Moving Hot Spots and Resonance in Adiabatic Packed-Bed Reactors

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An incentive to better understand the dynamic behavior of the nonisothermal packed-bed reactor (PBR) is that under transient operation the temperature may rise substantially above its steady-state maximum. Generally, transient behavior of the PBR has the character of traveling temperature and concentration waves which are sometimes called moving hot spots (MHS). Because of their high peak temperatures, MHS may compromise the safe and economical reactor operation.

The physical mechanisms of MHS formation in adiabatic PBR are described and it is demonstrated how they are based on the reactor's *convective instability* and *resonant frequency response* (Yakhnin et al., 1995). MHS may arise from a sudden drop of the temperature of feed—a phenomenon known as wrong-way behavior (see Pinjala et al., 1988)—or from a transient increase of the feed temperature. In the latter case, the initial perturbation generates a localized zone of elevated temperature, forced downstream by convection. Because of the large heat capacity of the bed, the hot spot propagates at a slow speed, much less than the gas flow velocity. Fast fluid flow continually supplies fresh reagents to the hot spot area and sustains the reaction at a high rate. This causes the MHS temperature to grow beyond the maximal temperature of the steady state.

The system favors MHS of a certain width: narrower hot spots are suppressed by heat dispersion, while in wider ones, heat release is not sufficiently localized to greatly increase the temperature of the bed. The optimal spatial scale of the MHS determines the position of resonance in the reactor's frequency response.

Model

We describe the standard reaction $A \rightarrow B + \text{heat}$ in the adiabatic PBR by the nondimensional equations

$$\dot{x}_1 = -f + \left(Pe_1^{-1}\partial_\xi^2 - \partial_\xi\right)x_1,$$
$$\dot{x}_2 = Le^{-1}\left[bf + \left(Pe_2^{-1}\partial_\xi^2 - \partial_\xi\right)x_2\right], \qquad (1)$$

where $f = Dax_1 \exp[\gamma(1 - 1/x_2)]$, similar to the equations used for example, by Jensen and Ray (1982). Here x_1 and x_2 are the normalized concentration and temperature; the dot denotes derivative with respect to dimensionless time τ. Da is the Damköhler number; γ is the normalized activation energy of reaction. Pe_1 and Pe_2 are the Peclet numbers for mass and heat dispersion, and ξ is the normalized spatial variable. The Lewis number Le represents the ratio of heat capacity of the fluid-solid medium to that of the fluid alone (for the PBR, $Le > 1$); b is the adiabatic temperature rise. The velocity of matter flow (the coefficient in front of the term with the first spatial derivative in the first of Eq. 1) equals 1, while that of heat flow $1/Le$. Since $Le > 1$, the latter is less than the former. This is due to the solid reactor packing, which introduces an additional heat capacity and slows down the transport of heat. Indeed, it is the difference $(1 - Le^{-1})$ of propagation speeds of concentration and temperature disturbances that is the physical cause of the convective instability (Rovinsky and Menzinger, 1992; Yakhnin et al., 1995) and of the resultant MHS in the packed-bed reactor. Equations 1 were supplemented with Danckwerts boundary conditions and solved numerically to produce the following results.

Moving Hot Spots

Figures 1 and 2 show, superimposed on the steady-state distribution, successive snapshots of the temperature and concentration profiles that evolve from negative (a) and positive (b) transient perturbation of the reactor inlet temperature. Each figure contains 3 snapshots, taken at time intervals 0.5 and 0.4, respectively, starting at $\tau = 2$ after the perturbation was applied. The initial state of the reactor was the steady state. Transient concentration and temperature profiles in front of and behind the evolving perturbation follow closely the steady-state distributions, so that only the deviant parts of the former are visible.

The negative perturbation induces a local temperature minimum in the reactor inlet area, which is forced downstream by convection. Because of the high thermal inertia of the bed, the temperature wave moves at a slow speed (about $1/Le$), much less than the fluid flow velocity ($= 1$). In the area of lowered temperature, the reaction rate is low com-

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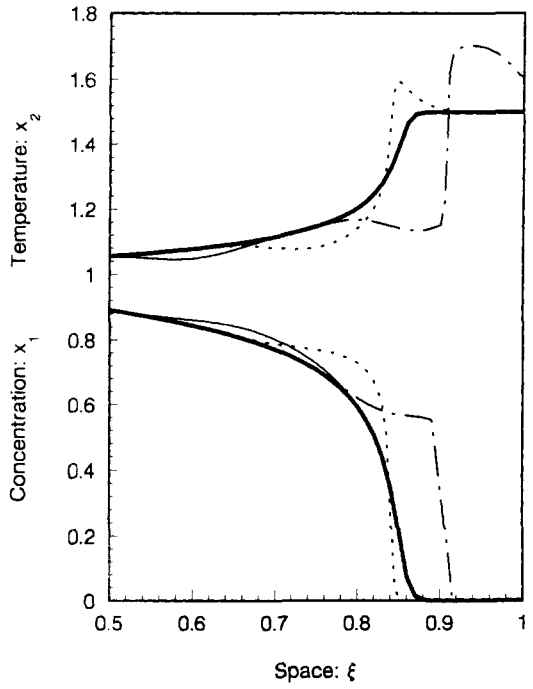

Figure 1. Development of a traveling wave in the PBR from a temporary drop in the temperature of feed.

The input perturbation is a single negative half-period of a harmonic oscillation with frequency $\nu = 1.2$ and amplitude $a = 0.01$. The thin solid, dotted, and dash-dotted lines in the upper part of the figure represent three transient temperature (x_2) profiles at successive moments of time; corresponding profiles of the reagent concentration x_1 are given in the lower part of the figure. The thick lines represent the steady-state concentration and temperature distributions. Parameter values are: $Pe_1 = 3Pe_2 = 3{,}000$, $Le = 3$, $b = 0.5$, $Da = 0.135$, $\gamma = 22$; only the downstream part (second half) of the reactor is shown.

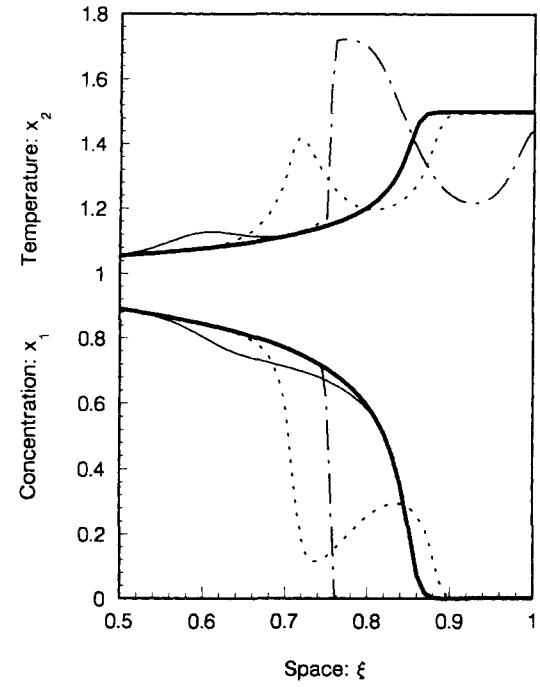

Figure 2. Same data as in Figure 1, but for the transient rise in the temperature of feed.

The perturbation is a single positive half-period of a harmonic oscillation with $\nu = 1.2$ and $a = 0.01$. Parameter values are equal to those of Figure 1.

pared to its steady-state value, and the concentration of the reagent is correspondingly high. In other words, the heat wave generates a matter wave—a moving zone of elevated reagent concentration. The fast fluid flow transfers the concentration wave downstream. This results in a phase shift between the concentration and temperature waves: the former precedes the latter. This dynamics is illustrated by the snapshot taken at the earlier time (thin solid lines in Figure 1).

The concentration wave enters the reaction zone well before the temperature wave. The reagent-enriched flow interacts now essentially with the steady-state temperature distribution that persists in the reaction zone. The resultant release of heat, enhanced by the excess of fresh reagent, causes the temperature in the reaction zone to grow beyond its steady-state maximum and the MHS to form, as illustrated by the snapshot shown in Figure 1 by the dotted lines. From a certain point on, the MHS begins to broaden (see the last snapshot: dash-dotted lines) and to accommodate, thereby, the reaction heat without further growth of temperature. Finally, the transient wave is washed out of the reactor by the flow, leaving it in the steady state. This sequence of events is essentially the same as in the usual case of wrong-way behavior, initiated by a sudden and persistent drop in the reactor inlet temperature (see, for example, Pinjala et al., 1988).

Formation of a pronounced MHS in response to a slight positive perturbation of the reactor inlet temperature is less obvious. For example, it (as well as wrong-way behavior) does not occur in the unpacked reactor. In the latter case a moving zone of elevated temperature may arise from a transient increase of the temperature of feed, but the depletion of reagent in the hot-spot area limits the growth of temperature to the level of the steady-state maximum. In the PBR, however, fast fluid flow continually supplies fresh reagent to the slow-moving hot spot. This counteracts its depletion and eliminates the above temperature limitation. This dynamic is illustrated in Figure 2. The earliest frame (thin full lines) shows a positive temperature wave and induced by it (through enhanced reagent consumption) a negative concentration wave. For the same reasons given above, the concentration wave is phase-shifted relative to the temperature wave. This alleviates somewhat the decrease of reagent concentration in the MHS area and sustains the reaction at a high rate. Local heat release in the moving hot zone, promoted by fresh reagent, leads to formation of a pronounced MHS (dotted lines in Figure 2). Eventually, there develops a substantial overshoot of the steady-state temperature maximum, as demonstrated by the last snapshot in Figure 2 (dash-dotted lines).

Resonance

An example of the PBR's response to periodic perturbation is given in Figure 3. It can be understood as a result of the combined operation of the above mechanisms invoked by positive and negative perturbations. This view sheds a new

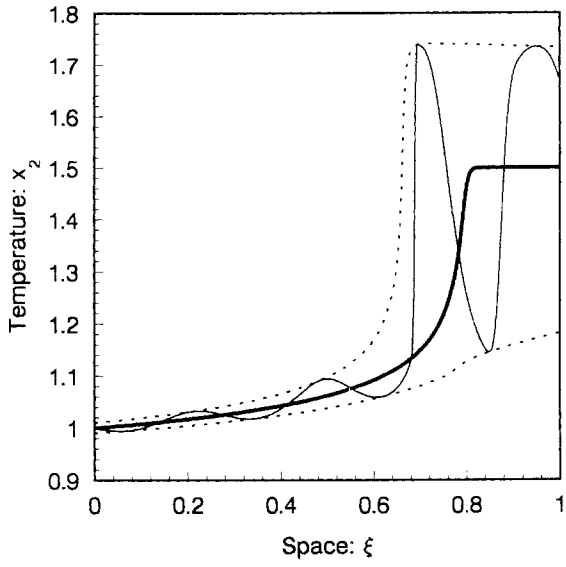

Figure 3. Temperature waves from continuous harmonic oscillation of the inlet temperature with frequency $\nu = 1.2$ and amplitude $a = 0.01$.

A snapshot of the temperature distribution (thin wavy curve) is shown together with the upper and lower temperature envelopes (dotted lines); the thick curve represents the steady-state profile; parameter values are as in Figure 1, except for $Da = 0.145$.

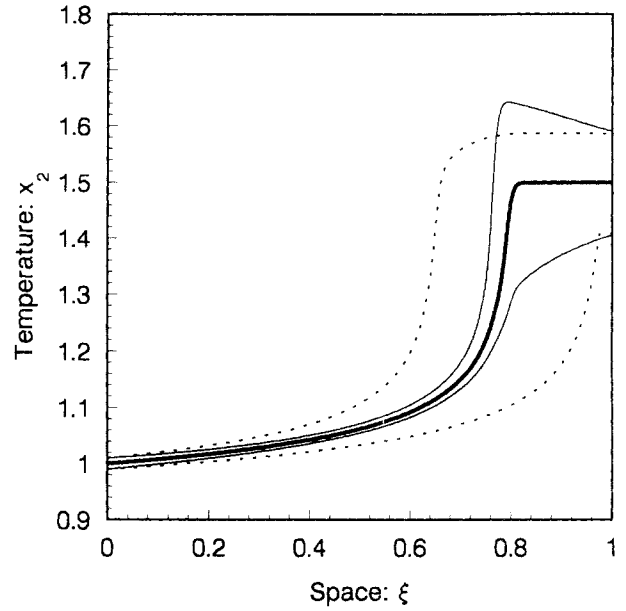

Figure 4. Upper and lower temperature envelopes (analogous to those in Figure 3) of the transient waves from harmonic oscillation of the inlet temperature.

It has high frequency $\nu = 3$ (thin full lines) and low frequency $\nu = 0.1$ (dotted lines); the thick solid curve represents the steady state; parameter values are as in Figure 3.

light on the mechanism of convective instability of the PBR (Yakhnin et al., 1995), based on the reactor response to periodic perturbation. The term *convective instability* is conventional in fluid mechanics and plasma physics (Briggs, 1964), where it refers to an open flow system which amplifies input perturbations but which is asymptotically stable since it is purged by the flow. [In hydrodynamics this type of instability is sometimes called convected to avoid confusion with thermal instability that leads to Benard convection in a fluid layer heated from below (Drazin and Reid, 1989).] This behavior is typical of the PBR. To distinguish the above dynamics from the instability associated with positive eigenvalues of the linear stability problem, the latter is termed *absolute instability* in this context. However, the difference between convective and absolute instabilities is to a certain degree conditional. The instability classified as convective in the laboratory reference frame is absolute in the reference frame co-moving with the perturbation.

Figure 4 illustrates the PBR response to high- ($\nu = 3$) and low- ($\nu = 0.1$) frequency perturbations. In both cases the maximal temperatures of the MHS are less than for the frequency $\nu = 1.2$ (Figure 3). Weak low-frequency perturbations tend to slightly displace the steady state as a whole, rather than generating pronounced localized MHS. High-frequency perturbations initiate narrow MHS that are damped by heat dispersion. Given this, one can expect that there exists an intermediate range of frequencies to which the PBR is especially responsive or, in other words, that the phenomenon of resonance takes place. This resonance is illustrated in Figure 5 which shows the Fourier-spectrum of the reactor's response to a multifrequency perturbation. The resonance has a spatial aspect, since the resonance frequency is related to the optimal width of the MHS favored by the system.

Generally, the resonance frequency is inversely proportional to the Lewis number Le. The value $Le = 3$, used in the present computations, is representative of liquid-phase

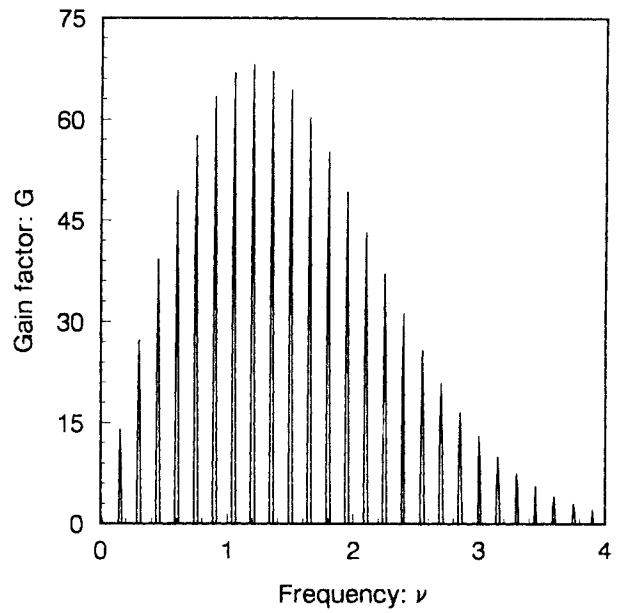

Figure 5. The gain-factor $G(\nu)$—the ratio of the amplitudes of output and input temperature variations at a given frequency ν.

The input signal consists of 31 frequency components with amplitudes $a = 10^{-5}$, random phases, and frequencies uniformly distributed in the range $\nu = [0 - 4.5]$. $G(\nu)$ is maximal and equal to 68 at the resonance frequency $\nu = 1.2$. Parameter values are as in Figure 1.

systems. At high values of *Le* of the order 10^3, typical of gas-phase systems, all the qualitative features of the reactor behavior remain unchanged; only the time scale becomes proportionally larger. A rough estimation of the resonance frequency is given by the inverse time of the reactor's thermal response. For gas-phase systems, the latter is of the order of 10 min to 1 h for laboratory reactors and 1–10 h for industrial units.

In the control-oriented literature, the PBR's frequency response has received considerable attention and some authors also observed a resonance (see, for example, Jorgensen and Hansen, 1976). However, this resonance has a different nature and is located further in the high-frequency domain. This type of resonance was also described for the passive heat exchanger (Cohen and Johnson, 1961) and is believed to be a general property of multivariable distributed systems. In contrast to that, the resonant behavior associated with the convective instability of the nonisothermal PBR results from two specific properties (Rovinsky and Menzinger, 1992; Yakhnin et al., 1995): from the autocatalytic nature of exothermic reactions and from the difference of the propagation speeds of concentration and temperature perturbations. The latter is introduced by the reactor packing. Resonance is a purely dynamic feature of the PBR's response. To expose it, we chose conditions where the reaction goes to completion. This minimizes the static component of the reactor response which, if present, interferes with the resonance at low frequencies (Sinai and Foss, 1970).

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Manuscript received July 3, 1997, and revision received Dec. 1, 1997.