# Large Activation Energy Analysis of the Ignition of Self-Heating Porous Bodies

**JOSÉ M. VEGA and A. LIÑÁN**

A large activation energy analysis of the problem of thermal ignition of self-heating porous bodies is carried out by means of a regular perturbation method. A correction to the well-known Frank-Kamenetskii estimate of the ignition limit is calculated, for symmetric bodies, by using similarity properties of the equations giving higher order terms in an expansion in powers of $1/E$ ($E$ = activation energy). Our estimate compares well with numerical results, and differs from others in the literature, which are not better than Frank-Kamenetskii's one from an asymptotic point of view. Dirichlet and Robin type of boundary conditions are considered.

A brief analysis of the extinction problem for no reactant consumption is also presented.

## 1. INTRODUCTION

The problem of thermal ignition of porous catalysts has received considerable attention in the literature. Frank-Kamenetskii's pioneering work [1] took advantage of the fact that the nondimensional activation energy $E$, defined below, is usually a large parameter. His solution for the ignition regime is the leading order term of an expansion in powers of $E^{-1}$ of the solution of the exact equation and satisfies the so-called Frank-Kamenetskii (F-K) equation. This equation has known closed-form solutions in one and two dimensions, and possesses similarity properties which make it possible to express the solution in three dimensions in terms of some canonical functions which can be calculated from a second order initial value problem (see Chandrasekhar and Wares [2] and Chambré [3]). It is seen, in particular, that no solution of the F-K equation (satisfying the appropriate boundary conditions) exists if the Damköhler number exceeds a certain critical value $\delta_I^0$, which is a first approximation, as $E \to \infty$, of the ignition limit $\delta_I$.

More recently, a number of workers tried to determine the dependence of $\delta_I$ on $E$. Parks [4] and Shouman et al. [5, 6] calculated $\delta_I$ by numerical computations of the exact problem; Shouman and Donaldson [7] used a power series expansion on the spatial variable to describe the solution of the exact problem. Bowes and Thomas [8] assumed that the temperature inside the body is uniform (see Thomas [9]) and made a large activation energy analysis of the simple resulting problem. Hardee et al. [10] replaced the Arrhenius term by a polynomial. Takeno [11] used the maximum temperature inside the body (which is an unknown), instead of the temperature at its surface, to make nondimensionalizations, and solved the leading order problem in the limit $E \to \infty$. Comparison with numerical results showed that Takeno's approximation is qualitatively good, at least for zero-order reactions; nevertheless the estimates of $\delta_I$ given in [11] are zero-order approximations as $E \to \infty$ and, therefore, they are not better than the original Frank-Kamenetskii estimate from an asymptotic point of view. Takeno's idea has been used also by Bazley and Wake [12], Takeno and Sato

[13], and Gill et al. [14, 15]. For a variational method for calculating $\delta_I$ see Fradkin and Wake [16].

In this note, we shall calculate higher order approximations, as $E \to \infty$, of the ignition limit. Such approximations will be given by problems having similarity properties which will allow them to be reduced to canonical initial value problems. We shall take into account the reactant consumption and the effect of external heat and mass transfer resistances.

The dimensionless heat and mass conservation equations and the boundary conditions to be considered are

$$-\bar{\gamma}\left(\frac{d^2\bar{\tau}}{dx^2}+\frac{j}{x}\frac{d\bar{\tau}}{dx}\right)=\frac{d^2\bar{c}}{dx^2}+\frac{j}{x}\frac{d\bar{c}}{dx}$$

$$=\bar{\gamma}\frac{\bar{\delta}}{\bar{E}}\bar{c}^n \exp\,(\bar{E}(\bar{\tau}-1)/\bar{\tau}), \tag{1}$$

$$\bar{\tau}'(0)=\bar{c}'(0)=0; \qquad \nu(1-\bar{\tau}(1))=\bar{\tau}'(1),$$

$$\sigma(1-\bar{c}(1))=\bar{c}'(1), \tag{2}$$

where $x$, $\bar{c}$, and $\bar{\tau}$ are the nondimensional space coordinate, concentration, and temperature; $n$ is the reaction order and $\bar{\delta}$, $\bar{E}$, and $\bar{\gamma}^{-1}$ are the Damköhler number, the nondimensional activation energy, and the nondimensional maximum adiabatic temperature rise; $j$ = 0, 1, and 2 for symmetric bodies in 1, 2, and 3 dimensions; and $\nu$ and $\sigma$ are the Biot numbers for external heat and mass transfer. Bars over variables and parameters will be used when considering boundary conditions of the type (2), while they will be omitted when using boundary conditions of the Dirichlet type.

We shall make the realistic hypothesis

$$\bar{E}\to\infty, \qquad \bar{\gamma}^{-1}\bar{E}\to\infty, \qquad \bar{\gamma}^{-1}=O(1),$$

$$\sigma^{-1}\bar{E}=O(1). \tag{3}$$

The first two of these are necessary for the F-K equation to give an approximate solution of the problem. The remaining two are not essential in the analysis; values of $\bar{\gamma}$ and $\sigma$ smaller than those considered here will require only algebraic changes in the analysis below.

## 2. THE DIRICHLET PROBLEM

Let us consider first the problem

$$-\gamma\left(\frac{d^2\tau}{dx^2}+\frac{j}{x}\frac{d\tau}{dx}\right)=\frac{d^2c}{dx^2}+\frac{j}{x}\frac{dc}{dx}$$

$$=\gamma\frac{\delta}{E}c^n \exp(E(\tau-1)/\tau), \tag{4}$$

$$\tau'(0)=c'(0)=0; \qquad \tau(1)=c(1)=1. \tag{5}$$

An integration of the first equation in (4) leads to the relation

$$\gamma\tau+c=\gamma+1, \tag{6}$$

which reduces (4) and (5) to a problem in $\tau$. This problem may be written as

$$\frac{d^2\phi}{dx^2}+\frac{j}{x}\frac{d\phi}{dx}+\delta\left(1-\frac{\gamma\phi}{E}\right)^n$$

$$\times\exp\left(\frac{\phi}{1+\phi/E}\right)=0, \tag{7}$$

$$\phi'(0)=\phi(1)=0 \tag{8}$$

in terms of the variable

$$\phi=E(\tau-1).$$

The simplest asymptotic analysis, as $E\to\infty$, of (7) and (8), requires the introduction of an expansion of the type

$$\phi=\phi_0+\frac{\gamma}{E}\phi_1+\frac{\gamma^2}{E^2}\phi_2+\frac{1}{E}\phi_3+O\left(\frac{\gamma}{E^2},\frac{\gamma^3}{E^3}\right)$$

into (7) and (8) to get a sequence of recursive problems giving $\phi_i$, $i$ = 0, 1, ... . ($E^{-1}$ and $\gamma E^{-1}$ are treated as independent small parameters to account for the case $1 \ll \gamma \ll E$). Then, the problems giving $\phi_i$, $i > 1$, are singular at the ignition limit. To avoid this difficulty, the Damköhler number will be expanded: $\delta=\delta_0+$

$(\gamma/E)\delta_1 + \cdots$. To define the unknowns $\delta_1$, $\delta_2$, $\cdots$, an arbitrary additional condition must be imposed on the problem giving $\phi_i$, for any $i > 1$. Such conditions can be chosen in such a way that (i) no singularity appears in the higher order problems and (ii) $\phi_i$, $i > 1$, can be expressed in terms of canonical functions.

A redefinition of $\phi$ will allow us to obtain $\phi_1$, $\phi_2$, and $\phi_3$ at the same time. Let us introduce

$$g = (1 - n\gamma/E)\phi, \qquad \Lambda = (1 - n\gamma/E)\delta \tag{9}$$

and the expansions

$$g = g_0 + (E^{-1} + n\gamma^2/2E^2)g_1 + \cdots,$$

$$\Lambda = \Lambda_0 + (E^{-1} + n\gamma^2/2E^2)\Lambda_1 + \cdots. \tag{10}$$

The problems giving $g_0$ and $g_1$ and found to be

$$\frac{d^2g_0}{dx^2} + \frac{j}{x}\frac{dg_0}{dx} + \Lambda_0 e^{g_0} = 0;$$

$$g_0'(0) = g_0(1) = 0, \tag{11}$$

$$\frac{d^2g_1}{dx^2} + \frac{j}{x}\frac{dg_1}{dx} + \Lambda_0 e^{g_0}$$

$$\times\left(g_1 + \frac{\Lambda_1}{\Lambda_0} - g_0^2\right) = 0;$$

$$g_1'(0) = g_1(1) = 0. \tag{12}$$

The equation and the boundary condition at $x = 0$ in (11) are invariant under the group of transformations

$$g_0 \to g_0 + \alpha, \qquad x \to \beta x, \qquad \Lambda_0 \to \Lambda_0/\beta^2 e^{\alpha}. \tag{13}$$

This invariance allows us to obtain an analytical solution of (11) (see [2,3]). Following Chambré [3], we define the new variables

$$\omega_0 = -xg_0' \qquad \theta_0 = \Lambda_0 x^2 e^{g_0}, \qquad s = g_0(0) - g_0, \tag{14}$$

which are invariant under the group (13), to write (11) as

$$d\omega_0/ds = 1 - j + \theta_0/\omega_0,$$

$$d\theta_0/ds = -\theta_0 + 2\theta_0/\omega_0, \tag{15}$$

$$\lim \omega_0/s = \lim \theta_0/(j+1)s = 2$$

$$\text{as} \quad s \to 0^+, \tag{16}$$

$$\theta_0(\bar{s}) = \Lambda_0, \qquad \omega_0(\bar{s}) = -g_0'(1)$$

$$\text{at} \quad \bar{s} = g_0(0). \tag{17}$$

For $j = 0$ and 1, (15) and (16) have closed-form solutions, while for $j = 2$, $\theta_0 = \theta_0(s)$ and $\omega_0 = \omega_0(s)$ may be obtained by numerical computations on (15) and (16). Observe [see (17)] that the functions $\theta_0 = \theta_0(s)$ and $\omega_0 = \omega_0(s)$ give $\Lambda_0$ and $-g_0'(1)$ in terms of $g_0(0)$; it is seen, in particular, that no solution of (11) exists if $\Lambda_0 > \Lambda_{0I} = \sup_{s\geq 0}\theta_0(s)$ ($\Lambda_{0I} = 0.879$, 2.000, and 3.322 for $j = 0$, 1, and 2, respectively).

The differential equation and the boundary condition at $x = 0$ in (12) are invariant under the group of transformations given by (13) and

$$g_1 \to g_1 + 2\alpha(1 + g_0) + \alpha^2.$$

As an additional condition for defining $\Lambda_1$, we select

$$g_1(0) = g_0(0)[2 + g_0(0)] + 2 - \Lambda_1/\Lambda_0, \tag{18}$$

which is invariant under the group. We introduce the new variables

$$\theta_1 = g_0[2 + g_0] - g_1 + 2 - \Lambda_1/\Lambda_0,$$

$$\omega_1 = x[2g_0' + 2g_0 g_0' - g_1'], \tag{19}$$

which are invariant under the group too, to write (12), (18) in the form

$$d\omega_1/ds = [(1-j)\omega_1 + 2\omega_0^2 - \theta_0\theta_1]/\omega_0,$$

$$d\theta_1/ds = \omega_1/\omega_0,$$

$$\lim \omega_1/4s^2 = \lim \theta_1/s^2 = 2/(3+j)$$

$$\text{as} \quad s \to 0^+,$$

$$\theta_1(\bar{s}) = 2 - \Lambda_1/\Lambda_0,$$

$$\omega_1(\bar{s}) = 2g_0'(1) + g_1'(1), \tag{20}$$

where $\bar{s}$ is defined in (17). The value of $g_1$ at $x = 0$ is readily obtained, in terms of $\bar{s}$, from (18) and (20):

$$g_1(0) = \theta_1(\bar{s}) + 2\bar{s} + \bar{s}^2. \tag{21}$$

Now, from (9), (10), (14), (17), (19), (20), and (21), we get

$$(1 - n\gamma/E)\delta = \theta_0(\bar{s})\{1 + (1/E + n\gamma^2/2E^2) \times [2 - \theta_1(\bar{s})] + O(\mu)\}, \tag{22}$$

$$E(1 - n\gamma/E)[\tau(0) - 1] = \bar{s} + (1/E + n\gamma^2/2E^2) \times [\theta_1(\bar{s}) + 2\bar{s} + \bar{s}^2] + O(\mu), \tag{23}$$

$$E(1 - n\gamma/E)\psi/(j+1)\gamma = \omega_0(\bar{s}) + (1/E + n\gamma^2/2E^2) \times [\omega_1(\bar{s}) + 2\omega_0(\bar{s})] + O(\mu), \tag{24}$$

where $\mu = \max\{\gamma/E^2, \gamma^3/E^3\}$, and $\psi = (j + 1)(dc/dx)_{x=1}$ is the observable reaction rate per unit volume. Equations (22)-(24) give parametrically, through $\bar{s}$, $\tau(0)$, and $\psi$ in terms of $\delta$. The ignition limit, $\delta_I$, corresponds to the first maximum of $\delta$; it is reached at $\bar{s} = \bar{s}_I$, where

$$\bar{s}_I = \alpha + \frac{(1/E + n\gamma^2/2E^2)\omega_0(\alpha)\omega_1(\alpha)}{[2 - \omega_0(\alpha)]^2 - 2[1 - j + \theta_0(\alpha)/\omega_0(\alpha)]} + O(\mu),$$

with $\alpha = 1.187$, 1.386, and 1.608, $\theta_0(\alpha) = 0.879$, 2.000, and 3.322, and $\omega_1(\alpha) = 3.250$, 2.580, and 1.980 for $j = 0$, 1, and 2, respectively, and $\omega_0(\alpha) = 2$ [$\alpha$ is the value of s at the first maximum of the function $\theta_0 = \theta_0(s)$]. Then

$$(1 - n\gamma/E)\delta_I = \theta_0(\alpha)\{1 + (1/E + n\gamma^2/E^2) \times [2 - \theta_1(\alpha)] + O(\mu)\}, \tag{25}$$

where $\theta_1(\alpha) = 0.9519$, 0.910, and 0.869 for $j = 0$, 1, and 2, respectively. Since $2 - \theta_1(\alpha) > 0$, $\delta_I$ increases as $E^{-1}$, $n$, or $\gamma$ increases. A comparison of the estimate (25) with numerical results given by Parks [4] is made in Fig. 1.

The temperature profiles are easily obtained in terms of the functions $\theta_0 = \theta_0(s)$ and $\theta_1 = \theta_1(s)$. From the definitions (14) and (19), $g_0(x)$ and $g_1(x)$ are seen to be given by

$$x = \sqrt{\theta_0(s)/\Lambda_0}\exp[(s - \bar{s})/2],$$

$$g_0 = \bar{s} - s,$$

$$g_1 = 2 - \Lambda_1/\Lambda_0 + (\bar{s} - s)[2 + \bar{s} - s] - \theta_1(s),$$

in terms of the parameter $s$, for $0 \leq s \leq \bar{s}$.

## 3. THE EFFECT OF HEAT AND MASS TRANSFER RESISTANCES

When using the new variables and parameters

$$\tau = \bar{\tau}/\bar{\tau}_s, \qquad c = \bar{c}/\bar{c}_s, \qquad E = \bar{E}/\bar{\tau}_s,$$

$$\gamma = \bar{\gamma}\bar{\tau}_s/\bar{c}_s,$$

$$\delta = \frac{\bar{\delta}{c_s}^n}{\bar{\tau}_s^2}\exp\left(\bar{E}\,\frac{\bar{\tau}_s - 1}{\bar{\tau}_s}\right), \tag{26}$$

$$\bar{c}_s = \bar{c}(1), \qquad \bar{\tau}_s = \bar{\tau}(1),$$

Eqs. (1) and (2) become Eqs. (4) and (5), which have been considered in the previous section. The boundary conditions (2) at $x = 1$ and the relation (6) lead to

$$\bar{c}_s = [1 + \psi/\sigma(j+1)]^{-1},$$
$$\bar{\tau}_s = 1 + \bar{c}_s\psi/\bar{\gamma}\nu(j+1). \tag{27}$$

When taking into account hypothesis (3), Eq. (24), and the definitions (26), Eqs. (27) become

$$\bar{c}_s = 1 + O(\bar{E}^{-2}),$$

$$\left(1 - n\frac{\bar{\gamma}}{\bar{E}}\right)(\bar{\tau}_s - 1) = \frac{1}{\bar{E}}\left\{\frac{\omega_0(\bar{s})}{\nu} + \frac{2}{\bar{E}}\left(\frac{\omega_0(\bar{s})}{\nu}\right)^2 + \left(\frac{1}{\bar{E}} + \frac{n}{2}\frac{\bar{\gamma}^2}{\bar{E}^2}\right) \times \frac{2\omega_0(\bar{s}) + \omega_1(\bar{s})}{\nu} + O(\bar{\mu})\right\},$$

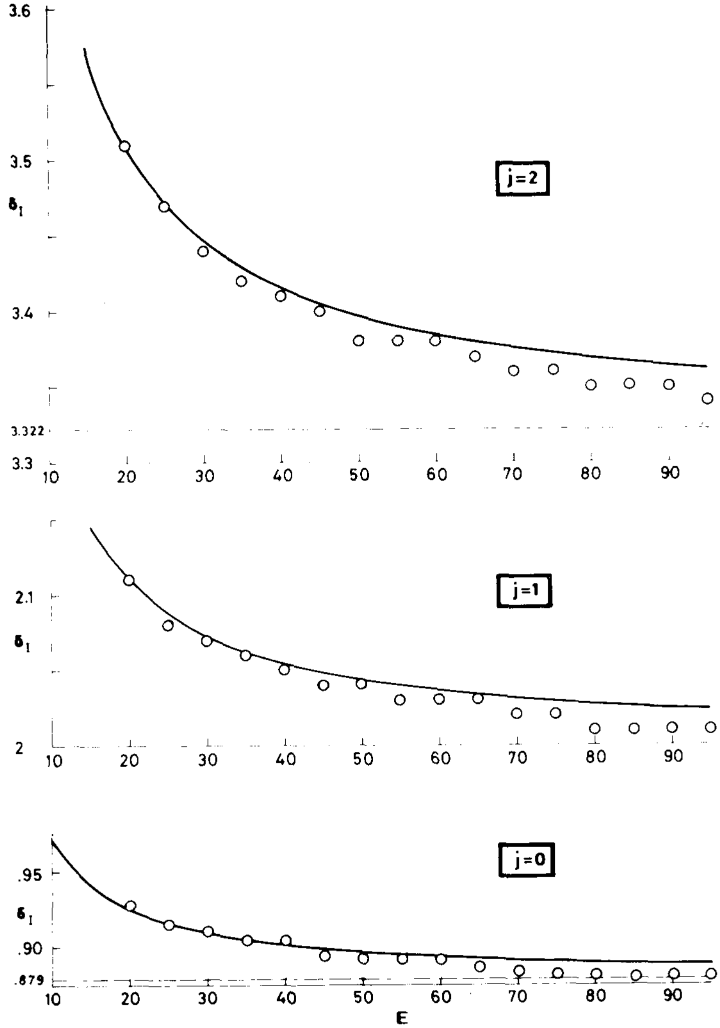


Fig. 1. A comparison between the present estimate of the ignition limit ( ) and numerical results of [4] (○) for $n = 0$ and no external heat and mass transfer resistances.

where $\bar{\mu} = \max\{\bar{\gamma}/\bar{E}^2, \bar{\gamma}^3/\bar{E}^3\}$. Then, from (26) we get

$$(1 - n\bar{\gamma}/\bar{E})\bar{\delta} = \Lambda_0(\bar{s}) + (2/\bar{E})\Lambda_1(\bar{s}) + (1/\bar{E} + n\bar{\gamma}^2/\bar{E}^2)\Lambda_2(\bar{s}) + O(\bar{\mu}), \tag{28}$$

where

$$\Lambda_0 = \theta_0 \exp[-\omega_0/\bar{\nu})],$$

$$\Lambda_1 = \Lambda_0(\omega_0/\bar{\nu}) \exp[-\omega_0/\bar{\nu})], \tag{29}$$

$$\Lambda_2 = \Lambda_0[2 - \theta_1 - (2\omega_0 + \omega_1)/\bar{\nu}],$$

$$\bar{\nu} = \nu(1 - n\bar{\gamma}/\bar{E}). \tag{30}$$

The ignition limit corresponds to the first maximum of $\bar{\delta} = \bar{\delta}(\bar{s})$, which is reached at a value of $\bar{s}$ which, in the first approximation, is given by the equation

$$\bar{\nu} = \frac{(1-j)\omega_0 + \theta_0}{2 - \omega_0}. \tag{31}$$

Remember that in (29)–(31), $\omega_i$ and $\theta_i$ are known

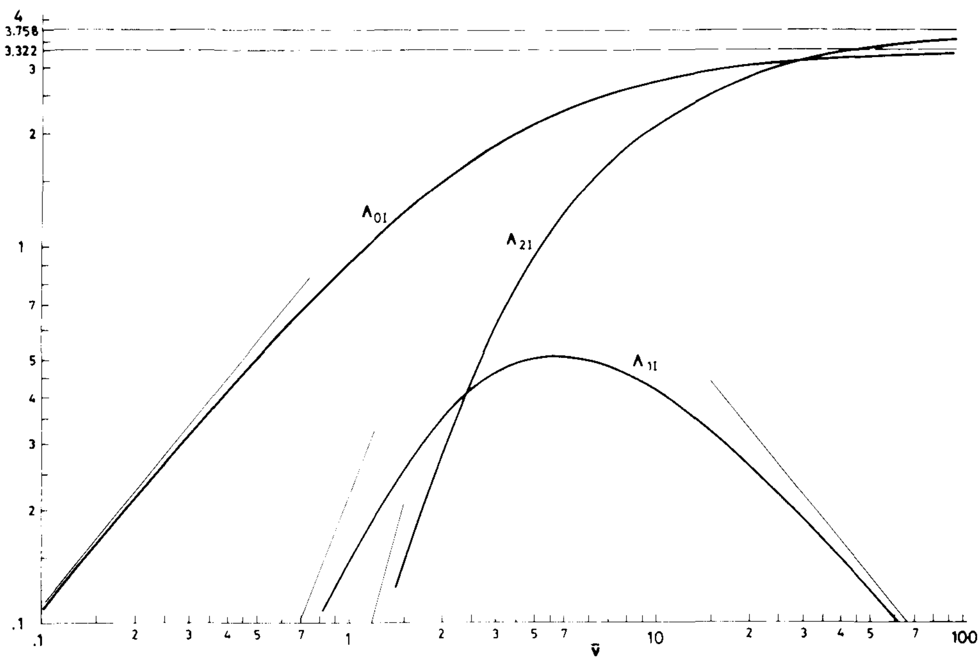


Fig. 2. $\Lambda_{01}$, $\Lambda_{11}$, and $\Lambda_{21}$ versus $\bar{\nu} = \nu(1 - n\bar{\gamma}/\bar{E})$, to be used in Eq. (28) to calculate the ignition limit.

functions of $\bar{s}$; therefore, (28) and (31) give a parametric representation, through $\bar{s}$, of the function $\bar{\delta}_I = \bar{\delta}_I(\bar{\nu})$. $\Lambda_{01}$, $\Lambda_{11}$, and $\Lambda_{21}$ are plotted versus $\bar{\nu}$ in Fig. 2 for the spherical geometry ($j = 2$). The function $\Lambda_{01} = \Lambda_{01}(\bar{\nu})$, which gives a first approximation of the ignition limit, was obtained by Thomas [17].

The temperature profiles may be obtained as in the previous section.

## 4. A NOTE ON THE EXTINCTION

The analysis given before describes the response of the porous body in a nearly frozen reacting mode, or ignition regime, which exists only for $\delta < \delta_I$. For $\delta$ larger than an extinction value $\delta_E$ ($\delta_E < \delta_I$), there is an additional fast reaction response mode, which is to be considered briefly.

In the limit $E \to \infty$, $\delta E$ = finite, the effect of reactant consumption must be taken into account. If $n > -1$ and the reaction term is assumed to vanish for $c = 0$, three distinguished zones appear in the porous body: (a) an internal core without reactant, (b) an external region where the chemical reaction is frozen, and (c) a thin reaction region, which is placed at the common boundary of regions (a) and (b), where the reactant arriving by diffusion from region (b) is completely consumed. A singular perturbation analysis of the problem is possible in this case, and provides an asymptotic approximation to the extinction limit $\delta_E$ (see [18–20]).

Here we shall consider only the case of no reactant consumption, whose analysis differs from those of Ref. [18–20]. If $E \to \infty$ but $\gamma E \to 0$, the concentration is $c \equiv 1$ in first approximation, and the conservation equation for the enthalpy takes the form

$$\frac{d^2T}{dx^2} + \frac{j}{x}\frac{dT}{dx} + \delta' \exp(-1/T) = 0,$$

$$\left(\frac{dT}{dx}\right)_{x=0} = 0, \qquad T(1) = \frac{1}{E}, \tag{32}$$

in terms of

$$T = \frac{\tau}{E} \quad \text{and} \quad \delta' = \frac{\delta}{E^2}\exp(E).$$

For the sake of brevity, we consider boundary conditions of the Dirichlet type in (32); an analysis of the Robin problem could be made by means of the same ideas as those used in Section 3.

For sufficiently large values of $E$, there is an interval, $[\delta_E', \delta_I']$, of multiplicity of solutions of (32). The upper multiplicity bound is

$$\delta_I' = \frac{\delta_I}{E^2} \exp(E),$$

where $\delta_I$ is the ignition limit calculated in Section 2. Observe that the temperature profiles of the ignition regime which were calculated in Section 2 correspond to the solution $T \equiv 0$ of (32) in the limit $E \to \infty$.

To calculate the lower multiplicity bound, $\delta_E'$, we introduce the expansions

$$\delta' = \delta_0' + E^{-1}\delta_1' + \cdots,$$

$$T = T_0 + E^{-1}T_1 + \cdots$$

to write (32), in first approximation, in the form

$$\frac{d^2T_0}{dx^2} + \frac{j}{x}\frac{dT_0}{dx} + \delta_0' \exp(-1/T_0) = 0,$$

$$\left(\frac{dT_0}{dx}\right)_{x=0} = 0, \qquad T_0(1) = 0. \tag{33}$$

A straightforward numerical analysis of (33) shows that it has two solutions if $\delta_0' > \delta_{0E}'$, and no solution if $\delta_0' < \delta_{0E}'$, where

$$\delta_{0E}' = 6.966,\ 16.837, \text{ and } 29.565$$

for $j = 0$, 1, and 2.

Then $\delta_E' = \delta_{0E}' + O(1/E)$. For an analysis of (33) in cylinders ($j = 1$) see Parter [21].

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