Approximate design of loop reactors

Olga Nekhamkina*, Moshe Sheintuch

Department of Chemical Engineering, Technion-I.I.T., Technion City, Haifa 32 000, Israel

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Abstract

A loop reactor (LR) is an $N$-unit system composed of a loop with gradually shifted inlet/outlet ports. This system was shown in our previous study [Sheintuch M., Nekhamkina O., 2005. The asymptotes of loop reactors. A.I.Ch.E. Journal 51, 224–234] to admit an asymptotic model for a loop of a fixed length with $N \to \infty$. Both the finite-unit and the asymptotic model exhibit a quasi-frozen or a frozen rotating pulse (FP) solution, respectively, within a certain domain of parameters that becomes narrower as feed concentration declines.

In the present paper we derive approximate solutions of the ignited pulse properties in an LR as a function of the external forcing (switching) rate. Analysis of these solutions enable us to determine the maximal temperature in the system, as well as the boundaries of the FP domain. For the optimal solution we determine the maximal temperature and conversion dependencies on the reactor length and on $N$.

The approximate solutions are verified by comparison with direct simulations of the asymptotic model and a good agreement was found. The obtained results can be successfully used for prediction of the finite unit LR.

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1. Introduction

The search for a technological solution for low-concentration VOC combustion has led to several conceptual solutions that combine a catalytic packed bed with enthalpy recuperation. The reverse-flow reactor (RFR), the best known example in this class, has been investigated for the past two decades and has been applied commercially. The loop reactor (LR), in the form of several units with gradual feed switching between them, has been conceptually proposed by Matros (1989) as one of the transient schemes that follow front propagation within the system. Such a reactor was numerically simulated for the case of two units (Haynes and Caram, 1994) or for three units (Brinkmann et al., 1999), for certain applications like VOC abatement and exothermic reversible reaction. The concept of LR has been extensively studied during the past five years focusing on the asymptotic solutions of its behavior (Sheintuch and Nekhamkina, 2005; Fissore et al., 2006a) as well as on its stability and dynamics (Russo et al., 2002; Altimary et al., 2006). The first experimental implementation of the LR was recently reported for an almost isothermal process (selective catalytic reduction, NH$_3$ + NO, Fissore et al., 2006b) and for the VOC combustion concept (ethylene oxidation, Madai and Sheintuch, in prep.).

In our recent study (Sheintuch and Nekhamkina, 2005) we demonstrated that there exists an asymptotic analytical solution by studying the LR of a fixed length ($L$) with increasing number of units ($N$) and by deriving an asymptotic (continuous) model for the case of infinitely large $N$. This model implies that increasing $N$ is accompanied by properly decreasing unit length $\Delta L = L/N$ and switching time $\tau_{SW}$, so that the switching velocity ($C_{SW} = \Delta L/\tau_{SW}$, i.e. unit length divided by switching time) is preserved. In such a case the LR can be described as a single unit of length $L$ with a moving feed/exit port at a position that follows $\zeta_{in} = \zeta_{in} + C_{SW} t$. It was shown that the asymptotic model (Sheintuch and Nekhamkina, 2005) can exhibit a rotating pulse solution, propagating with velocity $C_{SW}$, which is “frozen” in a rotating coordinate system within a certain domain of parameters. The finite-unit model (Haynes and

* Corresponding author. Tel.: +972 4 8293561.
E-mail addresses: aermwon@tx.technion.ac.il (O. Nekhamkina), cermsll@tx.technion.ac.il (M. Sheintuch).
Obviously, the front velocity cannot exceed the thermal front velocity \( V_{th} = v/Le \), which corresponds to an infinitely large temperature rise in the ideal front. Relatively simple integral balance relations were derived to determine \( T_m \) for a gas-less combustion (Zeldovich et al., 1959; Puszynski et al., 1987). Several attempts were made to account for the effect of convection in a catalytic bed (i.e., \( Le \gg 1 \)): Kiselev et al. (1980) and Kiselev (1993) using the narrow reaction zone assumption proposed by Frank-Kamenetski (1955) derived an approximate relation between \( T_m \) and \( V_{id} \) in the following dimensionless form:

\[
\frac{BPe_s (u - V_{id})^2}{(1 + y_m/\gamma)^2 Da \exp[y_m/(1 + y_m/\gamma)]} = 1 + \delta(y_m, V_{id}),
\]

where \( \delta(y_m, V_{id}) \) is a small term which can be neglected. Eqs. (1) and (2) allow to approximate the maximal temperature rise of an ideal front and its velocity. Kiselev’s approach (which has received little attention in the west) was successfully verified numerically (Burchardt et al., 1999).

In the present study we derived two approximate relations between the maximal temperature rise and the propagation velocity of a non-ideal front in a finite-length LR operating in the “frozen” mode following Kiselev’s approach and using the appropriate form of boundary conditions (BC). The first approximation is based on the assumption of the complete conversion at a point where the temperature achieves its maximum value (i.e. \( x_m(T_m) = 1 \) if \( T(T_m) = T_m \)), and differs from relation (2) only by additional terms on the right-hand side (RHS) that account the effect of BC. The second approach accounts for the incomplete conversion and includes an additional approximation with respect to \( x_m \). The obtained approximations are verified by comparison with direct simulations of the asymptotic LR model within a wide domain of operation conditions. In Section 5 we analyze the optimal solution, that is with \( C_{sw} = V_{th} \), that assures the highest temperatures and derive the relation between the maximal temperature and the exit conversion with the reactor length and the number of units. Thus, these approximations provide an easy approach for crude design, which should be fine-tuned by direct simulations.

The structure of this work is the following: in the next section we review the asymptotic LR model formulated in our previous study (Sheintuch and Nekhamkina, 2005). In the third section the approximate relations showing the effect of the switching velocity on the maximal temperature rise and the boundaries of the slow-switching domain are derived. These relations are verified in the fourth section by comparison with the direct simulation results of the asymptotic LR model within a wide domain of operation conditions following by brief recommendation concerning their implementation.

### 2. Reactor models

We limit our study to generic first-order activated and exothermic reactions with the Arrhenius kinetics (\( r = A \exp(-E/RT)C \)). To a first approximation the transport coefficients (\( k_e, D_f \)) and thermodynamic parameters (\( \rho, c_p \)) are assumed to be constant. With these assumptions the enthalpy

\[
\begin{align*}
\Delta T_m &= T_m - T_0 = \Delta T_{ad} \frac{v - V_{id}}{v - LeV_{id}}, \\
V_{id} &= \frac{\Delta T_m - \Delta T_{ad}}{Le\Delta T_m - \Delta T_{ad}}.
\end{align*}
\]
and mass balances may be written in the following dimensionless form:
\[ \frac{d\xi}{d\tau} + \frac{1}{Pe_x} \frac{d^2\xi}{d\zeta^2} = Da(1 - x) \exp \left( \frac{\gamma y}{\gamma + y} \right) = B(1 - x) f(y), \tag{3} \]
\[ \frac{d\xi}{d\tau} + \frac{1}{Pe_y} \frac{d^2\xi}{d\zeta^2} = Da(1 - x) \exp \left( \frac{\gamma y}{\gamma + y} \right) = (1 - x) f(y), \tag{4} \]
with appropriate initial and boundary conditions. In the case of a once-through operation Danckwerts’ BC are typically employed
\[ \xi = \xi_{\text{in}}, \quad \frac{1}{Pe_y} \frac{d\xi}{d\zeta} = v(y - y^{\text{in}}), \quad \frac{1}{Pe_x} \frac{d\xi}{d\zeta} = v(x - x^{\text{in}}), \tag{5} \]
\[ \xi = \xi_{\text{out}}, \quad \frac{d\xi}{d\zeta} = 0, \quad \frac{d\xi}{d\zeta} = 0. \]

Here conventional notation is used
\[ \tilde{\xi} = \frac{\zeta}{z_0}, \quad \tau = \frac{tu_0}{z_0}, \quad y = \frac{T - T_0}{T_0}, \quad x = 1 - C, \]
\[ v = \frac{u}{u_0}, \quad L = \frac{L}{z_0}, \]
\[ \gamma = \frac{E}{RT_0}, \quad B = \left( \frac{-\Delta H}{C_0} \right) \frac{\gamma}{(\rho C_p)f}, \quad Da = \frac{z_0}{u_0} A \exp(-\gamma), \]
\[ Le = \frac{(\rho C_p)T^2}{(\rho C_p) f}, \quad Pe_y = \frac{(\rho C_p)T^2 z_0 u_0}{k_e}, \quad Pe_x = \frac{(\rho C_p)T^2 z_0 u_0}{D}. \]

Note that we use arbitrary values for the velocity and the length scales \((u_0, z_0)\) in order to investigate the effect of length and velocity \((L, v)\) as independent parameters. Typically in our simulations, as well as in practical situations, \(Le \gg 1\) and \(Pe_y, Pe_x \gg 1\).

2.2. Asymptotic continuous model (infinite port model)

In the limiting case of an infinite-port LR \((N \to \infty)\) the stepwise functions \(\xi_{\text{in}}(\tau), \xi_{\text{out}}(\tau)\) can be replaced by continuously varying feed and exit positions described by the functions (Sheintuch and Nekhamkina, 2005)
\[ \tilde{\xi}_{\text{in}}(\tau) = \xi_{\text{in}}^0 - C_{sw}\tau, \quad \xi_{\text{out}}(\tau) = \xi_{\text{out}}^0 - C_{sw}\tau, \]
where the switching velocity \((C_{sw})\) is defined as \(C_{sw} = \Delta L / \tau_{sw}\).

In such a case it is convenient to transform the governing equations (3) and (4) using a moving coordinate system \((\tau' = \tau, \zeta = \xi - C_{sw}\tau)\) with fixed positions of the inlet and outlet:
\[ \frac{d\tilde{\xi}}{d\tau} + \frac{1}{(v - LeC_{sw}Pe_y)} \frac{d^2\tilde{\xi}}{d\zeta^2} \]
\[ = B(1 - x) \exp \left( \frac{\gamma y}{\gamma + y} \right) = B(1 - x) f(y), \tag{7} \]
\[ \frac{d\xi}{d\tau} + \frac{1}{(v - C_{sw}Pe_x)} \frac{d^2\xi}{d\zeta^2} \]
\[ = Da(1 - x) \exp \left( \frac{\gamma y}{\gamma + y} \right) = (1 - x) f(y). \tag{8} \]

Danckwerts’ BC conditions (see Eq. (5)) can be applied for the mass balance (8). For the energy balance in the case of slow switching the appropriate boundary conditions were shown (Sheintuch and Nekhamkina, 2005) to be
\[ \frac{1}{Pe_y} \left( \frac{\tilde{\xi}}{\xi_{\text{in}}} - \frac{\tilde{\xi}}{\xi_{\text{out}}} \right) = v(y - y^{\text{in}}), \quad y|_{\text{in}} = y|_{\text{out}}. \tag{9} \]
Note that the first of conditions (9) was derived as a simple combination of Danckwerts’ BC, while the second condition enable the formation of a pulse solution and was verified in our previous work by studying the convergence of the multi-port reactor solution to the asymptotic one with \(N \to \infty\).

3. Pulse characteristics

We derive now approximations for the maximal temperature rise \((\gamma_m)\) of the LR. Assuming a “frozen” solution in a moving coordinate system and ignoring the mass dispersion term (i.e. \(Pe_x \to \infty\)), we can rewrite Eqs. (7) and (8) in the following form:
\[ \frac{1}{Pe_y} \frac{d^2\tilde{\xi}}{d\zeta^2} - (v - LeC_{sw}) \frac{d\tilde{\xi}}{d\zeta} = -B(1 - x) f(y), \tag{10} \]
\[ (v - C_{sw}) \frac{d\xi}{d\zeta} = (1 - x) f(y), \tag{11} \]
\[ y(0) = y(L), \quad x(0) = 0, \quad \frac{1}{Pe_y} \{y(0) - y(L)\} = v[y(0) - y^{\text{in}}]. \tag{12} \]

Combining Eqs. (10) and (11) results in
\[ \frac{1}{Pe_y} \frac{d^2\tilde{\xi}}{d\zeta^2} - (v - LeC_{sw}) \frac{d\tilde{\xi}}{d\zeta} + B(v - C_{sw}) \frac{d\xi}{d\zeta} = 0. \tag{13} \]
Integrating this equation from $\zeta$ from 0 until $L$ yields
\[ \frac{1}{P_e y} \left[ y'_c(L) - y'_c(0) \right] + B(v - C_{sw}) x_{out} = 0, \] (14)
where $x_{out}$ denotes conversion at the reactor exit ($x_{out} = x(L)$). Comparing Eq. (14) and BC (12) we obtain
\[ y(0) = y^m + B \left( 1 - \frac{C_{sw}}{v} \right) x_{out}. \] (15)

Integrating Eq. (13) by $\zeta$ from 0 until $\zeta$ we get
\[ \frac{1}{P_e y} y''(v - LeC_{sw})y + B(v - C_{sw})x = -S_0, \] (16)
where
\[ S_0 = (v - LeC_{sw})y(0) - \frac{1}{P_e y} y''(0). \] (17)

Applying Eq. (16) at point $\zeta = \zeta_m$ corresponding to $y = y_m$ ($y'_m = 0$) with $x = x_m$ (we do not specify $x_m$ here) we obtain
\[ -(v - LeC_{sw})y_m + B(v - C_{sw})x_m = -S_0. \] (18)

It is also useful to write
\[ y'(0) = P_e y[B(v - C_{sw})x_m - (v - LeC_{sw}) (y_m - y(0))] \] (19)
and
\[ y'(L) = y'(0) - P_e yB(v - C_{sw})x_{out} \]
\[ = P_e y[B(v - c)(x_m - x_{out}) - (v - LeC_{sw})(y_m - y(0))]. \] (20)

Using an auxiliary relation
\[ B(v - C_{sw})x = \frac{x}{x_m} \left[ -S_0 + (v - LeC_{sw})y_m \right] \]
we can rewrite Eq. (16) as
\[ \frac{1}{P_e y} y''(v - LeC_{sw})y + \frac{x}{x_m} (v - LeC_{sw})y_m - \frac{x}{x_m} S_0 = -S_0 \]
or, with definition of a new variable $w = y/y_m$ as
\[ \frac{1}{P_e y} w'' - (v - LeC_{sw}) \left( w - \frac{x}{x_m} \right) = -S_0 \left( 1 - \frac{x}{x_m} \right) \frac{1}{y_m}. \] (21)

Combining this equation with Eq. (18) results in
\[ \frac{1}{P_e y} W'' = Bx_m \left( v - C_{sw} \right) \left( w - \frac{x}{x_m} \right) - \frac{S_0}{y_m} (1 - w). \] (22)

The maximal temperature of the forced front can be determined from Eqs. (11) and (22).

3.1. Complete combustion case $x_m = x_{out} = 1$

Following Kiselev’s approach (Kiselev, 1993) we can divide Eq. (11) by Eq. (22) resulting in
\[ \frac{dx}{dw} = \frac{y_m(1 - x) f(y_m w)}{(v - C_{sw}) P_e y [Bx_m (v - C_{sw}) (w - x/x_m) - S_0(1 - w)]}. \] (23)

Eq. (23) possesses a singularity at point $w = 1$, $x = x_m$. However, this expression becomes regular (see below) when $x_m = x_{out} = 1$ (the numerator and denominator tend to 0 simultaneously).

Note, that for the “ideal” front this assumption follows from the narrow reaction zone approach (Frank-Kamenetski, 1955) employed for an infinitely long system (Kiselev, 1993).

Assuming $x_m = 1$ we obtain
\[ \frac{dx}{dw} = p(w)g(w, x), \] (24)
where
\[ p(w) = \frac{y_m f(y_m w)}{P_e y B(v - C_{sw})^2}, \quad g(w, x) = \frac{1 - x}{(w - x) - S_0(1 - w)}, \]
\[ \tilde{S}_0 = \frac{S_0}{B(v - C_{sw})}. \] (25)

Now function $g(w, x)$ has a singularity if $(x, w) \to 1$, however the limit $g(w, x)$ as well as $dx/dw$ are finite
\[ \lim_{w, x \to 1} x' = p(1) \lim_{w, x \to 1} g(w, x) = p(1) \frac{-x'_w}{1 - x'_w + \tilde{S}_0} \]
So
\[ \lim_{w, x \to 1} x'_w = 1 + p(1) + \tilde{S}_0. \] (26)

Now we can estimate $g(w, x)$ around $w = 1$ (i.e. $y = y_m$), approximating $x(w) \simeq 1 - x'_w(1 - w)$
\[ g(w, x) \simeq \frac{x'_m(1 - w)}{w - 1 + x'_w(1 - w) - \tilde{S}_0(1 - w)} = 1 + \frac{1 + \tilde{S}_0}{p(1)}. \]

Integrating Eq. (24) by $dw$ $\int_{w(0)}^{1}$ and using the narrow zone assumption we obtain
\[ 1 \simeq \left[ 1 + \frac{1 + \tilde{S}_0}{p(1)} \right] \int_{w(0)}^{1} p(w) \ dw \]
\[ = \left[ 1 + \frac{1 + \tilde{S}_0}{p(1)} \right] \frac{y_m Da}{P_e y B(v - C_{sw})^2} \times \int_{0}^{1} \exp \left( \frac{y_m w}{\gamma + y_m w} \right) \ dw. \] (27)

To estimate the integral in the RHS of Eq. (27) consider the approximation of the power $(\gamma y_m w)/ (\gamma + y_m w)$ in the vicinity
\[ w = 1 \]
\[ \frac{y_m w}{1 + w y_m / \gamma} \simeq \frac{y_m}{1 + y_m / \gamma} + \frac{y_m (1 - w)}{(1 + y_m / \gamma)^2} + O((w - 1)^2). \]

So we have
\[ \int_{0}^{1} \exp \left( \frac{y_m w}{\gamma + y_m w} \right) \ dw \simeq \exp \frac{y_m}{1 + y_m / \gamma} \left( \frac{1 + y_m / \gamma}{y_m} \right)^2 \times \left[ 1 - \exp \left( -y_m[1 - w(0)] \right) \right]. \] (28)
and for large \( y_m \) the last term in the square brackets can be neglected in comparison with 1. Substituting this relation into Eq. (27) we obtain

\[
B Pe_y (v - C_{sw})^2 \left( 1 + y_m/\gamma \right)^2 Da \exp[ym/(1 + y_m/\gamma)] = 1 + \beta(y_m, C_{sw}), \quad (29)
\]

where

\[
\beta(y_m, C_{sw}) = \frac{1 + \bar{S}_0}{p(1)} = \frac{Pe_y (v - C_{sw}) (v - Le C_{sw})}{Da \exp[ym/(1 + y_m/\gamma)]}
\]

is a correction due to inhomogeneous BC. Note that Eq. (29) is reduced to the “ideal” front relation (2) if we set \( \delta = \beta = 0 \) and replace \( C_{sw} \) by \( V_{id} \).

3.2. Incomplete combustion case

Define conversion at the front (\( y = y_m \)) as \( x_m \equiv 1 - \varepsilon, \varepsilon > 0 \). In this case it is helpful to consider the inverse of Eq. (23), i.e.

\[
\frac{dw}{dx} = \frac{q(w, x)}{p(w)}, \quad (31)
\]

where \( p(w) \) is defined by Eq. (25) and

\[
q(w, x) = \frac{x_m (w - x/x_m) - \bar{S}_0 (1 - w)}{1 - x}, \quad (32)
\]

which can be reduced to \( 1/g(w, x) \) with \( x_m = 1 \). Now \( w'_m = 0 \) at \( \zeta = \zeta_m \) and \( w(x) \)-profile around this point approximately follows:

\[
w \simeq w_m + \frac{1}{2} w''_m (x - x_m)^2 + O((x - x_m)^3). \quad (33)
\]

Estimating \( w''_m \) using Eqs. (31) and (32) we obtain

\[
w''_m = \frac{1}{p(w)} \left. \frac{dq(w, x)}{dx} \right|_{w=1,x=1-\varepsilon} = -\frac{1}{\varepsilon p(1)}. \quad (34)
\]

Substituting this expression into Eq. (33) we obtain

\[
w(x) \simeq 1 - \frac{1}{2\varepsilon p(1)} (x - x_m)^2. \quad (35)
\]

Now we can estimate \( q(w, x) \) around \( \zeta = \zeta_m \)

\[
q(w, x) = \frac{x_m - x - (1 - u)(x_m + \bar{S}_0)}{1 - x} \\
\simeq \frac{(x_m - x)[1 - (x_m - x)(x_m + \bar{S}_0)] - 2\varepsilon p(1)}{x_m - x + \varepsilon}
\]

or

\[
q(w, x) = \frac{s(1 - ax)}{s + \varepsilon} = \tilde{q}(s), \quad (35)
\]

where

\[
s = x_m - x, \\
a = \frac{x_m + \bar{S}_0}{2\varepsilon p(1)} = \frac{(v - Le C_{sw})(v - C_{sw})}{2\varepsilon Da Pe_y \exp[ym/(1 + y_m/\gamma)]}, \quad (36)
\]

Integrating Eq. (31) and using the narrow zone assumption we obtain:

\[
J_L = \int_{w(0)}^{1} p(w) \, dw = \int_0^{x_m} q(w(x), x) \, dx \\
\simeq \int_0^{x_m} \tilde{q}(s) \, ds = J_R. \quad (37)
\]

The integral \( J_L \) in the LHS of Eq. (37) with the incorporation of Eq. (28) is

\[
J_L \simeq \frac{(1 + y_m/\gamma)^2 Da \exp[ym/(1 + y_m/\gamma)]}{B Pe_y (v - C_{sw})^2}, \quad (38)
\]

while integral \( J_R \) in the RHS of Eq. (37) accounts for corrections due to incomplete combustion \( \varepsilon \neq 1 \) and non-homogeneous BC

\[
J_R = \int_0^{x_m} \tilde{q}(z) \, dz \\
= x_m + \frac{ax_m (2\varepsilon - x_m)}{2} + (1 + a\varepsilon )x \ln \varepsilon. \quad (39)
\]

Now incorporating Eqs. (38) and (39) we find

\[
(1 + y_m/\gamma)^2 Da \exp[ym/(1 + y_m/\gamma)] \\
B Pe_y (v - C_{sw})^2 = x_m + \omega(x_m, y_m, C_{sw}). \quad (40)
\]

where

\[
\omega(x_m, y_m, C_{sw}) = \frac{ax_m (2\varepsilon - x_m)}{2} + (1 + a\varepsilon )x \ln \varepsilon, \quad (41)
\]

which differs from the corresponding relation for a complete combustion case (Eq. (29)) by RHs.

To determine the unknown \( x_m \) we can multiply both sides of Eq. (13) by \( \partial y/\partial \zeta \) and integrate by \( \zeta \) from 0 until \( \zeta_m \) yielding

\[
\frac{1}{2 Pe_y} \int_0^{\zeta_m} \frac{d}{d\zeta} (y^2_\zeta) d\zeta = (v - Le C_{sw}) \\
\times \int_0^{\zeta_m} y^2_\zeta \, d\zeta + B(v - C_{sw}) \int_0^{\zeta_m} y_\zeta x_\zeta d\zeta = 0 \quad (42)
\]

or

\[
-\frac{1}{2 Pe_y} (y^2_\zeta (0))^2 = (v - Le C_{sw}) \int_0^{\zeta_m} y^2_\zeta \, d\zeta \\
+ B(v - C_{sw}) \int_0^{\zeta_m} y_\zeta x_\zeta d\zeta = 0. \quad (43)
\]

To estimate the integral (\( J_1 \)) in the second term of Eq. (43) we can assume a parabolic profile \( y = y(\zeta) \) within interval \( \zeta \in [0, \zeta_m] \)

\[
y(\zeta) = y_m - A_1 (\zeta - \zeta_m)^2, \quad \zeta_m = 2 \frac{y_m - y(0)}{y'_\zeta(0)}, \quad A_1 = \frac{y'_\zeta(0)}{2 \zeta_m}. \quad (44)
\]
We checked the parabolic profile approximation Eq. (44) and found a good agreement with the simulations (Fig. 4c). Using Eq. (44) we obtain
\[ J_1 = \int_0^{\zeta_m} y^2 \, d\zeta = 4A_1 \frac{z_m}{3} \left( \zeta_m - \zeta_0 \right)^2 \left( \zeta_m - \zeta_0 \right) = \frac{8}{3} A_1 \frac{z_m^3}{3} \]
\[ = \frac{8}{3} \left[ y_m - y(0) \right] y(0). \]  
(45)
The integral \( J_2 \) in the third term of Eq. (43) after substituting of Eqs. (16) and (17) is reduced to
\[ J_2 = \int_0^{x_m} y \, dx = P e_y \left[ B(v - C_{sw}) \frac{y_m^3}{6} - (v - LeC_{sw}) \frac{y_m - y(0)}{y(0)} \right]. \]  
(46)

An inspection of the simulation results shows that the last term in the RHS of Eq. (46) is significantly smaller than the first one. Nevertheless, as is shown below, it is useful to take it into account using approximation (34), which results in a small correction of \( y_\zeta \) over the whole domain \( \zeta \in [0, \zeta_m] \). Thus,
\[ J_2 = P e_y \left[ B(v - C_{sw}) \frac{x_m^2}{2} - (v - LeC_{sw}) \frac{y_m - y(0)}{y(0)} \right]. \]  
(47)

Substituting Eqs. (45) and (47) into Eq. (43) we obtain
\[ \frac{1}{2} P e_y \left[ y_\zeta(0)^2 \right] - \frac{2}{3} (v - LeC_{sw}) [y_m - y(0)] y_\zeta(0) + \frac{P e_y}{2} \left[ B^2(v - C_{sw})^2 x_m^2 \right. \]
\[ - \frac{P e_y}{2} \left. B^2(v - C_{sw})^2 (v - LeC_{sw}) x_m^3 \right] \left[ \exp \left( y_m / (1 + y_m / y(0)) \right) \right] = 0 \]
(48)

and upon accounting for Eq. (19) the last equation is reduced to
\[ \left[ y_m - y(0) \right] \left( y_m - y(0) + 2B(v - C_{sw}) \right) \]
\[ = \frac{P e_y}{2} B^2(v - C_{sw})^2 x_m^3 \exp \left( y_m / (1 + y_m / y(0)) \right). \]  
(49)

The set of Eqs. (40) and (49) forms a system with respect to two unknown parameters \( y_m, x_m \) as functions of the switching velocity \( C_{sw} \).

As was pointed in Introduction, the “frozen” rotating solution can be maintained over a certain domain of switching velocities
\[ C_{sw}^{\min} < C_{sw} < C_{sw}^{\max}. \]  
(50)
The lower limit \( C_{sw}^{\min} \) can be estimated using the physically reasonable condition for \( y_\zeta(0) \) to be positive. Following Eq. (19) the necessary condition can be rewritten as
\[ B(v - C_{sw}) - (v - LeC_{sw}) \left[ y_m - y(0) - B(1 - C_{sw} / v) \right] > 0. \]  
(51)

Assuming \( C_{sw} \ll v \) (recall \( C_{sw} \sim O(v / Le) \) or \( 10^{-3} v \) in order of magnitude) this condition can be reduced to the following simplified form:
\[ C_{sw} > \frac{v}{Le} \frac{y_m - y(0) - B}{y_m - y(0) - B} = C_{sw}^{mn}. \]  
(52)
The upper limit \( C_{sw}^{\max} \) can be estimated using the other physically reasonable condition for \( y_\zeta(L) \) to be negative. An inspection of Eq. (20) shows that
\[ C_{sw}^{\max} = V_{th} / Le \quad \text{if} \quad x_{out} = x_m \]
and
\[ C_{sw}^{\max} = V_{th} \quad \text{if} \quad x_{out} > x_m. \]

Thus, assuming \( x_{out} > x_m \) (\( x_m < 1 \)), and using Eqs. (40), (49) and (20) we can derive the upper switching velocity boundary of the “frozen” pattern domain.

4. Comparison of analytical predictions and simulation results

To verify the approximations derived above we compare the predictions based on the assumptions of complete (Eq. (29), referred below as the first approach) and incomplete (Eqs. (40) and (49), the second approach) conversion with numerical simulations results for a set of parameters used earlier in a study of a flow reversal reactor (Eigenberger and Niienen, 1988): \( C_0 = 1.21 \times 10^{-4} \text{kmol/m}^3 \), \( E / R = 8000 \text{K} \), \( -\Delta H = 206000 \text{kJ/kmol}, A = 29732 \text{s}^{-1}, u_0 = 1 \text{m/s}, z_0 = 1 \text{m}, T_{in} = 293 \text{K}, D = 5 \times 10^{-3} \text{m}^2 / \text{s}, \kappa = 2.06 \times 10^{-3} \text{kW/m} \text{K}, (\rho C_p)_{x} = 0.5 \text{kJ/m}^3 \text{K}, (\rho C_p)_{e} = 400 \text{kJ/m}^3 \text{K} \), which result in \( \Delta H_{ad} = C_0 \Delta H / (\rho C_p)_{x} = 50 \text{kJ}, P e_y = 200; P e_x = 194; Le = 800 \) and \( B = B_0 = 0.523 \) (calculated with \( T_0 = 873 \text{K} \)). For this set the system attains an extinguished solution for the whole shown domain and we wish to predict the domain of ignited “frozen” pulse solutions.

4.1. Bifurcation diagram

We study the effects of switching velocity \( (C_{sw}) \), of feed concentration \( (B) \) and of convective velocity \( (v) \) on the sustained patterns.

Typical pattern transformation upon varying the switching velocity within FP domain is illustrated in Fig. 2 showing the temperature and conversion spatial profiles simulated with the asymptotic model in the moving coordinate system. The highest maximal temperatures are achieved around \( C_{sw} = V_{th} / Le \) for which the spatial profile (Figs. 2a and c) is linear both downstream and upstream of the reaction zone (peak point) since the heat is lost by conduction only (defined as “convection-less case” by Haynes and Caram, 1994). With increasing \( C_{sw} \) while \( C_{sw} < V_{th} \) the ignited front is shifted toward the reactor inlet (in a moving frame) and becomes steeper (Figs. 2a and b). This process is accompanied by increasing maximal temperature \( T_{m} \) with practically complete conversion (at \( z = z_m \) defined as point where \( T = 0.995T_m \) we have \( x_m \simeq x_{out} = 1 \)). The opposite
tendencies were detected in simulations with \( C_{sw} > V_{th} \); with increasing \( C_{sw} \) the “frozen” spatial profiles become smoother, the front (inflection point) is shifted downstream with respect to the reactor inlet (Figs. 2c and d) and \( T_m \) decreases. The conversion also declines and the temperature- and conversion-maximum locations (the last one can be defined as a point, where \( x = 0.99 x_{out} \)) diverge. Note that for most simulations conducted with \( C_{sw} > V_{th} \) we get a sufficiently high exit conversion (\( x_{out} > 0.95 \)) while \( x_m \) (at point \( T_m \)) can be significantly less than the maximal value.

Following the asymptotic model simulation results we can expect that approximations based on the assumption of complete conversion (\( x_m = 1 \), Eq. (29)) are suitable to predict solutions for \( C_{sw} < V_{th} \) while the second approach (Eqs. (40) and (49)) is more suitable for \( C_{sw} > V_{th} \). The analytically predicted lower switching boundary of the FP domain (\( C_{sw}^{mn} \) (Eqs. (29) and (52))) is in an excellent agreement with numerical simulation results (Figs. 3a and b). Velocity \( C_{sw}^{mn} \) gradually decreases with increasing \( B \) and intersects the ordinate-axis at \( B = B_{cr} \) (\( \simeq 13.8 B_0 \) for the parameters of Fig. 3a), i.e. beyond \( B_{cr} \) patterns can emerge in an LR without any forced switching (\( C_{sw} = 0 \)) and such a reactor can be constructed as a single section with properly matched inlet and outlet. (Actually a simple bed is ignited under these conditions.)

To calculate the upper boundary of the FP domain we set \( x_{out} = 1 \) (Eq. (20)) following the simulation results. The agreement between the asymptotic model results and \( C_{sw}^{mx} \) is satisfactory for low \( B \) (\( B \leq 4 \) in Fig. 3a), for larger \( B \) the results diverge.

With increasing convective velocity (\( v \)) the boundaries of FP domain defined via a normalized switching velocity \( C_{sw} = C_{sw}/V_{th} \) gradually approach each other (Fig. 3b) forming a cusp-like structure of the inverse form. Note that decreasing of the FP domain (\( \Delta C_{sw} \)) leads to drastic decrease of the switching time operation window

\[
\Delta \varepsilon_{sw} \sim \left( \frac{1}{C_{sw}^{mx}} - \frac{1}{C_{sw}^{mn}} \right) \frac{1}{C_{sw}^{2}} \}
\]

where \( (\bullet) \) denotes an averaged value over the switching domain.

### 4.2. Maximal temperature rise

The effect of the switching velocity \( C_{sw} \) on the maximal temperature rise is illustrated in Figs. 4 and 5 showing two sets of analytical predictions, based on the assumption of either complete (\( T_m^{(1)} \), Eq. (29), dashed lines) or incomplete (\( T_m^{(2)} \), Eqs. (40) and (49), solid lines) conversion. Direct numerical simulations (symbols) are presented also. Following the first approach the maximal temperature increases monotonically within the whole domain of \( C_{sw} > 0 \). Maximal temperature calculated by the second approach (\( T_m^{(2)} \)) exhibits a non-monotonic function of the switching velocity with maximum \( T_m \) beyond \( C_{sw} = V_{th} \). For all sets of parameters being considered we found that \( T_m^{(1)} > T_m^{(2)} \). The asymptotic model simulations exhibit maximal temperatures (\( T_m \)) that exceed \( T_m^{(1)} \) within subdomain \( C_{sw} < V_{th} \) and fall below \( T_m^{(2)} \) with \( C_{sw} > V_{th} \). The agreement between the asymptotic model and analytical predictions of \( T_m \) is satisfactory for low \( B \) and becomes poor with increasing \( B \).

To elucidate the reason of such distinctions we compare conversion \( x_m \) calculated by asymptotic model (7)–(9) with that of the incomplete combustion approach (Eqs. (40) and (49)). The “exact” (numerical) simulations revealed that \( x_m = 1 \) for most of the left part of the FP subdomain (i.e. with \( C_{sw} < V_{th} \)) and sharply decreases with increasing \( C_{sw} \) above \( V_{th} \) (Figs. 4b
Fig. 3. Comparison of the analytically (lines) and numerically (points) calculated boundaries of the FP domain in the $C_{sw}/V_{th}$ vs $B/B_0$ (a, $v = 1$) and the $C_{sw}/V_{th}$ vs $v$ (b, $B = 1$) planes. The lower switching boundary ($C_{mn}$, solid lines) is calculated using Eq. (29); the high switching boundary ($C_{mx}$, dashed lines) is calculated using Eqs. (20), (40) and (49) with $x_{out} = 1$. Other parameters as in Fig. 1.

Fig. 4. Comparison between the approximated (using Eq. (29) with $x_m = 1$, dashed lines or using Eqs. (40) and (49) with $x_m < 1$, solid lines) and “exact” numerical solutions (signs) calculated by asymptotic model (7) and (9). Plates (a) and (b) show the maximal temperature ($T_m$) and the corresponding conversion ($x_m$) as functions of dimensionless switching velocity ($C_{sw}/V_{th}$). Solutions of system (40) and (49) are shown for $V_{th} < C_{sw} < C_{mx}$. Numbers denote $B/B_0$-values, $v = 1$, other parameters as in Fig. 1.

Fig. 5. Comparison between the approximated (using Eq. (29), dashed lines; using Eqs. (40) and (49), solid lines) and “exact” solutions (signs) calculated by asymptotic model (7)–(9). Plate (a) shows the maximal temperature ($T_m$) of the FP as functions of varying dimensionless switching velocity ($C_{sw}/V_{th}$). Solutions of system (40) and (49) are shown for $V_{th} < C_{sw} < C_{mx}$. Numbers show $v$-values, $B = B_0 = 1$, other parameters as in Fig. 1.
and 5b). These results justify our previous assumption concerning preferential use of the first approach within subdomain $C_{sw} < V_{th}$, and of the second one within subdomain $C_{sw} > V_{th}$. Note, that conversion $x_m$ calculated with the incomplete conversion assumption (49) exhibits a non-monotonic function of the switching velocity with maximum $x_m$ around $C_{sw} = V_{th}$. The simulations are in a good agreement with the approximations near the boundary of the FP domain and becomes poor with decreasing $C_{sw}$.

4.3. Summary

Summarizing this comparison we can conclude that the two proposed analytical approaches assuming complete and incomplete conversion can be successfully used for prediction of the "frozen" rotating patterns within subdomains of $C_{swmin} < C_{sw} < V_{th}$ and $V_{th} < C_{sw} < C_{swmax}$, respectively. Derivation of a unique approach within the whole domain of the switching velocity will be a subject of the following study.

5. Optimal solution

Obviously, the optimal conditions are at $C_{sw} = V_{th} = v/Le$, which is within the FP domain and assures the highest temperature and a sufficiently high exit conversion. As was discussed below, in such a case the spatial temperature profile is linear both downstream and upstream of the reaction zone (which is narrow with respect to the reactor length). That allows to propose a relatively simple reactor design based on the piece-wise linear approximation of $y(z)$. Assuming $x_{out} = 1$ we can approximate the total balance equation (14) as

$$\frac{y_m - y(0)}{\varphi_m} - \frac{y(0) - y_m}{L - \varphi_m} = B Pe y v$$

or

$$y_m - y(0) = B Pe y v \varphi_m \left(1 - \frac{\varphi_m}{L}\right).$$

For the infinitely long system ($L \to \infty$) this relation is reduced to

$$\lim_{L \to \infty} y_m - y(0) = B Pe y v \varphi_m. \quad (54)$$

Noting that $\varphi_m$ varies only slightly with $L$ we set it constant at $\varphi_m = \varphi_m^\infty$, yielding

$$y_m^{\infty} - y(0) = B Pe y v \varphi_m^{\infty}.$$  

Similarly, we can estimate $x_m$ using the approximation of Eq. (20) and assuming $x_{out} = 1$

$$y'(L) \approx -\frac{y_m - y(0)}{L - \varphi_m} \approx B Pe y (x_m - 1),$$

or

$$x_m \approx 1 - \frac{y_m^{\infty} - y(0)}{Pe B v} \frac{1}{L - \varphi_m^{\infty}}. \quad (56)$$

To verify the obtained approximations we simulated the model with $C_{sw} = V_{th}$ for varying reactor length (Fig. 6a and b). The maximal temperature declines with $1/L$ (Fig. 6c) as predicted by Eq. (55). Linear extrapolation of the obtained results to $1/L = 0$ yields $T_m^{\infty}$ (marked by star in Fig. 6c). Using relation (56) and $T_m^{\infty} (y_m^{\infty})$ we can estimate the slope ($A_L$) of $x_m$ dependence on $1/L$. For the set of parameters employed in Fig. 6 we obtained $A_L = -0.10$ which is in a good agreement with the numerically calculated value $A_L^{num} = -0.093$. 

![Fig. 6. Effect of the reactor length (L) on the optimal solution ($C_{sw} = V_{th}$) showing spatial temperature (a) and conversion (b) profiles, and the maximal temperature (c) and the corresponding conversion (d) as functions of 1/L. The star in (c) marks $T_m^{\infty}$ obtained by linear extrapolation. $B = B_0 = 1$, $v = 1$, the other parameters as in Fig. 1.](image-url)
6. Concluding remarks

We have suggested an approximate procedure for designing an LR for simple irreversible exothermic reactions. It involves the following steps:

1. Determine the maximal operation temperature allowed in the system, and find the corresponding operating conditions (flow rate) that will maintain this temperature in the asymptotic \((N \rightarrow \infty)\) long reactor solution using Eq. (29) with \(C_{sw} = V_{th} = v/Le\).

2. Find the windows of switching velocities corresponding to these conditions from Eq. (50) and determine if this domain is too narrow or comfortable. In the former case, incorporate a control procedure to maintain it at the optimal value. Such control was suggested by Barresi et al. (1999) and it switched the port position as a feedback to the difference of the temperature at a certain position from its setpoint value.

3. Find the maximal temperature and the corresponding conversion dependencies on \(L\) (Eqs. (54)–(56)) and determine an acceptable reactor length.

4. Find the maximal temperature and the exit conversion dependencies on \(N\) and determine an acceptable number of units.

5. Proceed with detailed simulations of the reactor dynamics.

Notation

- \(a\) parameter defined by Eq. (36)
- \(A\) rate constant
- \(B\) dimensionless exothermicity
- \(c_p\) volume-specific heat capacity
- \(C\) key component concentration
- \(C_{p}\) heat capacity
- \(C_{sw}\) switching velocity
- \(D\) axial dispersion coefficient
- \(Da\) Damkohler number
- \(E\) activation energy
- \(g\) function defined by Eq. (25)
- \(\Delta H\) reaction enthalpy
- \(k_e\) effective conductivity
- \(\Delta L, L\) dimensionless length of a single unit and total reactor length
- \(Le\) Lewis number
- \(N\) number of the reactor units
- \(p\) fluid
- \(Pe_y, Pe_x\) Peclet numbers of heat- and mass dispersion
- \(q\) function defined by Eq. (32)
- \(r\) reaction rate
- \(S_0\) parameter defined by Eq. (17)
- \(t\) time
- \(T\) temperature
- \(u, v\) dimension and dimensionless fluid velocities
- \(V\) front velocity
- \(w\) dimensionless temperature
- \(x\) conversion
- \(y\) dimensionless temperature
- \(z\) spatial coordinate

Greek letters

- \(\gamma\) dimensionless activation energy
- \(\theta\) switching period
- \(\varepsilon\) \(1 - x_m\)
- \(\xi, \zeta\) dimensionless coordinate
- \(\rho\) density
- \(\tau\) dimensionless time

Subscripts

- \(ad\) adiabatic
- \(e\) effective value
- \(f\) fluid
- \(in\) at the inlet
- \(id\) ideal
- \(m\) maximal
- \(out\) at the outlet
- \(sw\) switching parameter
- \(0\) reference value

Superscripts

- \(in\) feed

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References


