Novel Scheme for Delaying Reverse-Flow Reactor Runaway

Jason M. Keith
Dept. of Chemical Engineering, Michigan Technological University, Houghton, MI 49931

The reverse-flow packed-bed reactor has been proposed for use in the chemical process industries because of its ability to store thermal energy within the bed (Boreskov and Matros, 1983). During periods of high fuel concentration, large thermal spikes may form within the reactor upon flow reversal. If the duration of high fuel concentration is large, thermal runaway may result since the spikes grow in magnitude upon each other. A new scheme is proposed here which strategically reduces the flow reversal time with each half-cycle in order to utilize the entire bed to store thermal spike energy. Alternatively, the principles outlined here can be used to reduce the startup time of reverse-flow reactors.

Reverse-Flow Reactor Operation

In this study, numerical simulations of reverse-flow reactor dynamics are presented. The analysis begins with the governing thermal energy and fuel concentration conservation equations while invoking a pseudohomogeneous model (Eigenberger and Nieken, 1988)

$$\frac{\partial T}{\partial t}+\frac{U}{\gamma}\frac{\partial T}{\partial x}=\alpha\frac{\partial^2 T}{\partial x^2}-\frac{\Delta H R'}{(\rho C_p)_s} \tag{1}$$

for thermal energy conservation where $\gamma=(1-\epsilon)(\rho C_p)_s/(\epsilon(\rho C_p)_g)$ is the solid/gas capacitance ratio and

$$\epsilon U\frac{dC}{dx}=-(1-\epsilon)R' \tag{2}$$

for the fuel conservation, where quasi-steady dynamics are assumed as the concentration rapidly equilibrates in comparison to the thermal equilibration time scale. As a model problem, this study shall utilize parameters from the reverse-flow CO oxidation reactor of Purwono et al. (1994), where R' is measured in mol/m$^3-$s

$$R'=\frac{k_o e^{E_1/RT}CT}{(1+KCTe^{E_2/RT})^2} \tag{3}$$

Table 1. Material Properties

Parameter	*Identification*	*Value*
C_o	Feed concentration	2.5×10^{-1} mol/m^3
E_1	Activation energy parameter	-3502 J/mol
E_2	Activation energy parameter	5451 J/mol
ΔH	Heat of reaction	-2.83×10^5 J/mol
k_o	Pre-exponential parameter	2.11×10^{-2} s$^{-1}\cdot$K^{-1}
K	Pre-exponential parameter	6.29×10^{-4} m^3/mol$\cdot$K
$\langle k\rangle$	Mean reaction rate constant	3.05 s^{-1}
L	Reactor length	6.0 m
l_{rxn}	Characteristic reaction length	0.39 m
Pe	Peclet number, $Pe=UL/\gamma\alpha$	2.0×10^4
R	Gas constant	8.314 J/mol$\cdot$K
t_f	Thermal front time	12,000 s
t_{rxn}	Time to form thermal spike	780 s
T_{crit}	Critical reactor temperature	1,000 K
T_{in}	Feed temperature	400 K
ΔT_{ad}	Adiabatic temperature rise	111 K
U	Gas velocity	2.2 m/s
α	Thermal diffusivity	1.5×10^{-7} m^2/s
γ	Solid/gas capacitance ratio	4.4×10^3
ϵ	Bed void fraction	0.35
$(\rho C_p)_g$	Gas heat capacitance	6.36×10^2 J/m$^3\cdot$K
$(\rho C_p)_s$	Solid heat capacitance	1.51×10^6 J/m$^3\cdot$K

Table 1 lists important model parameters for the simulations presented here. Since packed beds generally operate with large values of the Peclet number $Pe = UL/\gamma\alpha$ (here, $Pe = 2.0\times10^4$), axial thermal dispersion in the bed is negligible compared to axial convection and the second derivative term in Eq. 1 can be ignored giving rise to a hyperbolic system

$$\frac{\partial T}{\partial t}+\frac{U}{\gamma}\frac{\partial T}{\partial x}=-\frac{\Delta H R'}{(\rho C_p)_s} \tag{4}$$

The above equation can also be derived from a heterogeneous model with separate conservation equations for the thermal energy in both the gas and solid phases in the bed and assuming instantaneous equilibration between them.

During rich fuel periods, thermal spikes can form within the reverse-flow reactor, as seen in Figure 1. The physical mechanism for thermal spike formation is akin to wrong-way behavior (Oh and Cavendish, 1982; Pinjala et al., 1988). If the rich fuel persists, thermal runaway can occur quite read-

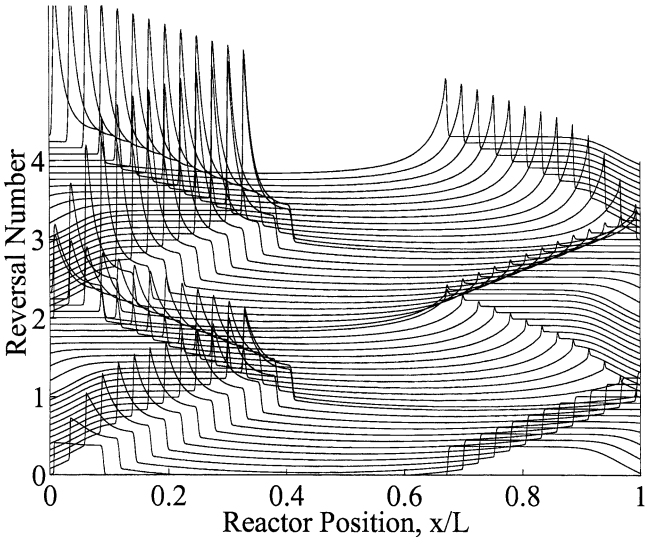

Figure 1. Performance of reverse-flow reactor during extended rich feed.

The time elapsed between snapshots of the simulated thermal profile is 1/13th of a half-cycle. Note that the maximum temperature grows with each full cycle.

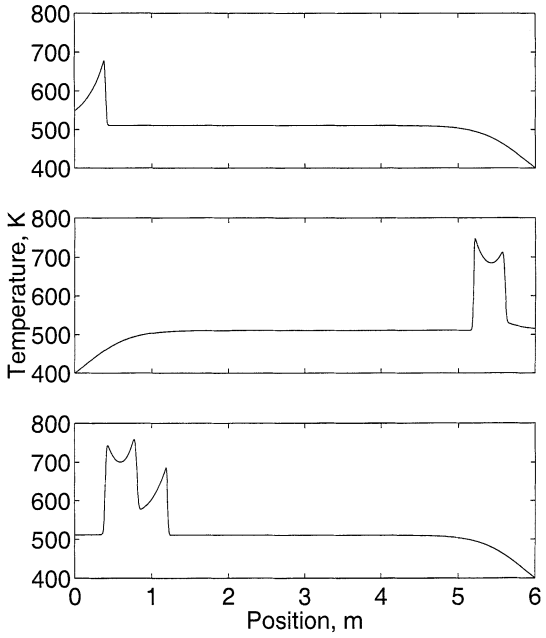

Figure 2. Temperature profiles within the reverse-flow reactor.

(a) Snapshot after the completion of the first half-cycle where one spike is present (gas flow right to left, $t^1_{\text{rev}} = 11{,}220$ s, elapsed time $t_{\text{total}} = 11{,}220$ s). (b) Snapshot after the completion of the second half-cycle where two spikes are present (gas flow left to right, $t^2_{\text{rev}} = 10{,}440$ s, elapsed time $t_{\text{total}} = 21{,}660$ s). (c) Snapshot after the completion of the third half-cycle where three spikes are present (gas flow right to left, $t^3_{\text{rev}} = 9{,}660$ s, elapsed time $t_{\text{total}} = 31{,}320$ s).

ily upon consecutive flow reversals (after an elapsed time of about 1.0×10^4 s, assuming a typical reversal time of 3.6×10^3 s).

New Dynamic Strategy for Reverse-Flow Reactors

A key parameter of interest in reverse-flow reactors is the reaction length l_{rxn} over which the concentration is depleted

$$l_{rxn} = \epsilon U/(1-\epsilon)\langle k\rangle \tag{5}$$

where $\langle k\rangle$ is a mean reaction rate which can be estimated by the following formula (Keith et al., 1999)

$$\langle k\rangle = \frac{\int_{T_{in}}^{T_{in}+\Delta T_{ad}} k dT}{\Delta T_{ad}} \tag{6}$$

The reaction length l_{rxn} also serves as an estimation of the width of a thermal spike within the packed bed.

During the new strategy, one begins by operating at the residence time that it takes a thermal front to pass through the reactor $t_{\text{rev}} = t_f = L\gamma/U$. The key principle used in invoking the new strategy is recognizing that the spikes are of a characteristic width l_{rxn}. Thus, it is the aim of the design to pack multiple spikes within the bed by reducing the characteristic flow reversal time t_{rev} for the next half-cycle by the time it takes a thermal front to move a distance l_{rxn}, which is equal to $t_{rxn} = l_{rxn}\gamma/U$. Thus, the reversal time during half-cycle i should be adjusted according to the following schedule

$$t^i_{\text{rev}} = t_f - i\cdot t_{rxn} \tag{7}$$

The number of half cycles that the reactor can be operated without experiencing a potential for runaway (defined here as when thermal spikes grow on top of each other and exceed a critical temperature $T_{\text{crit}} \sim 1{,}000$ K) is equal to $L/l_{rxn} - 1 \sim 14$ half cycles. Figure 2 shows the temperature profile within the bed at the completion of the first, second, and third half-cycles, illustrating the mechanism by which the spikes traverse the reactor length, packing themselves inside of the reactor. Meanwhile, Figure 3 shows the temperature profile after the fourteenth half cycle. The total amount of time before runaway can be estimated from the sum

$$t_{\text{total}} = \sum_{i=1}^{L/l_{rxn}-1} t^i_{\text{rev}} = \frac{1}{2} t_{\text{rxn}} \left(\frac{L}{l_{rxn}}\right)\left(\frac{L}{l_{rxn}} - 1\right) \tag{8}$$

For the system being studied here, $t_{\text{total}} = 8.2 \times 10^4$ s, which is significantly longer than the 1.1×10^4 s typical of the standard reverse-flow with a constant t_{rev}, as seen in Figure 1. It is also clear to see from Figure 3 that the maximum temperature remains relatively unchanged after the first flow reversal when the first thermal spike is formed.

One could also invoke this strategy during reactor startup to rapidly heat up the entire bed to a prescribed operating temperature, as opposed to using a constant reversal time. This is possible if the thermal dispersion within the bed is sufficient (Matros, 1985; Keith et al., 1999; Yakhnin and Menzinger, 1999). This new operating procedure uses con-

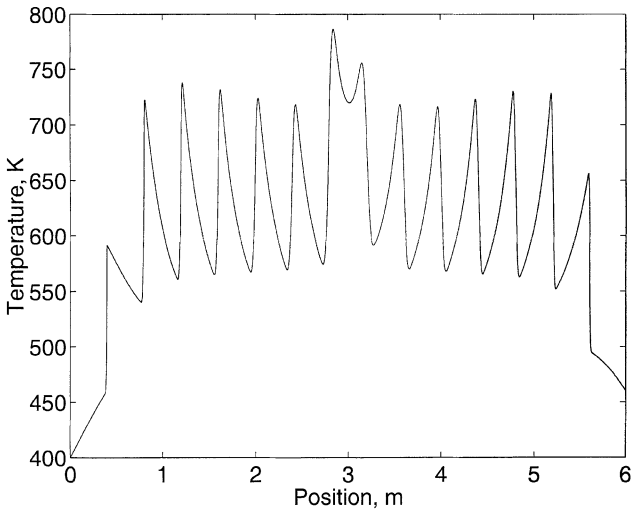

Figure 3. Temperature profile of the reverse-flow reactor after completing the 14th half cycle, where 14 spikes are present.

Gas flow right to left, t_{rev}^{14} = 1,080 s, elapsed time = 86,100 s. Thermal spikes are now distributed throughout the entire reactor length.

vection to heat the entire bed in 14 half-cycles. Keith et al. (1999) showed, for a constant reversal time, that the number of cycles required to heat up the bed center is dependent upon axial thermal dispersion and is on the order of 100 half-cycles. Operation under such a strategy could give a nearly uniform bed temperature while using less fuel to ignite the bed.

Conclusions

We have demonstrated the utility of varying the key operating parameter, the reversal time, within a packed bed in order to maintain thermal stability. Such a procedure can be invoked by measuring temperatures at a distance approximately equal to the reaction length l_{rxn} away from the ends of the bed in order to determine that the feed is fuel-rich. Another way of mitigating thermal spike formation within packed beds involves the placement of cylindrical metal rods within the bed (Keith et al., 1999; Keith, 2002) which in turn invokes a transient Taylor-Aris thermal dispersion mechanism (Taylor, 1953; Aris, 1956; Keith et al., 2001). Without having detailed data on transient temperature profiles, some thermal dispersion near the entrance should make it easier for the temperature sensors to detect these spikes and control the reactor.

Literature Cited

Aris, R. "On The Dispersion of a Solute in a Fluid Flowing Through a Tube," *Proc. of Royal Society of London*, **A235**, 67 (1956).

Boreskov, G. K., and Y. S. Matros, "Unsteady-State Performance of Heterogeneous Catalytic Reactions," *Catal. Rev.-Sci. Eng.*, **25**, 551 (1983).

Eigenberger, G., and U. Nieken, "Catalytic Combustion with Periodic Flow Reversal," *Chem. Eng. Sci.*, **43**, 2109 (1988).

Keith, J. M., D. T. Leighton, and H.-C. Chang, "A New Design of Reverse-Flow Reactors with Enhanced Thermal Dispersion," *Ind. and Eng. Chemistry Res.*, **38**, 67 (1999).

Keith, J. M., "Controlling Reverse-Flow Reactors via Multiscale Transient Thermal Dispersion," *Advances in Env. Res.*, in press (2002).

Keith, J. M., H.-C. Chang, and D. T. Leighton, "Designing a Catalytic Converter System," *AIChE J.*, **47**, 650 (2001).

Matros, Y. S. *Unsteady Processes in Catalytic Reactors*, Elsevier, Amsterdam (1985).

Oh, S. H., and J. C. Cavendish, "Transients of Monolithic Catalytic Converters: Response to Step Changes in Feedstream Temperature as Related to Controlling Automobile Emission," *Ind. and Eng. Chemistry Res.*, **22**, 29 (1982).

Pinjala, V., Y. C. Chen, and D. Luss, "Wrong-Way Behavior of Packed Bed Reactors: II. Impact of Thermal Dispersion," *AIChE J.*, **34**, 1553 (1988).

Purwono, S., et. al., "Runaway in Packed Bed Reactors Operating With Periodic Flow Reversal," *Chem. Eng. Sci.*, **49**, 5473 (1994).

Taylor, G. I., "Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube," *Proc. of Royal Soc. of London*, **A219**, 186 (1953).

Yakhnin, V. Z., and M. Menzinger, "Convective Instability and its Suppression in Packed-Bed and Monolith Reactors," *Chem. Eng. Sci.*, **54**, 4547 (1999).

Manuscript received Oct. 12, 2001, and revision received Feb. 13, 2002.