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

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ABSTRACT

This paper analyzes the exothermic reaction of an initially cold gaseous mixture flowing with a moderately large Reynolds number along a cylindrical pipe with constant wall temperature. An overall irreversible reaction with an Arrhenius rate having a large activation energy is used for the chemistry description. The flow is chemically frozen in the cold entrance region, where the velocity evolves towards the Poiseuille profile as the gas temperature increases towards the wall value, ushering in a reaction stage during which the rate of heat transfer from the wall changes from positive to negative. The subsequent downstream evolution of the flow depends critically on the competition between the heat released by the chemical reaction and the heat-conduction losses to the wall, as measured by the Damköhler number δ, first introduced by Frank-Kamenetskii in his seminal analysis of thermal explosions in cylindrical vessels. For values of δ below the critical value $\delta = 2$ corresponding to the quasi-steady explosion limit, heat losses to the wall keep the gas temperature close to the wall value, so that the chemical reaction occurs slowly along the pipe in a flameless mode, which is analyzed to give an implicit expression for the streamwise reactant distribution. By way of contrast, for $\delta > 2$ the slow reaction rates occur only in an initial ignition region, which ends abruptly when very large reaction rates cause a temperature runaway, or thermal explosion, at a well-defined location, whose computation must account for the temperature found at the end of the entrance region. The predictions of the large-activation-energy analyses, including ignition distances for $\delta > 2$ and flameless reactant consumption rates for $\delta \leq 2$, show good agreement with numerical computations of the reactive pipe flow for finite values of the activation energy.

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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], who studied a reacting mixture undergoing an exothermic chemical reaction in a centrally symmetric closed vessel with constant wall temperature. His analysis employed an overall irreversible reaction with an Arrhenius rate having a large activation energy, an appropriate model to represent the strong temperature dependence of the rate-controlling oxidation reactions in typical fuel–air mixtures [2,3]. The resulting gas-temperature distribution is 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 (i.e. the homogeneous thermal-explosion time at constant pressure) evaluated at the wall temperature [3]. A slowly reacting flameless mode of combustion is found for values of δ 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]. More recent analyses of slowly reacting mixtures in closed vessels have addressed additional aspects of the problem, including the effects of pressure increase on the ignition time [6] and of buoyancy-induced motion on explosion limits [7–10].

The results of the FK analysis find direct application in connection with the 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,

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analyzed previously in a simplified configuration [11]. Specifically, we consider below the discharge of a reactant mixture stored in a cold vessel at temperature T_l' through a pipe whose wall temperature is kept at a constant temperature $T_o' > T_l'$ with $T_o' - T_l' \sim T_o'$. The Damköhler number δ introduced by Frank-Kamenetskii for the analysis of thermal explosions in cylindrical vessels emerges as the main governing parameter [11]. Our analysis identifies the existence of an entrance region with negligible chemical reaction, where the gas temperature increases from T_l' towards T_o' by heat conduction from the wall, immediately followed by a region of incipient chemical reaction that governs the transition towards a persistent slowly reacting mode of combustion for $\delta \leq 2$ or the development of a thermal runaway for $\delta > 2$. Ignition events are analyzed to determine the explosion distance for $\delta > 2$, a computation that requires consideration of the upstream chemically frozen region of temperature accommodation. Specific attention is given to near-critical conditions with delayed ignition events. The development includes also an analytic description of the slowly reacting mode of combustion established downstream the transition region in subcritical configurations with $\delta \leq 2$.

2. Formulation

Consider a gaseous reactant mixture with initial temperature, density, and reactant mass fraction T_l', ρ_l', and Y_o discharging from a storage vessel along a pipe of radius a whose wall temperature is kept at a fixed value $T_o' > T_l'$. As in Frank-Kamenetskii'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

$$\dot{m}/\rho' = k(T')Y_r = B\exp[-E/(RT')]Y_r, \tag{1}$$

where ρ', T', and Y_r represent the density, temperature and reactant mass fraction. The temperature-dependent reaction-rate constant

$$k = B\exp[-E/(RT')] = B\exp[-E/(RT_o')]\exp[\beta(T'-T_o')/T'], \tag{2}$$

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. A direct consequence of this strong temperature dependence is that, for initially cold mixtures with $T_o' - T_l' \sim T_o'$, the case considered here, the chemical reaction is effectively frozen in the storage vessel.

In this overall-reaction model 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—evaluated at T_o' with the initial reactant mass fraction Y_o—to increase the enthalpy by an amount $c_p T_o'/\beta$, proportional to the FK temperature $RT_o'^2/E$, is given by

$$t_e = \frac{1}{\alpha\beta B\exp[-E/(RT_o')]}, \tag{3}$$

where $\alpha = (qY_o)/(c_p T_o')$ is the dimensionless temperature rise, based on T_o', for constant-pressure adiabatic combustion, with c_p representing the specific heat at constant pressure, taken as constant for simplicity. In relevant combustion applications the parameter α takes values that are of the order of, although typically larger than, unity. The chemical time t_e defined in (3) can be compared with the characteristic heat-conduction time across the pipe

$$t_c = a^2/D_T, \tag{4}$$

where D_T is the thermal diffusivity evaluated at T_o', to define the FK parameter

$$\delta = t_c/t_e = (a^2/D_T)\alpha\beta B\exp[-E/(RT_o')], \tag{5}$$

a Damköhler number characterizing the slowly reacting mode of combustion of enclosed reactant mixtures, with the value $\delta = 2$ identifying the explosion limit in cylindrical vessels [1–3].

The discharge is assumed to occur at low Mach numbers, resulting in spatial pressure differences in the pipe that are small compared with the vessel pressure, so that the equation of state can be written in the simplified form $\rho'T' = \rho_l'T_l'$. 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 $\rho_o' = \rho_l'T_l'/T_o'$ 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 Reynolds number $Re \sim Pe$ in the range $10 \lesssim Re \lesssim 2000$, 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

$$\frac{\partial}{\partial x}(\rho u) + \frac{1}{r}\frac{\partial}{\partial r}(r\rho v) = 0 \tag{6}$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial r} = -P_l(x) + \frac{Pr}{r}\frac{\partial}{\partial r}\left(rT^\sigma\frac{\partial u}{\partial r}\right) \tag{7}$$

$$\rho u \frac{\partial T}{\partial x} + \rho v \frac{\partial T}{\partial r} = \frac{1}{r}\frac{\partial}{\partial r}\left(rT^\sigma\frac{\partial T}{\partial r}\right) + \frac{\delta}{\beta}\rho Y\exp[\beta(T-1)/T] \tag{8}$$

$$\rho u \frac{\partial Y}{\partial x} + \rho v \frac{\partial Y}{\partial r} = \frac{1}{Le\, r}\frac{\partial}{\partial r}\left(rT^\sigma\frac{\partial Y}{\partial r}\right) - \frac{\delta}{\alpha\beta}\rho Y\exp[\beta(T-1)/T] \tag{9}$$

for $x > 0$ and $0 < r < 1$ supplemented with the equation of state

$$\rho T = 1 \tag{10}$$

and subject to the initial conditions

$$x = 0: \quad u - T_l = T - T_l = Y - 1 = 0 \tag{11}$$

at the pipe entrance, and the boundary conditions

$$\frac{\partial u}{\partial r} = v = \frac{\partial T}{\partial r} = \frac{\partial Y}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{12}$$

and

$$u = v = T - 1 = \frac{\partial Y}{\partial r} = 0 \quad \text{at} \quad r = 1 \tag{13}$$

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 $u_l' = G/(\rho_l'\pi a^2)$ becomes $u_l'/U = \rho_o'/\rho_l' = T_l$ when expressed in dimensionless form, as shown in (11). 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 $P_l(x)$, to be determined as