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Heat and mass transport in a nonlinear fixed-bed catalytic reactor: Hot spots and thermal runaway

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ABSTRACT

Transient heat and mass transport in a wall-cooled tubular catalytic bed reactor is numerically investigated. A two-dimensional pseudo-heterogeneous model, accounting for transport in the solid and fluid phases, with axial and radial dispersions is used to describe transport in the reactor. The effects of inlet process conditions, viz., temperature and concentration, are investigated and their impact on the development of thermal runaway and hot spots in the reactor is analyzed. Under typical process conditions the calculation results show the development of a hot spot downstream the reactor inlet. At reduced feed temperature thermal runaway develops for an inlet concentration of 0.505 mol/m^3. A criterion for thermal runaway limit has been developed whereby runaway can be detected at a point in time during the process when the time derivative of temperature increases monotonously with time throughout the bed. Under low feed concentration and temperature a simpler pseudo-homogeneous model can be used to describe the reactor.

1. Introduction

Fixed-bed catalytic reactors serve as the workhorse of the chemical industry with widespread use in economic sectors of vital importance such as petroleum refining, chemicals manufacturing, and environmental clean-up. Exothermic reactors, such as those used for oxidation and hydrogenation reactions, are generally operated under process conditions that potentially give rise to a rich palette of nonlinear behaviors, e.g., multiple steady-states, hot spot, and runaway. These are fundamentally due to strong feedback mechanisms between various transport phenomena – namely, heat and mass transfers – and chemical reaction kinetics, and depend on operation conditions, e.g., see [1–4] and references therein. While fixed-bed reactors, relatively to other types of catalytic reactors, are flexible, efficient, low-cost, and require low maintenance, their most serious disadvantage is poor heat transfer with attendant poor temperature control [4]. Heat transfer and temperature control can be facilitated through external or internal heat exchange and a judicious choice of process parameters. Owing to the large number of design parameters in such processes there has been a concerted research effort to gain a better understanding of their behaviors and performance. While the rate of chemical reactions is generally a complex exponential function of temperature, if no or inadequate cooling is applied to the reactor, the temperature will increase very rapidly along the reactor potentially resulting in a temperature spike or hot spot [5]. This phenomenon can cause damage to both catalyst (via sintering) and reactor vessel (via thermal stresses). Consequently, the operation of such processes may incur high maintenance costs, staggering safety, and loss in productivity. Process selectivity may also deteriorate through the initiation of undesired side chemical reactions. In addition to the development of a hot spot in the reactor, the latter can also be prone to large parametric sensitivities, or thermal runaway, due to the inherent feedback mechanism. However, running the reactor near thermal runaway conditions is potentially advantageous to the catalytic process as it may result in optimum reactor operation. This is especially attractive if energy savings can be attained.

Experimental observations of nonlinear behaviors in catalytic reactors are still scarce. Hot spots have been reported in commercial packed-bed reactors [6,7], and recently rotating thermal patterns have been observed on a cylindrical surface with radial flow catalyzing carbon monoxide oxidation on a platinum/alumina catalyst [8]. Difficulties encountered in experimental observation of nonlinear behaviors have triggered an increasing need for a fundamental understanding of catalytic reactors using mathematical modeling. There are two main categories of reactor models in use: the homogenous model in which gradients between the phases are neglected, and the heterogeneous model, which accounts for both phases and transport exchange between them. Both models are based on the volume averaging of constitutive transport equations

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Nomenclature

a	specific area (m^2/m^3)
Bi	Biot number (−)
cp	heat capacity (J/K/mol)
C	dimensionless molar concentration (−)
D	diffusivity (m^2/s)
Da	Damköhler number (−)
E_a	activation energy (J/mol)
ΔH_r	heat of reaction (J/mol)
ΔH_i^{ads}	heat of adsorption of i (J/mol)
k	thermal conductivity (W/m/K)
L	reactor length (m)
p, p_i	pressure, partial pressure (Pa)
Pe	Peclet number (−)
r	radial coordinate (−)
R	dimensionless reaction rate (−)
$\Re$	reaction rate (mol/kg/s)
Re	Reynolds number (−)
R_g	gas constant (J/K/mol)
R_t	tube radius (m)
St	Stanton number (−)
t	dimensionless time (−)
T	temperature (K)
u_o	fluid superficial velocity (m/s)
z	axial coordinate (−)

Greek letters

ε	void fraction (−)
ν	CO stoichiometric coefficient (−)
θ	dimensionless temperature (−)
$\Delta\theta^*_{ad}$	adiabatic temperature rise (K)
ρ	density (kg/m^3)

Subscripts

a	axial
eff	effective
f	fluid
h	heat
i	species i
in	inlet
m	mass
p	particle
r	radial
s	solid
t	tube

Superscripts

ads	adsorption
*	absolute quantity
◦	pre-exponential constant

[9]. Generally, homogeneous models, due to their relative simple numerical implementation, have been used most for the description of fixed-bed reactors but not without serious shortcomings, especially when inter-phase thermal and concentration gradients exist. In a previous study of a fixed-bed reactor, with the same model reaction as the one used in the present work and at reactor inlet temperature of 385 K, a pseudo-homogeneous model without axial dispersion was found to be inadequate to describe the thermal behavior of the reactor [10]. In the present work we extend the previous study by using a transient pseudo-heterogeneous model to describe transport in the reactor under various reactor inlet conditions. The pseudo-heterogeneous model, which recognizes the two-phase nature of the system, is more suitable than the pseudo-homogeneous model. The effective transport parameters in this model still lump the heat transport in both phases, whilst the reaction rate is calculated using the temperature of the solid phase [11].

This study aims at investigating transient heat and mass transport in a two-dimensional tubular fixed-bed catalytic reactor using numerical modeling. The effects of process conditions, namely temperature and concentration, at the reactor inlet are investigated and their impact on the dynamic behavior of the system in question is analyzed. The focus is on hot spot and thermal runaway development in the reactor. The suitability of a pseudo-homogeneous model for the description of transport in the reactor is also discussed.

2. Reactor model and data

2.1. Model formulation

The system consists of a packed bed of catalyst (s: solid phase, hereafter) and gaseous reactants (f: fluid phase, hereafter). The reactor tube is placed in a cooling jacket. A simple cross-sectional view of the reactor system is illustrated in Fig. 1. In the present work, we consider the well-documented exothermic oxidation reaction of carbon monoxide, CO, into carbon dioxide, CO_2, over copper chromite as the catalyst [10,12,13]. See the Appendix A for further details. The pseudo-heterogeneous model with axial dispersion describes the reactor via two partial differential equations, account-

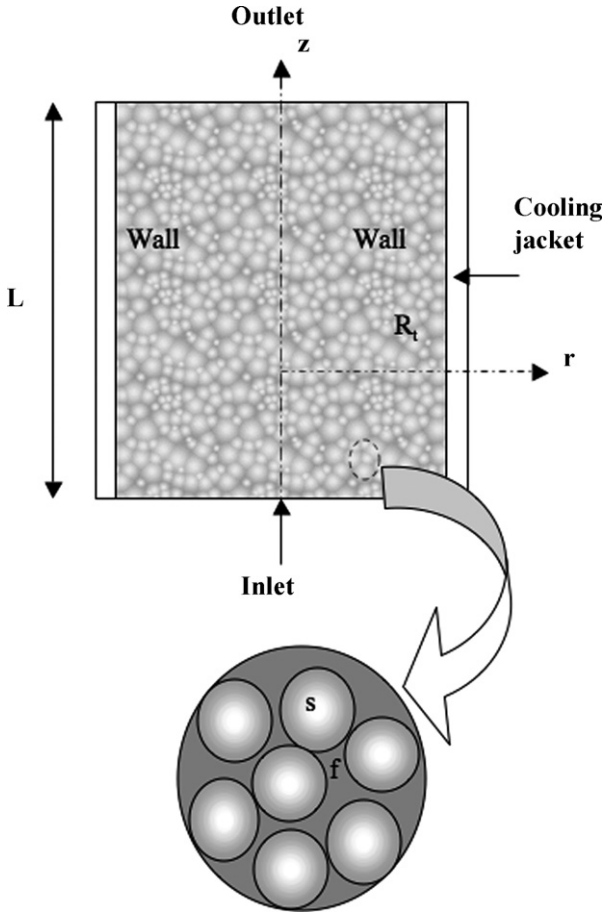

Fig. 1. Simplified schematics of the catalytic fixed-bed reactor.