modifications.

In real furnace flames the combustion process is exceedingly complex, and pollutant formation is affected not only by the chemistry of combustion but also by the physical processes that control the environment in which the chemistry takes place. It is known that flame characteristics can markedly affect the percent fuel nitrogen converted to NO. One of the pitfalls for a researcher in this field is to apply the results obtained for a premixed system directly to turbulent diffusion flames, only to find that the predicted NO is much higher than that measured in practice. This is because, in the presence of O_2, there is no sufficiently rapid route to form the N≡N bond from, say, N atoms.

There is a need therefore to develop a model that allows the investigation of kinetic mechanisms in a turbulent diffusion flame so that the results can be related directly to field operating data. Realistic kinetic mechanisms of pollutant formation, however, usually involve a large number of reactions and reactive species, and the usual steady state or equilibrium assumptions are not valid.

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To incorporate these mechanisms into exact physical models is quite difficult, only rarely successful, and according to other workers, results in excessive computer time.

A more fruitful approach is to develop an approximate physical model that describes the salient features of a turbulent diffusion flame but that easily allows the incorporation of existing computational tools for the study of complex kinetic mechanisms. Using the work of Gibson and Libby (1972) and Fendell (1965) as a guide it is possible to develop a film model in which the reaction zone has a finite structure. The method of matched asymptotic expansions then produces an outer solution valid outside the reaction zone, and an inner solution which, for a single reaction, has already been investigated by Friedlander and Keller (1963). Further approximations allow their solution to be generalized to include multireaction systems, in a simple way. The resulting model can then be used to gain valuable insight into which furnace and combustion variables can be adjusted in order to obtain a minimum amount of nitrogen oxide emissions.

CONCLUSIONS AND SIGNIFICANCE

The model of a turbulent diffusion flame developed consisted essentially of a well stirred stage, or point wise, calculation in which the (hypothetical) volume was determined by the diffusion flux of oxygen into the reaction zone. This volume can be related to combustion intensity and the effect of turbulent mixing can be qualitatively examined. Long lazy flames, or poorly mixed flames such as are expected in tangential firing, for example, lead to a low combustion intensity and a large reaction volume. The converse is true for intense, well mixed flames.

The mechanism of fuel nitrogen conversion in a hydrogen air diffusion flame was investigated using this model and a kinetic scheme of 17 reactions and 10 species. Fuel nitrogen was simulated by nitrogen atoms. It was found that the conversion of nitrogen atoms to NO was in the correct range and that it decreased with increasing N atom concentration, as it should from data reported in the literature. In addition, it was found that NO formation from fuel nitrogen occurred at a much lower temperature than is necessary for NO formation from N_2 fixation. This agrees with field data showing that flue gas recirculation, which decreases the flame temperature, is not effective in eliminating NO_x emissions from fuel nitrogen. There is, however, still a significant effect of temperature, and this appears to substantiate the claim of Martin and Berkau (1972) that flue gas recirculation can reduce but not eliminate fuel NO from combustion processes.

It was also shown that, at a given temperature, combustion intensity is an important variable in determining conversion of fuel nitrogen to NO. This agrees qualitatively with plant data, relating fuel nitrogen conversion to flame characteristics.

So far, agreement between the model and actual plant data is qualitative rather than quantitative, and this may be due to shortcomings both in the kinetic mechanism chosen and in the model. It would be valuable to relate our expression for the combustion intensity of turbulent diffusion flames quantitatively to burner and firebox variables. This will involve further work using concepts of flame stretch models and turbulent jets.

Recent interest in nitrogen oxide emissions has centered on the role of fuel nitrogen and its conversion to NO and N_2 under various combustion conditions. It has been shown (Martin and Berkau, 1972; Turner et al., 1972) that many abatement methods proven effective for the reduction of NO arising from atmospheric fixation are largely ineffective for the abatement of NO arising from fuel nitrogen conversion. There is therefore a need to understand the factors affecting the convertion of fuel nitrogen both to NO and to N_2. The hope is that with this understanding some progress can be made in NO_x abatement by combustion modifications.

In investigating kinetic mechanisms of NO formation from fuel nitrogen, a reasonable first attempt is to simulate bound nitrogen by free nitrogen atoms. This is based on the idea that reactions such as

$$CN + O = CO + N \qquad (I)$$

may be important in the flame. If the mechanisms of NO formation are investigated in a premixed environment in the presence of oxygen, it turns out that there is no sufficiently rapid mechanism to form the N≡N bond and at realistic N atom concentrations of 1% wt, or below, too much NO is formed when compared to experimental data (Turner et al., 1972). This is because

$$N + O_2 \rightarrow NO + O \qquad (II)$$

is much more rapid (Baulch et al., 1970) than, for example,

$$N + NO \rightarrow N_2 + O \qquad (III)$$

or

$$N + N + M \rightarrow N_2 + M \qquad (IV)$$

Thus either the premixed model or the kinetic mechanism appears to be inadequate

The fuels which contain large amounts of chemically bound nitrogen are coal and residual oils, both of which are usually burned in turbulent diffusion flames. The environment in which the N≡N bond is formed is thus significantly different from that in a premixed system. An idealized mathematical model of the diffusion flame involving both the physical and chemical aspects is, therefore, expected to be a useful tool in improving our understanding of the fuel nitrogen reactions. The simplest model of a diffusion flame developed by Burke and Schumann (1928) pictures all the combustion reactions as occurring at a flame sheet of infinitesimal thickness. This has been investigated for NO formation by fixation by Williams and Sarofim (1970). The location of the flame sheet adjusts itself so that the rates of diffusion of fuel and of oxidizer up to the flame sheet are in exact stoichiometric ratio. For determining overall rates of combustion, flame lengths, flame temperatures, etc., this is a reasonably accurate picture when the combustion rates are indeed very fast compared to rates of diffusion. However, for predicting the products of combustion, the flame sheet model must be elaborated to take into account the fact that some of the combustion reactions are faster than others. For example, in burning hydrogen, it is found that the steps consuming hydrogen are much faster than those forming NO (Seery and Bowman, 1970).

There are several ways in which the flame sheet model may be extended to permit the calculation of the products of combustion. Figure 1 shows some of the mechanistic models for representing various types of laminar and turbulent diffusion flames, both attached and separated from particles in motion. If proper ignition has occurred and if the rates of diffusion and stretching are not too great, there will be a flame sheet of small thickness somewhere between the fuel and oxidizer. Very rapid mixing can serve to blow out the flame so that the mixing is largely completed before combustion, in which case models based on premixed flames are more appropriate than flame sheet models. The formation of NO is known to involve interactions between the combustion reactions, free radicals, and NO production reactions, and quasi global kinetics are generally not valid (Thompson et al., 1972). What is needed is to formulate the essential features of a diffusion flame in such a way that detailed kinetic calculations involving many reactions and many stiff kinetic equations can be made. It was with this objective in mind that we devised our method of simulating a diffusion flame. One useful approach to this problem is that of Jones et al. (1972) who developed a complete finite kinetic mathematical model of an opposed jet diffusion flame. A possible disadvantage of their model is, however, its complexity and the long computer time necessary to obtain a single solution. In order to test a wide variety of kinetic mechanisms, we believed our purpose would be better served by a more simplified model which describes the salient features of a diffusion flame, but which still allowed the use of complex finite rate kinetic mechanisms.

Our basic idea was to develop a model in which the environment in which the fuel nitrogen reacted was controlled by the diffusion of fuel and oxidant. The work of Fendell (1965) provided some interesting leads. Using the method of matched asymptotic expansions he investigated the structure of the reaction zone in an opposed jet diffusion flame. In addition, he showed that Arrhenius kinetics led to a three-branched steady solution of which the middle branch is physically unstable and rarely observed. This result is remarkably analogous to that obtained from stability calculations of a well stirred reactor and led us to develop the simpler concept of a diffusion flame which is modeled as a well stirred stage, the feeds to which are controlled entirely by diffusion. It is apparent, however, that further justification of this concept is necessary, and so it is useful to examine this idea more carefully.

DIFFUSION FLAMES MODELED BY THE WHITMAN TWO-FILM THEORY

In real furnace diffusion flames, the physical conditions near the flame front are influenced in a very complex way by the turbulence in the system. We cannot hope to model these processes very exactly. Following the lead of Gibson and Libby (1972) we first assume a quasi steady process in which diffusion and reaction are occurring through two gas films as shown in Figure 1B. This is the conventional chemical engineering approach of using equivalent film thicknesses as in the Whitman Two-Film Model in which the film thicknesses are determined by the fluid mechanics of the system. The physical problem thus reduces to one similar to that studied by Friedlander and Keller (1963) for a single diffusion controlled reaction. An important distinction, however, is that in our model the total film thickness is finite and is controlled by the turbulence of the system.

The basic physical situation is shown in Figure 2. We can consider five zones arranged parallel to a flame front. The bulk of the fuel and of the oxidizer gas can be considered to be uniform in composition and temperature due to the fact that the influence of the flame has not yet been felt by them. Between these two layers the composition and temperature vary due to the diffusion and convection of heat and mass up to or away from the flame front. In Zone A there is no oxygen and, hence, no reaction. Similarly, in Zone B there is no fuel and also no reaction. In Zone R, of small thickness relative to Zones A and B there is reaction since both fuel and oxygen are present.

Our approach now is to solve the problem for a single reaction

$$\nu_F F + \nu_O O \rightarrow P \qquad \text{(V)}$$

and then by making some approximations to generalize for many reactions. With the additional approximations that the use of binary diffusion coefficients is valid, that the number of moles is conserved, and that all properties are constant, it can be shown (Friedlander and Keller, 1963) that the equations to be solved are

$$\frac{d}{dx}\left(D_F \frac{dC_F}{dx}\right) = \nu_F R \qquad (1)$$

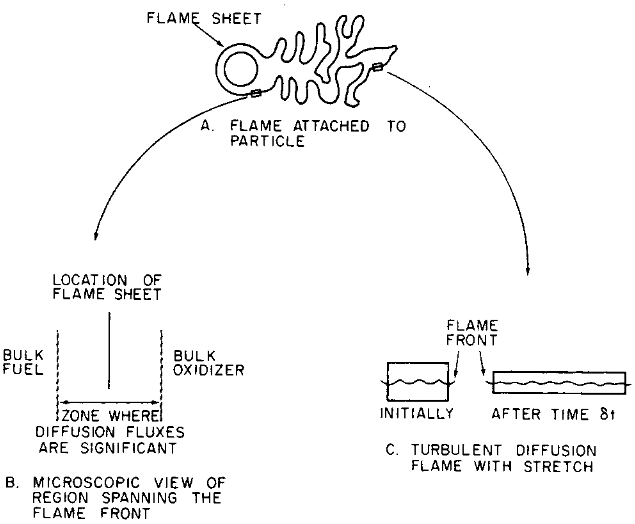

Fig. 1. Mechanistic models of flame sheets occurring in diffusion flames.

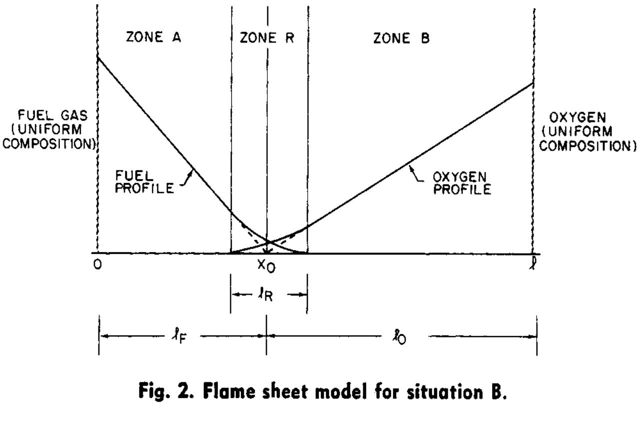

Fig. 2. Flame sheet model for situation B.

$$\frac{d}{dx}\left(D_O \frac{dC_O}{dx}\right) = \nu_O R \tag{2}$$

with the boundary conditions

$$x = 0 \quad C_F = C_F{}^0 \quad C_O = 0, \quad \frac{dC_O}{dx} = 0 \tag{3}$$

$$x = l \quad C_F = 0 \quad C_O = C_O{}^0, \quad \frac{dC_F}{dx} = 0 \tag{4}$$

Following the general approach of Friedlander and Keller (1963), but applying different boundary conditions it can be shown that

$$C_O = \frac{\nu_O}{D_O{}^0} \frac{D_F C_F}{\nu_F} + J\left(x - \frac{C_F{}^0 D_F}{\nu_F}\right) \tag{5}$$

where

$$J = -\frac{D_F}{\nu_F} \frac{dC_F}{dx}\bigg|_{x=0} = \frac{D_O}{\nu_O} \frac{dC_O}{dx}\bigg|_{x=l} \tag{6}$$

Define x_0 as the position of the Burke Schumann flame front:

$$x_0 = \frac{C_F{}^0 D_F}{\nu_F J} \tag{7}$$

and substitute into Equation (1) to obtain for the fuel

$$\frac{D_F}{\nu_F} \frac{d^2 C_F}{dx^2} = k_2\, C_F \frac{\nu_O}{D_O} \left[\frac{D_F}{\nu_F} C_F + J\,(x - x_0)\right] \tag{8}$$

Nondimensionalizing

$$y_1 = \frac{x - x_0}{x_0} \tag{9}$$

$$C_1 = C_F / C_F{}^0 \tag{10}$$

we obtain for the fuel

$$\frac{d^2 C_1}{dy_1{}^2} = \frac{k_2 C_F{}^0 \nu_O x_0{}^2}{D_O} [C_1{}^2 + C_1 y_1] \tag{11}$$

or

$$\lambda_1{}^3 \frac{d^2 C_1}{dy_1{}^2} = C_1{}^2 + C_1 y_1 \tag{12}$$

where

$$\lambda_1 = \left[\frac{D_O}{k_2 C_F{}^0 \nu_O x_0{}^2}\right]^{1/3} = \left[\frac{D_O D_F}{k_2 \nu_O \nu_F J}\right]^{1/3} \frac{1}{x_0}$$

$$= \frac{\text{reaction zone thickness}}{\text{fuel film length}} \tag{13}$$

Similarly, it can be shown for the oxidant, where

$$C_2 = \frac{C_O}{C_O{}^0} \tag{14}$$

$$y_2 = \frac{x_0 - x}{l - x_0} \tag{15}$$

$$\lambda_2{}^3 \frac{d^2 C_2}{dy_1{}^2} = C_2{}^2 + C_2 y_2 \tag{16}$$

where

$$\lambda_2 = \frac{D_F}{k_2 C_O{}^0 \nu_F (l - x_0)^2} = \left[\frac{D_O D_F}{k_2 \nu_O \nu_F J}\right]^{1/3} \frac{1}{(l - x_0)}$$

$$= \frac{\text{reaction zone thickness}}{\text{oxidant film thickness}} \tag{17}$$

The outer solution, for $\lambda_1 \approx \lambda_2 \approx 0$, is of course the Burke Schumann solution

$$C_1 = y_1 \quad -1 < y_1 < 0 \quad C_1 = 0 \quad y_1 > 0 \tag{18}$$

$$C_2 = y_2 \quad -1 < y_2 < 0 \quad C_2 = 0 \quad y_2 > 0 \tag{19}$$

We investigate in inner solution, for small λ_1, λ_2 by stretching coordinates

$$\eta_1 = \frac{y_1}{\lambda_1}; \quad \eta_2 = \frac{y_2}{\lambda_2} \tag{20}$$

and transforming variables

$$\xi_1 = \frac{c_1}{\lambda_1}; \quad \xi_2 = \frac{c_2}{\lambda_2} \tag{21}$$

to obtain

$$\xi_1'' = \xi_1 + \xi_1 \eta_1; \quad \xi_2'' = \xi_2 + \xi_2 \eta_2 \tag{22}$$

B.C.'s match the outer solution at $\eta_1, \eta_2 = \pm\, \infty$:

$$\begin{gathered} \eta_1 = +\,\infty \quad \xi_1 = 0 \quad \eta_2 = +\,\infty \quad \xi_2 = 0 \\ \eta_1 = -\,\infty \quad \xi_1' = -1 \quad \eta_2 = -\,\infty \quad \xi_2' = -1 \end{gathered} \tag{23}$$

This equation is now identical to that solved by Friedlander and Keller using the analog computer, and so it is permissable to use their numerical results.

The dimensionless reaction rate

$$\frac{d^2 \xi_1}{d\eta_1{}^2} = \frac{d^2 \xi_2}{d\eta_2{}^2} = \left(\frac{\lambda_1 x_0}{J}\right) \frac{D_F}{\nu_F} \frac{d^2 C_F}{dx^2}$$

$$= \left(\frac{\lambda_2 (l - x_0)}{J}\right) \frac{D_O}{\nu_O} \frac{d^2 C_O}{dx^2} \tag{24}$$

was shown by Friedlander and Keller to vary from 0.080 at $\eta_1 = -2.2$ (at the edge of the reaction zone) to 0.302 at $\eta_1 = 0$ and to be symmetrical about $\eta_1 = 0$. We now make some radical approximations to the above theory in order to adapt it for complex multireaction systems. Nonetheless we wish to retain the concept of a finite width reaction zone.

First let us assume that all dimensionless concentration profiles inside reaction zone are quadratic in η_1, that is,

$$\xi_1 = a_0 + a_1 \eta_1 + a_2 \eta_1{}^2 \tag{25}$$

The physical implication of this quadratic approximation is that we assume no reaction at all outside the reaction zone and a constant reaction rate inside the zone given by

$$\frac{d^2 \xi_1}{d\eta_1{}^2} = 2a_2 \tag{26}$$

This is shown in Figure 3 in which our approximation is

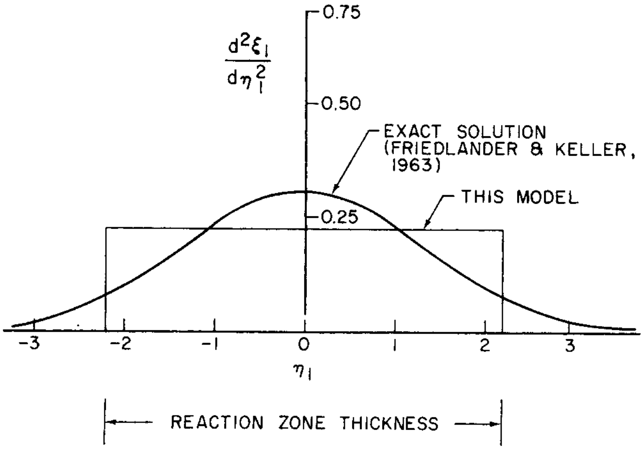

Fig. 3. Comparison of approximate and exact models for dimensionless reaction rate.

compared to the exact solution of Friedlander and Keller (1963). Using Friedlanders and Kellers results, and making the integrated reaction rates equal we obtain

$$\int_{-\infty}^{+\infty} \frac{d^2\xi_1}{d\eta_1{}^2}\, d\eta_1 = \int_{-2.2}^{2.2} 2a_2\, d\eta_1 = 1$$

Thus

$$a_2 = 1/8.8 = 0.113 \tag{28}$$

Then we convert back to dimensional quantities using Equations (24), (7), and (1) to obtain

$$R = \frac{2a_2 J}{\lambda_1 x_0} \tag{29}$$

$$= \frac{0.226\, J}{l_R} \tag{30}$$

where l_R is the reaction zone thickness given by

$$l_R = \left[\frac{D_O D_F}{k_2 \nu_O \nu_F J}\right]^{1/3} \tag{31}$$

Let $C_{i,r}$ be the set of concentrations which will give a reaction rate equal to R. In addition the flux J now equals, for the fuel,

$$J = -\frac{D_F\,(C_F{}^0 - C_{F,r})}{\nu_F\, x_0} \tag{32}$$

giving for the fuel

$$R(C_{i,r}) = -\frac{0.226}{l_R x_0}\,\frac{D_F}{\nu_F}\,(C_F{}^0 - C_{F,r}) \tag{33}$$

and for the oxidant

$$R(C_{i,r}) = -\frac{0.226}{l_R(l - x_0)}\,\frac{D_O}{\nu_O}\,(C_O{}^0 - C_{O,r}) \tag{34}$$

These transcendental equations are analogous to those for a well stirred reactor:

$$-V\,R_i(C_{i,r}) = F_T(C_i{}^0 - C_{i,r}) \tag{35}$$

Since oxygen is common to all combustion kinetics be it first stage or second stage and since we are primarily interested in reactions between N atoms and oxygen, we set

$$\frac{V}{F_T} = \frac{l_R\,(l - x_0)}{0.226\, D_O} \tag{36}$$

Thus our model for a turbulent diffusion flame is

$$-R_i(C_1, C_2 \ldots\ldots C_n)\,\frac{V}{F_T} = C_i{}^0 - C_{i,r} \tag{37}$$

with V/F_T given by Equation (36). Essentially we take the volume of our hypothetical well stirred stage to be determined entirely by the diffusion flux of oxygen into the reaction zone.

PHYSICAL INTERPRETATION OF MODEL

Our model of a diffusion flame in terms of a well stirred stage or point wise calculation implies that the reaction zone thickness or volume of this hypothetical well stirred stage is determined entirely by the diffusion flux of oxygen into the reaction zone. One can define a combustion intensity C_I of a diffusion flame.

$$C_I = \frac{\text{Rate of reaction}}{\text{Unit volume}} \tag{38}$$

$$= \frac{0.226\, J}{l_R}\ \alpha\ \frac{l_O\, J}{D_O\,(V/F_T)} \tag{39}$$

$$\alpha\ \frac{\Delta C}{(V/F_T)} \tag{40}$$

where ΔC is the oxidant concentration difference across the film. Since the reaction zone thickness is small

$$\Delta C \approx C_{O_2}{}^0 = \text{constant}$$

Therefore

$$C_I\ \alpha\ \frac{1}{(V/F_T)} \tag{41}$$

The type of fuel to air mixing in a turbulent diffusion flame will affect the combustion intensity by changing the film thicknesses. Long lazy flames will have large film thicknesses while the converse is true for short well mixed flames. Indeed the thickness is determined by the turbulent shear rate, as shown by Gibson and Libby (1972).

Since the combustion intensity

$$C_I\ \alpha\ \frac{J}{l_R}$$

$$\alpha\ \frac{J}{\left(\dfrac{D_O D_F}{k_2 \nu_O \nu_F J}\right)^{1/3}}$$

and since

$$J\ \alpha\ \frac{D_O C_O{}^0}{l_O}$$

it can be shown

$$C_I\ \alpha\ 1/(l_O)^{4/3} \tag{42}$$

for given kinetics and diffusion coefficients. Thus as the film thickness increases, or the mixedness decreases, the combustion intensity, as defined here, will decrease and the hypothetical reaction volume (V/F_T) will increase. This model can therefore be used to investigate qualitatively the effect of turbulent mixing on fuel nitrogen conversion, merely by studying the behavior of complex kinetics for well stirred stages of various volumes. Much remains to be done, however, before these volumes can be quantitatively correlated to burner hardware design.

In terms of kinetics of fuel nitrogen conversion it would appear that high combustion intensity will lead to high O_2 concentrations in the flame front and hence will probably favor such reactions as

$$N + O_2 \rightarrow NO + O \qquad \text{II}$$

over such reactions as

$$N + NO \rightarrow N_2 + O \qquad \text{III}$$

It is to be expected that increasing combustion intensity will therefore lead to increasing conversions of fuel nitrogen to NO.

APPROACH

Some calculations were made using this idea of the equivalent well-stirred reactor to investigate the combustion of mixtures of H_2 and HCN. The HCN, which is one of the products of pyrolysis of fuel compounds containing nitrogen, is simulated by N atoms. The kinetic scheme used is shown in Table 1. The hydrogen combustion scheme was selected to exhibit most of the known features of hydrogen flames (Dixon-Lewis, 1970). For conversion of the nitrogen atoms, only the Zeldovich reactions and the direct three-body recombination of N were used. Future studies would certainly involve more reactions.

Our approach was to use a computer program to solve the set of transcendental Equations (37) for each species and adiabatic temperature. This computer program con-

TABLE 1. REACTIONS USED IN HYDROGEN DIFFUSION FLAME

Combustion reactions

1.	BROK 18	$H_2 + M$	$= H + H + M$
2.	JOHN 11	$O_2 + M$	$= O + O + M$
3.	HOMER 1	$H + OH + H_2O$	$= H_2O + H_2O$
4.	HOMER 2	$H + OH + M$	$= H_2O + M$
5.	BROK 4A	$H + O_2 + H_2O$	$= HO_2 + H_2O$
6.	BROK 4B	$H + O_2 + M$	$= HO_2 + M$
7.	LDSB 1	$H_2 + O$	$= H + OH$
8.	LDSB 3	$H_2 + OH$	$= H_2O + H$
9.	LDSB 5	$H_2O + O$	$= OH + OH$
10.	LDSC 1	$O_2 + H$	$= O + OH$
11.	BROK 6	$H + HO_2$	$= OH + OH$
12.	BROK 7	$HO_2 + OH$	$= O_2 + H_2O$
13.	BROK 8	$O + HO_2$	$= OH + O_2$
14.	BROK 10	$H + HO_2$	$= H_2 + O_2$

Reactions involving *N*

15.	LDSD 1	$NO + N$	$= N_2 + O$
16.	LDSD 3	$O_2 + N$	$= NO + O$
17.	NEWH 4	$N + N + M$	$= N_2 + M$

tains a reaction rate library where each reaction name on Table 1 is a mnemonic representative of the source of rate coefficient data. Thus reactions with the name BROK have rate coefficients from Brokaw and Bittker (1970), those with the name HOMER from Homer (1970), those with names LDSB, LDSC, LDSD from Baulch et al. (1968-1970), those with name NEWH from Newhall (1969).

In this investigation the effect of combustion intensity as defined by Equation (41) and the effect of fuel nitrogen content in the fuel on fuel N conversion were examined as a function of temperature. In each case the simulation of a diffusion flame by a point wise calculation [Equation (37)] was made.

RESULTS

Results are plotted in Figure 4, showing the calculated effects of combustion intensity and of temperature on NO_x emissions originating from a given concentration of fuel nitrogen. The effect of various fuel nitrogen levels on conversion to nitrogen oxides is shown on Table 2.

It is seen from Table 2 that the diffusion flame model predicts that conversion of fuel N to NO decreases with increasing N level in the fuel and that at about 0.7% wt N (or 0.001 N atom/H_2 molecule mole ratio) the conversion can range from 27.7% to 73.0% depending on combustion intensity and temperature. These results are in rough agreement with those observed in field and pilot plant experiments (Turner et al., 1972; Bartok et al., 1969; Martin and Berkau, 1972). Furthermore, according to Figure 4, our model predicts a large effect of combustion intensity such that more rapid combustion leads to more NO and less N_2 and lower combustion intensity leads to less NO for a given fuel nitrogen content. This effect has also been observed (Bartok et al., 1969) in real combustion units. In tangential firing, mixing between fuel and air is poor, the combustion intensity is low and the conversion of fuel nitrogen to nitrogen oxides is also lower than for front fired units. The model thus predicts that NO emissions arising from fuel nitrogen conversion can be decreased by combustion modifications.

The effect of combustion intensity can be understood in terms of the competing reactions

$$N + O_2 \rightarrow NO + O \qquad \text{II}$$

$$N + NO \rightarrow N_2 + O \qquad \text{III}$$

Low combustion intensity leads to consumption of almost all of the O_2 in the reaction zone permitting Reaction III to compete effectively with Reaction II. It is interesting to note, however, that the Zeldovich reaction pair provide a mechanism for making both NO and N_2. We found that simple N atom recombinations (Reaction IV) did not account for significant N_2 formation.

Figure 4 also shows that significant nitrogen oxide emissions arise even when the temperature is relatively low, compared to 1800°K, below which no fixation from N_2 occurs. However, there is an effect of temperature, and Figure 4 shows that low temperature favors conversion of fuel nitrogen to N_2, at least for the very simple mechanism tested. Such an effect was observed experimentally by Martin and Berkau (1972). On the other hand, recirculation of flue gas, which ought to give lower combus-

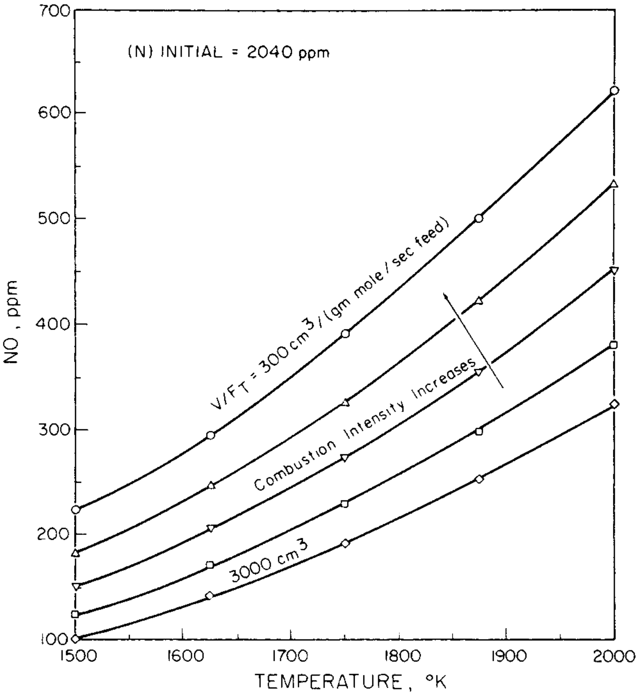

Fig. 4. Effect of temperature and combustion intensity on NO production in H_2 diffusion flame.

TABLE 2. CONVERSION OF FUEL NITROGEN IN A HYDROGEN DIFFUSION FLAME

Temp., °K	Volume V/F_T, $\frac{cm^3\ s}{mole}$	% fuel nitrogen converted to NO Atoms of fuel N/molecules H_2 0.001	0.01	0.03	0.10
2000	300	73.0	21.3	9.06	3.12
	949	68.8	16.7	6.74	2.24
	3,000	65.2	12.9	4.98	1.61
	9,490	62.7	10.0	3.68	
	30,000	61.2	7.75	2.72	
1875	300	62.7		7.38	2.49
	949	55.8		5.38	1.77
	3,000	49.0		3.90	1.25
	9,490	42.7		2.82	
	30,000	37.3	5.74	2.03	
1750	300	57.2		5.89	1.95
	949	48.4		4.21	1.36
	3,000	40.8		3.00	0.95
	9,490	33.9	5.93	2.13	
	30,000	27.7		1.52	

tion temperatures, was observed by Turner (1972) not to change significantly the fractional conversion of fuel nitrogen to NO.

CONCLUSIONS

A model framework was developed for the study of the complex kinetic mechanisms describing the conversion of fuel nitrogen to nitrogen oxides and to nitrogen molecules in turbulent diffusion flames. Results for a hydrogen diffusion flame with fuel nitrogen simulated by nitrogen atoms gave observed results relating fuel nitrogen conversion to fuel nitrogen content. In addition the model predicted an important effect of combustion intensity and showed that fuel nitrogen conversion did depend on temperature, although not as strongly as do the fixation reactions.

The model did not yet give exact quantitative agreement with experimental data and this may be due both to deficiencies in the model and deficiencies in the kinetic mechanism. Further work on this type of diffusion flame model should consider a more realistic set of reactions for fuel nitrogen combustion. For example, it may be more realistic to simulate fuel nitrogen by NH rather than N atoms and to use our model to investigate the competition between reactions such as

$$NH + OH \rightarrow NO + H_2 \qquad \text{V}$$

$$NH + OH \rightarrow N_2 + OH \qquad \text{VI}$$

in a diffusion flame environment. It would also be valuable to make quantitative estimates of combustion intensity and to relate our expression for combustion intensity to burner and firebox variables. This will involve further work using concepts of flame stretch models and turbulent jets.

One of the strengths of our present model, however, is that it allows existing kinetics computer programs, presently applicable to premixed systems, to be used as a tool to investigate kinetic mechanisms in diffusion flames. This will help researchers in gaining the insight and understanding necessary to solve an important air pollution problem.

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NOTATION

a_0, a_1, a_2 = coefficients in Equation (25)
C_I = combustion intensity, defined by Equation (38)
C_F, C_O = fuel and oxygen concentrations
C_F^0, C_O^0 = bulk fuel and oxygen concentrations
C_1, C_2 = dimensionless fuel and oxidant concentrations
D_F, D_O = pseudo binary diffusion coefficient for fuel and oxygen
$C_{i,r}$ = concentration of species i to give reaction rate equal to $R(C_{i,r})$
F = fuel
F_T = feed rate to hypothetical well stirred stage
J = diffusion flux, defined by Equation (6)
k_2 = reaction rate coefficient, where $R = k_2 C_F C_O$
l = total stagnant film thickness
l_F = fuel diffusion film thickness
l_O = oxygen diffusion film thickness
l_R = reaction zone thickness
R = reaction rate per unit volume
R_i = rate of formation through reaction of species i
V = volume of hypothetical well stirred stage
x = distance
x_0 = location of Burke Schumann flame front defined by Equation (7)
y_1, y_2 = dimensionless distances for fuel and oxygen

Greek Letters

λ_1, λ_2 = dimensionless ratios defined by Equations (13) and (17)
ν_F, ν_O = fuel and oxygen stoichiometric coefficients
ξ_1, ξ_2 = transformed dimensionless concentrations of fuel and oxidant for inner solutions
η_1, η_2 = stretched coordinates for fuel and oxidant

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