Electronic Journal of Differential Equations, Vol. 2014 (2014), No. 187, pp. 1–12.
ISSN: 1072-6691. URL: http://ejde.math.txstate.edu or http://ejde.math.unt.edu
ftp ejde.math.txstate.edu

STABILITY OF A BINARY MIXTURE WITH CHEMICAL SURFACE REACTIONS IN THE GENERAL CASE

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Abstract. In this article we consider the stability of a chemical equilibrium of a thermally conducting two-component reactive viscous mixture, in a horizontal layer heated from below and experiencing a catalyzed chemical reaction at the bottom plate. After reformulating the perturbation evolution equations in a suitable equivalent form, we study the nonlinear Lyapunov stability and, assuming the validity of the principle of exchange of stabilities, we find a region of the parameter space in which the linear and nonlinear stability bounds coincide.

1. Introduction

The convective instability and the nonlinear stability of a chemically inert fluid heated from below, in a gravitational field, i.e. the classical Bénard problem, is a well-known interesting problem in several fields of fluid mechanics.

Recently, in [1, 2, 14, 15] reactive fluids of technological interest have been studied. For these fluids chemical reactions can give temperature and concentration gradients, which influence the transport process and can alter hydrodynamic stabilities. Successively, in [14] the nonlinear convective stability has been studied by the method of the energy and some nonlinear stability criteria was found.

In this article we reconsider the linear and nonlinear stability problem of the chemical equilibrium for a reactive fluid, reformulating the perturbation evolution equations in a suitable form, to allow us a more advantageous symmetrization of the linear problem and an easier formulation of the variational problem of the nonlinear stability.

The model adopted in the present paper is that of Bdzil and Frisch [1, 2, 14, 15]. We consider a fluid mixture composed of a dimer and a monomer [1, 2, 14, 15] in a horizontal layer heated from below, the bottom plate being catalytic. We evaluate the effects of heterogeneous surface catalyzed reactions on the hidrodynamic stability of the chemical equilibrium.

We consider a Newtonian fluid model and derive the evolution equation for the perturbation energy following the approach from [4, 5, 6, 7, 8, 9, 17], which generalizes the Joseph's parametric differentiation method reported in [11, 12].

2000 *Mathematics Subject Classification.* 76E15, 76E30.
Key words and phrases. Nonlinear stability; horizontal thermal convection; energy method.

Submitted January 23, 2014. Published September 10, 2014.

In Section 2 we formulate the initial boundary value problem by splitting some given perturbation fields, in terms of some new unknown functions satisfying 'simpler' boundary conditions, and allowing us the use of inequalities like the Poincare's and Wirtinger's ones.

In Section 3 we determine evolution equation for the perturbation energy reducing the number of scalar fields, which represent the velocity perturbation field, by using the representation theorem for solenoidal vectors in a plane layer [12, 18].

In Section 4 we formulate the maximum problem of the nonlinear stability in terms of the new perturbation fields introduced by splitting the concentration perturbation field, in such a way all integrals on the boundaries involved in the maximum problem disappear from the Euler Lagrange equations.

We can formulate the maximum problem with or without the integrals on the boundary. We determine, in subsections 4.1, 4.2 and 4.3 a region of the parameter space in which the linear and nonlinear stability bounds are coincident, when the Prandtl and Schmidt numbers coincide, and we recover the results found in [8, 9], by using some other approaches of symmetrization technique.

2. Initial/boundary value problem for the perturbation

We consider a mixture described by a Newtonian model to which we apply the Boussinesq approximation in the layer bounded by the surfaces $z = 0$ and $z = 1$, in a Cartesian frame of reference, the lower surface being catalytic, [1, 2, 15].

The chemical equilibrium S_0 is characterized by the temperature ($\overline{T}$) and degree of dissociation (fraction of pure monomers present) ($\overline{C}$) fields [1, 2, 15], and $0 \le z \le 1$:

$$\overline{T}(z) = T_1 + \beta(1 - z), \quad \overline{C}(z) = C_1 + \gamma(1 - z), \tag{2.1}$$

where C_1 and T_1 are the values of C and T at $z = 1$ and the constants β and γ are given in [1, 2, 15].

Let us now perturb S_0 up to a cellular motion (convection-diffusion) characterized by a velocity $\vec{u} = \vec{0} + \vec{u}$, a pressure $\pi = \bar{P} + p$, a temperature $T = \bar{T} + \theta$ and a concentration $C = \bar{C} + \gamma$, where $\vec{u}, p, \theta, \gamma$ are the corresponding perturbation fields and $\vec{0}, \bar{P}, \bar{T}, \bar{C}$ represent the basic state S_0 (the expression of $\bar{P}$ follows from the momentum balance equation for S_0).

The perturbation fields satisfy the following equations which express the balance of the momentum, energy and concentration, written in nondimensional coordinates [19],

$$\begin{gathered}\frac{\partial}{\partial t}\vec{u} + (\vec{u} \cdot \nabla)\vec{u} = -\nabla p + \Delta\vec{u} + (\mathcal{R}\theta + \mathcal{C}\gamma)\vec{k}, \\ P_r(\frac{\partial}{\partial t}\theta + \vec{u} \cdot \nabla\theta) = \Delta\theta - \mathcal{R}w, \\ S_c(\frac{\partial}{\partial t}\gamma + \vec{u} \cdot \nabla\gamma) = \Delta\gamma + \mathcal{C}w,\end{gathered} \tag{2.2}$$

in the set $\mathcal{N}$ given by

$$\begin{gathered}\mathcal{N} = \big\{(\vec{u}, p, \theta, \gamma) \in L^2((0, \infty) \times V)) : \nabla \cdot \vec{u} = 0;\ u_z = v_z = w = 0 \text{ on } \partial V_2, \\ \vec{u} = 0 \text{ on } \partial V_1, \quad \theta = \gamma = 0 \text{ on } \partial V_2, \quad \theta_z = -s\gamma,\ \gamma_z = r\gamma \text{ on } \partial V_1\big\},\end{gathered} \tag{2.3}$$

where $\nabla f \equiv (f_x, f_y, f_z)$ for an arbitrary function f, $\vec{u} = (u, v, w)$, $V = \mathcal{V} \times [0, 1]$ denotes the three dimensional box over the rectangle $\mathcal{V}$, periodic in the x, y directions, with $z \in [0, 1]$, ∂V is the boundary of V, $\partial V_1 = \partial V \cap \{z = 0\}$, $\partial V_2 = \partial V \cap \{z = 1\}$.

The perturbation fields depend on the time t and space $\vec{x} = (x, y, z)$ and $\mathcal{R}^2$, $\mathcal{C}^2$, P_r and S_c are the thermal and concentrational numbers of Rayleigh, Prandtl and Schmidt, respectively. In addition, $r, s > 0$ are dimensionless surface reactions numbers [1, 2, 15]. The basic state S_0 corresponds to the zero solution of the initial-boundary value problem for (2.2) in the class $\mathcal{N}$.

In this paper we reformulate this initial boundary value problem by splitting some given perturbation fields to allow us a much more advantageous symmetrization. In the particular case $r < 1$, we replace the initial temperature and concentration fields with the following functions

$$\Phi_1 = r\theta + s\gamma, \quad \Phi_2 = \gamma(1 - rz), \quad \Phi_4 = rz\gamma \quad \forall z \in [0, 1]. \tag{2.4}$$

We observe that, for arbitrary γ, the functions Φ_2 and Φ_4 are functionally independent, namely the vectors $\nabla\Phi_2$ and $\nabla\Phi_4$ can be coincident iff $\Phi_2 = 0$, or $\Phi_2 = \Phi_2(z)$, that is the only case when the rank of the matrix

$$\begin{pmatrix} \Phi_{2x} & \Phi_{2y} & \Phi_{2z} \\ \Phi_{4x} & \Phi_{4y} & \Phi_{4z} \end{pmatrix}$$

is less than two.

If $r \geq 1$ we can proceed similarly, introducing $\Phi_2 = \gamma \exp(-rz)$, $\Phi_4 = \gamma(1 - \exp(-rz))$ for all $z \in [0, 1]$. The treatment of the stability problem is the same in both cases $r \geq 1$, $r < 1$.

In terms of Φ_1, Φ_2 and Φ_4, the the initial perturbation evolution equations (2.2) can be written in the equivalent form

$$\frac{\partial}{\partial t}\vec{u} + (\vec{u} \cdot \nabla)\vec{u} = -\nabla p + \Delta\vec{u} + \frac{\mathcal{R}}{r}\Phi_1\vec{k} + e\big(\Phi_2 + \Phi_4\big)\vec{k}, \tag{2.5}$$

$$\frac{\partial}{\partial t}\Phi_1 + \vec{u} \cdot \nabla\Phi_1 = \frac{1}{P_r}\Delta\Phi_1 + b\Delta(\Phi_2 + \Phi_4) + aw, \tag{2.6}$$

$$\frac{\partial}{\partial t}(\Phi_2 + \Phi_4) + \vec{u} \cdot \nabla(\Phi_2 + \Phi_4) = \frac{1}{S_c}\Delta(\Phi_2 + \Phi_4) + \frac{\mathcal{C}}{S_c}w, \tag{2.7}$$

with

$$a = \frac{\mathcal{C}s}{S_c} - \frac{\mathcal{R}r}{P_r}, \quad b = \frac{s(P_r - S_c)}{P_r S_c}, \quad e = \frac{\mathcal{C}r - \mathcal{R}s}{r},$$

in the subset (2.3) written as

$$\begin{aligned} \mathcal{N} = \big\{ &(\vec{u}, p, \Phi_1, \Phi_2, \Phi_4) \in L^2((0, \infty) \times V) : \nabla \cdot \vec{u} = 0,\ u_z = v_z = w = 0 \text{ on } \partial V_2, \\ &\vec{u} = 0 \text{on } \partial V_1,\ \ \Phi_1 = \Phi_2 = \Phi_4 = 0 \text{ on } \partial V_2,\ \ \Phi_{1_z} = \Phi_{2_z} = \Phi_4 = 0, \text{ on } \partial V_1 \big\}. \end{aligned} \tag{2.8}$$

Let us define

$$\Phi_3 = a_1\Phi_1 + a_2(\Phi_2 + \Phi_4), \tag{2.9}$$

where a_1, a_2, are some constants to be determined later.

From (2.6)-(2.7) we obtain

$$\frac{\partial}{\partial t}\Phi_3 + \vec{u} \cdot \nabla\Phi_3 = -\frac{a_1}{a_2}\frac{b}{s}(sa_1 + a_2)\Delta\Phi_1 + (\frac{a_1 b}{a_2} + \frac{1}{S_c})\Delta\Phi_3 + (\frac{\mathcal{C}a_2}{S_c} + aa_1)w, \tag{2.10}$$

3. Evolution equation for the perturbation energy

Taking into account the solenoidality condition for the velocity perturbation field $\nabla \cdot \vec{u} = 0$, using the representation theorem of solenoidal vectors [12, 18], in a plane layer, into toroidal and poloidal fields, we reduce the number of scalar fields, deriving a system of equivalent perturbation evolution equations.

If the mean values of u, v, w vanish over V [18]; that is, if the conditions

$$\int_{\mathcal{V}} u(x,y,z)\,dx\,dy = \int_{\mathcal{V}} v(x,y,z)\,dx\,dy = \int_{\mathcal{V}} w(x,y,z)\,dx\,dy = 0, \quad z \in [0,1],$$

hold, the velocity perturbation $\vec{u}$ has the unique decomposition [12, 18]

$$\vec{u} = \vec{u}_1 + \vec{u}_2, \tag{3.1}$$

with

$$\nabla \cdot \vec{u}_1 = \nabla \cdot \vec{u}_2 = \vec{k} \cdot \nabla \times \vec{u}_1 = \vec{k} \cdot \vec{u}_2 = 0, \tag{3.2}$$

$$\vec{u}_1 = \nabla \chi_z - \vec{k}\Delta\chi \equiv \nabla \times \nabla \times (\chi\vec{k}), \quad \vec{u}_2 = \vec{k} \times \nabla\psi = -\nabla \times (\vec{k}\psi), \tag{3.3}$$

where the poloidal and toroidal potentials χ and ψ are doubly periodic and satisfy the equations [12, 18]

$$\Delta_1\chi \equiv \chi_{xx} + \chi_{yy} = -\vec{k}\vec{u}, \quad \Delta_1\psi = \vec{k} \cdot \nabla \times \vec{u}. \tag{3.4}$$

The boundary conditions for χ and ψ are [12]:

$$\begin{gathered} \chi = \chi_z = \psi = 0, \quad z = 0, \\ \chi = \chi_{zz} = \psi_z = 0, \quad z = 1. \end{gathered} \tag{3.5}$$

From (3.2)-(3.3) it follows that $\vec{u} \cdot \vec{k} = \vec{u}_1 \cdot \vec{k} = -\Delta_1\chi$.

Multiplying (2.5) by $\vec{u}$, (2.6) by $b_1\Phi_1$, (2.10) by $b_3\Phi_3$, where b_1 and b_3 are some positive constants, integrating the resulted equations over V, taking into account the boundary conditions from (2.8), and adding the resulted equations we obtain the evolution equation for the energy $E(t)$, we derive

$$\frac{d}{dt}E(t) = \mathcal{I} - \mathcal{D}, \tag{3.6}$$

where,

$$E(t) = \frac{1}{2}\frac{d}{dt}(|\vec{u}|^2 + b_1|\Phi_1|^2 + b_3|\Phi_3|^2),$$

with $|f|^2 = \langle f, f\rangle$, and $\langle f, g\rangle = \int_V fg\,dv$ in $L_2(V)$, respectively. In (3.6) $\mathcal{I}$ and $\mathcal{D}$ are given by

$$\begin{aligned} \mathcal{I} = & -A_1\langle\Phi_1, \Delta_1\chi\rangle - A_2\langle(\Phi_2 + \Phi_4), \Delta_1\chi\rangle + B_1\langle\nabla\Phi_1, \nabla(\Phi_2 + \Phi_4)\rangle \\ & - 2B_3\langle\nabla\Phi_2, \nabla\Phi_4\rangle + C_1(\langle\Phi_1, \Phi_{2z} > + < \Phi_2, \Phi_{1z}\rangle) + C_2\langle\Phi_2, \Phi_{2z}\rangle \end{aligned} \tag{3.7}$$

$$\begin{aligned} \mathcal{D} = & |\nabla\chi_{xz}|^2 + |\nabla\chi_{yz}|^2 + |\nabla\Delta_1\chi|^2 + |\nabla\psi_x|^2 + |\nabla\psi_y|^2 + D_1|\nabla\Phi_1|^2 \\ & B_3|\nabla\Phi_2|^2 + B_3|\nabla\Phi_4|^2, \end{aligned} \tag{3.8}$$

with

$$A_1 = \frac{\mathcal{R}}{r} + ab_1 + a_1^2 b_3(a + \frac{\mathcal{C}}{S_c}\frac{a_2}{a_1}), \quad A_2 = e + a_2^2 b_3(\frac{\mathcal{C}}{S_c} + a\frac{a_1}{a_2}), \tag{3.9}$$

$$B_1 = -b_3a_1a_2\frac{1}{P_r} - (b_3a_1B_{12} + bb_1), \quad B_{12} = ba_1 + \frac{a_2}{S_c}, \quad B_3 = a_2b_3B_{12}, \tag{3.10}$$

$$C_1 = r(b_3a_1B_{12} + bb_1), \quad C_2 = 2rb_3a_2B_{12}, \quad D_1 = \frac{1}{P_r}(b_3a_1^2 + b_1). \tag{3.11}$$

From the boundary conditions (2.8) it follows that

$$\begin{aligned}\langle\Phi_i, \Delta\Phi_4\rangle &= \int_{\partial V} \Phi_i\nabla\Phi_4 \cdot \vec{n}d\sigma - \langle\nabla\Phi_i, \nabla\Phi_4\rangle \\ &= r\int_{\partial V} \Phi_i\Phi_2\vec{k} \cdot \vec{n}d\sigma - \langle\nabla\Phi_i, \nabla\Phi_4\rangle \\ &= r(\langle\Phi_i, \Phi_{2z} > + < \Phi_2, \Phi_{iz}\rangle) - \langle\nabla\Phi_i, \nabla\Phi_4\rangle \quad (i = 1, 2),\end{aligned} \tag{3.12}$$

$$\langle\Phi_4, \Delta\Phi_i\rangle = -\langle\nabla\Phi_i, \nabla\Phi_4\rangle \quad (i = 1, 2), \tag{3.13}$$

$$\langle\Phi_4, \Delta\Phi_4\rangle = -\langle\nabla\Phi_4, \nabla\Phi_4\rangle. \tag{3.14}$$

From $(3.11)_3$ it follows that $D_1 > 0$, then if we define $\Phi_1' = \Phi_1\sqrt{D_1}$ to obtain

$$\begin{aligned}\mathcal{I} = &-\frac{A_1}{\sqrt{D_1}}\langle\Phi_1', \Delta_1\chi\rangle - A_2\langle\Phi_2 + \Phi_4, \Delta_1\chi\rangle + \frac{B_1}{\sqrt{D_1}}\langle\nabla\Phi_1', \nabla(\Phi_2 + \Phi_4)\rangle \\ &- 2B_3\langle\nabla\Phi_2, \nabla\Phi_4\rangle + \frac{C_1}{\sqrt{D_1}}(\langle\Phi_1', \Phi_{2z}\rangle + \langle\Phi_2, \Phi_{1z}'\rangle) + C_2\langle\Phi_2, \Phi_{2z}\rangle\end{aligned} \tag{3.15}$$

$$\begin{aligned}\mathcal{D} = &|\nabla\chi_{xz}|^2 + |\nabla\chi_{yz}|^2 + |\nabla\Delta_1\chi|^2 + |\nabla\psi_x|^2 + |\nabla\psi_y|^2 + |\nabla\Phi_1'|^2 \\ &+ B_3|\nabla\Phi_2|^2 + B_3|\nabla\Phi_4|^2.\end{aligned} \tag{3.16}$$

By introducing, in the case $A_1 \neq 0$, $\mathcal{I} = \mathcal{I}^*A_1$, the energy relation (3.6) becomes

$$\frac{d}{dt}E(t) = \mathcal{D}(\mathcal{I}^*\frac{A_1}{\mathcal{D}} - 1). \tag{3.17}$$

The boundedness of the functional $\frac{\mathcal{I}^*}{\mathcal{D}}(\chi, \psi, \Phi_1, \Phi_2, \Phi_4)$ can be proved, in the class $\mathcal{N}$, by using inequalities like Poincare's, Schwartz's, Wirtinger's and some other in [13].

It is well-known that the inequality

$$\frac{dE}{dt} \leq 0 \tag{3.18}$$

represents a sufficient condition for global nonlinear Lyapunov stability. In our case the stability or instability of S_0 depends on the six physical parameters P_r, $S_c = \tau P_r$, $\mathcal{R}$, $\mathcal{C} \equiv \alpha\mathcal{R}$, r and s. Whence, the basic state is nonlinearly stable if

$$\frac{d}{dt}E(t) \leq -\mathcal{D}(1 - \frac{|A_1|}{2\sqrt{R_{a*}}}) \equiv -\mathcal{D}(1 - \frac{\mathcal{R}}{\mathcal{R}_E}), \tag{3.19}$$

where,

$$\frac{1}{\sqrt{R_{a*}}} = \max_{(\vec{u},\Phi_1,\Phi_2,\Phi_4)\in\mathcal{N}} \frac{2\mathcal{I}^*}{\mathcal{D}}. \tag{3.20}$$

Whence, the condition

$$|A_1| < 2\sqrt{R_{a*}} \Leftrightarrow \mathcal{R} < \mathcal{R}_E \tag{3.21}$$

represents a criterion of nonlinear global Lyapunov stability.

4. The maximum problem and the stability bound

Let us study the variational problem (3.20) and later determine the parameters a_1, a_2, b_1, b_3 in terms of the physical quantities, such that the stability domain is maximal. The associated Euler Lagrange equations are:

$$\begin{gathered}
-\frac{A_1}{\sqrt{D_1}}\Delta_1\Phi_1' - A_2\Delta_1(\Phi_2+\Phi_4) + A_1\frac{1}{\sqrt{R_{a*}}}\Delta\Delta_1\chi = 0,\\
-\frac{A_1}{\sqrt{D_1}}\Delta_1\chi - \frac{B_1}{\sqrt{D_1}}\Delta(\Phi_2+\Phi_4) + A_1\frac{1}{\sqrt{R_{a*}}}\Delta\Phi_1' = 0,\\
-A_2\Delta_1\chi - \frac{B_1}{\sqrt{D_1}}\Delta\Phi_1' + 2B_3\Delta\Phi_4 + A_1B_3\frac{1}{\sqrt{R_{a*}}}\Delta\Phi_2 = 0,\\
-A_2\Delta_1\chi - \frac{B_1}{\sqrt{D_1}}\Delta\Phi_1' + 2B_3\Delta\Phi_2 + A_1B_3\frac{1}{\sqrt{R_{a*}}}\Delta\Phi_4 = 0,\\
\Delta\Delta_1\psi = 0.
\end{gathered}\tag{4.1}$$

They are equivalent to the following equations:

$$\begin{gathered}
-\frac{A_1}{\sqrt{D_1}}\Delta_1\Phi_1' - A_2\Delta_1(\Phi_2+\Phi_4) + A_1\frac{1}{\sqrt{R_{a*}}}\Delta\Delta_1\chi = 0,\\
-\frac{A_1}{\sqrt{D_1}}\Delta_1\chi - \frac{B_1}{\sqrt{D_1}}\Delta(\Phi_2+\Phi_4) + A_1\frac{1}{\sqrt{R_{a*}}}\Delta\Phi_1' = 0,\\
-A_2\Delta_1\chi - \frac{B_1}{\sqrt{D_1}}\Delta\Phi_1' + B_3\Delta(\Phi_2+\Phi_4) + A_1\frac{B_3}{2}\frac{1}{\sqrt{R_{a*}}}\Delta(\Phi_2+\Phi_4) = 0,\\
B_3(1 - A_1\frac{1}{2\sqrt{R_{a*}}})\Delta(\Phi_2-\Phi_4) = 0,\\
\Delta\Delta_1\psi = 0.
\end{gathered}\tag{4.2}$$

From $(4.2)_4$ it follows that we can consider the cases

$$B_3 = 0, \quad 1 - A_1\frac{1}{2\sqrt{R_{a*}}} = 0, \quad \Delta\Phi_2 = \Delta\Phi_4.$$

4.1. **Case:** $B_3 = 0$. In this case

$$B_3 = 0 \Longleftrightarrow b_3a_2B_{12} = 0,$$

if $B_{12} = 0$, that is $ba_1 + \frac{a_2}{S_c} = 0$, to preserve the boundedness of the functional $\frac{\mathcal{I}^*}{\mathcal{D}}(\chi,\psi,\Phi_1)$ we must impose $A_2 = B_1 = C_1 = C_2 = 0$; i.e., $a_2 = b = e = 0$. In terms of physical parameters we have

$$P_r = S_c, \quad \mathcal{C}r - \mathcal{R}s \equiv \mathcal{R}(\alpha r - s) = 0 \Leftrightarrow r\alpha = s.$$

The Euler Lagrange equations become

$$\begin{gathered}
\frac{\sqrt{D_1}}{\sqrt{R_{a*}}}\Delta\Delta_1\chi - \Delta_1\Phi_1' = 0,\\
-\Delta_1\chi + \frac{\sqrt{D_1}}{\sqrt{R_{a*}}}\Delta\Phi_1' = 0,\\
\Delta\Delta_1\psi = 0.
\end{gathered}\tag{4.3}$$

Taking into account the poloidal and toroidal fields, the steady problem obtained by linearizing (2.5)-(2.6) about the solution (2.1), is

$$\begin{gathered}
\Delta\Delta\Delta_1\chi - \frac{\mathcal{R}}{r}\Delta_1\Phi_1 = 0,\\
-a\Delta_1\chi + \frac{1}{P_r}\Delta\Phi_1 = 0,\\
\Delta\Delta_1\psi = 0.
\end{gathered} \tag{4.4}$$

The operator associated to the system (4.4) is not symmetric. If $\alpha > 1$ its symmetrical form is given by

$$\begin{gathered}
\Delta\Delta\Delta_1\chi^* - \mathcal{R}\sqrt{\alpha^2-1}\Delta_1\Phi_1^* = 0,\\
-\mathcal{R}\sqrt{\alpha^2-1}\Delta_1\chi^* + \Delta\Phi_1^* = 0,\\
\Delta\Delta_1\psi = 0,
\end{gathered} \tag{4.5}$$

where, $\chi^* = \chi$, $\Phi_1^* = \sqrt{\mu_2}\Phi_1$, $\sqrt{\mu_2} = r\sqrt{\alpha^2-1}$.

Let the matricial partial differential operator associated with the system (4.5) be

$$A \equiv \begin{pmatrix} -\Delta\Delta\Delta_1 & \mathcal{R}\sqrt{\alpha^2-1}\Delta_1 & 0\\ \mathcal{R}\sqrt{\alpha^2-1}\Delta_1 & -\Delta & 0\\ 0 & 0 & -\Delta\Delta_1 \end{pmatrix}.$$

The system (4.5) reads $A\vec{V} = \vec{0}$, where $\vec{V} = (\chi^*, \Phi_1^*, \psi)^T$.

The system coincide with the Euler Lagrange equations for the functional

$$\langle A\vec{V}, \vec{V}\rangle = \mathcal{F}(\vec{V}),$$

where

$$\begin{aligned}
\mathcal{R}\,\mathcal{F}(\vec{V}) &= -\langle\chi^*, \Delta\Delta\Delta_1\chi^*\rangle - \langle\psi, \Delta\Delta_1\psi\rangle + \mathcal{R}\sqrt{\alpha^2-1}\langle\chi^*, \Delta_1\Phi_1^*\rangle\\
&\quad + \sqrt{\alpha^2-1}\langle\Phi_1^*, \Delta_1\chi^*\rangle - \langle\Phi_1^*, \Delta_1\Phi_1^*\rangle.
\end{aligned} \tag{4.6}$$

Taking into account the boundary conditions it follows that

$$\begin{aligned}
\mathcal{F}(\vec{V}) &= |\nabla\chi_{xz}^*|^2 + |\nabla\chi_{yz}^*|^2 + |\nabla\Delta_1\chi^*|^2 + |\nabla\psi_x|^2 + |\nabla\psi_y|^2 + |\nabla\Phi_1^*|^2\\
&\quad + 2\mathcal{R}\sqrt{\alpha^2-1}\langle\Phi_1^*, \Delta_1\chi^*\rangle.
\end{aligned}$$

In terms of $\vec{u}, \Phi_1^*$ we have

$$\begin{aligned}
\mathcal{F}(\vec{V}) &= |\nabla\vec{u}|^2 + |\nabla\Phi_1^*|^2 - 2\mathcal{R}\sqrt{\alpha^2-1}\langle\Phi_1^*, w\rangle\\
&\geq (|\nabla\vec{u}|^2 + |\nabla\Phi_1^*|^2)\Big(1 - \frac{2\mathcal{R}\sqrt{\alpha^2-1}}{\alpha_p^2}\Big).
\end{aligned}$$

A is a positive definite operator, for $2\mathcal{R}\sqrt{\alpha^2-1} < \alpha_p^2$, where α_p^2 is a constant [13] , therefore we have $\min\mathcal{F}(\vec{V}) = 0$, implying that the minimum of the functional $\frac{|\nabla\vec{u}|^2+|\nabla\Phi_1^*|^2}{2\langle\Phi_1^* w\rangle}$ is $\mathcal{R}\sqrt{\alpha^2-1}$. In this case

$$\frac{\mathcal{I}^*}{\mathcal{D}} = \frac{1}{\sqrt{D_1}}\frac{\langle\Phi_1', w\rangle}{|\nabla\vec{u}|^2 + |\nabla\Phi_1'|^2},$$

and the Euler Lagrange equations, associated to the maximum,

$$\frac{1}{\sqrt{R_a}} = \max_{(\vec{u},\Phi_1)\in\mathcal{N}} \frac{2\langle\Phi_1', w\rangle}{|\nabla\vec{u}|^2 + |\nabla\Phi_1'|^2} \tag{4.7}$$

are:

$$\begin{aligned} \Delta\Delta\Delta_1\chi - \sqrt{R}_a\Delta_1\Phi_1' &= 0,\\ -\sqrt{R}_a\Delta_1\chi + \Delta\Phi_1' &= 0,\\ \Delta\Delta_1\psi &= 0. \end{aligned} \tag{4.8}$$

They coincide with the Euler Lagrange equations (4.3), namely $\frac{\sqrt{D_1}}{\sqrt{R_{a*}}} = \frac{1}{\sqrt{R_a}}$, and with the linear equations.

Comparing (4.5) and (4.8) it follows that the chemical equilibrium has a linear stability bound $\mathcal{R}_L$ which satisfies the relation

$$\sqrt{R}_a = \mathcal{R}_L\sqrt{\alpha^2 - 1}. \tag{4.9}$$

The inequality (3.21), in terms of physical parameters, becomes

$$\sqrt{P}_r\frac{\frac{R}{r} + ab_1}{\sqrt{b_1}} < 2\sqrt{R}_a.$$

The stability domain attains its maximum if

$$\frac{d}{db_1}\frac{\frac{R}{r} + ab_1}{\sqrt{b_1}} = 0 \ \Leftrightarrow\ b_1 = \frac{R}{ar}.$$

In terms of the physical quantities, the non linear stability bound is the following

$$\mathcal{R}_E \equiv \sqrt{R}_{a*}\Big(\sqrt{(\frac{s}{r})^2 - 1}\Big)^{-1}, \tag{4.10}$$

whence, $\mathcal{R}_L = \mathcal{R}_E$.

Theorem 4.1. *For physical parameters $P_r = S_c$, $\mathcal{C} = \alpha\mathcal{R}$, $\frac{s}{r} = \alpha$, $(\frac{s}{r})^2 > 1$, the zero solution of* (2.2)*, corresponding to the basic conduction state* (2.1)*, is linearly and nonlinearly asymptotically stable if $\mathcal{R} < \mathcal{R}_E$, where $\mathcal{R}_E$ is given by* (4.10)*.*

It is easy to verify that the asymptotic stability follows from (3.20) by introducing

$$\xi^2 = \min_{(\vec{u},\Phi_1)\in\mathcal{N}}\frac{|\nabla\vec{u}|^2 + |\nabla\Phi_1|^2}{|\vec{u}|^2 + b_1|\Phi_1|^2}, \tag{4.11}$$

taking into account the boundary conditions in the class $\mathcal{N}$.

4.2. **Case: $\Delta\Phi_2 = \Delta\Phi_4$.** In this section we investigate on the existence, for different Prandtl and Schmidt numbers, of a a region of the parameter space, in which the linear and nonlinear stability bounds are coincident.

Taking into account that we must impose $B_3 > 0$, we can define

$$\Phi_2' = \Phi_2\sqrt{B_3}, \quad \Phi_4' = \Phi_4\sqrt{B_3}.$$

From the boundary conditions it follows that

$$\begin{gathered} \langle\nabla\Phi_2', \nabla\Phi_4'\rangle = 2r\langle\Phi_2', \Phi_{2z}'\rangle + |\nabla\Phi_2'|^2,\\ \langle\nabla\Phi_2', \nabla\Phi_4'\rangle = |\nabla\Phi_4'|^2,\\ |\nabla\Phi_4'|^2 - |\nabla\Phi_2'|^2 = 2r\langle\Phi_2', \Phi_{2z}'\rangle = -r\int_{z=0}{\Phi_2'}^2 d\sigma,\\ \langle\nabla\Phi_1', \nabla\Phi_2'\rangle = \langle\nabla\Phi_1', \nabla\Phi_4'\rangle - r(\langle\Phi_1', \Phi_{2z}'\rangle + \langle\Phi_2', \Phi_{1z}'\rangle). \end{gathered}$$

It follows that

$$\begin{aligned}\mathcal{I} = &-\frac{A_1}{\sqrt{D_1}}\langle\Phi_1', \Delta_1\chi\rangle - \frac{A_2}{\sqrt{B_3}}\langle\Phi_2' + \Phi_4', \Delta_1\chi\rangle \\ &+ \frac{B_1}{\sqrt{D_1 B_3}}\langle\nabla\Phi_1', \nabla(\Phi_2' + \Phi_4')\rangle + \frac{C_1}{\sqrt{D_1 B_3}}(\langle\Phi_1', \Phi_{2z}'\rangle + \langle\Phi_2', \Phi_{1z}'\rangle),\end{aligned} \tag{4.12}$$

$$\begin{aligned}\mathcal{D} = &|\nabla\chi_{xz}|^2 + |\nabla\chi_{yz}|^2 + |\nabla\Delta_1\chi|^2 + |\nabla\psi_x|^2 + |\nabla\psi_y|^2 + |\nabla\Phi_1'|^2 \\ &+ 2|\nabla\Phi_2'|^2 + 2|\nabla\Phi_4'|^2.\end{aligned} \tag{4.13}$$

The linear problem written in terms of the variables $\chi, \psi, \Phi_1, \gamma$ takes the form

$$\begin{gathered}\Delta\Delta\Delta_1\chi - \frac{\mathcal{R}}{r}\Delta_1\Phi_1 - e\Delta_1\gamma = 0, \\ -aP_r\Delta_1\chi + \Delta\Phi_1 + bP_r\Delta\gamma = 0, \\ -(\frac{\mathcal{C}a_2}{S_c} + aa_1)\Delta_1\chi + \frac{a_1}{P_r}\Delta\Phi_1 + B_{12}\Delta\gamma = 0, \\ \Delta\Delta_1\psi = 0.\end{gathered} \tag{4.14}$$

The operator associated with (4.14) is not symmetric, but, taking into account that $B_{12} \neq 0$, if $e \neq 0$, it can be symmetrized as follows. Introducing

$$\chi = \sqrt{\mu_1}\chi^*, \quad \Phi_1 = \sqrt{\mu_2}\Phi_1^*, \quad \gamma = \sqrt{\mu_3}\gamma^*,$$

the system (avoiding $*$) reads equivalently

$$\begin{gathered}\Delta\Delta\Delta_1\chi - \frac{\mathcal{R}}{r}\frac{\sqrt{aP_r r}}{\sqrt{R}}\Delta_1\Phi_1 - e\sqrt{\frac{ar}{bP_r\mathcal{R}X}}\Delta_1\gamma = 0, \\ -\frac{\mathcal{R}}{r}\frac{\sqrt{aP_r r}}{\sqrt{R}}\Delta_1\chi + \Delta\Phi_1 + b\sqrt{\frac{1}{bX}}\Delta\gamma = 0, \\ -e\sqrt{\frac{ar}{bP_r\mathcal{R}X}}\Delta_1\chi + b\sqrt{\frac{1}{bX}}\Delta\Phi_1 + \Delta\gamma = 0, \\ \Delta\Delta_1\psi = 0,\end{gathered} \tag{4.15}$$

where,

$$\frac{\mu_2}{\mu_1} = \frac{aP_r r}{R}, \quad \frac{\mu_3}{\mu_1} = \frac{1}{eB_{12}}(\frac{\mathcal{C}}{S_c}a_2 + aa_1), \quad \frac{\mu_3}{\mu_2} = \frac{a_1}{P_r^2 bB_{12}}, \tag{4.16}$$

and it must have $a > 0$ and $bX > 0$.

Furthermore, from (4.16) it follows that

$$a_2 = a_1\frac{S_c}{R\alpha}a(\frac{re}{bP_r R} - 1) \equiv a_1 Y; \tag{4.17}$$

therefore,

$$\begin{gathered}B_{12} = a_1 X, \quad X = b + \frac{Y}{S_c}, \quad (\frac{\mathcal{C}a_2}{S_c} + aa_1) = aa_1\frac{re}{bP_r R}, \\ \frac{\mu_2}{\mu_1} = \frac{aP_r r}{R}, \quad \frac{\mu_3}{\mu_1} = \frac{ar}{bP_r\mathcal{R}X}, \quad \frac{\mu_3}{\mu_2} = \frac{1}{P_r^2 bX}.\end{gathered} \tag{4.18}$$

The system (4.15) represents the Euler Lagrange system for the functional

$$\mathcal{G}\vec{V} = \langle B\vec{V}, \vec{V}\rangle, \quad \vec{V} \equiv (\chi, \Phi_1, \gamma, \Psi),$$

where B is the matricial partial differential operator given by:

$$B = \begin{pmatrix} \Delta\Delta\Delta_1 & -\frac{\mathcal{R}}{r}\frac{\sqrt{aP_r r}}{\sqrt{R}}\Delta_1 & -e\sqrt{\frac{ar}{bP_r\mathcal{R}X}}\Delta_1 & 0 \\ -\frac{\mathcal{R}}{r}\frac{\sqrt{aP_r r}}{\sqrt{R}}\Delta_1 & \Delta & b\sqrt{\frac{1}{bX}}\Delta & 0, \\ -e\sqrt{\frac{ar}{bP_r\mathcal{R}X}}\Delta_1 & b\sqrt{\frac{1}{bX}}\Delta & \Delta & 0 \\ 0 & 0 & 0 & \Delta\Delta_1 \end{pmatrix},$$

and

$$\begin{aligned} \mathcal{G}\vec{V} &= -|\nabla\chi_{xz}|^2 - |\nabla\chi_{yz}|^2 - |\nabla\Delta_1\chi|^2 - |\nabla\psi_x|^2 - |\nabla\psi_y|^2 - |\nabla\Phi_1|^2 - |\nabla\gamma|^2 \\ &\quad + \int_{\partial V}\gamma\nabla\gamma\cdot\vec{n}d\sigma - 2e\sqrt{\frac{ar}{bP_r\mathcal{R}X}}\langle\gamma,\Delta_1\chi\rangle - 2\frac{\mathcal{R}}{r}\frac{\sqrt{aP_r r}}{\sqrt{R}}\langle\chi,\Delta_1\Phi_1\rangle \\ &\quad + b\sqrt{\frac{1}{bX}}\langle\gamma,\Delta\Phi_1\rangle + b\sqrt{\frac{1}{bX}}\langle\Phi_1,\Delta\gamma\rangle. \end{aligned}$$

As a functional $\mathcal{G}$ of $(\chi,\psi,\Phi_1,\Phi_2,\Phi_4)$, it is given by

$$\begin{aligned} \mathcal{G}\vec{V} &= -|\nabla\chi_{xz}|^2 - |\nabla\chi_{yz}|^2 - |\nabla\Delta_1\chi|^2 - |\nabla\psi_x|^2 - |\nabla\psi_y|^2 - |\nabla\Phi_1|^2 \\ &\quad - 2|\nabla\Phi_2|^2 - 2|\nabla\Phi_4|^2 - 2e\sqrt{\frac{ar}{bP_r\mathcal{R}X}}\langle\Phi_2+\Phi_4,\Delta_1\chi\rangle - 2\frac{\mathcal{R}}{r}\frac{\sqrt{aP_r r}}{\sqrt{R}}\langle\Delta_1\chi,\Phi_1\rangle \\ &\quad - 2b\sqrt{\frac{1}{bX}}\langle\nabla\Phi_1,\nabla(\Phi_2+\Phi_4)\rangle + rb\sqrt{\frac{1}{bX}}(\langle\Phi_1\Phi_{2z}\rangle + \langle\Phi_2\Phi_{1z}\rangle). \end{aligned}$$

The value $\mathcal{G}\vec{V}$ can be written as $\mathcal{I}-\mathcal{D}$, with $\mathcal{I}$ and $\mathcal{D}$ given by (4.12) and (4.13) if and only if

$$\begin{gathered} \frac{A_1}{2\sqrt{D_1}} = \frac{\mathcal{R}}{r}\frac{\sqrt{aP_r r}}{\sqrt{R}}, \quad \frac{A_2}{2\sqrt{B_3}} = e\sqrt{\frac{ar}{bP_r\mathcal{R}X}}, \\ \frac{B_1}{2\sqrt{D_1B_3}} = -bP_r\sqrt{\frac{1}{P_r^2bX}}, \quad \frac{C_1}{\sqrt{D_1B_3}} = +rbP_r\sqrt{\frac{1}{P_r^2bX}} \end{gathered} \tag{4.19}$$

are true.

In this situation, system (4.19) gives us a region of the parameter space where the linear and nonlinear stability bounds coincide.

After some calculations it may be proved that equations $(4.19)_3$ and $(4.19)_4$ admit no solution if $b \neq 0$; i.e. for different Prandtl and Schmidt numbers. However, we observe explicitly that the surface integrals do not contribute to the Euler Lagrange equations, because of they have the first variation identically zero. Indeed, in the next Section, by comparing the Euler Lagrange equations with the linear problem we obtain exactly the relations $(4.19)_{1,2,3}$.

4.3. **Case:** $1 - A_1\frac{1}{2\sqrt{R_{a*}}} = 0$. In this last case, to determine a region of parameter space where the liinear and nonlinear stability bounds coincide we consider the

Euler equations written as

$$\begin{aligned} &\Delta\Delta\Delta_1\chi - \frac{A_1}{2\sqrt{D_1}}\Delta_1\Phi_1' - \frac{A_2}{2\sqrt{B_3}}\Delta_1(\Phi_2' + \Phi_4') = 0,\\ &-\frac{A_1}{2\sqrt{D_1}}\Delta_1\chi + \Delta\Phi_1' - \frac{B_1}{2\sqrt{D_1}\sqrt{B_3}}\Delta(\Phi_2' + \Phi_4') = 0,\\ &-\frac{A_2}{2\sqrt{B_3}}\Delta_1\chi - \frac{B_1}{2\sqrt{D_1}\sqrt{B_3}}\Delta\Phi_1' + \Delta(\Phi_2' + \Phi_4') = 0,\\ &\Delta\Delta_1\psi = 0. \end{aligned} \tag{4.20}$$

They coincide with the linear symmetric problem (4.15) if and only if $(4.19)_{1,2,3}$ are satisfied.

After some calculations it can be proved that, in this case too, system $(4.19)_2$–$(4.19)_3$ admits no solution if $b \neq 0$, i.e. for different Prandtl and Schmidt numbers. Hence, we have proved, in all the considered cases, the following theorem.

Theorem 4.2. *For physical parameters $P_r = S_c$, $\mathcal{C} = \alpha\mathcal{R}$, $\frac{s}{r} = \alpha$, $(\frac{s}{r})^2 > 1$, the zero solution of* (2.2)*, corresponding to the basic conduction state* (2.1)*, is linearly and nonlinearly asymptotically stable, if $\mathcal{R} < \mathcal{R}_E$, where $\mathcal{R}_E$ is given by* (4.10)*.*

Conclusions

We studied the nonlinear stability of the chemical equilibrium for a binary mixture in a horizontal layer heated from below and experiencing a catalyzed chemical reaction at bottom plate, using the energy method, improved as in [4, 5, 6, 7], by taking into account an idea from [11, 12].

The presence of some chemical reactions at the bottom plate suggests us to split some perturbations fields to reformulate the perturbation evolution equations, allowing us first an easier handling of the maximum problem governing the nonlinear stability theory, and second a more advantageous symmetrization of the involved operators.

Our method uses a variant of some symmetrization techniques in [4, 5, 6, 7], by choosing the new unknown in such a way to simplify the variational problem of the non linear stability. In terms of the new perturbation fields, introduced by splitting the concentration perturbation field, the contributions of all integral on the boundaries disappear from the Euler Lagrange equations.

We can formulate, in an equivalent form, the maximum problem with or without the integrals on the boundaries, simplifying the variational approach. In such a way we can determine, in any case, a region of the parameter space in which the linear and nonlinear stability bounds coincide, only when the Prandtl and Schmidt numbers coincide.

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