Chemical Engineering Journal 154 (2009) 115–119

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Approximate characteristics of a moving temperature front in a fixed-bed catalytic reactor: Effect of mass dispersion

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ARTICLE INFO

Article history:
Received 30 November 2008
Received in revised form 19 March 2009
Accepted 17 April 2009

Keywords:
Packed bed
Moving fronts
Maximal temperature rise
Front velocity
Approximations

ABSTRACT

We derive approximate relations for the propagation velocity and the maximal temperature rise of an "ideal" 1-D front in a pseudo-homogeneous packed bed reactor (PBR) model with a first order activated kinetics, accounting for a finite mass Peclet number (Pe_C). These relations are compared with known approximations for $Pe_C \to \infty$ and are verified by direct numerical simulations showing a good agreement within a wide domain of parameters if $Pe_C > Pe_T$, which typically applies for PBRs.

1. Introduction

Heterogeneous catalytic packed bed reactors (PBRs) are extensively used in chemical and petrochemical reactors and for abatement of environmental pollutants typically by catalyzing exothermic reactions (e.g., oxidation, hydrogenation). Such reactors are known to exhibit thermal fronts propagating in the axial direction. The maximal temperature rise behind the front (ΔT_m) and front velocity (V_f) are essential parameters that need to be determined for proper reactor design. A good design will use conditions that will not expel the front from the reactor and lead to extinction. The fronts are also of significance for design of the reverse-flow reactor (RFR, see, for example Matros [1] and Eigenberger et al. [2]) and of the recently proposed loop reactor (LR, Matros [3]) in which the maximal temperature rise can significantly exceed the adiabatic temperature rise (ΔT_{ad}).

The front parameters are also crucial in analysis of a transversal pattern formation in PBRs: The temperature (and conversion) distributions, which are assumed to be uniform across the reactor cross section in an adiabatic case may undergo symmetry breaking in the transversal (normal to the flow) direction (see review Viswanathan et al. [4]). In our recently published study (Nekhamkina, Sheintuch [5]) we derived a new criterion which suggests that a planar front can undergo symmetry breaking if the ratio the mass to heat Pe numbers is smaller then the ratio of the adiabatic to maximal temperature rises ($Pe_C/Pe_T < \Delta T_{ad}/\Delta T_m$).

During the last decades significant efforts were directed to derive approximate relations for the maximal temperature rise and front velocity (V_f). In an "ideal" front (propagating with a constant form in an infinitely long system with complete conversion) these parameters follow the relations (Wicke, Vortmeyer [6]):

$$\Delta T_m = \Delta T_{ad}\frac{1-V_f}{1-LeV_f},\ V_f = \frac{\Delta T_m - \Delta T_{ad}}{Le\Delta T_m - \Delta T_{ad}}, \quad (1)$$

for any Pe_T, Pe_C. An inspection of Eq. (1) shows that i) in a stationary front the maximal temperature rise is equal to the adiabatic one, i.e. $\Delta T_m = \Delta T_{ad}$, ii) in a downstream propagating front the velocity ($V_f > 0$) cannot exceed the thermal front velocity $V_{th} = 1/Le$, which corresponds to an infinitely large ΔT_m, and iii) in an upstream propagating front V_f (< 0) can formally decrease indefinitely while ΔT_m is bounded by a limit value ($\Delta T_{ad}/Le$), i.e.

$$-\infty < V_f < V_{th},\quad \frac{\Delta T_{ad}}{Le} < \Delta T_m < \infty \quad (2)$$

Note that relations (1), (2) are valid with any value of axial Pe_T and Pe_C, assuming that conversion at the reactor exit is complete.

To form a closed system that will allow to calculate the two unknown variables (V_f, T_m) we need to couple Eq. (1) with an additional relation involving the main kinetic, thermodynamic and transport parameters. The approximate relation for PBRs published in literature was derived by Kiselev [7,8] for the limiting case of $Pe_C \to \infty$ using the narrow reaction zone assumption (Frank-Kamenetski [9], Zeldovich, Barenblatt [10]). This relation in the

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doi:10.1016/j.cej.2009.04.043

Nomenclature

A	rate constant
B	dimensionless exothermicity
c_p	volume-specific heat capacity
C	key component concentration
C_p	heat capacity
D	dispersion coefficient
Da	Damkohler number
E	activation energy
f	function defined by Eq. (6)
F, G	groups defined by Eq. (30)
ΔH	reaction enthalpy
k_e	effective conductivity
L	reactor length
Le	Lewis number
Pe_T, Pe_C	Peclet numbers of heat- and mass dispersion
R_i, S	groups defined by Eqs. (38) and (37)
t	time
T	temperature
u	fluid velocities
v	auxiliary variable used in Eq. (32)
V_f	front velocity
$w = y/y_m$	dimensionless temperature
x	conversion
y	dimensionless temperature

Greek letters

α	group defined by Eq. (21)
β	group defined by Eq. (28)
γ	dimensionless activation energy
ε	porosity
ξ, ζ	dimensionless coordinate
ρ	density
τ	dimensionless time

Subscripts

ad	adiabatic
e	effective value
f	fluid
in	at the inlet
m	maximal
C	mass
T	temperature
0	reference value

Superscripts

num	numerical
$appr$	approximated

dimensionless form can be written as following:

$$\frac{(1+y_m/\gamma)^2 Da \exp[y_m/(1+y_m/\gamma)]}{BPe_T(1-V_f)^2} = 1 \tag{3}$$

The purpose of this study is to derive the approximate relations for the propagation velocity and the maximal temperature rise of an ideal 1-D front in a PBR, accounting for a finite but large mass dispersion. These approximations are verified by comparison with direct numerical simulations of a 1-D front within a wide domain of operating conditions. The structure of this paper is as follows: in the next section we present a 1-D pseudo-homogeneous PBR model and derive the approximate relations for front velocity and the maximal temperature rise, which are verified numerically in Section 3 In concluding remarks we discuss the obtained results and also address the future implementation of the obtained approximations for estimation of parameters of a loop and a reverse flow reactors, as well as for prediction of symmetry breaking conditions of a planar 1-D front.

2. Reactor model and parameters of a planar front

The balance equations of the generic 1-D pseudo-homogeneous model of a fixed-bed reactor catalyzing a first order reaction of Arrhenius-kinetics assuming non-catalytic reactor walls may be written in the following dimensionless form:

$$\frac{\partial x}{\partial \tau} + \frac{\partial x}{\partial \xi} - \frac{1}{Pe_C}\frac{\partial^2 x}{\partial \xi^2} = (1-x)f(y) \tag{4}$$

$$Le\frac{\partial y}{\partial \tau} + \frac{\partial y}{\partial \xi} - \frac{1}{Pe_T}\frac{\partial^2 y}{\partial \xi^2} = B(1-x)f(y), \tag{5}$$

$$f(y) = Da\exp\left(\frac{\gamma y}{\gamma + y}\right) \tag{6}$$

$$\xi = 0, \quad \frac{1}{Pe_C}\frac{\partial x}{\partial \xi} = x, \quad \frac{1}{Pe_T}\frac{\partial y}{\partial \xi} = y, \quad \xi = \bar{L}, \quad \frac{\partial x}{\partial \xi} = 0, \quad \frac{\partial y}{\partial \xi} = 0. \tag{7}$$

Here conventional notation is used:

$$x = 1 - \frac{C}{C_{in}}, y = \gamma\frac{T - T_{in}}{T_{in}}, \xi = \frac{z}{z_0}, \quad \tau = \frac{tu}{z_0},$$

$$\gamma = \frac{E}{RT_{in}}, \Delta T_{ad} = \frac{(-\Delta H)C_{in}}{(\rho C_p)_f}, B = \gamma\frac{\Delta T_{ad}}{T_{in}}, Da = \frac{z_0}{u}A\exp(-\gamma),$$

$$Le = \frac{(\rho c_p)_e}{(\rho c_p)_f}, Pe_T = \frac{(\rho c_p)_f z_0 u}{k_e}, Pe_C = \frac{z_0 u}{\varepsilon D_f},$$

We derive now approximations for the maximal temperature rise and velocity of an "ideal" front, i.e. a front propagating in an infinitely long system subject to the conditions:

$$\xi \to -\infty, x = 0, y = 0, dx/d\xi = 0, dy/d\xi = 0;$$

$$\xi \to \infty, x = 1, y = y_m, dx/d\xi = 0, dy/d\xi = 0; \tag{8}$$

Assuming a "frozen" solution in a moving coordinate system ($\zeta = \xi - V_f\tau$) we can rewrite the balance equations in the following form:

$$(1 - LeV_f)y' - \frac{1}{Pe_T}y'' = B(1-x)f(y) \tag{9}$$

$$(1 - V_f)x' - \frac{1}{Pe_C}x'' = (1-x)f(y) \tag{10}$$

Here primes denote derivatives with respect to ζ. Combining Eqs. (9) and (10) results in:

$$(1 - LeV_f)y' - B(1 - V_f)x' - \frac{1}{Pe_T}y'' + \frac{B}{Pe_C}x'' = 0 \tag{11}$$

Integrating this equation by ζ from $-\infty$ until ∞ while accounting for boundary conditions (BC) (8) yields:

$$(1 - LeV_f)y_m - B(1 - V_f) = 0 \tag{12}$$

or

$$y_m = B\frac{1 - V_f}{1 - LeV_f}, V_f = \frac{y_m - B}{Ley_m - B} \tag{13}$$

which present a non-dimensional form of relations (1). Integrating Eq. (11) up to local ζ with account for (13) yields:

$$\frac{B}{Pe_C}x' - \frac{1}{Pe_T}y' = B(1-V_f)\left[x - \frac{y}{y_m}\right] \tag{14}$$

As was mentioned in Section 1, Kiselev et al. ([7,8]), for the limiting case of negligible mass dispersion ($Pe_C \to \infty$), derived an approximate relation between front velocity and the maximum temperature rise (3) using a set of two first order ODEs [Eqs. (10) and (14) with $Pe_C^{-1} = 0$] and implementing a narrow reaction zone assumption ([9]). In the present study we follow this approach while accounting for a finite mass dispersion. As the first step we eliminate the term including x'' from Eq. (10). For this purpose we can differentiate Eq. (10) yielding:

$$(1-V_f)x'' - \frac{1}{Pe_C}x''' = -x'f(y) + (1-x)f'_y y' \tag{15}$$

With account for the function $f(y)$ (6) we obtain

$$x'' = \frac{1}{1-V_f}\left[-x'f(y) + \frac{(1-x)f(y)}{(1+y/\gamma)^2}y'\right] - \frac{1}{(1-V_f)Pe_C}x''' \tag{16}$$

After substituting Eq. (4) into Eq. (10) while neglecting terms of $O(1/Pe_C^2)$ we find:

$$x'\left[(1-V_f) + \frac{f(y)}{Pe_C(1-V_f)}\right] - y'\frac{(1-x)f(y)}{Pe_C(1-V_f)(1+y/\gamma)^2} = (1-x)f(y) \tag{17}$$

Eqs. (14) and (17) form a linear algebraic system with respect to derivatives x', y' yielding

$$x' \sim -\frac{(1-x)f(y)}{Pe_T}\left[1 - \frac{B(x-y/y_m)}{Pe_C/Pe_T(1+y/\gamma)^2}\right] \tag{18}$$

$$y' \sim -B(1-V_f)^2\left(x - \frac{y}{y_m}\right)\left[1 + \frac{f(y)}{Pe_C(1-V_f)^2}\left(1 - \frac{1-x}{x-y/y_m}\right)\right] \tag{19}$$

Combining these equations we obtain a single first order equation, which after introducing a new variable $w = y/y_m$ can be written in the following form:

$$\frac{dx}{dw} = p(w)g(w,x)q\left(w, x, \frac{Pe_C}{Pe_T}, \alpha\right) \tag{20}$$

where

$$p(w) = \frac{y_m f(y_m w)}{BPe_T(1-V_f)^2}, g(w,x) = \frac{1-x}{w-x},$$

$$q(w,x,\alpha) = \frac{[1-B(x-w)]/[Pe_C/Pe_T(1+y_m w/\gamma)^2]}{1+\alpha p(w)[1+g(w,x)]},$$

$$\alpha = \frac{BPe_T}{y_m Pe_C} \tag{21}$$

The appropriate BCs are:

$$w = 0, x = 0; w = 1, x = 1. \tag{22}$$

In the limiting case $Pe_C \to \infty$ we have $\alpha \to 0$, $q(w,x,\alpha) \to 1$ and Eqs. (20)–(22) are reduced to the problem statement considered in Refs. [7,8], where the desirable relation (3) was obtained as an integral of reduced Eq. (20).

The function $g(w,x)$ has a singularity if $(x,w) \to 1$, however the limits of $g(w,x)$ and dx/dw are finite:

$$\lim_{w,x\to 1} x'_w = p(1)\frac{-x'_w}{(1-x'_w)}\frac{1}{1+\alpha p(1)[1-x'_w/(1-x'_w)]}$$

Thus,

$$x'_w = \frac{1+p(1)+\alpha p(1)}{1+2\alpha p(1)} \tag{23}$$

Now, according to the narrow reaction zone assumption we can estimate all functions in the right hand side of Eq. (20) around $w = 1$: For the function $g(w,x)$ we have:

$$g(w,x) = \frac{1-x}{w-x} \simeq \frac{x'_w}{x'_w - 1} = \frac{1+p(1)(1+\alpha)}{p(1)(1-\alpha)}$$

or, since $p(1) \gg 1$,

$$g(w,x) = \frac{1+\alpha}{1-\alpha} = const(w) \tag{24}$$

Consider the correction function $q(w,x,Pe_C)$ (21) around $w = 1$, while neglecting the term proportional to $(x-w)$ in the numerator:

$$q(w,x,Pe_C) \simeq \frac{1}{1+\alpha p(w)[1+(1+\alpha)/(1-\alpha)]} = \frac{1}{1+2\alpha/(1-\alpha)p(w)} \tag{25}$$

Substituting Eqs. (24) and (25) into Eq. (20) we obtain:

$$\frac{dx}{dw} = \frac{(1+\alpha)p(w)}{1-\alpha+2\alpha p(w)} \tag{26}$$

Integrating this equation we have:

$$\frac{1}{1+\alpha} = \int_0^1 \frac{p(w)}{1-\alpha+2\alpha p(w)}dw \tag{27}$$

Estimating the power of the exponent in $p(w)$ around $w = 1$:

$$\frac{y_m w}{1+y_m w/\gamma} \simeq \frac{y_m}{1+y_m/\gamma} + \beta(w-1),\ \beta = \frac{y_m}{(1+y_m/\gamma)^2} \tag{28}$$

we obtain

$$p(w) = F\exp\left(\frac{y_m w}{1+y_m w/\gamma}\right) \simeq FG\exp[\beta(w-1)] \tag{29}$$

where

$$F = \frac{Day_m}{BPe_T(1-V_f)^2},\ G = \exp\left(\frac{y_m}{1+y_m/\gamma}\right) \tag{30}$$

Substituting (29) in Eq. (27) we get:

$$\frac{1}{1+\alpha} = FG\int_0^1 \frac{\exp[\beta(w-1)]}{1-\alpha+2\alpha FG\exp[\beta(w-1)]}dw \tag{31}$$

Introducing a new variable $v = \exp[\beta(w-1)]$, $dv = v\beta dw$ we obtain

$$\frac{1}{1+\alpha} = \frac{FG}{\beta}\int_{v(0)}^1 \frac{dv}{1-\alpha+2\alpha FGv} = \frac{FG}{\beta}\frac{1}{2\alpha FG}\log(1-\alpha+2\alpha FGv)|_{v(0)}^1 \tag{32}$$

Assuming that the value of the logarithm at the lower limit is significantly less then that at the upper limit we obtain

$$\frac{1}{1+\alpha} = \frac{1}{2\alpha\beta}\log[1+\alpha(2FG-1)] \simeq \frac{1}{2\alpha\beta}\log(1+2\alpha FG) \tag{33}$$

and finally

$$\frac{2\alpha}{1+\alpha} = \frac{1}{\beta}\log(1+2\alpha FG) \tag{34}$$

Eq. (34) coupled with relation (13) form a closed system with respect to two unknown parameters: y_m and V_f. An inspection of

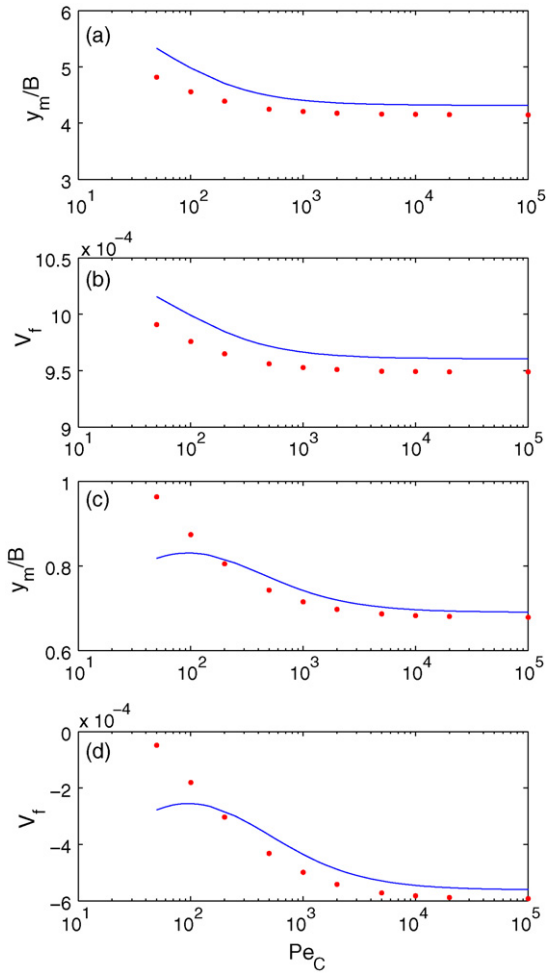

Fig. 1. (Color online) Comparison of approximate [Eqs. (13) and (34), lines] and numerically calculated (points) dimensionless temperature rise (y_m/B, a, c) and front velocity (V_f, b, d) with varying mass Peclet (Pe_C). $B = 30$ (a, b), 300 (c, d). Other parameters are: $Le = 800$, $Pe_T = 200$, $Da = 4 \times 10^{-8}$, $\gamma = 27$.

Eq. (34) shows that in the limiting case $\alpha \to 0$ (i.e. $Pe_C \to \infty$) this equation is reduced to

$$1 \simeq \frac{FG}{\beta} \tag{35}$$

which is equivalent to Eq. (3). With moderate and large α Eq. (34) can be reduced to

$$\frac{2\alpha}{1+\alpha} = \frac{1}{\beta}\log(2\alpha F) + 1 + \frac{y_m}{\gamma} \tag{36}$$

3. Validation of the proposed approximations

To verify approximate relations derived above we simulated model (4), (5) in a wide domain of operating conditions: The maximal temperature rise and front velocity essentially depend on the mass Peclet number for both a downstream—[small B, Fig. 1 (a,b)] and an upstream—[large B, Fig. 1(c,d)] propagating fronts, tending to the corresponding asymptotic values with $Pe_C \to \infty$. A reasonable agreement between the approximated (denoted by lines) and the simulated (symbols) results was obtained with moderate and large Pe_C ($Pe_C \geq Pe_T$, Figs. 1–3); note that this is the physically feasible operation domain for PBRs. The divergence between the approximated and simulated results increases with decreasing Pe_C/Pe_T.

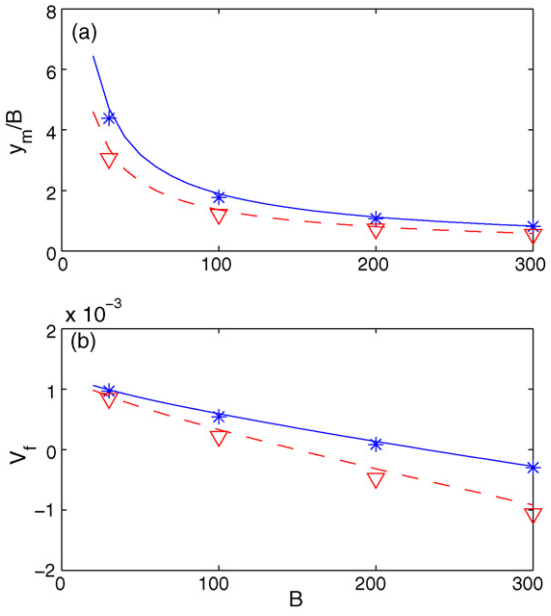

Fig. 2. (Color online) Comparison of approximate [Eqs. (13) and (34), lines] and numerically calculated (symbols) dimensionless temperature rise (y_m/B, a) and front velocity (V_f, b) with varying dimensionless adiabatic temperature rise B. $Da = 4 \times 10^{-8}$ (stars, solid lines), 4×10^{-7} (triangulars, dashed lines), $Pe_C = 200$, other parameters as in Fig. 1.

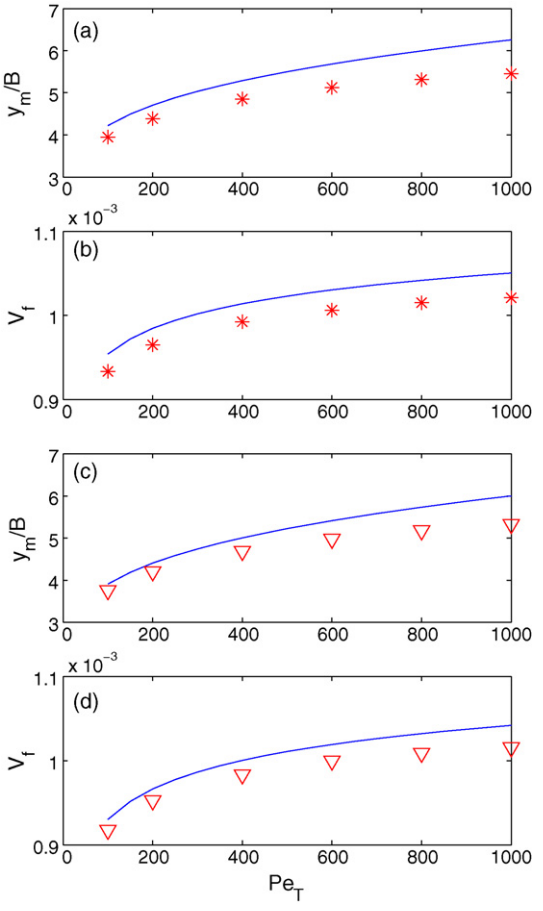

Fig. 3. (Color online) Comparison of approximate [Eqs. (13) and (34), lines] and numerically calculated (symbols) dimensionless temperature rise (y_m/B, a, c) and front velocity (V_f, b, d) with varying Peclet number with equal $Pe_C = Pe_T$; other parameters as in Fig. 1.

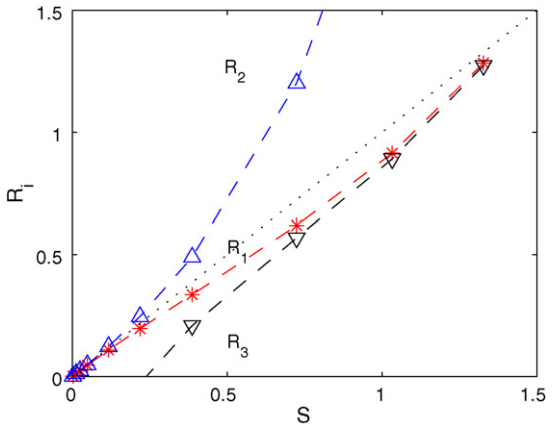

Fig. 4. (Color online) Comparison of approximate relations (37) showing numerically calculated complexes R_i, $i = 1, 2, 3$ vs S [Eq. (38)], symbols connected by dashed lines]. $B = 100$, other parameters as in Fig. 1. Dotted line shows $R_i = S$.

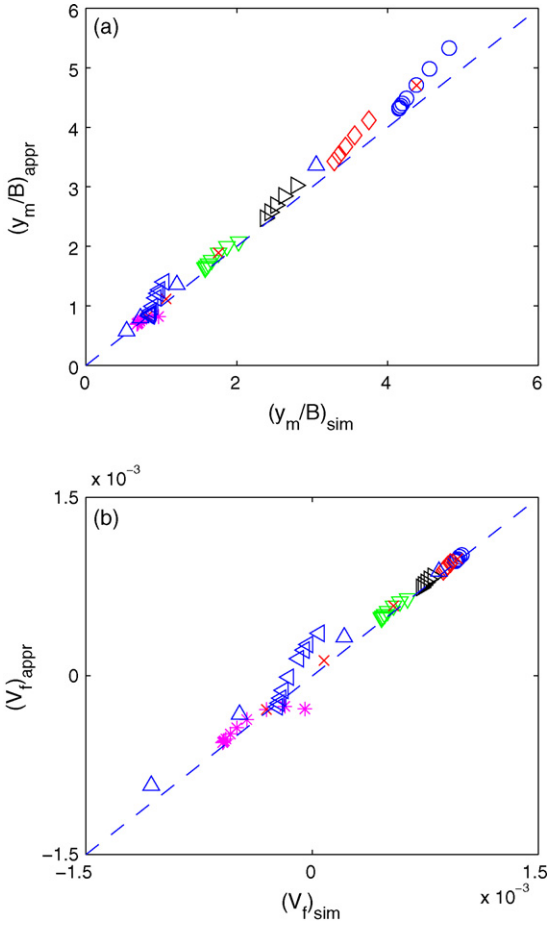

Fig. 5. Comparison of approximate [relations (13), (34)] and simulated values of the dimensionless temperature rise (y_m/B, a) and front velocity (V_f, b). $Pe_T = 200$, other parameters: $Da = 4 \times 10^{-8}$, $\gamma = 27$, $Pe_C = 75 - 10^4$, $B = 30$ (○), 40 (◊), 60 (◁), 100 (▽); 300 (∗); $Da = 4 \times 10^{-7}$, $\gamma = 27$, $Pe_C = 200$, $B = 30$–300 (△); $Da = 4 \times 10^{-8}$, $\gamma = 27$, $Pe_C = 200$, $B = 30$–300 (x); $Da = 4 \times 10^{-8}$, $\gamma = 35$, $Pe_C = 75 - 10^4$, $B = 100$ (◁). Dashed lines show the lines of perfect agreement.

Relations (34)–(36), which will be used for comparison with numerical results, can be rewritten as

$$S \equiv \frac{2\alpha}{1+\alpha} = R_i,\ i = 1, 2, 3 \tag{37}$$

where

$$R_1 = \frac{1}{\beta}\log(1+2\alpha FG),\ R_2 = \frac{2\alpha FG}{\beta(1+\alpha)},\ R_3 = \frac{1}{\beta}\log(2\alpha F)+1+\frac{y_m}{\gamma} \tag{38}$$

The calculated results, expressed as the complexes R_i vs S (Fig. 4), follow Eq. (34) in a wide domain of α. As expected, relation (35) can be successfully applied with small α, while relation (36) is valid for large α.

The obtained results are summarized in Fig. 5 showing the comparison between the approximated and the simulated parameters. The agreement is satisfactory over a wide domain of parameters suggesting that approximation (34) is well validated.

4. Conclusion remarks

We proposed approximate relations for the maximal temperature rise and velocity of a 1-D ideal moving front in a PBR catalyzing a first-order activated reaction. These relations are validated in a wide domain of parameters with $Pe_C \geq Pe_T$, which is a feasible condition for commercial reactors. The obtained relations are both of theoretical and of practical interest. The proposed approach can be extended to predict the parameters and the operating domain boundaries of the loop reactor (i.e. accounting for effect of non-ideal boundary conditions, Nekhamkina and Sheintuch [11]) and the parameters of the reverse flow reactor in the sliding regimes (following Matros [3]). Moreover, the obtained approximations can be extended to the case of a curvilinear front, which in turn, allow to formulate the symmetry breaking condition of a 1-D planar front using a bifurcation condition $dV_f/dK_{K=0} = 0$, where K is the local front curvature. The last issue will be addressed in the future publication.

Acknowledgments

This work is supported by Israel-US BSF. ON is partially supported by the Center for Absorption in Science, Ministry of Immigrant Absorption State of Israel. MS is a member of the Minerva Center of Nonlinear Dynamics and Complex Systems.

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