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Kinetic effects on transversal instability of planar fronts in packed-bed reactors

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HIGHLIGHTS

- A criterion for transversal instability of planar fronts in packed beds is derived.
- *n*th order or Langmuir–Hinshelwood kinetics is considered.
- The heat to mass Peclet numbers ratio should surpass a kinetic-dependent value.
- Transversal patterns can emerge in upstream propagating fronts.
- The minimal reactor radius that can exhibit transversal patterns is approximated.

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ABSTRACT

We derive a new criterion for transversal instability of planar fronts in packed bed reactors (PBR's) in which *n*th order or Langmuir–Hinshelwood kinetics reaction occurs using a pseudo-homogeneous two-variables (C,T)-model. The derivation follows the analysis of combustion of reaction–diffusion systems by Sivashinsky, Comb. Sci. Tech. 15 (1977). The new criterion is expressed as a complicated relation of the ratio of the heat to mass dispersivities on the kinetic parameters. A necessary (but not sufficient) condition for emerging patterns in the reactor cross-section for the kinetic models studied is that $(\Delta T_{ad}/\Delta T_m)/(Pe_C/Pe_T) > 1$, where ΔT_{ad} and ΔT_m are the adiabatic and the maximal temperature rise, respectively, Pe_C and Pe_T are the mass and the heat Peclet numbers, respectively. This condition agrees with our previous results that were limited to first order kinetics and is unlikely to be satisfied in PBR's. Also, unlike the previous condition, the new criterion allows to determine the critical wave number (minimal reactor radius) that can exhibit transversal patterns. The new criterion is verified by comparison with the linear stability results and with 3-D simulations.

1. Introduction

Design of packed bed reactors (PBRs) is physically based on simulations of 1-D models and analysis of the state (concentrations, temperature) profiles. This is typically the practice even with highly exothermic reactions, like oxidation or hydrogenation reactions, or self inhibited reactions, like CO and hydrocarbon oxidation reactions, situations known to induce such phenomena as traveling fronts and multiple solutions (profiles) in 1-D systems [1–7].

The use of 1-D solutions is based on the assumption that the solution is homogeneous in the direction transversal to the flow. An extensive literature exists on conditions that induce transversal patterns in moving fronts. Such traveling fronts occur in a variety of physical systems like combustion flames, population invasions, virus infections, tumor growth, chemical waves, crystallization and many others.

Similarly, transversal patterns emergence in catalytic reactors was investigated in the past decade. Catalytic reactors are reaction–diffusion–advection (RDA) systems, that bear resemblance to other RDA systems, like combustion reactors, or to reaction–diffusion (RD) systems like flame combustion and self-propagating high-temperature synthesis. Catalytic systems differ from these two in their high heat capacity and intricate kinetics.

Several experimental studies used IR imaging to monitor 2-D patterns and can be interpreted as transversal patterns. These include the exterior surface of a radial flow reactor [8], the shallow packed-bed reactors [8] or the surface of a catalytic cloth [9] under oscillatory conditions (which employed a micro-kinetic model to account for the results) and other results on PBRs reviewed in Ref. [7]. Technologies that monitor 3-D states are quite expensive and at this stage the 3-D patterns can be inferred from theory only.

Most studies of transversal patterns in packed beds employed first order Arrhenius kinetics and the main results are listed below.

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Nomenclature

Roman symbols

B	dimensionless exothermicity
c	dimensionless concentration
c_p	volume-specific heat capacity
C	key component concentration
D	dispersion coefficient
Da	Damkohler number
E_a	activation energy
f	reaction rate
ΔH	reaction enthalpy
k	perturbation wave number
k_e	effective conductivity
L	reactor length
Le^*	Lewis number
Pe_T, Pe_C	Peclet numbers of heat- and mass dispersion
R	reactor radii
t	time
T	temperature
u	fluid velocity
V_f	front velocity
x	conversion
y	dimensionless temperature defined by Eq. (67)
Z	axial coordinate

Greek symbols

α	parameter defined by Eq. (2)
γ	dimensionless activation energy
ε	porosity
θ	dimensionless temperature scaled by T_m
κ	parameter defined by Eq. (36)
ξ, ζ	dimensionless coordinate
ρ	density
σ_c, σ_T	parameters defined by Eq. (23)
ϕ	angular coordinate
Φ	function defined by Eq. (65)
ω	perturbation growth rate
τ	dimensionless time

Subscripts

ad	adiabatic
e, ef	effective value
f	fluid
in	at the inlet
m	maximal
C	mass
T	temperature
0	reference value
$\perp$	transversal

Superscripts

in	inner
lim	limiting
out	outer
simul	simulated
$*$	threshold

The simplest mathematical model that captures the main properties of PBRs is a pseudo-homogeneous model (i.e. interphase gradients of mass and heat are ignored), with "frozen hydrodynamics" (i.e. with constant axial velocity), accounting for two variables: temperature (T) and concentration of a limiting species (C).

The two-variable RD and RDA systems are known to exhibit transversal instabilities of two types: (i) Turing-like instability [10] can emerge if the ratio of the inhibitor to activator diffusivities exceeds a certain critical value, (ii) Instability due to kinetic effects that can emerge even in the limiting case of a non-diffusive inhibitor [6].

Instability of the first type was studied in a pioneering work of Sivashinsky [11] on cellular front propagation in a stationary gas, showing the bifurcation condition to be

$$\rho C_p D_i/k > 1 \tag{1}$$

Similarly, in a reaction–diffusion (RD) system with a formal cubic kinetics patterns can emerge if the ratio of the diffusion coefficients of the inhibitor (D_{inh}) to the activator (D_{act}) exceeds a certain critical value ($\simeq$2.3). This bifurcation condition was verified for different RD models both by experiments [12,13] and by numerical simulations [14–17].

The second type of instability takes place if the 1-D front exhibits an oscillatory behavior and is less relevant to packed beds, with the class of models considered here, since oscillatory behavior does not emerge due to the large heat capacity.

Linear stability analysis (LSA) of the 1-D solution is used as the main tool to predict the system behavior [6]. The dispersion relation curves showing the growth rate (ω) dependence on the wave number (k) exhibit qualitatively different behavior for the two cases: For the oscillatory 1-D behavior $\omega(k)$ is typically complex and the system admits Hopf bifurcations yielding formation of moving transversal patterns. For diffusive patterns $\omega(k)$ is typically real within the instability domain and exhibits a well-distinguished maximum which predicts formation of stationary patterns. This issue was intensively studied for various homogeneous models. A comprehensive study of a three-variable system is outlined in Ref. [18] accounting for two ratios of the diffusivity to the conductivity ($\rho c_p D_i/k$) associated with the fuel and the inhibitor.

Pseudohomogeneous and heterogeneous thermokinetic PBR models were used in several numerical studies [19–24]. Analytical criteria concerning transversal instability, using even simplified pseudohomogeneous models, are more difficult to derive (compared with the models considered above) due to the following peculiar features: (i) the maximal temperature rise over the front depends on the front velocity and both are not defined analytically, (ii) the time scales of the activator (T) and the inhibitor differ by several orders of magnitude due to the large ratio of solid to gas phase heat capacities (Le^* number). Note, that the latter feature practically eliminates the instability of kinetic type that can emerge in PBRs with oscillatory kinetics. Such a model was considered in our previous papers [25,26] and is not addressed here.

Analysis of transversal instability of planar fronts was mainly conducted by numerical simulations. Transversal patterns were simulated with sufficiently large $Pe_{T\perp}/Pe_{C\perp}$ where Pe_T and Pe_C are the heat and the mass Peclet numbers defined below, respectively (the symbol $\perp$ marks the transversal direction). For example, stationary ("frozen") patterns were simulated [19] with a three-variable (two species and temperature) pseudohomogeneous model and the Langmuir–Hinshelwood kinetics with $Pe_{T\perp}/Pe_{C\perp} > 2$. Studies of heterogeneous models showed that the interphase heat and mass transfer resistances had a major influence on the occurrence of transversely non-uniform states and can significantly extend the instability domain [22]. However, such effects can be accounted only by numerical simulations.

The first analytical result of transversal instability in PBRs was obtained using a simplified shallow reactor model [27] that is valid