

Parametric Study of Nitrogen Oxide Formation During Combustion of Uniform Methane–Air Mixtures

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UDC 536.46: 777.4

Translated from *Fizika Goreniya i Vzryva*, Vol. 35, No. 2, pp. 9–15, March–April 1999.
Original article submitted March 10, 1998.

With a model for the propagation of normal flame fronts in methane–air mixtures as an example, estimates are made of the contribution of various NO_x formation mechanisms with varying pressure, temperature, and mixture composition. During combustion of near stoichiometric mixtures, the thermal mechanism is found to predominate, while in lean mixtures, the N_2O mechanism predominates and in rich mixtures, the “prompt” mechanism. These results are compared with a direct solution of the kinetic problem and it is shown that this simpler model provides a satisfactory description of NO_x formation in lean and nearly stoichiometric flames.

INTRODUCTION

The reduction of nitrogen oxide NO_x emissions is the most complicated problem that arises in improving the ecological characteristics of combustion chambers for power plants. During burning of traditional gaseous fuels, the oxides NO_x are formed mainly through oxidation of the nitrogen in air in the highest temperature regions of the combustion chamber. There are three main mechanisms for this [1, 2]:

- (i) thermal (the Zel'dovich mechanism), with direct oxidation of the nitrogen by oxygen in the high temperature zones;
- (ii) “prompt” NO , through reactions of N_2 with hydrocarbon radicals;
- (iii) the N_2O mechanism, through reactions with formation of N_2O as an intermediate substance.

In traditional combustion chambers with separate fuel and air feed, the main chemical processes take place in regions with nearly stoichiometric compositions (diffusion flame). Here the bulk of the NO is produced by the thermal mechanism (i). The existing theoretical models [3] and experimental data indicate that it is extremely difficult to reduce the NO_x emissions to an acceptable level in this type of combustion chamber.

In recent years, combustion chambers with premixing of the fuel and oxidant, in which burning of a

homogeneous mixture predominates, have been developed. A sharp reduction in the NO_x emission (by a factor of 2–4 for existing industrial systems compared to “diffusion chambers”) is achieved by varying the composition of the mixture and lowering the temperature in the reaction zones. The search for methods to further improve combustion chambers with premixing continues. Thus, there is considerable interest in modelling the details of the physicochemical processes leading to NO_x production in mixed flames. In fact, reducing the temperature of the premixed mixture and changing its composition in the reaction zones during combustion reduces the contribution of the thermal mechanisms for NO_x production. Thus, unlike in traditional combustion chambers, the emission properties (and the limits on their improvement) in premixing combustion chambers will be determined, to a great extent, by mechanisms (ii) and (iii).

The purpose of this article is to evaluate the possible contribution of the different mechanisms to NO_x production under typical conditions in power plants of different types (combustion chambers in gas-turbine plants, etc.) which operate with premixed natural gas (methane) and air. As a model problem for obtaining these estimates, we consider the conventional propagation of a normal flame front.

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MATHEMATICAL MODEL

The major aspects of problem statement for the steady-state propagation of a laminar flame have been discussed elsewhere [4]. It was shown that a steady-state isobaric uniform flow of the fuel mixture obeys the following system of equations:

$$\rho u \frac{dc}{dx} + \frac{dJ}{dx} - \mathbf{W} = 0, \quad (1)$$

where x is the coordinate along the normal to the flame front, ρ is the density, u is the velocity ($\rho u = \text{const}$), $c = \{h, c_1, \dots, c_K\}^T$, K is the number of components, h is the enthalpy of the mixture, c_k is the mass fraction of the k th component ($k = 1, \dots, K$), $\mathbf{W} = \{0, W_1, \dots, W_K\}^T$, W_k is the rate of formation/consumption of the k th component, $\mathbf{J} = \{q, J_1, \dots, J_K\}^T$, q is the heat flux, and J_k is the diffusion flux of the k th component. Radiative heat transfer is neglected.

The thermal and caloric equations of state have the form

$$\rho = \frac{p\mu}{RT}, \quad h = \sum_{k=1}^K c_k h_k(T),$$

where p is the pressure (specified), μ is the molecular mass of the mixture, T is the temperature, R is the universal gas constant, $h_k(T) = h_k^0 + \int_{T_0}^T c_{p,k}(T) dT$ is the specific enthalpy of the components including the enthalpy of formation h_k^0 , and $c_{p,k}$ are the specific heats of the components at constant pressure.

The specific enthalpies of the components were approximated by seventh order polynomials in the temperature with coefficients taken from [5].

The kinetics of methane oxidation and nitrogen oxide formation were approximated by the Miller-Bowman scheme [1]. The total kinetic scheme includes 235 elementary reactions among 51 components. The rate constants for the reverse reactions were obtained from those for the forward reactions and the equilibrium constants, which, in turn, were calculated using the approximations of [5] for the enthalpy and entropy.

Since the problem was solved numerically, the boundary conditions were specified at a finite distance from the reaction zone at several quite distant points. The composition c_k^0 and temperature T^0 of the initial mixture were specified at the inlet (left) boundary (the superscript zero denotes parameters of the initial mixture). In order to reduce the effect of the finite length of the computational region, asymptotic conditions of the form $d^2T/dx^2 = 0$ and $d^2c_k/dx^2 = 0$ were specified at the outlet (right) boundary.

The propagation velocity of the flame front relative to the cold mixture was determined by specifying an additional condition (any of the equivalent conditions) $dT/dx = 0$ or $dc_k/dx = 0$ on the left boundary, where c_k can be taken to be the concentration of any of the reacting components.

In the transport model, thermal diffusion and the diffusive thermal effect were neglected. The diffusion fluxes of the components in Eq. (1) were determined from the Stefan-Maxwell relations [6] written in a form proposed in [7]. The thermal flux q in system of Eqs. (1) was calculated using the formula

$$q = -\lambda \frac{dT}{dx} + \sum_{k=1}^K h_k J_k,$$

and the thermal conductivity λ of the mixture, using the approximate formula of Mason and Saxena [8]. The internal degrees of freedom of the polyatomic components were taken into account using the Aiken correction [6]. The binary diffusion coefficients and thermal conductivities of the individual components were calculated using the formulas of molecular gas kinetic theory [6] using a Lennard-Jones interaction potential for the molecules. The collision integrals were approximated using the formulas of N. A. Anfimov as functions of the reduced temperature $T_{ik}^* = T/\theta_{ik}$, where θ_{ik} is the characteristic temperature [9]. The parameters of the Lennard-Jones potential for molecules of the same type, θ_{kk} and σ_{kk} (the collision diameter), were taken from [10], and those for molecules of different types were determined using the following approximate formulas [6]:

$$\sigma_{ik} = (\sigma_{ii} + \sigma_{kk})/2, \quad \theta_{ik} = \sqrt{\theta_{ii}\theta_{kk}}.$$

COMPUTATIONAL PROCEDURE

The system of Eqs. (1) was solved numerically by a relaxation method. The concentration of one of the components (molecular nitrogen) was determined in each iteration from the normalization condition. The transition from a known layer in the relaxation variable τ^n to a new layer τ^{n+1} was taken using the implicit difference scheme:

$$\left\{ \rho^n + \Delta\tau \left[(\rho u)^n I \frac{d}{dx} - \frac{d}{dx} D^n \frac{d}{dx} \right] - \left(\frac{\partial \mathbf{W}}{\partial c} \right)^n \right\} \Delta c = \Delta\tau \left[\mathbf{W}^n - (\rho u)^n \frac{dc^n}{dx} - \frac{dJ^n}{dx} \right], \quad (2)$$

where $\Delta c = c^{n+1} - c^n$, $\Delta\tau = \tau^{n+1} - \tau^n$, I is the unit matrix, D is the diagonal matrix with elements $D_{00} = \lambda/c_p$ and $D_{kk} = \rho D_k$ ($k = 1, \dots, K$). Here we have used the approach proposed in [11]: the ef-

fective diffusion coefficients D_k of the components in the implicit part of Eq. (2) were calculated using the approximate formulas of Wilke [12]. It should be emphasized that this sort of approximation for the implicit part does not affect the accuracy of the steady-state solution, since the right hand side of the scheme (2), which determines the stationary solution, contains diffusion fluxes calculated using the Stefan-Maxwell relations.

For approximating the convective terms on the left of Eqs. (2), a first order scheme was used with differences compared to the flow, and the convective terms on the right of Eq. (2) were approximated by a limited third order scheme [13]. The diffusion terms in Eq. (2), as well as the derivatives in the expression for the heat flux and the Stefan-Maxwell relations were approximated by a second order central difference scheme.

To linearize the heat flux and the chemical sources, the differential of the temperature was expressed in terms of the differentials of the enthalpy and the concentrations of the components:

$$dT = \frac{dh}{c_p} - \sum_{k=1}^K \frac{h_k}{c_p} dc_k. \quad (3)$$

The chemical source terms W_k were linearized in terms of the concentrations of the components and enthalpy. Here the elements of the Jacobi matrix $(\partial W_k / \partial c_j)$ were calculated analytically using Eqs. (3). This way of linearizing the source terms while simultaneously solving the system of Eqs. (2) ensured a fairly high stability and rate of convergence for the numerical procedure.

In order to satisfy the conservation condition for the computational procedure, the main flow parameters (h , T , c_k , and ρ) were determined at the nodes of the difference scheme and the transport coefficients and the thermal and diffusion fluxes were determined in the middle of the intervals $[x_i, x_{i+1}]$.

The resultant matrix for the finite difference system (2) has a block-tridiagonal form and was transformed (at each layer with respect to the relaxation variable τ) by matrix iteration.

The calculations were done using a composite adaptive grid in the spatial variable. The grid consisted of a segment with a uniform partition in the chemical reaction zone and exponential segments in the directions of the initial mixture and combustion products.

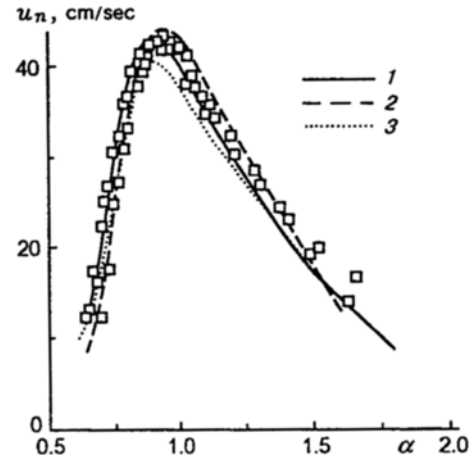


Fig. 1. The propagation velocity of a normal flame front in methane-air mixtures with different excess air coefficients for $p = 0.1$ MPa and $T^0 = 300$ K: the points are experimental data from various authors collected [15]; curve 1 refers to the present calculation and curves 2 and 3 to calculations of [15] and [14], respectively.

COMPUTATIONAL ACCURACY

In order to monitor the effect of the grid partition, the propagation of a flame through a stoichiometric methane-air mixture at $p = 0.1$ MPa and $T^0 = 300$ K was calculated using three grids (45, 90, and 180 nodes). An extrapolation to a zero grid step showed that for the grid consisting of 180 points, the accuracy in predicting all the concentrations (including radicals) at the extrema was better than 1%. This grid was used in the main series of calculations.

In order to estimate the validity of the models used, the calculated normal flame front propagation velocity u_n was compared with published data from several experiments and calculations [14, 15] (Fig. 1). It is clear that the computational results and their accuracy are as good as the known simulation results.

TABLE 1

The Computational Cases

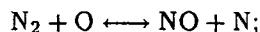
Variant	p , MPa	T^0 , K	α
A1	0.1	300	1.0
A2	1.0	600	1.0
B1	1.0	600	1.8
B2	1.0	600	0.65

RESULTS AND DISCUSSION

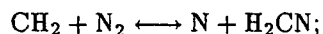
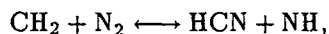
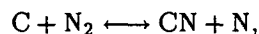
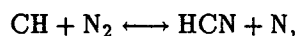
Table 1 is a summary of the base operating conditions for which the main series of calculations were done. They correspond approximately to the typical parameters in the boilers of heating and electric power stations (A1) and in the combustion chambers of gas-turbine power plants (B1 and B2).

The contribution of mechanisms (i)–(iii) to NO formation in the various regimes were determined from their portion of the consumption of N_2 molecules:

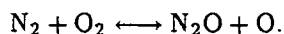
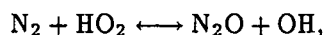
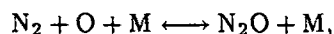
(1) Thermal mechanism (Zel'dovich mechanism), from the rate of consumption of N_2 in the reaction



(2) "Prompt" mechanism, from the rate of consumption of N_2 in the reactions



(3) N_2O mechanism, from the rate of consumption of N_2 in the reactions



The rates of these reactions were integrated to obtain the total amount of N_2 that had reacted through a given mechanism up to a given time. Of course, the rate of N_2 consumption does not always coincide with the rate of NO production, since it can proceed through the formation of intermediate substances. Nevertheless, the breakup of molecular nitrogen is a slow stage, so its balance is a good means of estimating the contribution of the various mechanisms [2].

The results of these calculations are presented in the same form as in [2], i.e., as dependences on the residence time from the rate of consumption of N_2 in the reaction

$$t = \int_{x_0}^x \frac{dx'}{u(x')},$$

where $u(x)$ is the velocity of the reacting mixture and the origin is taken to be the point x_0 at which the temperature of the mixture reached 1000 K.

Some quantitative results of the calculations are listed in Table 2.

Figure 2a (see also Table 2) illustrates the balance of molecular nitrogen for case A1 ($p = 0.1$ MPa, $T^0 = 300$ K, and excess air coefficient $\alpha = 1$). It is clear that, under these conditions, the thermal mechanism predominates. The prompt mechanism is significant only within the main reaction zone ($t < 1$ msec). The contribution of the N_2O mechanism increases slowly with time simultaneously with a decrease in the contribution of the prompt mechanism (the amount of nitrogen expended through the prompt mechanism is essentially constant after $t = 1$ msec). These results are in good agreement with the calculations of [2]. The small ($\approx 5\%$) differences in the NO concentrations are explained by a difference in the components of the mathematical models.

The dominance of the thermal mechanism in the combustion of nearly stoichiometric mixtures is retained at high pressures, as well (variant A2). The estimated contributions of the mechanisms in this case are essentially the same as in variant A1 (see Table 2).

The formation of NO_x in lean mixtures at high p and T^0 is of special interest, since these conditions are realized in planned gas-turbine plants. The mixture is depleted by lowering the flame temperature and, with it, the contribution of the thermal mechanism. The contributions of the different mechanisms in variant B1 ($p = 1.0$ MPa, $T^0 = 600$ K, and $\alpha = 1.8$) are shown in Fig. 2b (see Table 2, as well). It is clear that here the picture is entirely different from case A1. The main contribution is from the N_2O mechanism, in agreement with [16], and in the initial stage this mechanism ensures the reaction of a large amount of nitrogen and later it leads to recovery of more than half of this nitrogen. By $t = 2$ msec, the rate of expenditure of molecular nitrogen through the N_2O mechanism approaches zero. This sort of change in the balance of molecular nitrogen occurs because not all the products of the destruction of nitrogen through the N_2O mechanism oxidize finally to NO. Part of these substances again form molecular nitrogen after a certain time, and a significant fraction of the N_2O is retained in the combustion products in the form of a stable compound until the equilibrium state is reached.

For rich mixtures, the contribution of the thermal mechanism decreases, and the prompt mechanism becomes decisive (variant B2, Fig. 2c, and Table 2). On the whole, the calculations showed that the thermal mechanism can be neglected for $\alpha < 0.7$. The computational results indicate that the N_2O mechanism cannot be left out of a correct quantita-

TABLE 2

Results of the Calculations. The Contributions of the Different Mechanisms for Destruction of N_2 and Concentrations of the Main N-Containing Substances at Time $t = 5$ msec

Variant	Relative contributions to loss of N_2 , %			Concentration of N-containing substances, ppm			
	thermal	"prompt"	N_2O mechanism	NO	N_2O	NH_3	NCH
A1	84	4	12	83	—	—	—
A2	88	≈ 1	11	830	—	—	—
B1	18	3	79	5.3	0.5	—	—
B2	≈ 1	86	13	4.3	—	4.6	4.6

Note: The results are given for a residence time $t = 2$ msec in variant A2.

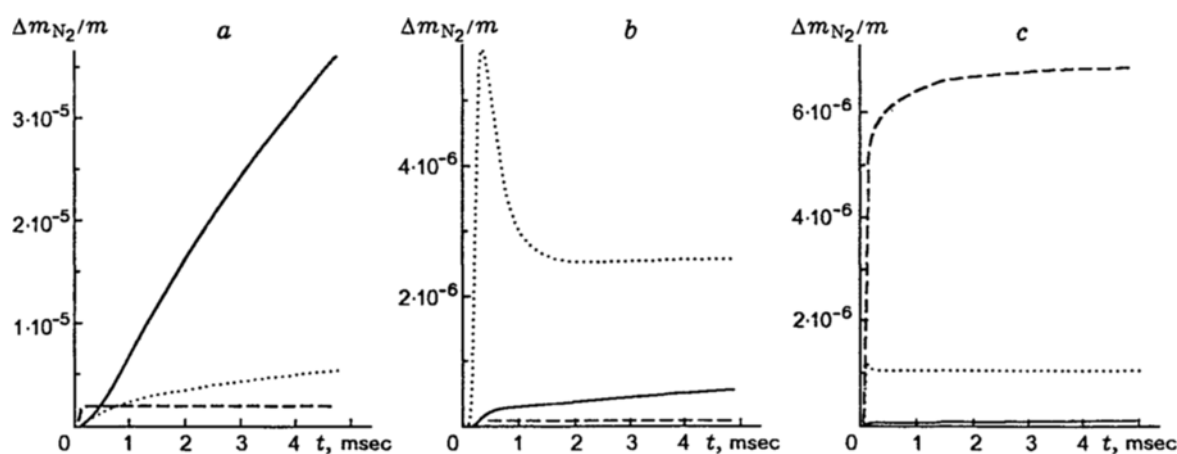


Fig. 2. Consumption balance of molecular nitrogen for $p = 0.1$ MPa and $T^0 = 300$ K and $\alpha = 1.0$ (a), $T^0 = 600$ K and $\alpha = 1.8$ (b), and $T^0 = 600$ K and $\alpha = 0.65$ (c): the solid, dashed, and dotted curves refer to thermal, "prompt," and N_2O mechanisms, respectively; m is the mass of the mixture and Δm_{N_2} is the decrease in the mass of N_2 .

tive description of the formation of NO in rich mixtures (Fig. 2c). Here it is also important that, during combustion of rich mixtures, reduction of NO plays a significant role and the combustion products contain a considerable amount of NH_3 and HCN. In our calculations for $\alpha < 0.7$, the concentrations of NH_3 and HCN in the combustion products were comparable to that of NO.

The results of some parametric calculations of the distribution of the molar fraction of NO in a normal flame front for different values of α are shown in Fig. 3 for $p = 1.0$ MPa and $T^0 = 600$ K. It is clear that they are in good agreement with the conclusions based on examining the consumption balance for molecular nitrogen.

These calculations have shown that the change in the NO concentration as the pressure is varied is rather complicated (often even nonmonotonic), especially (with respect to α) where the contributions of all three mechanisms in the consumption of N_2 are comparable, since their pressure dependences differ. We believe that this should greatly narrow the

range of validity and limit the universality of the various semiempirical formulas often used in engineering practice for estimating the emission of nitrogen oxides as a function of the burner parameters (pressure, excess air coefficient, residence time, etc.).

The emission characteristics of combustion chambers are often estimated using calculations of the time evolution of the reacting mixture obtained by solving the direct kinetic problem:

$$\rho \frac{dc}{dt} - W = 0.$$

Here molecular transport effects are neglected and an intense chemical reaction wave is initiated by applying a heat pulse of quite high power to the system [17]. It was interesting to compare the predictions of this model with calculations of the production of NO_x in a laminar flame front. Three regimes were chosen: $\alpha = 0.65$ (dominant "prompt" mechanism), $\alpha = 1.0$ (dominant thermal mechanism), and $\alpha = 1.8$ (dominant N_2O mechanism) for $p = 1.0$ MPa and $T^0 = 600$ K. The results of the comparative cal-

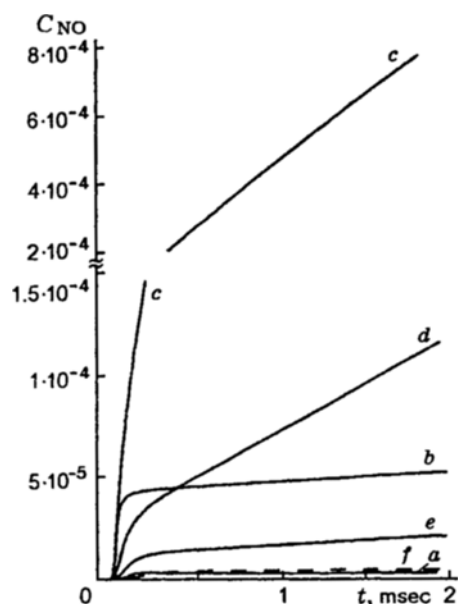


Fig. 3. Effect of the excess air coefficient in the mixture on the NO concentration in a laminar flame: $p = 1.0$ MPa and $T^0 = 600$ K; $\alpha = 0.65$ (a), 0.8 (b), 1.0 (c), 1.3 (d), 1.5 (e), and 1.8 (f).

culations are shown in Fig. 4. Evidently, the new method does not lead to any significant errors, while the nitrogen oxides are mainly generated in the post-flame zone by the thermal mechanism ($\alpha = 1$). The difference in the predictions increases when the role of the "front" NO increases ($\alpha = 1.8$). On the whole, however, the direct kinetic calculation gives a satisfactory description of the generation of NO through the N_2O mechanism in the post-flame zone during combustion of a depleted mixture, and the difference from the laminar flame model calculations is small. Significant differences in the predictions were obtained for combustion of rich mixtures ($\alpha = 0.65$). In fact, under these conditions, nitrogen oxide generation is controlled by the "prompt" mechanism, in which molecular nitrogen is destroyed by reaction (ii) with the participation of hydrocarbon radicals (CH and CH_2). An analysis showed that the procedure of initiating a chemical reaction wave by applying a heat pulse to the system often employed in the direct kinetic regime does have a significant effect hydrocarbon radicals in the reaction zone. The peak values of the concentrations of CH and CH_2 obtained in these calculations differ by almost an order of magnitude from the laminar flame calculations. Thus, the different predictions for the NO concentrations during combustion of rich mixtures reveal a fundamental difference in these models for analyzing processes inside a flame front.

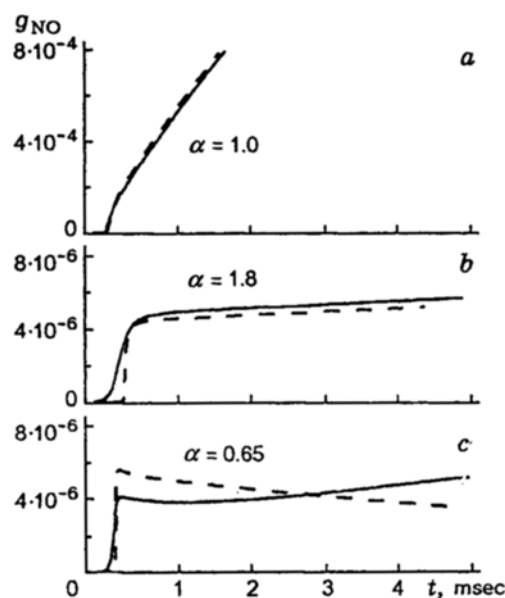


Fig. 4. A comparison of the mass fraction of NO calculated by the laminar flame method (solid curves) and by the direct kinetic method (dashed curves).

We thank M. Kh. Strelets, M. L. Shur, and Yu. E. Egorov (GIPKh, St. Petersburg), with whom we collaborated closely in creating the first version of the program for calculating steady-state laminar flame propagation. We also thank A. P. Tishin (TsNIIMash, Moscow), who, to a great extent, initiated this work.

This work was partially supported by the Russian Foundation for Fundamental Research (Grant Nos. 98-01-00153 and 98-01-00785).

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