

ANALYSIS OF PRODUCTION OF OXIDES OF NITROGEN IN METHANE-AIR DIFFUSION FLAME

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Abstract. *The production of oxides of nitrogen in laminar diffusion flames is analyzed through three main mechanisms: thermal, prompt and nitrous oxide. In this sense, a six-step flame chemistry is employed, in which one of them deals with the formation of NO. NO_x emission indices are calculated in a first approximation as functions of scalar dissipation rates for different pressures and boundary temperatures, and its values and tendencies compared among the three mechanisms.*

Keywords: *diffusion flame, NO.*

1. Introduction

Methane is the simplest hydrocarbon fuel, and its combustion may provide important information for the combustion of more complex hydrocarbon fuels. The study of diffusion flames, in which CH_4 reacts with air, is a valuable tool to try to understand the production level of nitric oxide, one of the responsible for air pollution. Although most practical applications involve turbulent combustion, the turbulent flames usually are in the reaction-sheet regime, in which the turbulent combustion occurs in an ensemble of laminar flamelets [Hewson and Williams, 1999].

[Hewson and Williams, 1999] analyzed the production rates of oxides of nitrogen in laminar methane-air diffusion flames, with thermal, prompt and nitrous oxide mechanisms taken into account, as well as consumption processes collectively termed reburn. For this purpose, they extended the well-known four-step flame-chemistry description to six steps, with acetylene taken out of steady-state and one-step production of nitric oxide included. Emission indices were calculated as functions of the rate of scalar dissipation at the stoichiometric mixture fraction for near-atmospheric pressures and shown to be in reasonable agreement with results obtained from numerical integrations.

In the article of [Li, Williams and Gebert, 1999], a simplified, fundamentally based method was developed for calculating burning rates and NO_x emissions in turbulent lean-premixed flames. The approach relates the rates to elementary chemical-kinetic parameters. Reasonable predictions of motor emissions were obtained when comparisons were made with results of experiments on a dual-fuel diesel engine.

Laminar diluted hydrogen flames have been studied in a counterflow burner by [Rørteit *et al.*, 2002]. Measurements of temperature profiles and $[NO]$ were made, which were compared with predictions from numerical computations. The hydrogen stream was diluted with the inerts N_2 , CO_2 and He. Differences between the influences of the various diluents were discussed in terms of differences in heat capacities, thermal-radiative properties, and effects on chemical reactions. Numerical predictions showed good agreement with experiments for both temperatures and $[NO]$ at lower temperatures.

[Li and Williams, 1999] made measurements and computations of structures of two-stage counterflow methane-air flames at normal atmospheric pressure and a feed-stream temperature of about 300 K, in order to try to understand how staged combustion aids in reducing emissions of oxides of nitrogen from gas turbines. The fuel stream was partially premixed, with equivalence ratios from 1.5 to 3.0, and to the air stream was added up to 10% by mass of water spray, carbon dioxide or nitrogen. Results of numerical integrations were in improved agreement with experimental results when suitable selections were made of certain critical elementary reaction-rate constants.

Following existing convention, NO_x is considered here to consist of NO and NO_2 , since N_2O generally is treated separately, and in addition, N_2O emissions are small compared with those of NO and NO_2 [Hewson and Williams, 1999]. In the present work, the levels of emissions of oxides of nitrogen in a laminar diffusion methane-air flame are analytically analyzed. Their dependencies on scalar dissipation rates are compared among thermal, prompt and nitrous oxide mechanisms. Two different pressures were employed, in order to observe their influences.

2. Problem Analysis

The combustion on a laminar methane-air diffusion flame is analyzed. For this purpose, it is necessary to know the set of elementary reactions and their associated reaction-rate parameters. In this work, the elementary steps of [Hewson and Williams, 1999] were employed, and the variables names presented here belong to that article.

2.1 Combustion Parameters

The well-known four-step flame chemistry description was extended to six steps, derived from some reactions of Tab. 1 and 2 from [Hewson and Williams, 1999] by introduction of steady-state approximations for reaction intermediaries.

The six-step reduced mechanism is written below.



In this reduced scheme, step (1) is the fuel-consumption step, which is seen also to consume radicals. Step (2) is the step for production of C_2 species not in steady state, important for obtaining correct CH profiles. Step (3) is the water-gas shift that burns CO . The oxygen is consumed by step (4), which is the source of radical production through the hydrogen-oxygen branched chain. Step (5) describes the three-body radical recombination. Finally, step (6) includes the three mechanisms of NO production, as well as reburn.

To achieve a formulation that is independent of the flame configuration, the mixture fraction, Z , is employed as the independent variable. The connection to physical coordinates is made through the gradient, ∇Z , or more conventionally through the so-called scalar dissipation rate (χ),

$$\chi = \frac{2|\nabla Z|^2 \lambda}{\rho c_p} \quad (7)$$

where λ denotes the thermal conductivity, ρ the density, and c_p the specific heat at constant pressure for the mixture.

The stoichiometric mixture fraction, Z_{st} , can be stated as:

$$Z_{st} = \frac{1}{S + 1} \quad (8)$$

where

$$S = \frac{\nu}{Y_{O_\infty}} \frac{L_O}{L_F} \quad (9)$$

In Eq. (9), ν is the stoichiometric relation between the oxidant mass and methane mass, Y_{O_∞} is the oxygen mass fraction far from the flame, and L_O and L_F are the oxidant and fuel Lewis Numbers in the flame, respectively.

The Lewis Numbers (L) for H , H_2 , CO , O_2 , CH_4 and C_2H_2 are, respectively, 0.18, 0.3, 1.1, 1.06, 0.97, 1.19.

It can be stated that

$$Z^0 = Z_{st} + \epsilon \eta^0 \quad (10)$$

$$X_{O_2}^0 = 2L_{O_2} b \epsilon \left(\frac{z^0}{2} - \eta^0 \right) \quad (11)$$

$$X_{H_2}^0 = \frac{2L_{H_2} b \epsilon z^0}{1 + \alpha^0} - L_{H_2} b \nu \quad (12)$$

$$X_{H_2O}^0 = 2X_{CO_2}^0 = 2b(1 - Z_{st}) Z^0 \quad (13)$$

and

$$T^0 = T_{st} - b \epsilon T_r [2qz^0 - (1 - Z_{st}) \eta^0] \quad (14)$$

where the superscript 0 refers to the fuel-consumption zone and X is the symbol for molar fraction. The definition for η is:

$$\eta = \frac{Z - Z_{st}}{\epsilon} \quad (15)$$

According to [Hewson and Williams, 1999], there is a relationship between z^0 and η^0 , given as:

$$z_{g\nu=0}^0 = 1.184 + 0.5262\eta^0 + 0.2027(\eta^0)^2 + 0.05282(\eta^0)^3 + 0.008324(\eta^0)^4 + 0.00007043(\eta^0)^5 + 2.437 \cdot 10^{-5}(\eta^0)^6 \quad (16)$$

where

$$g_V = bT_r \epsilon (1 - Z_{st}) \left[\frac{E_V}{R(T^0)^2} + \frac{(n_{8f} - 2)}{T^0} \right] \quad (17)$$

T_r is a reference temperature, E_V is the overall activation energy and R is the universal gas constant.

The parameter α is defined as:

$$\alpha = \frac{K_3 L_{H_2} X_{CO_2}}{K_{14} L_{CO} X_{H_2O}} \quad (18)$$

The parameter b is a stoichiometric parameter, defined as:

$$b = \frac{Y_{O_2, O} \bar{W}}{2W_{O_2} Z_{st}} \quad (19)$$

where the subscript O refers to air stream conditions and \bar{W} is the mixture mean molecular mass.

The thickness of the oxygen consumption zone, that is the thickest one, is represented by ϵ :

$$\epsilon = [4b^2 D_V (1 + \Theta_V)]^{-\frac{1}{4}} \quad (20)$$

where the Damköhler Number corresponding to step (5) is

$$D_V = \frac{4p^2 k_{8f}^0 X_M^0 \left[\frac{K_1^0 (K_3^0)^3}{K_4^0} \right]^{\frac{1}{2}} (L_{H_2} L_{O_2})^{\frac{3}{2}}}{\chi^0 (\bar{R}T^0)^2 X_{H_2O}^0 (1 + \alpha^0)^{\frac{3}{2}}} \quad (21)$$

The pressure is represented by p , k is the reaction-rate constant, X means molar fraction, $K_j \equiv k_{jf}/k_{jb}$, \bar{R} is the universal gas constant and T is the temperature.

Θ_V is defined as:

$$\Theta_V \equiv \left(\frac{k_{7f}^0}{k_{8f}^0} \right) \left(\frac{K_1^0 K_3^0}{K_4^0} \right)^{\frac{1}{2}} \left(\frac{X_{H_2}^0}{X_{O_2}^0} \right)^{\frac{1}{2}} \quad (22)$$

The parameter ν is expressed as

$$\nu = \frac{(1 - \alpha^0)}{[(1 + \alpha^0)^3 D_{III}]} \quad (23)$$

where

$$D_{III} = \left(\frac{2}{\chi^0} \right) \frac{p}{\bar{R}T^0} k_{14f}^0 L_{CO} \left(\frac{K_1^0 K_3^0 X_{O_2}^0 X_{H_2}^0}{K_4^0} \right)^{\frac{1}{2}} \quad (24)$$

2.2 NO Production

The production of nitric oxide is due mainly to thermal, prompt and nitrous oxide mechanisms. The emission index in general is defined as the mass of pollutant emitted per unit mass of fuel consumed. In quasi steady diffusion flames, this is the ratio of the mass flux of pollutant out of the flame to the mass rate of consumption of fuel per unit flame area.

2.2.1 The Thermal Mechanism

The thermal mechanism is characterized by the large activation energy of its initiating reaction, $O + N_2 \rightarrow NO + N$, and is thus centered around the region of peak temperature at $Z = Z^0$. In this mechanism, the NO mass production rate per unit flame area can be written as:

$$\tilde{\omega}_T = 2W_{NO} \left(\frac{p}{\bar{R}T^0} \right)^2 \frac{k_{54f}^0 K_1^0 K_3^0 X_{H_2}^0 X_{O_2}^0 X_{N_2}^0}{|\nabla Z|^0 X_{H_2O}^0} \frac{T^{02}}{bT_r T_T} \left(\frac{1}{1 - Z_{st} - 2q} + \frac{1}{Z_{st}} \right) \quad (25)$$

where W refers to molecular mass, and T_r is a reference temperature given by

$$T_r \equiv W_{CH_4} \frac{T_{st} - T_O}{Y_{CH_4,F} \overline{W} Z_{st}} \quad (26)$$

In Eq. (26), the subscript F refers to the fuel stream. In Eq. (25), T_T is

$$T_T = \frac{E_{54f} + E_{1f} - E_{1b} + E_{3f} - E_{3b}}{R} + (n_{54f} - 2) T^0 \quad (27)$$

The parameter q of Eq. (25) is the enthalpy release (normalized by total heat release of the overall reaction in the consumption of a fuel molecule).

The normalized by the fuel-consumption rate is

$$E_T = \frac{2000 W_{NO_2} \frac{\tilde{\omega}_T}{\overline{W}_{NO}} c_p \overline{W}}{b |\nabla Z|^0 \lambda^0 W_{CH_4}} \quad (28)$$

2.2.2 The Prompt Mechanism

The initial reaction responsible for prompt NO_x is $CH + N_2 \rightarrow HCN + N$, where, to a first approximation, HCN and N lead ultimately to NO . The temperature dependence of this reaction is not large, and CH radicals exist only within the fuel-consumption zone, so the terms may all be evaluated using the values from this layer with the temperature fixed at T^0 .

The mass production rate of prompt NO across the flame per unit flame area is:

$$\tilde{\omega}_P = P_1 I_3 + P_2 J_3 \quad (29)$$

where

$$I_3 \equiv \int_{-\infty}^{\infty} \frac{y_{CH_4} y_H^3}{y_H^2 + c} d\xi \quad (30)$$

$$J_3 \equiv \int_{-\infty}^{\infty} y_{C_2H_2} y_H^3 d\xi \quad (31)$$

$$P_1 = \frac{16b^3 \delta^4 W_{NO} \left(\frac{p}{RT^0}\right)^2 k_{57f}^0 k_{20f}^0 M_1 L_H X_{N_2}^0}{\left(k_{15}^0 X_{O_2}^0 + k_{16}^0 X_{CO_2}^0 + k_{17f}^0 X_{H_2O}^0\right) |\nabla Z|} \quad (32)$$

$$P_2 = \frac{16b^3 \delta^5 \kappa W_{NO} \left(\frac{p}{RT^0}\right)^2 k_{57f}^0 k_{20f}^0 M_2 L_H X_{N_2}^0}{k_{15}^0 X_{O_2}^0 + k_{16}^0 X_{CO_2}^0 + k_{17f}^0 X_{H_2O}^0 |\nabla Z|} \quad (33)$$

In Eq. (32) and (33) there is a parameter named δ , defined as:

$$\delta = (2bD_I)^{-\frac{1}{3}} \quad (34)$$

The acetylene scale factor is:

$$\kappa = \frac{p \left(k_{36f}^0 + k_{37f}^0\right) \left(k_{38f}^0 + \gamma k_{39f}^0\right)^2 L_{CH_4}^2 \delta}{2\chi^0 \overline{RT}^0 \left(\beta k_{33}^0 L_H\right)^2} \quad (35)$$

The Damköhler Number of step (1) is:

$$D_I = \frac{2}{\chi^0} \frac{p}{RT^0} \left(k_{38f}^0 + \gamma^0 k_{39f}^0\right) L_H L_{CH_4} \quad (36)$$

where

$$\gamma = \frac{X_{H_2O}}{K_3 X_{H_2}} \quad (37)$$

M_1 and M_2 are given as:

$$M_1 = \frac{k_{27f}^0 (k_{38f}^0 + k_{39f}^0 \gamma^0) L_{CH_4} L_H}{k_{33}^0 \beta^0 \left[(k_{23}^0 + k_{24}^0) X_{O_2}^0 + \frac{k_{27b}^0}{K_{25}^0} X_{H_2}^0 \right]} \quad (38)$$

$$M_2 = \frac{(k_{42}^0 + k_{43}^0) \beta^0 L_{C_2H_2} L_H^2}{(k_{23}^0 + k_{24}^0) X_{O_2}^0 + \frac{k_{27b}^0}{K_{25}^0} X_{H_2}^0} \quad (39)$$

The parameter β is defined as:

$$\beta = \frac{K_4 X_{H_2O}}{K_3^2 X_{H_2}^2} \quad (40)$$

It can be said that the prompt contribution to the emission index is:

$$E_P = \frac{2000 W_{NO_2} \frac{\tilde{\omega}_P}{W_{NO}} c_p \bar{W}}{b |\nabla Z|^0 \lambda_{st} W_{CH_4}} \quad (41)$$

An approximation for $X_{O_2}^0$ is used in the expressions for M_1 and M_2 given by:

$$X_{O_2}^0 = B \frac{\chi^0}{p} \quad (42)$$

where $B \approx 10^2$ s·Pa. Use of $X_{O_2}^0$ from Eq. (11) leads to predictions of prompt production rates which are reasonable near extinction conditions but roughly five times too small for $\chi^0 < 1$ [Hewson and Williams, 1999].

2.2.3 The Nitrous Oxide Mechanism

This mechanism is responsible for converting a small fraction of nitrous oxide to nitric oxide. It is important in the oxygen-consumption layer, where N_2O as well as all radicals are in steady state.

The mass production rate of NO across the flame per unit flame area is:

$$\tilde{\omega}_N = 2W_{NO} \left(\frac{p}{RT^0} \right)^2 \left(\frac{k_{72b}^0 k_{96b}^0 K_1^0 K_3^0 X_{H_2}^0 X_{O_2}^0 X_{N_2}^0}{k_{97f}^0 X_{H_2O}^0 |\nabla Z|^0} \right) \frac{T^{0^2}}{b T_r T_N} \frac{1}{1 - Z_{st} - 2q} \quad (43)$$

where

$$k'_{72b} = k_{72b} \left(1 + \frac{k_{98}}{k_{72b}} \sqrt{\frac{K_1 K_4 X_{O_2}}{K_3^3 X_{H_2}}} \right) \quad (44)$$

$$k'_{96b} = k_{96b} \left(1 + \frac{k_{94f} p}{k_{96b} K_{92} \bar{RT}} \sqrt{\frac{K_1 K_3^3 X_{H_2}^3 X_{O_2}}{K_4 X_{H_2O}^2}} \right) \quad (45)$$

$$k'_{97f} = k_{97f} \left(1 + \frac{k_{96f} \bar{RT}}{k_{97f} p} \sqrt{\frac{K_4 X_{H_2O}^2}{K_1 K_3^3 X_{H_2}^3 X_{O_2}}} \right) \quad (46)$$

$$T_N = \frac{E_{72b} + E_{96b} - E_{97f} + E_{1f} - E_{1b} + E_{3f} - E_{3b}}{\bar{R}} - 2.83T^0 \quad (47)$$

The emission index of the nitrous oxide mechanism is given as:

$$E_N = \frac{2000 W_{NO_2} \frac{\tilde{\omega}_N}{W_{NO}} c_p \bar{W}}{b |\nabla Z|^0 \lambda_{st} W_{CH_4}} \quad (48)$$

In order to calculate k_{96f} and k_{96b} , a third body concentration was calculated based on [Seshadri and Peters, 1990], and the Lindemann form utilized based on [Kee *et al.*, 1996].

3. Results

The variation of the emission index of oxides of nitrogen with the scalar dissipation rate was plotted for pressures of 10^5 Pa and $2 \cdot 10^5$ Pa.

Figure 1 represents the temperature in the fuel-consumption zone. A small decrease on its values can be observed for increasing scalar dissipation rates, and higher pressures cause higher temperatures.

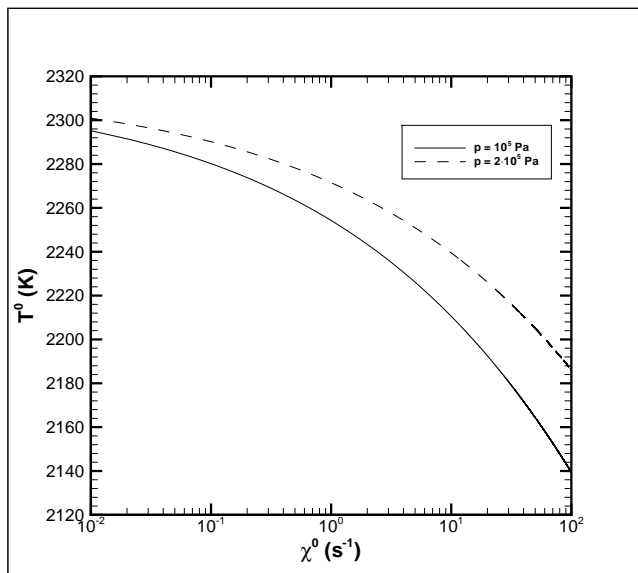


Figure 1. Variation of temperature in fuel-consumption zone for boundary temperature of 300 K and pressures of 10^5 Pa and $2 \cdot 10^5$ Pa.

Figure 2 illustrates the case for E_T . It can be seen that the thermal contribution to the emission index presents lower values for higher values of the scalar dissipation rate. There is also a small difference in E_T when different pressures are considered

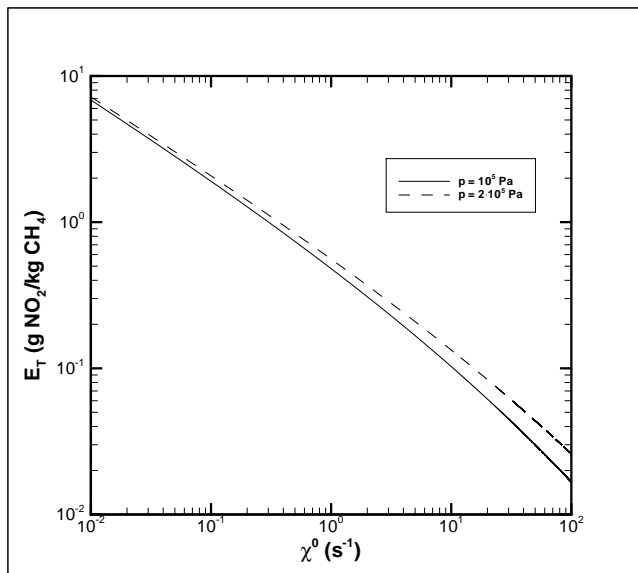


Figure 2. Variation of thermal emission index for boundary temperatures of 300 K, and pressures of 10^5 Pa and $2 \cdot 10^5$ Pa.

Figure 3 shows the dependence of the prompt emission index with the scalar dissipation rate. As far as the scalar dissipation factor increases, the prompt emission index decreases. An interesting behavior can be seen near $\chi^0 = 1 s^{-1}$. At this point, there is a change between the lines, the one with the smallest values acquiring the highest ones.

Finally, Fig. 4 illustrates the changes of E_N with χ^0 . Again, opposite behaviors take place between the nitrous oxide index and the scalar dissipation rate. A small dependence on pressure is observed.

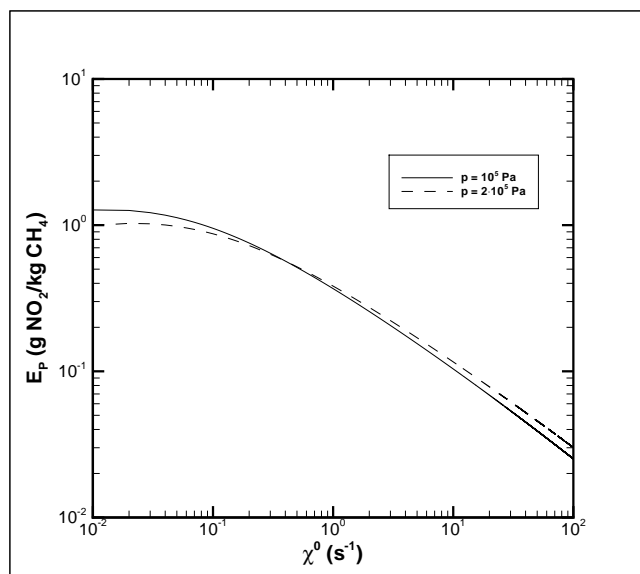


Figure 3. Variation of prompt emission index for boundary temperatures of 300 K, and pressures of 10^5 Pa and $2 \cdot 10^5$ Pa.

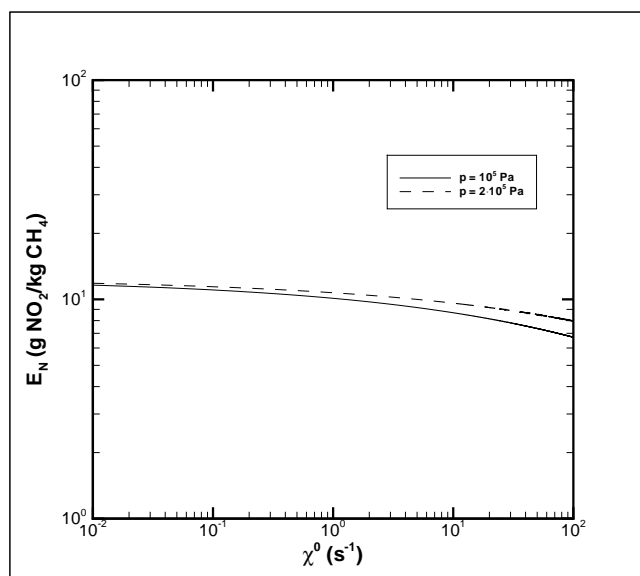


Figure 4. Variation of nitrous oxide emission index for boundary temperatures of 300 K, and pressures of 10^5 Pa and $2 \cdot 10^5$ Pa.

4. Conclusions

Emission indexes for oxides of nitrogen for thermal, prompt and nitrous oxide mechanisms were analytically calculated for a laminar methane-air flame. Its variations with the scalar dissipation rate were plotted for boundary temperatures of 300 K, and for pressures of 10^5 Pa and $2 \cdot 10^5$ Pa.

It can be concluded that, in the three mechanisms, for the two pressures considered, there is a small dependence of the emission indexes on them. Besides that, the higher the values of the dissipation rates, the lower the ones of the emission indexes.

An interesting phenomenon occurs in the prompt mechanism. Increasing pressure leads to reduced CH mole fractions, and for smaller values of χ^0 reduces the net prompt-emission index so that results for $2 \cdot 10^5$ Pa lie below those for 10^5 Pa [Hewson and Williams, 1999]. This effect is mitigated because the overall reaction rates increase at higher pressures, and at high dissipation rates, the numerical results indicate that increased pressure actually causes a slight increase in the prompt contribution to the emission index [Hewson and Williams, 1999].

5. References

- Hewson, J. C. and Williams, F. A., 1999, "Rate Ratio Asymptotic Analysis of Methane-Air Diffusion-Flame Structure for Predicting Production of Oxides of Nitrogen", *Combustion and Flame*, Vol. 117, No. 3, pp. 441-476.
- Kee, R. J., Rupley, F. M., Meeks, E. and Miller, J. A., 1996, "Chemkin III: a Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical and Plasma Kinetics", UC-405/SAND96-8216, USA, 162 p..
- Li, S. C. and Williams, F. A., 1999, " NO_x Formation in Two-Stage Methane-Air Flames", *Combustion and Flame*, Vol. 118, No. 3, pp. 399-414.
- Li, S. C., Williams, F. A. and Gebert, K., 1999, "A Simplified, Fundamentally Base Method for Calculating NO_x Emissions in Lean Premixed Combustors", *Combustion and Flame*, Vol. 119, No. 3, pp. 367-373.
- Rørteit, G. J., Hustad, J., Li, S. C. and Williams, F. A., 2002, "Effects of Diluents on NO_x Formation in Hydrogen Counterflow Flames", *Combustion and Flame*, Vol. 130, No. 1, pp. 48-61.
- Seshadri, K. and Peters, N., 1990, "The Inner Structure of Methane-Air Flames", *Combustion and Flame*, Vol. 81, No. 2, pp. 96-118.

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