# Rate-Ratio Asymptotic Analysis of the Structure and Mechanisms of Extinction of Nonpremixed $CH_4/N_2$–$O_2/N_2O/N_2$ Flames

Kalyanasundaram Seshadri[(1)], Xue-Song Bai [(2)], and Forman A. Williams[(1)]
[(1)]Department of Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, California 92093-0411, USA
[2],Division of Fluid Mechanics, Department of Energy Sciences, Lund University, Box 118 SE-22100 Lund, Sweden

**Abstract**

Rate-ratio asymptotic analysis is carried out to elucidate the structure and mechanisms of extinction of nonpremixed $CH_4/N_2$–$O_2/N_2O/N_2$ flames. Steady, axisymmetric, laminar flow of two counterflowing streams toward a stagnation plane is considered here. One stream, called the fuel stream, is made up of a mixture of methane ($CH_4$) and nitrogen ($N_2$). The other stream, called the oxidizer stream is made up of a mixture of oxygen ($O_2$), nitrous oxide ($N_2O$), and $N_2$. A reduced five-step mechanism is deduced from a detailed chemical kinetic mechanism. This five-step mechanism is employed in the asymptotic analysis. Chemical reactions are presumed to take place in a thin reaction zone that is established in the vicinity of the stagnation plane. On either side of this thin reaction zone, the flow field is inert. These inert regions are called the outer structure. In the thin reaction zone chemical reactions are presumed to take place in three layers—$CH_4$-consumption layer, the $O_2$-consumption layer, and the $N_2O$ consumption layer. Asymptotic analysis of these layers gives the value of the scalar dissipation rate, $\chi$ at extinction. The strain rates at extinction are calculated from the scalar dissipation rate. They are compared with experimental data and those computed using detailed mechanisms.

## 1 Introduction

The gas-phase combustion of nitramines can be described as a collection of a number of subsystems. One such subsystem is the reaction between methane ($CH_4$) and nitrogen containing oxidizers for example nitrogen dioxide ($NO_2$) and nitrous oxide ($N_2O$). An improved understanding of the combustion taking place in these subsystems is required to model the combustion of nitramines. Here a rate-ratio asymptotic study is carried out to elucidate the structure and extinction of nonpremixed $CH_4/N_2$–$O_2/N_2O/N_2$ flames. Asymptotic flame theories provide valuable insights on mixing and chemical reactions taking place during combustion [1–3]. This work is to be considered as the first step in understanding combustion processes with nitrogen containing oxidizers. It is focused on studies with $N_2O$ as one of reactants because experimental data is available for testing the prediction of the asymptotic analysis. The tools developed here will be extended later to include studies on systems that include $NO_2$ as oxidizer. Very little experimental data with $NO_2$ as oxidizer is available because this compound is extremely toxic and requires special handling.

Correspondence to: seshadri@ucsd.edu

## 2 Formulation

Steady, axisymmetric, laminar flow of two counterflowing streams toward a stagnation plane is considered here. One stream, called the fuel stream, is made up of a mixture of $CH_4$ and nitrogen ($N_2$). The other stream, called the oxidizer stream is made up of a mixture of oxygen ($O_2$), $N_2O$, and $N_2$. The origin is placed on the axis of symmetry at the stagnation plane. Far from the stagnation plane the mass fraction of fuel and nitrogen in the fuel stream is represented by $Y_{\mathrm{F},1}$ and $Y_{\mathrm{N}_2,1}$, respectively, and the temperature by $T_1$. Far from the stagnation plane the mass fraction of oxygen, nitrogen and nitrous oxide in the oxidizer stream is represented by, $Y_{\mathrm{O}_2,2}$, $Y_{\mathrm{N}_2,2}$, and $Y_{\mathrm{N_2O},2}$ respectively, and the temperature by $T_2$. In asymptotic analysis of the flame structure, it is convenient to use a conserved scalar quantity $\xi$, called the mixture fraction, as an independent variable [4]. This conserved scalar is defined such that $\xi$ = 0 at the oxidizer stream far from the stagnation plane and $\xi$ = 1 at the fuel stream far from the stagnation plane. The scalar dissipation rate, $\chi$ is given by

$$\chi = 2\left[\lambda/\left(\rho c_{\mathrm{p}}\right)\right]\left|\nabla\xi\right|^2, \tag{1}$$

where $\lambda$ is the thermal conductivity, $\rho$ the density, and $c_{\mathrm{p}}$ the heat capacity per unit mass of the mixture. The quantity $\chi$ plays a central role in asymptotic analyses. The goal of the present analysis is to predict the scalar dissipation rate at extinction.

The structure of the reactive flow-field depends on the three independent boundary values of mass fractions of reactants given by $Y_{\mathrm{F},1}$, $Y_{\mathrm{O}_2,2}$, and $Y_{\mathrm{N_2O},2}$, and the temperatures, $T_1$ and $T_2$. Thus the chemical reaction time $\tau_c$ depends on these five independent quantities. The residence time is characterized by the strain rate $\tau_f$. The overall Damköhler number, $\Delta_{\mathrm{o}} = \tau_f/\tau_c$, is defined as the ratio between the characteristic residence time and the characteristic reaction time. For large values of $\Delta_{\mathrm{o}}$ the flow-field comprises two chemically inert regions separated by a thin reaction zone [1, 3, 5]. In the limit $\Delta_{\mathrm{o}} \to \infty$, the thickness of the reaction zone approaches zero. The stoichiometric mixture fraction, $\xi_{\mathrm{st}}$, is evaluated using the equation

$$\xi_{\mathrm{st}} \equiv \left[\frac{Y_{\mathrm{O}_2,2}}{2W_{\mathrm{O}_2}} + \frac{Y_{\mathrm{N_2O},2}}{4W_{\mathrm{N_2O}}}\right]\left[\frac{Y_{\mathrm{F},1}}{W_{\mathrm{F}}} + \frac{Y_{\mathrm{O}_2,2}}{2W_{\mathrm{O}_2}} + \frac{Y_{\mathrm{N_2O},2}}{4W_{\mathrm{N_2O}}}\right]^{-1}, \tag{2}$$

where $W_{\mathrm{F}}$, $W_{\mathrm{O}_2}$ and $W_{\mathrm{N_2O}}$ are the molecular weights of $CH_4$, $O_2$ and $N_2O$ respectively. The quantity $\xi_{\mathrm{st}}$ represents the position of the reaction zone in the limit $\Delta_{\mathrm{o}} \to \infty$ with the Lewis number of the reactants assumed to be equal to unity. The Lewis number is defined as $Le_i = \lambda/(\rho c_{\mathrm{p}} D_{\mathrm{i}})$, where $D_{\mathrm{i}}$ is the diffusion coefficient of species $i$.

## 3 Experimental and Computational Studies

To guide the asymptotic analysis, experimental and computational studies are carried out to characterize the influence of $N_2O$ on the structure and extinction of nonpremixed methane flames. It has been established from asymptotic analysis [1–3, 5] that the scalar dissipation rate at extinction depends on the strain rate, the stoichiometric mixture fraction, $\xi_{\mathrm{st}}$ and the adiabatic flame temperature $T_{\mathrm{st}}$. The adiabatic temperature is a function of $Y_{\mathrm{F},1}$, $Y_{\mathrm{O}_2,2}$, $Y_{\mathrm{N_2O},2}$, $T_1$ and $T_2$. To elucidate the influence of combustion chemistry of $N_2O$ on the structure and mechanisms of extinction of $CH_4$ flames, studies are carried out at fixed values of $\xi_{\mathrm{st}}$, $T_{\mathrm{st}}$, $T_1$, and $T_2$. This fixes the values of four of the five independent variables. The system now has only one independent variable. The quantity $Y_{\mathrm{N_2O},2}$ is selected as the independent

variable. Thus the experimental and computational studies are carried out for various values of $Y_{\mathrm{N_2O},2}$.

The counterflow configuration is employed in the experimental and computational study. The counterflow burner used in the experimental study has two ducts. From one duct, called the fuel-duct, a reactant stream made up of methane and nitrogen is injected toward the mixing layer. From the other duct, called the oxidizer duct, a mixture of oxygen, nitrous oxide, and nitrogen is injected. The magnitude of the injection velocity of the reactants at the the fuel duct is represented by $V_1$, and the magnitude of the injection velocity at the oxidizer duct is represented by $V_2$. The flow-field is characterized by the strain rate, $a$, given by [6]

$$a = \frac{2|V_2|}{L}\left(1 + \frac{|V_1|\sqrt{\rho_1}}{|V_2|\sqrt{\rho_2}}\right). \tag{3}$$

Here $\rho_1$ and $\rho_2$ are the densities at the reactant streams at the injection plane of the fuel duct and at the injection plane of the oxidizer duct respectively. The separation distance between the ducts is $L$.

The experiments were conducted with $T_1 = T_2 = 298\,\mathrm{K}$. At a selected value of $Y_{\mathrm{N_2O},2}$, the values of $Y_{\mathrm{F},1}$, and $Y_{\mathrm{O_2},2}$, were so chosen that $\xi_{\mathrm{st}} = 0.054$, and $T_{\mathrm{st}} = 2200\,\mathrm{K}$. At these selected values of the mass fractions and temperatures of the reactants a flame was established. Figure 1 shows a photograph of a flame stabilized in the counterflow burner. The photograph shows two reaction zones. After the

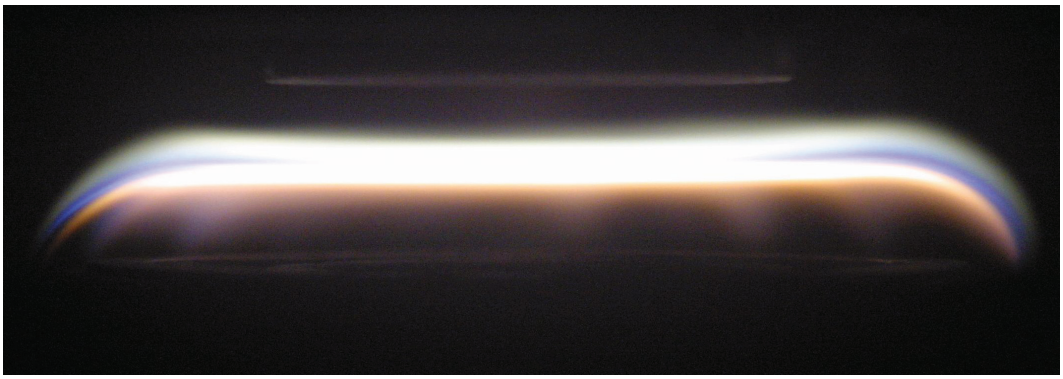

Figure 1: Photograph of a Nonpremixed $CH_4$/$N_2$–$N_2O$/$O_2$/$N_2$ flame. Fuel stream: $Y_{\mathrm{F},1} = 0.75$, $T_1 = 298\,\mathrm{K}$, Oxidizer Stream: $Y_{\mathrm{N_2O},2} = 0.4$ , $Y_{\mathrm{O_2},2} = 0.1165$, $T_2 = 298\,\mathrm{K}$. Strain rate $a_2 = 175\,\mathrm{s}^{-1}$.

flame is established, the values of $V_1$ and $V_2$ were increased until extinction was observed. The strain rate at extinction, $a_{2,\mathrm{e}}$, was recorded as a function of the mass fraction of $N_2O$, $Y_{\mathrm{N_2O},2}$.

Computations were performed using the San Diego Mechanism [7, 8]. The mechanism is comprised of 288 reversible reactions among 53 reactive species. Comparisons were made with predictions of the much larger Milano mechanism (more than one thousand reactions and more than one hundred species) [9]. Figure 2 shows the computed structure of a $CH_4$/$N_2$–$N_2O$/$O_2$/$N_2$ flame at different strain rates with fixed $T_{\mathrm{st}} = 2200\,\mathrm{K}$, $\xi_{\mathrm{st}} = 0.054$, and $Y_{\mathrm{N_2O},2} = 0.102$. The structure at $a_2 = 100\,\mathrm{s}^{-1}$ is far from extinction and the structure at $a_2 = 100\,\mathrm{s}^{-1}$ is close to extinction. The normalized carbon mass fraction in Fig. 2 is the ratio of the mass fraction of carbon at a given location to the mass fraction of carbon in the fuel stream at $\xi = 1$. Figure 2 clearly shows that consumption of $CH_4$ and $N_2O$ takes place in two separate layers. They are called the $CH_4$-consumption layer and the $N_2O$-consumption layer respectively. In the layer where $CH_4$ is consumed, the fuel reacts with radicals, and the intermediate species CO and $H_2$ are formed. In the $N_2O$-consumption layer, $N_2O$ reacts with radicals to form

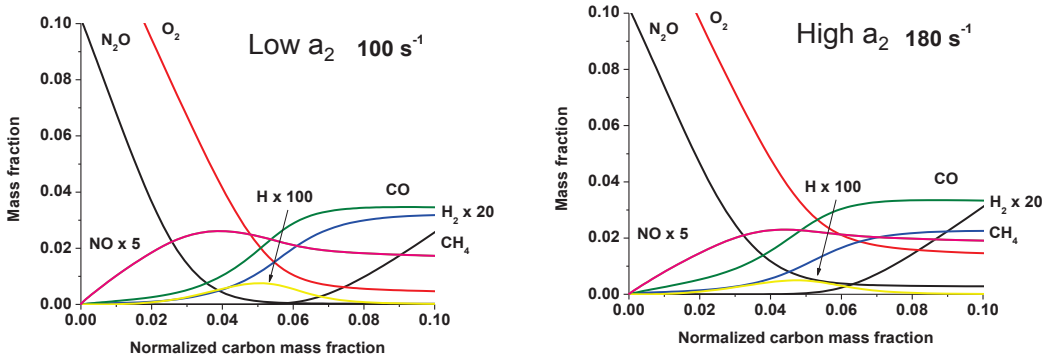


Figure 2: Computed structure of a $CH_4/N_2$–$N_2O/O_2/N_2$ flame at different strain rates with fixed $T_{\rm st} = 2200\,{\rm K}$, $\xi_{\rm st} = 0.054$, $Y_{\rm N_2O,2} = 0.102$. The computations were done using the San Diego Mechanism [7, 8].

NO. Consumption of $H_2$, CO, $O_2$, and NO, take place in the layer between the $CH_4$-consumption layer and the $N_2O$-consumption layer. This layer is called the $O_2$-consumption layer. In the $O_2$-consumption layer, radicals are formed. These radical diffuse into the $CH_4$-consumption layer and $N_2O$-consumption layer. The computed flame structure shown in Fig. 2 is used in the asymptotic analysis to separate the reaction zone into different reaction layers.

Figure 3 shows the strain rate at extinction, $a_{2,\rm e}$, as a function of the mass fraction of $N_2O$ in the

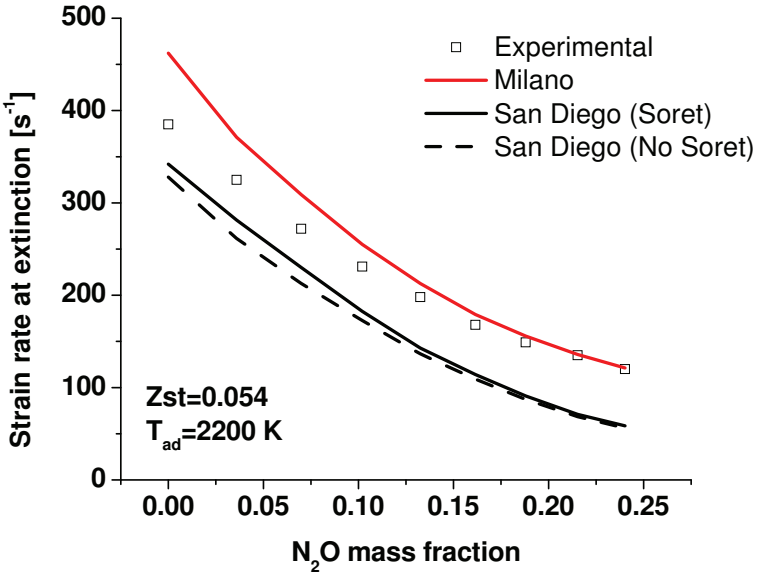


Figure 3: The strain rate at extinction, $a_{2,\rm e}$ of nonpremixed $CH_4/N_2$–$N_2O/O_2/N_2$ flames as a function of the mass fraction of nitrous oxide, $Y_{\rm N_2O,2}$, with fixed $T_{\rm st} = 2200\,{\rm K}$, $\xi_{\rm st} = 0.054$. The symbols represent experimental data. The solid lines and dotted lines are results of computations. The solid line above the experimental data are computations with the Milano mechanism [9]. The solid line below the experimental data and the dashed line are computations with the San Diego Mechanism [7, 8].

oxidizer stream, $Y_{\rm N_2O,2}$. The symbols are experimental data and the solid lines and dashed lines are results of computations performed using the San Diego Mechanism [7,8] and the Milano mechanism [9].

Experimental data and computations show that $a_{2,\mathrm{e}}$ decreases with increasing $Y_{\mathrm{N_2O},2}$. Thus $N_2O$ inhibits the flame. Computations with the San Diego Mechanism [7,8] and the Milano mechanism [9] agree well with experimental data.

## 4 Asymptotic Analysis

A reduced chemical-kinetic mechanism made up of five global steps is employed to describe the combustion of $CH_4/N_2$–$O_2/N_2O/N_2$ flames. The five-step mechanism is

$$\begin{aligned}
\mathrm{CH_4 + 2\,H + H_2O} &\rightleftharpoons \mathrm{CO + 4\,H_2}, && \mathrm{I}\\
\mathrm{CO + H_2O} &\rightleftharpoons \mathrm{CO_2 + H_2}, && \mathrm{II}\\
\mathrm{H + H + M} &\rightleftharpoons \mathrm{H_2 + M}, && \mathrm{III}\\
\mathrm{O_2 + 3\,H_2} &\rightleftharpoons \mathrm{2\,H + 2\,H_2O}, && \mathrm{IV}\\
\mathrm{N_2O + 2\,H + H_2O} &\rightleftharpoons \mathrm{2\,NO + 2\,H_2}. && \mathrm{V}
\end{aligned}$$

The reduced mechanism is derived from the detailed San Diego Mechanism [7, 8] after assuming that all reactive species, except those shown in the reduced mechanism, maintain steady states. The first four steps of this five-step mechanism was employed in previous rate-ratio asymptotic analysis of non-premixed methane flames [10]. The principal elementary reactions contributing to the rates of these global reactions are

$$\begin{aligned}
\mathrm{CH_4 + H} &\rightleftharpoons \mathrm{CH_3 + H_2}, && \mathrm{I}\\
\mathrm{CO + OH} &\rightleftharpoons \mathrm{CO_2 + H}, && \mathrm{II}\\
\mathrm{H + O_2 + M} &\rightleftharpoons \mathrm{HO_2 + M}, && \mathrm{III}\\
\mathrm{H + O_2} &\rightleftharpoons \mathrm{OH + O}, && \mathrm{IV}\\
\mathrm{N_2O + H} &\rightleftharpoons \mathrm{N_2 + OH}. && \mathrm{V}
\end{aligned}$$

The Damköhler numbers constructed from the ratio of the characteristic residence time to the characteristic chemical time obtained from the rates of elementary reactions of the five-step mechanism are presumed to be large. At conditions close to extinction, the reactive flow-field is presumed to be made up of a thin reaction zone where chemical reactions take place. This reaction zone is presumed to be located at $\xi = \xi_{\mathrm{p}}$. Oxygen is presumed to leak from the reaction zone to the leading order. The value of $\xi_{\mathrm{p}}$ depends on $\chi$. The chemically inert regions outside this thin reaction zone is called the outer zone.

The profiles of mass fraction of $CH_4$, $O_2$, $N_2O$, $CO_2$, $H_2O$, and $N_2$ represent the outer structure of the flame. They are presumed to be of the order of unity. Analysis of the outer structure provides the matching conditions for analyzing the structure of the reaction zone.

As shown in Figure 2, the reaction zone is made up of three layers, the $CH_4$-consumption layer, the $O_2$-consumption layer, and the $N_2O$-consumption layer. The global reactions of the reduced five-step mechanism take place in various layers within the reaction zone. The global steps I and IV are the main reactions taking place in the $CH_4$-consumption layer, global steps II. II, and IV in the $O_2$-consumption layer and global steps IV and V in the $N_2O$-consumption layer. Asymptotic analysis of these layers gives the value of the scalar dissipation rate, $\chi$ at extinction. The strain rate is evaluated from $\chi$ [11]. The results are compared with experimental data and those computed using the detailed mechanisms shown in Fig. 3.

## References

[1] F. A. Williams, *Combustion Theory*, 2nd ed. Redwood City, CA: Addison-Wesley Publishing Company, 1985.

[2] N. Peters, *Turbulent Combustion*. Cambridge, England: Cambridge University Press, 2000.

[3] A. Liñán and F. A. Williams, *Fundamental Aspects of Combustion*, ser. Oxford Engineering Science Series. Oxford University Press, New York, 1993, vol. 34.

[4] N. Peters, "Partially premixed diffusion flamelets in non-premixed turbulent combustion," *Proceedings of the Combustion Institute*, vol. 20, pp. 353–360, 1984.

[5] K. Seshadri, "Multistep asymptotic analyses of flame structures," *Proceedings of the Combustion Institute*, vol. 26, pp. 831–846, 1996.

[6] K. Seshadri and F. A. Williams, "Laminar flow between parallel plates with injection of a reactant at high Reynolds number," *International Journal of Heat and Mass Transfer*, vol. 21, no. 2, pp. 251–253, 1978.

[7] P. Saxena, "Numerical and experimental studies of ethanol flames and autoignition theory for higher alkanes," Ph.D thesis, University of California at San Diego, Department of Mechanical and Aerospace Engineering, 2007.

[8] "The San Diego Mechanism," http://maeweb.ucsd.edu/combustion/.

[9] http://creckmodeling.chem.polimi.it.

[10] X. S. Bai and K. Seshadri, "Rate-ratio asymptotic analysis of non-premixed methane flames," *Combustion Theory and Modelling*, vol. 3, pp. 51–75, 1999.

[11] J. S. Kim and F. A. Williams, "Theory of counterflow mixing of fuel with hot reaction products," vol. 73, pp. 575–588, 1990.