

Large-activation-energy analysis of gaseous reacting flow in pipes

Daniel Moreno-Boza¹, Immaculada Iglesias², Antonio L. Sánchez¹

¹ University of California, San Diego, La Jolla CA 92093-0411, USA

² Universidad Carlos III de Madrid, Leganés 28911, Spain

1 Introduction

The safe storage and transportation of reactant gas mixtures requires conditions that ensure a negligibly small reaction rate, achieved in storage vessels and transport pipes by lowering sufficiently the wall temperature. The seminal investigation of this problem is due to Frank-Kamenetskii (FK) [1, 2], who employed an overall irreversible reaction with large activation energy to study a reacting mixture undergoing an exothermic chemical reaction in a centrally symmetric closed vessel with constant wall temperature. The resulting gas-temperature distribution was seen to depend on the competition of the heat released by the chemical reaction and the heat losses to the wall, characterized by the Damköhler number δ , defined as the ratio of the conduction time across the vessel to the relevant characteristic time evaluated at the wall temperature [3]. A slowly reacting flameless mode of combustion is found for values of below a critical value, when the heat losses to the wall are able to limit the temperature rise, in such a way that the reaction rate does not change in order of magnitude from its near-wall value. Since the overall heat-release rate is proportional to the volume of reacting gas while the heat-loss rate to the wall is proportional to the wall surface, for a given wall temperature there exists a limiting size, corresponding to a critical value of δ , above which a slow reaction cannot be maintained, and is replaced by a localized temperature runaway that leads to the formation of a flame [4, 5]. These classical results find direct application in connection with the safety storage of reactant mixtures, defining critical sizes for thermal explosions in chemically reacting systems. A related problem addressed here is that of reactant transportation in pipes, with specific consideration given to the entrance region adjacent to the storage container.

2 Formulation

Consider a gaseous reactant mixture with initial temperature, density, and reactant mass fraction T'_i , ρ'_i , and Y_o discharging from a storage vessel along a pipe of radius a whose wall temperature is kept at a fixed value $T'_o > T'_i$. As in FK's work [1], our analysis considers an overall Arrhenius reaction, with the mass of reactant consumed per unit volume per unit time \dot{m} given by $\dot{m}/\rho' = k(T')Y_r = B \exp[-E/(RT')]Y_r$, where ρ' , T' , and Y_r represent the density, temperature and reactant mass fraction. The temperature-dependent reaction-rate constant $k = B \exp[-E/(RT')] = B \exp[-E/(RT'_o)] \exp[\beta(T' - T'_o)/T']$, includes a frequency factor B and an activation energy E , with R denoting the universal gas constant. The characteristic activation temperature E/R is assumed to be large compared with the wall temperature, resulting in a temperature-sensitive rate constant that changes from its wall value $B \exp[-E/(RT'_o)]$ by a factor of order unity when $T' - T'_o \sim RT'_o{}^2/E = T'_o/\beta \ll T'_o$, where $RT'_o{}^2/E$ is the so-called FK temperature and $\beta = E/(RT'_o) \gg 1$ is the nondimensional activation energy.

The heat-release rate of the reaction per unit volume is given by $q\dot{m}$, where q denotes the amount of heat released per unit mass of reactant consumed. Correspondingly, the time t_e needed for the heat-release rate of the chemical reaction to increase the enthalpy by an amount $c_p T'_o/\beta$, proportional to the FK temperature $RT'_o{}^2/E$, is given by $t_e = \exp[E/(RT'_o)]/\alpha\beta B$ where $\alpha = (qY_o)/(c_p T'_o) \sim 1$ is the dimensionless temperature rise, based on T'_o , for constant-pressure adiabatic combustion, with c_p representing the constant specific heat at constant pressure. The

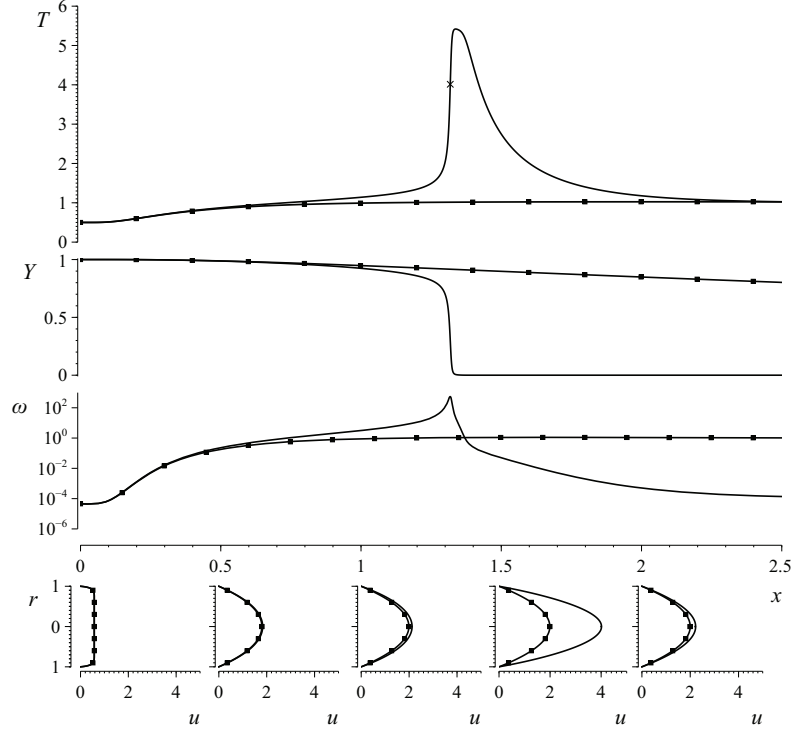


Figure 1: The variation with axial distance of T , Y , and $\omega = Y \exp[\beta(T - 1)/T]$ at $r = 0$ obtained by numerical integration of (1)–(4) with $Pr = 0.7$, $Le = 1.0$, $\beta = 10$, $\alpha = 5$, and $T_I = 0.5$ for $\delta = 1.0$ (squares) and $\delta = 5.0$ (plain); the bottom plots show the axial velocity profiles at five different locations.

chemical time can be compared with the characteristic heat-conduction time across the pipe $t_c = a^2/D_T$, where D_T is the thermal diffusivity evaluated at T'_o , to define the FK parameter $\delta = t_c/t_e = (a^2/D_T)\alpha\beta \exp[-E/(RT'_o)]$, a Damköhler number characterizing the slowly reacting mode of combustion of enclosed reactant mixtures, with the value $\delta = 2$ identifying the explosion limit [1–3]. A convenient characteristic value for the streamwise flow velocity $U = G/(\rho'_o \pi a^2)$ can be defined from the known mass flow rate G by using the density $\rho'_o = \rho'_i T'_i/T'_o$ evaluated at $T' = T'_o$. This velocity defines the Peclet number of the pipe flow $Pe = Ua/D_T$, comparable in magnitude to the associated Reynolds number $Re = Pe/Pr$, with Pr denoting the order-unity Prandtl number of the gaseous mixture. The following analysis pertains to configurations with moderately large values of the Peclet number for which the flow in the pipe is stable and slender, with a characteristic streamwise development length $\ell = Pe a$ much larger than the pipe radius a . The resulting steady laminar flow can be analyzed in the boundary-layer approximation by integrating

$$\frac{\partial}{\partial x}(\rho u) + \frac{1}{r} \frac{\partial}{\partial r}(r \rho v) = 0 \quad (1)$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial r} = -P_l(x) + \frac{Pr}{r} \frac{\partial}{\partial r} \left(r T^\sigma \frac{\partial u}{\partial r} \right) \quad (2)$$

$$\rho u \frac{\partial T}{\partial x} + \rho v \frac{\partial T}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left(r T^\sigma \frac{\partial T}{\partial r} \right) + \frac{\delta}{\beta} \rho Y \exp[\beta(T - 1)/T] \quad (3)$$

$$\rho u \frac{\partial Y}{\partial x} + \rho v \frac{\partial Y}{\partial r} = \frac{1}{Le r} \frac{\partial}{\partial r} \left(r T^\sigma \frac{\partial Y}{\partial r} \right) - \frac{\delta}{\alpha \beta} \rho Y \exp[\beta(T - 1)/T] \quad (4)$$

for $x > 0$ and $0 < r < 1$ supplemented with the equation of state $\rho T = 1$ and subject to the initial conditions $u - T_I = T - T_I = Y - 1 = 0$ at the pipe entrance, and the boundary conditions $\partial_r u = v = \partial_r T = \partial_r Y = 0$ at

$r = 0$ and $u = v = T - 1 = \partial_r Y = 0$ at $r = 1$ for $x > 0$, as corresponds to axially symmetric flow bounded by a non-permeable constant-temperature wall with non-slip flow.

In the formulation the axial and radial coordinates x' and r' are scaled with $\ell = Pe a$ and a according to $x = x'/\ell$ and $r = r'/a$, while their associated velocity components u' and v' are scaled with U and D_T/a to give $u = u'/U$ and $v = v'/(D_T/a)$, respectively. With the scale selected for the axial velocity, its initial uniform value $u'_i = G/(\rho'_i \pi a^2)$ becomes $u'_i/U = \rho'_o/\rho'_i = T_i$ when expressed in dimensionless form. The reactant mass fraction Y_r is normalized with its initial value Y_o to give $Y = Y_r/Y_o$, and the temperature and density are scaled with T'_o and ρ'_o to give the nondimensional variables $T = T'/T'_o$ and $\rho = \rho'/\rho'_o$. The unknown streamwise pressure gradient $P_i(x)$ has been scaled with its characteristic value $\rho'_o U^2/\ell$. The problem essentially depends on four nondimensional parameters, namely, the activation energy $\beta = E/(RT'_o)$, the heat-release parameter $\alpha = (qY_o)/(c_p T'_o)$, the Damköhler number δ , and the initial-to-wall temperature ratio $T_i = T'_i/T'_o < 1$. The analysis below considers the simplified solution that arises for moderately large values of β with $\alpha \sim 1$, $\delta \sim 1$, and $1 - T_i \sim 1$. A full numerical integration of the problem is displayed in Fig. 1 for two representative subcritical and supercritical cases.

3 The chemically frozen entrance region

As discussed above, the flow in the tube includes an entrance development region of characteristic length $\ell = Pe a$, corresponding to values of x of order unity, where the velocity profile evolves from an initial uniform profile $u = T_i$ to a Poiseuille profile $u = 2(1 - r^2)$ while the temperature evolves from the initial value $T = T_i < 1$ to the wall value $T = 1$. As a consequence of the exponential temperature dependence of the reaction rate discussed earlier, the chemical reaction can be entirely neglected as long as $1 - T \gg \beta^{-1}$, so that the reactant mass fraction remains equal to its initial value $Y = 1$ in this entrance region, as can be seen by integrating the chemically frozen version of (4) with initial condition $Y = 1$ at $x = 0$ and boundary conditions $\partial_r Y = 0$ at $r = 0$ and $r = 1$. The associated distributions of u and T are obtained by integration of (1)–(3) with the corresponding initial and boundary conditions given above; the chemical reaction being discarded in (3). The solution depends on the initial temperature T_i and on the transport description through the values of σ and Pr , with the realistic values $\sigma = 0.7$ and $Pr = 0.7$ selected in the integrations reported below, as is appropriate for fuel-air gas mixtures [8].

As seen in Fig. 1, depending on the conditions, the temperature either continues to increase, leading to a thermal runaway at a finite distance downstream, or reaches a maximum value $T - 1 \sim \beta^{-1}$ corresponding to a quasisteady balance between the heat released by the chemical reaction and the heat losses to the walls. The asymptotic temperature distribution for the non-reacting gaseous pipe flow at $x \gg 1$ is given by

$$T - 1 = -C \exp(-\lambda_1^2 x/2) \exp(-\lambda_1 r^2/2) L_{(\lambda_1-2)/4}(\lambda_1 r^2), \quad (5)$$

as can be obtained by using separation of variables in

$$2(1 - r^2) \frac{\partial}{\partial x}(T - 1) = \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r}(T - 1) \right], \quad (6)$$

derived by linearizing (3) for $T - 1 \ll 1$ with $u \simeq 2(1 - r^2)$ and $v \simeq 0$. Here $L_{(\lambda_1-2)/4}$ is the Laguerre polynomial of order $(\lambda_1 - 2)/4$, with the value of $\lambda_1 = 2.704$ determined as the smallest root of the equation $L_{(\lambda-2)/4}(\lambda) = 0$ associated with the condition $T = 1$ at $r = 1$. The factor C is an unknown positive constant obtained from the numerical integration of the entrance flow.

4 Slowly reacting flow

The exponential temperature decay (5) is modified as the chemical reaction begins to have a significant effect, which occurs when the temperature drop from the wall value $1 - T$ decreases to values of order β^{-1} across most of the pipe section. The condition $1 - T = \beta^{-1}$ evaluated with use made of the temperature drop along the axis $1 - T(x, 0) = C \exp(-\lambda_1^2 x/2)$ given in (5) provides $x_d = (2/\lambda_1^2) \ln(C\beta)$, as an expression for the downstream location x_d where the reaction becomes important, marking the end of the chemically frozen flow. The following region of incipient

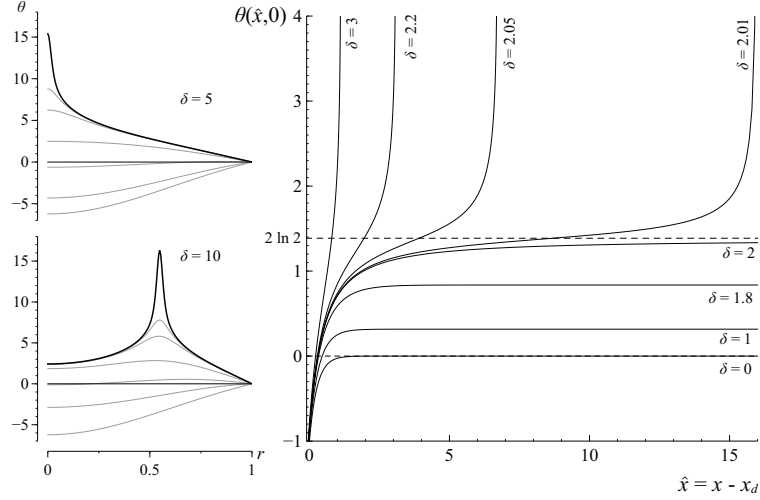


Figure 2: The temperature evolution obtained by integration of (8) with corresponding initial and boundary conditions for different values of δ , including the evolution with distance of the temperature along the axis for subcritical and supercritical cases along with selected temperature profiles for $\delta = 5$ [$\hat{x} = (0, 0.999, 4.999, 9.299, 9.678, 9.686, 9.687)$] and $\delta = 10$ [$\hat{x} = (0, 2.010, 4.826, 5.933, 6.028, 6.032, 6.033)$].

chemical reaction can be described in terms of $\hat{x} = x - x_d$ and $\theta = \beta(T' - T'_o)/T'_o$, reducing the problem to the integration of

$$2(1 - r^2) \frac{\partial \theta}{\partial \hat{x}} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta}{\partial r} \right) + Y \delta e^\theta \quad \text{and} \quad 2(1 - r^2) \frac{\partial Y}{\partial \hat{x}} = \frac{1}{Le r} \frac{\partial}{\partial r} \left(r \frac{\partial Y}{\partial r} \right) - \frac{1}{\alpha \beta} Y \delta e^\theta \quad (7)$$

with initial conditions $\theta + \exp(-\lambda_1^2 \hat{x}/2) \exp(-\lambda_1 r^2/2) L_{(\lambda_1-2)/4}(\lambda_1 r^2) = Y - 1 = 0$ as $\hat{x} \rightarrow -\infty$ and boundary conditions $\partial_r \theta = \partial_r Y = 0$ at $r = 0$ and $\theta = \partial_r Y = 0$ at $r = 1$. The FK linearization $\exp[\beta(T - 1)/T] = \exp[\theta/(1 + \theta/\beta)] \simeq e^\theta$ has been employed in writing the reaction rate in (7), as it is appropriate in the limit $\beta \gg 1$ with $\theta \sim 1$.

5 The first reaction stage

The analysis of the chemical reaction at distances $\hat{x} = x - x_d \sim 1$ determines whether the solution undergoes a thermal runaway, as occurs for supercritical cases with $\delta > 2$, or whether the flow evolves into a quasisteady slow mode of combustion that persists farther downstream, as occurs for $\delta \leq 2$. In this transition region $x \sim 1$ with $\theta \sim 1$ the change in reactant mass fraction is small, of order $1 - Y \sim (\alpha\beta)^{-1} \ll 1$, as follows from (7), so that the problem reduces to the integration of

$$2(1 - r^2) \frac{\partial \theta}{\partial \hat{x}} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta}{\partial r} \right) + \delta e^\theta \quad (8)$$

subject to the initial and boundary conditions given above. Selected results of computations are shown in Fig. 2. For subcritical cases with $\delta \leq 2$ the temperature evolves towards the steady distribution

$$\theta_{\text{FK}} = 2 \ln \left\{ \frac{2/(1 + \sqrt{1 - \delta/2})}{1 + (\delta/2)[r/(1 + \sqrt{1 - \delta/2})]^2} \right\} \quad (9)$$

corresponding to the cylindrical FK problem

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{d\theta_{\text{FK}}}{dr} \right) = -\delta e^{\theta_{\text{FK}}}, \quad \frac{d\theta_{\text{FK}}}{dr}(0) = \theta_{\text{FK}}(1) = 0. \quad (10)$$

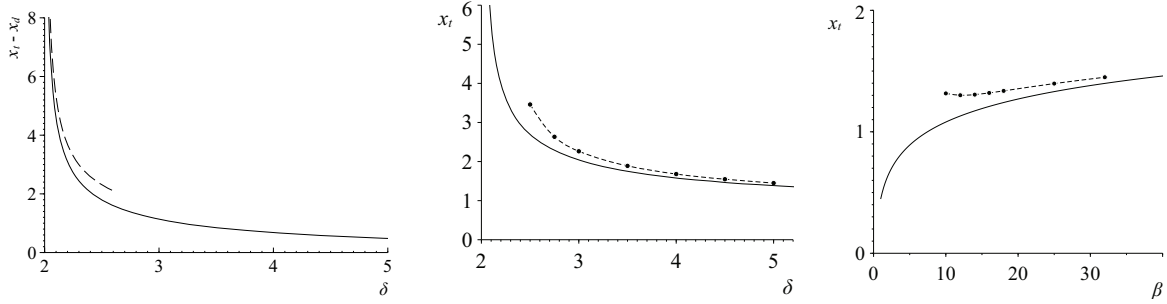


Figure 3: (left) The variation with $\delta > 2$ of the thermal-runaway distance $\hat{x}_t = x_t - x_d$, with the dashed curve representing the near-critical asymptotic result $\hat{x}_t \simeq 1.62(\delta - 2)^{-1/2}$. (middle and right) Comparison of the thermal-runaway distance with the full numerical computations (dots) as a function of δ and β , respectively, for $Pr = 0.7$, $\alpha = 5$, $Le = 1$ and $T_I = 0.5$.

The associated temperature along the axis $\theta(\hat{x}, 0)$ is seen to approach $\theta(\hat{x}, 0) = 2 \ln[2/(1 + \sqrt{1 - \delta/2})]$ for $x \gg 1$, with the limiting value $\theta(\hat{x}, 0) = 2 \ln 2$ reached for the critical case $\delta = 2$. On the other hand, for $\delta > 2$ the transition stage ends with a thermal runaway at a finite downstream location $\hat{x}_t = x_t - x_d \sim 1$.

The resulting thermal-runaway location \hat{x}_t , a decreasing function of δ , is shown in Fig. 3, together with a comparison with numerical results. The ignition distance computed here differs by a factor of order unity from that computed earlier in [7], where integrations of (8) were started with an initially uniform gas temperature, equal to the wall value. The present analysis, accounting for the presence of the reaction-free entry region, provides a prediction for the distance from the entrance of the pipe x'_t at which ignition occurs, given in nondimensional form $x_t = x'_t/[G/(\pi\rho'_o D_T)]$ by $x_t = x_d(T_I, \beta) + \hat{x}_t(\delta) = (2/\lambda_1^2) \ln C + (2/\lambda_1^2) \ln \beta + \hat{x}_t$.

6 Downstream flameless combustion for $\delta \leq 2$

For subcritical values of the Damköhler number $\delta \leq 2$ the temperature in the pipe evolves towards the quasi-steady distribution (9) for moderately large values of \hat{x} . Most of the reactant consumption, negligibly small in the entrance and transition regions, occurs downstream, at distances of order $\alpha\beta\ell$, such that the rescaled coordinate $X = (x - x_d)/(\beta\alpha)$ is of order unity, when Eqs. (7) become

$$\frac{2}{\alpha\beta}(1 - r^2) \frac{\partial\theta}{\partial X} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial\theta}{\partial r} \right) + Y\delta e^\theta, \quad \text{and} \quad 2(1 - r^2) \frac{\partial Y}{\partial X} = \frac{\alpha\beta}{Le r} \frac{\partial}{\partial r} \left(r \frac{\partial Y}{\partial r} \right) - Y\delta e^\theta, \quad (11)$$

to be solved with the boundary conditions given earlier. Equations (11) indicates that during this second stage transverse diffusion of the reactant is so fast that its mass fraction remains spatially uniform across the pipe at leading order, so that $Y \simeq \bar{Y}(X)$ with errors of order $1/(\alpha\beta)$, while the temperature evolves in a quasi-steady manner as dictated by

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial\theta}{\partial r} \right) + \bar{Y}\delta e^\theta = 0, \quad (12)$$

in the limit $\beta\alpha \gg 1$. As can be inferred from (10), the solution to (12) subject to $\partial\theta/\partial r = 0$ at $r = 0$ and $\theta = 0$ at $r = 1$ is just given by

$$\theta = 2 \ln \left\{ \frac{2/(1 + \sqrt{1 - \delta\bar{Y}/2})}{1 + (\delta\bar{Y}/2)[r/(1 + \sqrt{1 - \delta\bar{Y}/2})]^2} \right\} \quad (13)$$

obtained by writing the FK temperature distribution (9) with δ replaced by the instantaneous Damköhler number $\delta\bar{Y}$. The evolution of $\bar{Y}(X)$ is described, after some algebra, by

$$\delta X = \left(1 - \frac{\delta}{2}\right)^{1/2} - \left(1 - \frac{\delta\bar{Y}}{2}\right)^{1/2} - \ln \left[\frac{1 - (1 - \delta\bar{Y}/2)^{1/2}}{1 - (1 - \delta/2)^{1/2}} \right] \quad (14)$$

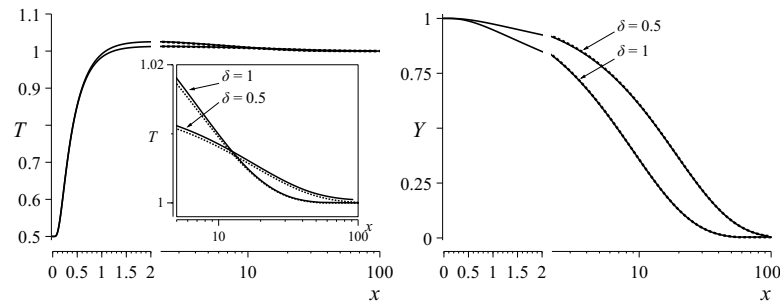


Figure 4: Axial evolution of temperature, given by (13) with $r = 0$ and $T = \theta/\beta + 1$, and mass fraction \bar{Y} , given by (14), valid for $X = (x - x_d)/(\alpha\beta) \sim 1$ (dashed lines), compared with the full numerical simulation of (1)-(4) for $\delta = 0.5$ and 1, with $\alpha = 5$, $\beta = 10$, $Pr = 0.7$, $T_I = 0.5$ and $Le = 1$.

as an implicit representation for the reactant mass fraction as a function of the rescaled streamwise distance $X = (x - x_d)/(\alpha\beta)$. The above expression applies for subcritical cases with $\delta \leq 2$ and a comparison with the full numerical integration of the problem is available in Fig. 4.

7 Concluding remarks

The flow of an initially cold reactant mixture in a hot cylindrical pipe at moderately large values of the Reynolds number has been analyzed in the limit of large activation energies. The flow includes an entrance region where the gas temperature adapts to the wall value, followed by a shorter region of incipient reaction where the flow evolves to give either a rapid thermal runaway leading to the generation of a flame or a quasi-steady flameless mode of combustion that persists downstream along the pipe. Appropriate rescaled problems have been formulated, analyzed and compared with full numerical integrations in the different regions, leading to predictions for the ignition distance in supercritical cases and for the slow downstream reactant consumption encountered in subcritical cases.

References

- [1] D.A. Frank-Kamenetskii, The temperature distribution in a reaction vessel and the time-independent theory of thermal explosions, *Zh. Fiz. Khim* 13 (1939) 738–755.
- [2] D.A. Frank-Kamenetskii, *Diffusion and heat transfer in chemical kinetics*, Second ed., Plenum Press, New York, NY, 1969.
- [3] Ya. B. Zel'dovich, G. I. Barenblatt, V. B. Librovich, and G. M. Makhviladze, *The Mathematical Theory of Combustion and Explosions*, Consultants Bureau, New York., 1985.
- [4] J.W. Dold, Analysis of the early stage of thermal runaway, *Q. J. Mech. Appl. Math.* 38 (1985) 361–387.
- [5] J.W. Dold, Analysis of thermal runaway in the ignition process, *SIAM J. Appl. Math.* 49 (1989) 459–480.
- [6] A. Liñán, D. Moreno-Boza, I. Iglesias, A.L. Sánchez, F. A. Williams, The slowly reacting mode of combustion of gaseous mixtures in spherical vessels. Part 1: transient analysis and explosion limits, *Combust. Theor. Model.* 20 (2016) 1010–1028.
- [7] G.I. Barenblatt, A.J. Chorin, and A. Kast, The influence of the flow of the reacting gas on the conditions for a thermal explosion, *Proc. Natl. Acad. Sci. USA* 94 (1997) 12762–12764.
- [8] D.E. Rosner, *Transport processes in chemically reacting flow systems*, Dover Publications, Inc., Mineola, New York, 2000.