Mixing by Thermal Convection in a Biochemical Reactor

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Abstract: The mixing process of a solute in a cubical cavity filled with water and heated from below is investigated numerically. The conservation equation of the solute species is discretized by means of a fourth-order accurate finite-volume scheme. The resulting set of ODE’s is advanced in time by means of a seventh-eight order Runge-Kutta method with adaptive time step. Initially, all of the solute is concentrated into a small portion of the cavity. In all of the cases investigated, a complete dispersion of the solute through the cavity is achieved at a time much smaller than the time-scale of molecular diffusion. The case of an enzymatic biochemical reaction taking place at the bottom wall is also considered. It is found that the efficiency of the discontinuous reactor system is larger than $\eta = 0.60$ in all of the cases investigated. Natural convection seems therefore to be an interesting alternative to mechanical devices as a drive for mixing in bioreactors.

Key–Words: Rayleigh-Bénard convection, mixing, finite–volume, bioreactor, Michaelis-Menten

1 Introduction

Most chemical and biochemical reactions take place on a catalyst surface or pellets. In a typical reactor fluid system, molecules are convected from the bulk of fluid into the vicinity of the surface (and viceversa) and then transported to the surface itself by molecular diffusion. When mixing is provided by a mechanical device, convection is very fast so that the process is controlled either by the rate of molecular diffusion or by the rate of reaction. However, mechanical devices such as impellers produce high levels of shear, which may be harmful when biological entities are involved. Recently, Al-Shannag et al. [1] have investigated the mixing ability of the lid-driven cavity flow with an enzymatic reaction taking place at the bottom surface of the cavity. They concluded that the wall-driven cavity configuration can be seen a highly promising alternative bioreactor system. Notwithstanding, an obvious drawback of such a system is the presence of the moving lid itself.

The alternative system that is investigated here uses no mechanical device at all. It consists of a cubical cavity with perfectly conducting sidewalls and heated from below. The stability and the main characteristics of the convection flow patterns for this particular Rayleigh-Bénard configuration have been recently investigated by the authors [2]. In the present work, it is assumed that the cavity is filled with water (having a Prandtl number of $Pr = 6$). The value of the Rayleigh number is fixed as $Ra = 7 \times 10^4$ and it is assumed that a flow pattern of the $B_3$ type, stable (and thus physically realizable) for the current conditions of $Ra$ and $Pr$ [2], is developed.

The first objective of the present research is to assess the ability of the natural convection flow as a mixer. Simó et al. [3] used dynamical systems tools to analyze the mixing properties of the current Rayleigh–Bénard system but for a different Prandtl number, $Pr = 130$, and flow patterns other than $B_3$. The approach that will be used here is different since it is based on a continuum model where the partial differential equation for the conservation of a chemical species is solved numerically. The second objective is to assess the efficiency of the current configuration as an alternative for a bioreactor system.
this case the species conservation equation is solved with a boundary condition at one of the walls which emulates a catalyst-driven surface reaction having a kinetic law of the Michaelis-Menten type.

2 Mathematical Model and Numerical Method

2.1 Flow System

An incompressible steady flow of a Newtonian fluid confined in a cube with six rigid walls is studied. The top and bottom horizontal walls are kept at constant temperatures $T_c$ and $T_h$ ($T_c < T_h$), respectively, and the four lateral walls are assumed to be perfectly conducting, i.e. a linear vertical temperature profile is assumed. The domain, shown in Fig. 1, is scaled and is represented by $\Omega = [ -0.5, 0.5 ] \times [ -0.5, 0.5 ] \times [ -0.5, 0.5 ]$. The problem is governed by the three-dimensional incompressible Navier–Stokes equations and the energy conservation equation. The flow within the cavity depends on two non-dimensional parameters which are the Rayleigh number, $Ra$, and the Prandtl number, $Pr$. These parameters are defined as $Ra = \beta(\Delta T)gL^3/\alpha \nu$ and $Pr = \nu/\alpha$, where $g$ is the acceleration of gravity, $\beta$ is the coefficient of thermal expansion, $\nu$ is the kinematic viscosity, $\alpha$ is the thermal diffusivity and $\Delta T = T_h - T_c$. In the current work the cavity is assumed to be filled with water and the Prandtl number is fixed to $Pr = 6$.

![Figure 1: A sketch of the problem geometry.](image)

2.2 Governing Equations

The dimensionless conservation equation for a given chemical species may be written as,

$$\frac{\partial s}{\partial \tau} = - \left( \frac{Sc}{Pr} \right) Ra^\frac{1}{2} \cdot (\nabla) s + \Delta s \quad (1)$$

where $s$ is the molal concentration of the species considered to be the solute, $Sc$ is the Schmidt number and $\tau$ denotes dimensionless time. The Schmidt number, $Sc = \nu/D$, is the ratio between the fluid kinematic viscosity and the coefficient of molecular diffusion of the solute in the solution, $D$, and the quantity $L^2/D$ is used to scale the dimensional time $t$. The volume-averaged value of $s$, $\bar{s}$, is set to one at the initial time $\tau = 0$ in all of the present calculations.

The levels of solute concentration are assumed to be small enough to not perturb the convective motion of water. Under this assumption, the velocity field $\mathbf{u}$ is independent of $s$ and it can be calculated separately. The method that was used to previously calculate $\mathbf{u}$ for the $B_3$ flow pattern at $Ra = 7 \times 10^3$ and $Pr = 6$ is explained elsewhere [2].

In the absence of chemical reaction, the boundary conditions for equation (1) are,

$$\frac{\partial s}{\partial x} = 0 \quad \text{along} \quad |x| = 0.5 \quad (2)$$

$$\frac{\partial s}{\partial y} = 0 \quad \text{along} \quad |y| = 0.5 \quad (3)$$

$$\frac{\partial s}{\partial z} = 0 \quad \text{along} \quad |z| = 0.5 \quad (4)$$

In those calculations where a chemical reaction is prescribed the boundary condition (4) at the bottom surface of the cavity is replaced by,

$$\frac{\partial s}{\partial z} = \frac{\phi s}{1 + \beta s} \quad \text{along} \quad z = -0.5 \quad (5)$$

Equation (5) assumes that there is no accumulation of the solute at the catalyst surface and that the rate of the reaction follows a kinetic law of the Michaelis-Menten type, with $\phi$ and $\beta$ being the Thiele modulus and the saturation parameter, respectively; see Ref. [1] for details.

2.3 Numerical Method

Equation (1) is discretized in space using a finite-volume scheme with uniform grids of identical size in each of the three coordinate directions. In all of the calculations discussed below the number of cells in each direction is $N = 100$, yielding a total of $N^3 = 10^6$ volume cells uniformly distributed along the cavity. This size has been chosen as a compromise between accuracy and computational cost. Several test calculations were performed using coarser ($N = 80$) as well as finer ($N = 120$) meshes. In all cases, the results obtained on the coarsest mesh are only slightly different from those obtained with $N = 100$ while the latter are basically identical to the results obtained on the finest mesh.
Values of the three components of velocity at the center of the faces of each control volume, which were calculated previously, remain stored at the computer memory during the whole extent of the calculation. The partial derivatives of \( s \) at the cell faces are computed using a fourth-order centered finite-difference approximation. The values of \( s \) at the center of each face are interpolated using a five-point stencil with either a 2-3 or a 3-2 scheme chosen depending on the sign of velocity normal to the face. A special treatment is needed for the discretization of the boundary condition (5). Thus, the values of \( s \) at the reactive surface must be recalculated whenever the concentration field is updated. For each surface value of \( s \), \( s_w(i,j) = s_w(t, x_i, y_j) \) the substitution of the partial derivative in (5) by its finite-difference approximation yields a quadratic algebraic equation. The new values of \( s_w \) at the center of each boundary face are the positive solution of these quadratic equations.

The space discretization of equation (1) results in a system of \( N^3 \) ordinary differential equations (ODE’s). These ODE’s are advanced in time using an explicit seventh-eighth order Runge-Kutta-Fehlberg method. At each time step the r.h.s. of each ODE has to be evaluated 13 times but this workload is worth paying because the method is highly accurate and at the same time it provides an estimate of the optimal next value of the time-step. One of two different initial conditions is chosen for each particular calculation. The simplest one sets a uniform concentration \( s_0(x, y, z) = 1 \) in each computational cell of the cavity. A more challenging initial distribution of \( s \) is:

\[
s_0(x, y, z) = 1000 \text{ in a small cubical region with } -0.05 \leq x, y, z \leq 0.05 \text{ and } -0.05 \leq d \text{ and } z \leq 0.1 \text{ while } s_0(x, y, z) = 0 \text{ is set elsewhere.}
\]

The second condition is used in the calculations aimed to assess the mixing properties of the flow system.

3 Results

3.1 Convective Flow Pattern

As discussed above, a unique velocity field \( u \) is used in all of the present calculations. A suitable method to visualize flow patterns is the plot of an isosurface of a zero values of \( \lambda_2 \), the second largest eigenvalue of the sum of the squared symmetric and antisymmetric parts of the velocity gradient tensor [4]. The \( \lambda_2 \)-plot for the \( B_3 \) pattern at \( Ra = 7 \times 10^4 \) and \( Pr = 6 \), colored with levels of the z-velocity component \( w \). The vertex with \( x = y = z = -0.5 \) is marked with a big dot.

Figure 2: Plot of the \( \lambda_2 = 0 \) isosurface for the \( B_3 \) flow pattern at \( Ra = 7 \times 10^4 \) and \( Pr = 6 \), colored with levels of the z-velocity component \( w \). The vertex with \( x = y = z = -0.5 \) is marked with a big dot.

Figure 3: Poincaré maps at the horizontal planes (a) \( z = 0 \) and (b) \( z = 0.3 \). Upwards and downwards velocities are colored in black and grey, respectively.
visualize the flow from a dynamical point of view, is the plot of Poincaré maps [3]. Poincaré maps are obtained by integrating the paths of individual inert particles that are convected by the flow motion and then plotting the points where these trajectories cut the reference section. Figures 3a and 3b show Poincaré maps for the horizontal planes $z = 0$ and 0.3, respectively. These plots reveal that a chaotic mixing is to be expected in most of the volume of the cavity. However, relatively small zones of regularity, which act as barriers to mixing, are also detected.

### 3.2 Dispersion of a Small Cube of Solute

Poincaré maps are a valuable tool to assess the mixing capability of a given flow pattern as provided by convection alone. On the other hand, the solution of equation (1) will provide a simulation of a mixing process in the presence of both convection and molecular diffusion. To this purpose, the initial condition consisting of a small solute cube that is placed on the bottom surface is set for three different calculations with Schmidt numbers $Sc = 12, 120$ and 1200, respectively. Note that the $(Sc/Pr)$ ratio denotes the relative strength of convection to molecular diffusion in equation (1). Figure 4 shows the evolution in time of the spreading ratio $\Phi$, defined as the ratio of the volume of the cavity where solute concentration fulfills the condition $s \geq 0.5$. As expected, when $(Sc/Pr)$ increases the mixing process is faster in terms of the dimensionless time $\tau$ (note however that, for a given value of $\tau$, the real time $t = \tau L^2/D$ would be 100 times higher for $Sc/Pr = \alpha/D = 200$ than it is for $Sc/Pr = 2$ because in the former case $D$ is 100 times smaller).

Figure 4 also shows that in the two cases with higher $Sc$ the mixing process becomes diffusion-

![Figure 4: Evolution in time of the spreading ratio $\Phi$ for three different values of $Sc$.](image)

![Figure 5: Contours of $s$ at the $z = 0$ plane for $Sc = 12$ at times (a) $\tau = 0.02$ and (b) $\tau = 0.04$ and (c) $Sc = 1200$ at time $\tau = 0.01$.](image)
controlled after the spreading ratio reaches a value about $\Phi = 0.6$. The reason of this phenomenon is better understood when looking at the plots of concentration contours in the horizontal midplane ($z = 0$) that are shown in Figs. 5a-c. As shown in Fig. 5a for the case with $Sc = 12$, the solute, initially concentrated in the vicinity of the bottom surface, is convected upwards along two of the vertical edges of the cavity by the upwelling flow of water (see Fig. 2). At a later time, $\tau = 0.08$, part of the solute molecules that had crossed the midplane moving upwards have been convected downwards while molecular diffusion keeps dispersing the solute through the whole volume of the cavity. Figure 5c shows the midplane contours of $s$ at dimensionless time $\tau = 0.01$ for the calculation with $Sc = 1200$. Here, as convection is much faster than molecular diffusion ($Sc/Pr = 200$) solute particles have already been convected up and down many times and as a result the contours of $s$ near the four vertical edges are very similar. Note also in Fig. 5c that regions of basically zero $s$ are still present at $\tau = 0.01$. Although convection is very fast compared to diffusion, in the absence of the latter solute molecules would never reach certain regions of the cavity. Note that despite such impediment convection plays a decisive role in spreading solute throughout most of the volume of the cavity. Thus, the typical length, say $\lambda$, where solute transport is driven by molecular diffusion alone becomes relatively small. If we assume, for example, $\lambda/L \approx 0.2$ then the diffusion time scale would be 0.04 times the standard ($L^2/D$) time, in qualitative agreement with the fast mixing that is observed in Fig. 4.

### 3.3 Discontinuous Reactor Model

Here a catalyst-driven enzymatic reaction having a kinetic law according to equation (5), with $\phi = 5$ and $\beta = 0.1$, is assumed to occur at the bottom horizontal wall ($z = -0.5$). An initial uniform reactant distribution $s_0 = 1$ is considered first. In a perfect-mixing, ideal reactor model, the value of $s$ at any point of the cavity, including the reactive wall itself, would be equal to its volume-averaged value $\bar{s}(t)$. Integrating in time the overall mole balance for the reactant yields therefore,

$$\tau = \frac{1}{\phi} [\beta (1 - \bar{s}) - \ln \bar{s}] \quad (6)$$

The evolution in time of $\bar{s}$ obtained in a calculation with $Sc = 12$ is compared in Fig. 6a with the corresponding evolution given by equation (6). The time needed to reach a reactant conversion of about 90% ($\bar{s} = 0.1$) is about 3/2 the time that would be required in the perfect-mixing limit. Note that the time needed for reaction to be completed is much larger than the time needed to completely mix the solute in Fig. 4. The corresponding Alternatively, the efficiency of the discontinuous reactor system may be assessed by a quantity, $\eta(t)$, defined as the ratio of the surface-averaged reaction rate (as given by the r.h.s. of equation (5)) to the maximum reaction rate, $\phi \bar{s}/(1 + \beta \bar{s})$. Figure 6b shows the evolutions in time of $\eta$ obtained in three calculations with $Sc = 12, 120$ and 1200, respectively. In all of the three cases, after a relatively short time $\eta$ reaches an almost constant value. As expected, this plateau-like value of $\eta$ increases with $Sc$ and it seems not to tend to $\eta = 1$ in the limit of $Sc \to \infty$. This fact is not surprising since, as seen above, even at high values of $Sc$ molecular diffusion plays a decisive role in spreading the solute throughout some regions in the cavity.

**Figure 6:** Evolution in time of (a) the concentration average $\bar{s}$ for the case with $Sc = 12$ and (b) the efficiency factor $\eta$ for three different values of $Sc$.

Finally, for the most challenging conditions of $Sc = 12$ a calculation has also been performed with the initial condition of the small cube of reactant being placed, in this particular case, in the vicinity of the top wall. Figure 7 shows the influence of initial conditions on the time evolution of $\bar{s}$. For the small cube initial condition (solid line), the reaction rate is zero
until some reactant first reaches the bottom wall. Interestingly, after a time about $\tau = 0.1$ the evolution of $\bar{s}$ is basically independent of the particular initial condition. Figure 8 shows the contours of $s$ on the reactive surface at the instant $\tau = 0.2$. The concentration of reactant is considerably higher near the two vertical edges where water is flowing down. The lowest values of $s$ are observed at the two corners where the transport of reactant into the surface is more diffusion-controlled.

![Graph](image_url)

Figure 7: Influence of the initial conditions on the evolution of $\bar{s}$ for the case with $Sc = 12$.

![Graph](image_url)

Figure 8: Contours of $s$ on the catalyst surface ($z = -0.5$) for $Sc = 12$ at time $\tau = 0.2$.

## 4 Conclusions

A new bioreactor system where mixing is provided by natural convection has been investigated. Present results strongly suggest that the new system is a promising alternative to classical reactors where mixing is provided by mechanical devices. In the most realistic conditions investigated ($Sc = 1200$), the discontinuous reactor system achieves an asymptotic efficiency as high as $\eta = 0.76$. Moreover, in practical conditions values of the Rayleigh number as high as $Ra = 10^6$ will be easily attained. The increase in $Ra$ should lead to even higher efficiencies since not only the relative weight of the convection term in equation (1) would increase but the dynamics of mixing would most probably be fully chaotic throughout the whole volume of the cavity.

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