

OPTIMAL TEMPERATURE AND FEED-RATE POLICIES FOR SYSTEMS WITH TWO REACTIONS

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Abstract: The optimization of batch process operation is a natural choice for reducing production costs, improving product quality, and meeting safety and environmental regulations. The optimal solution can be implemented easily if it is determined by the constraints of the optimization problem, i.e. it is not *inside* the feasible region. For semi-batch two-reaction systems, this paper provides conditions which guarantee that the optimal temperature and feed-rate policies be determined by path constraints. It is shown that, for the majority of two-reaction schemes, the optimal feed rate is indeed determined by constraints. The theoretical developments are illustrated by computing the optimal solution for three different examples.

Keywords: Batch processes, Semi-batch reactors, Dynamic optimization, Optimal temperature profile, Optimal feed-rate profile.

1. INTRODUCTION

Batch and semi-batch processes are of considerable importance in the batch chemical industry. A wide variety of specialty chemicals, pharmaceutical products, and polymers are manufactured in batch operations (Macchietto, 1998).

The operation of batch processes typically involves following recipes that have been developed in the laboratory. However, at the production level, operational decisions such as temperature and feed-rate profiles are subject to various technical and operational constraints regarding quality and safety aspects, for the satisfaction of which an optimization approach can be used (Wiederkehr, 1988; Marchal-Brassely *et al.*, 1992; Garcia *et al.*, 1995).

The optimization of dynamic systems with a finite terminal time typically results in a discontinuous solution that involves several intervals (Ray, 1981). These intervals are of two types, depending

on whether or not the solution therein is determined by active constraints such as input bounds, state and terminal constraints (Srinivasan *et al.*, 2002):(i) If the optimal solution is determined by a path constraint, the interval is referred to as a *constraint-seeking* interval; (ii) Otherwise, if the optimal solution is inside the feasible region in order to push the cost sensitivity to zero, the corresponding interval is labeled a *sensitivity-seeking* interval. An optimal solution that consists only of constraint-seeking intervals can be implemented easily through tracking of the active path constraints using on-line measurements (Visser *et al.*, 2000). Thus, it is of considerable interest to be able to provide conditions that guarantee that the optimal solution be on the boundary of the feasible region.

Whether or not the solution is determined by constraints depends on the compromises present in the optimization problem. These compromises stem from the individual inputs having multiple opposing effects on the objective function so that

intermediate values of the inputs are needed for the sake of optimality. This paper analyses if such compromises are ever possible in systems with two reactions. If there are no intrinsic compromise, the optimal inputs in each interval are determined by active path constraints (input bounds and state constraints).

Semi-batch reaction systems with two reactions are considered. The objective is to maximize some performance criterion such as productivity or product distribution at final time (Levien, 1992). Both the temperature and the feed rate are considered as manipulated inputs as they represent appropriate handles for dealing with productivity and selectivity aspects (Uhlemann *et al.*, 1994). Conditions that guarantee the absence of sensitivity-seeking arcs are presented. For the case of the temperature, these conditions are based on the sensitivity of the objective function with respect to the extents of the side reaction and the difference in activation energies. This work provides an analytical basis for some of the qualitative results presented in (Rippin, 1983; Uhlemann *et al.*, 1996). For the feed-rate policy, however, the derived conditions do not depend on the formulation of the optimization problem (terminal cost and constraints) but *only* on the dynamic model. It will be shown that, for the vast majority of semi-batch reaction systems with two reactions, the optimal feed rate is indeed determined by the constraints of the problem.

The paper is organized as follows. Section 2 briefly reviews the formulation of the optimization problem and the modeling of chemical reaction systems. The main theoretical results are stated in Sections 3 and 4 for the temperature and the feed-rate policies, respectively. Section 4 also presents a catalogue of semi-batch two-reaction systems with a clear indication on whether or not the optimal feed rate is determined by path constraints. Three examples are provided in Section 5 to illustrate the theoretical developments, and conclusions are drawn in Section 6.

2. PRELIMINARIES

2.1 Optimization of dynamic systems

A typical optimization problem that involves meeting certain specifications only at the *end* of the batch can be written as:

$$\max_{u(t)} J = \phi(x(t_f)) \quad (1)$$

$$s.t. \quad \dot{x} = f(x, u), \quad x(0) = x_0 \quad (2)$$

$$S(x, u) \leq 0, \quad (3)$$

where J is the scalar performance index to be maximized, x the state vector with the initial conditions x_0 , u the input vector, S the vector of path constraints that include state constraints and input bounds, f the smooth vector field describing the dynamics of the system, ϕ the smooth scalar function representing the terminal cost, and t_f the final time which can be either fixed or free.

To derive the conditions of optimality, Pontryagin's Maximum Principle uses the Hamiltonian (Bryson and Ho, 1975; Kirk, 1970)

$$H = \lambda^T f + \mu^T S \quad (4)$$

with

$$\dot{\lambda}^T = -\frac{\partial H}{\partial x} = -\lambda^T f_x - \mu^T S_x, \quad \lambda^T(t_f) = \phi_x|_{t_f} \quad (5)$$

where $\lambda(t) \neq 0$ are the adjoints (Lagrange multipliers for the system equations), and $\mu(t) \geq 0$ the Lagrange multipliers for the path constraints. The notation $a_b = \frac{\partial a}{\partial b}$ is used.

The *first-order necessary* conditions of optimality for Problem (1)-(3) can be obtained as:

$$H_u = \lambda^T f_u + \mu^T S_u = 0, \quad \mu^T S = 0 \quad (6)$$

The *second-order necessary* conditions of optimality require in addition that the second derivatives of the Hamiltonian be negative semi-definite:

$$H_{uu} = \lambda^T f_{uu} + \mu^T S_{uu} \leq 0 \quad (7)$$

The formulation (1)-(3) does not consider terminal constraints. These can be included by considering the augmented terminal cost $\bar{\phi}(x(t_f)) = \phi(x(t_f)) + \nu^T C(x(t_f))$ that combines the terminal cost ϕ and the terminal constraints C , where $\nu \geq 0$ are the Lagrange multipliers for the terminal constraints.

2.2 Model of chemical reaction systems

Consider a homogeneous, constant-density, semi-batch chemical reaction system comprising S species and R reactions. It is assumed that the reactor temperature is a manipulated variable. The component balances and total mass equations read:

$$\begin{aligned} \dot{n} &= K r_n(n, V, T) V + c_{in} F & n(0) &= n_0 \\ \dot{V} &= F & V(0) &= V_0 \end{aligned} \quad (8)$$

where n is the S -dimensional vector of numbers of moles, F the inlet volumetric flowrate, T the temperature, V the reactor volume, K the $S \times R$ stoichiometric matrix, r_n the R -dimensional reaction rate vector expressed in terms of n , c_{in} the molar concentrations of the inlet stream, n_0

the initial numbers of moles, and V_0 the initial volume. The terms $Kr_n V$ and $c_{in} F$ represent the effect of the reactions and the inlet stream on the numbers of moles, respectively. The molar concentrations are given by $c = n/V$.

Instead of using $(S + 1)$ states to represent the dynamic system as in (8), some *appropriate* extents of reaction can be used to represent the same system with only $(R + 1)$ states (Srinivasan *et al.*, 1998). The R -dimensional extent of reaction vector ξ is defined from the following relationship:

$$n = n_0 + K\xi + c_{in}(V - V_0) \quad (9)$$

Note that the elements of ξ are not dimensionless in the range $0 - 1$, but rather they express the changes in the numbers of moles due to the chemical reactions. Using (9) in (8) gives the $(R + 1)^{st}$ -order dynamic system with the inputs T and F :

$$\begin{aligned} \dot{\xi} &= r(\xi, V, T) V & \xi(0) &= 0 \\ \dot{V} &= F & V(0) &= V_0 \end{aligned} \quad (10)$$

where r is the reaction rate vector expressed in terms of ξ .

This study is limited to two-reaction systems. Among the two reactions, one is considered as the desired one, for which the objective function improves with the extent of reaction. The other reaction, which may or may not be desirable, is referred to as the side reaction. The two reactions are labeled $(\cdot)_d$ and $(\cdot)_s$, respectively. Thus, the three state variables are ξ_d , ξ_s and V , and the corresponding adjoint variables λ_d , λ_s and λ_V .

In addition, the following notations are used:

- A and B are the main reactants
- B is the reactant fed in the inlet steam with concentration $c_{B_{in}}$.
- X is another reactant present in the reactor.
- C and D are products.
- The desired reaction is represented by $a_d A + b_d B \rightarrow \gamma C$.
- The side reaction is represented generically by $a_s A + b_s B + c_s C + d_s D + x_s X \rightarrow \delta D$, although it involves only 1 or 2 reactants.

It is assumed that the two reaction rates obey *power-law kinetics*, i.e. $r_d = k_d c_A^{a_d} c_B^{b_d} > 0$ and $r_s = k_s c_A^{a_s} c_B^{b_s} c_C^{c_s} c_D^{d_s} c_X^{x_s} > 0$. Furthermore, the kinetic constant k_i , $i = \{d, s\}$, is assumed to be of the Arrhenius type, i.e. $k_i = k_{i0} e^{-\frac{E_i}{RT}}$ with k_{i0} the pre-exponential factor and E_i the activation energy. Upon expressing the concentrations in terms of ξ , the two reaction rates read:

$$r_d(\xi, V, T) = k_{d0} e^{-\frac{E_d}{RT}} \left(\frac{n_{A_0} + K_A \xi}{V} \right)^{a_d} \left(\frac{n_{B_0} + K_B \xi + c_{B_{in}}(V - V_0)}{V} \right)^{b_d} \quad (11)$$

$$r_s(\xi, V, T) = k_{s0} e^{-\frac{E_s}{RT}} \left(\frac{n_{A_0} + K_A \xi}{V} \right)^{a_s} \left(\frac{n_{B_0} + K_B \xi + c_{B_{in}}(V - V_0)}{V} \right)^{b_s} \left(\frac{n_{C_0} + K_C \xi}{V} \right)^{c_s} \left(\frac{n_{D_0} + K_D \xi}{V} \right)^{d_s} \left(\frac{n_{X_0} + K_X \xi}{V} \right)^{x_s} \quad (12)$$

where K_j is the row of the stoichiometric matrix corresponding to the j^{th} species, $j = \{A, B, C, D, X\}$.

3. OPTIMAL TEMPERATURE PROFILE FOR SYSTEMS WITH TWO REACTIONS

Equations (11)-(12) show that T appears nonlinearly in the system equations (10). Thus, the first-order necessary condition $H_T = 0$ contains T explicitly and can be used to determine T . This section exploits the first- and second-order necessary conditions of optimality, $H_T = 0$ and $H_{TT} \leq 0$, to provide sufficient conditions for the temperature to be determined by active path constraints, i.e. the optimal solution is on the boundary of the feasible region.

Theorem 1. For a two-reaction system, if the side reaction (i) does not worsen the objective function, $\frac{\partial \phi}{\partial \xi_s} \geq 0$, or (ii) does not have the largest activation energy, $E_s \leq E_d$, then the optimal temperature profile is necessarily on the boundary of the feasible region.

Proof (can be skipped without loss of continuity): The contraposition of the theorem will be proven, namely: If the optimal temperature profile is inside the feasible region, then the side reaction (i) worsens the objective function, $\frac{\partial \phi}{\partial \xi_s} < 0$, and (ii) has the largest activation energy, $E_s > E_d$.

The optimal temperature being inside the feasible region requires $\mu = 0$, i.e. no active path constraints. The first-order necessary condition then reads:

$$H_T = \lambda^T f_T = \left(\lambda_d \frac{\partial r_d}{\partial T} + \lambda_s \frac{\partial r_s}{\partial T} \right) V = 0 \quad (13)$$

It follows from (11)-(12), for $i = \{d, s\}$:

$$\frac{\partial r_i}{\partial T} = \frac{E_i r_i}{RT^2} \quad (14)$$

$$\frac{\partial^2 r_i}{\partial T^2} = \left(\frac{E_i - 2RT}{R^2 T^4} \right) E_i r_i \quad (15)$$

Using (14) in (13) gives:

$$\lambda_s = -\lambda_d \left(\frac{E_d r_d}{E_s r_s} \right) \quad (16)$$

The signs of λ_d and λ_s are studied next. Inside the feasible region ($\mu = 0$), the first two adjoint equations (5) read:

$$\dot{\lambda}_i = -\lambda_i \frac{\partial r_i V}{\partial \xi_i} - \lambda_k \frac{\partial r_k V}{\partial \xi_i}, \quad \lambda_i(t_f) = \frac{\partial \phi}{\partial \xi_i}(t_f) \quad (17)$$

for $i, k = \{d, s\}, i \neq k$ or upon using (16) in (17):

$$\dot{\lambda}_i = -\lambda_i \left(\frac{\partial r_i V}{\partial \xi_i} - \frac{E_i r_i}{E_k r_k} \frac{\partial r_k V}{\partial \xi_i} \right), \quad \lambda_i(t_f) = \frac{\partial \phi}{\partial \xi_i}(t_f) \quad (18)$$

This differential equation has the following analytical solution:

$$\lambda_i(t) = \lambda_i(t_f) e^{\int_t^{t_f} \left(\frac{\partial r_i V}{\partial \xi_i} - \frac{E_i r_i}{E_k r_k} \frac{\partial r_k V}{\partial \xi_i} \right) d\tau} \quad (19)$$

The exponential term is always positive and thus $\lambda_i(t)$ will have the sign of $\lambda_i(t_f) = \frac{\partial \phi}{\partial \xi_i}(t_f)$. Furthermore, $\lambda_d(t_f) = \frac{\partial \phi}{\partial \xi_d}(t_f)$ is positive by definition since the objective function improves with the extent of the desired reaction. Hence, $\lambda_d(t) > 0$ for all t . It follows from (16) that $\lambda_s(t) < 0$ for all t , and using the same argument, $\lambda_s(t_f) = \frac{\partial \phi}{\partial \xi_s}(t_f) < 0$. Thus, condition (i) is verified.

The second-order necessary condition leads to:

$$H_{TT} = \left(\lambda_d \frac{\partial^2 r_d}{\partial T^2} + \lambda_s \frac{\partial^2 r_s}{\partial T^2} \right) V \leq 0 \quad (20)$$

Substituting (15) and (16) into (20) gives:

$$H_{TT} = V \left(\frac{E_d r_d}{R^2 T^4} \right) \lambda_d (E_d - E_s) \leq 0 \quad (21)$$

Since E_d , r_d and λ_d are positive, (21) requires $E_s \geq E_d$. When $E_s = E_d$, $H_{TT} = 0$ and so are the further derivatives of H with respect to T . This situation corresponds to an inflexion point and not to a maximum. Thus, the optimum being inside the feasible region requires $E_s > E_d$, and condition (ii) is verified. \square

Figure 1 illustrates the solution type in terms of the sensitivity of the objective function with respect to the extent of the side reaction and the difference in activation energies.

Interpretation:

This result can be interpreted intuitively as follows. Suppose that the amount of material produced by the desired reaction has to be maximized in the presence of a side reaction that uses some of the reactant. With $E_d > E_s$, the differential selectivity of the desired reaction increases with

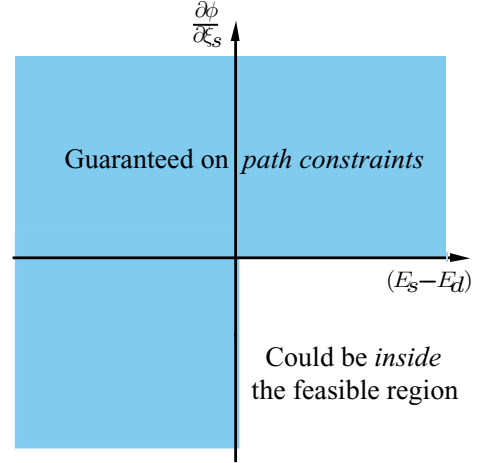


Fig. 1. Type of solution in terms of the sensitivity of the objective function ϕ with respect to the extent of the side reaction ξ_s and the difference in activation energies ($E_s - E_d$).

temperature. Since the productivity (extent of the desired reaction) also increases with temperature, it is best to keep the temperature at its maximum allowed value. On the contrary, if $E_s > E_d$, a compromise may occur since the temperature has to be increased for productivity and decreased for selectivity. All the two-reaction systems given in Tables 2 and 3 of (Rippin, 1983) can be analyzed rigorously using Theorem 1.

Remarks:

- (1) Theorem 1 involves the terminal cost $\phi(x(t_f))$ (and also possible terminal constraints via the augmented cost) but not the path constraints $S(x, u) \leq 0$. Thus, it is applicable to any type of path constraints (e.g. maximum heat generation, maximum or minimum concentrations, maximum cooling rate, etc.) and not only to bounds on T .
- (2) Theorem 1 indicates that if the side reaction worsens the objective function, $\frac{\partial \phi}{\partial \xi_s} < 0$, and has the largest activation energy, $E_s > E_d$, then there exists the possibility of a sensitivity-seeking interval. However, it has to be emphasized that this is only a possibility and not a guarantee that the solution will indeed be inside the feasible region. The guarantee of a sensitivity-seeking arc requires complete knowledge of the optimization problem (objective function as well as path and terminal constraints).
- (3) If the optimal temperature profile is inside the feasible region, it can be obtained as either a function of the adjoint variables or the solution of a differential equation. For the former case, the temperature profile can be calculated from (16) and r_d and r_s using explicit temperature dependency:

$$T = \frac{E_s - E_d}{R \ln \left(-\frac{\lambda_s E_s k_{s0} r_s k_d}{\lambda_d E_d k_{d0} r_d k_s} \right)} \quad (22)$$

To obtain a differential equation for T , (16) needs to be differentiated once with respect to time. Then, $\dot{\lambda}$ is obtained from (17), and \dot{r}_i , $i = \{d, s\}$, can be expressed as $\dot{r}_i = \frac{\partial r_i}{\partial \xi_d} \dot{\xi}_d + \frac{\partial r_i}{\partial \xi_s} \dot{\xi}_s + \frac{\partial r_i}{\partial V} \dot{V} + \frac{\partial r_i}{\partial T} \dot{T}$, with $\dot{\xi}_d$, $\dot{\xi}_s$, and \dot{V} taken from (10) and \dot{T} retained as a free variable. Using (16) again, the adjoint variables can be eliminated to give the following differential equation for the optimal temperature:

$$\dot{T} = -RT^2 \left(\frac{r_s}{E_d r_d} \frac{\partial r_d V}{\partial \xi_s} + \frac{r_d}{E_s r_s} \frac{\partial r_s V}{\partial \xi_d} + \frac{F}{(E_d - E_s)} \left(\frac{1}{r_d} \frac{\partial r_d}{\partial V} - \frac{1}{r_s} \frac{\partial r_s}{\partial V} \right) \right) \quad (23)$$

4. OPTIMAL FEED RATE FOR SYSTEMS WITH TWO REACTIONS

Unlike the temperature, the feed rate appears linearly in the system equations (10). Thus, the first-order necessary condition $H_F = 0$ is independent of F , which implies that H_F needs to be differentiated with respect to time to determine the optimal value of F . Moreover, if F does not appear in the successive time differentiations of H_F , the optimal solution will necessarily be on the boundary of the feasible region. This section presents the scenarios for which it can be guaranteed that the optimal solution is on the boundary of the feasible region.

Theorem 2. Consider a two-reaction system and let α_i be the total order of the i^{th} reaction, $i = \{d, s\}$. For the scenarios of Table 1, the optimal feed rate profile is on the boundary of the feasible region.

Scenario	a_d	b_d	α_s	b_s	$a_s \times c_s$
I	0,1	free	1	0	0
II	1	1	2	0	0
III	1	free	$b_d + 1$	b_d	0

Table 1. Scenarios for which the optimal feed rate is guaranteed to lie on the boundary of the feasible region.

Proof (can be skipped without loss of continuity): The proof proceeds by *contradiction*. With the assumptions that the optimal feed rate lies inside the feasible region and the reaction rates are strictly positive, it will be shown that the necessary conditions of optimality are inconsistent with these assumptions.

Let the optimal feed rate be inside the feasible region. Then, with $\mu = 0$, the first-order necessary

condition of optimality requires $H_F = \lambda^T f_F = \lambda_V = 0$. Since this condition is independent of F , taking its time derivative and using (5) gives:

$$\frac{dH_F}{dt} = \dot{\lambda}_V = -\lambda^T f_V = -\lambda_d \frac{\partial r_d V}{\partial V} - \lambda_s \frac{\partial r_s V}{\partial V} = 0 \quad (24)$$

Since (24) is still independent of F , it has to be differentiated further with respect to time:

$$\frac{d^2 H_F}{dt^2} = \lambda_d W_d + \lambda_s W_s - F \left(\lambda_d \frac{\partial^2 (r_d V)}{\partial V^2} + \lambda_s \frac{\partial^2 (r_s V)}{\partial V^2} \right) = 0 \quad (25)$$

with

$$W_i = \frac{\partial r_i V}{\partial \xi_d} \frac{\partial r_d V}{\partial V} + \frac{\partial r_i V}{\partial \xi_s} \frac{\partial r_s V}{\partial V} - \frac{\partial^2 r_i V}{\partial V \partial \xi_d} r_d V - \frac{\partial^2 r_i V}{\partial V \partial \xi_s} r_s V \quad (26)$$

for $i = \{d, s\}$. Solving (24) for λ_d and substituting it into (25) gives:

$$\frac{d^2 H_F}{dt^2} = \frac{\lambda_s}{\frac{\partial r_d V}{\partial V}} (\mathcal{W} - FC) = 0 \quad (27)$$

with

$$\mathcal{C} \equiv \frac{\partial (r_d V)}{\partial V} \frac{\partial^2 (r_s V)}{\partial V^2} - \frac{\partial (r_s V)}{\partial V} \frac{\partial^2 (r_d V)}{\partial V^2} \quad (28)$$

$$\mathcal{W} \equiv \frac{\partial (r_d V)}{\partial V} W_s - \frac{\partial (r_s V)}{\partial V} W_d \quad (29)$$

For the power-law kinetics (11) and (12), analytical expressions for the partial derivatives can be obtained:

$$\frac{\partial r_i V}{\partial V} = r_i \left(1 - \alpha_i + b_i \frac{c_{B_{in}}}{c_B} \right) \quad (30)$$

for $i = \{d, s\}$ and with

$$\alpha_d = a_d + b_d \quad (31)$$

$$\alpha_s = a_s + b_s + c_s + d_s + x_s \quad (32)$$

Similarly,

$$\frac{\partial^2 r_i V}{\partial V^2} = \frac{r_i}{V} \left(\alpha_i (\alpha_i - 1) - 2(\alpha_i - 1) b_i \frac{c_{B_{in}}}{c_B} + b_i (b_i - 1) \frac{c_{B_{in}}^2}{c_B^2} \right) \quad (33)$$

The stage is now set to show the contradiction in the scenarios of Table 1. The basic idea is the following: If the optimal feed rate lies inside the

feasible region, it should be possible to compute it from $H_F = 0$ and its time derivatives (Srinivasan *et al.*, 2002). It will be shown next that, in the three scenarios of Table 1, the input cannot be computed from the time derivatives of H_F . In the first and third cases, F has no effect on H_F and thus the necessary conditions cannot be used to determine F . In Scenario II, on the other hand, the system has to be on a surface to satisfy the necessary conditions of optimality, and this surface is shown to be infeasible.

- (1) *Scenario I: The side reaction is first order and does not involve the added species, i.e. $\alpha_s = 1$, $b_s = 0$.* From (30), $\frac{\partial r_s V}{\partial V} = 0$ for all t , which with (24) leads to $\lambda_d \frac{\partial r_d V}{\partial V} = 0$. It also follows that $\frac{\partial^2 r_s V}{\partial V^2} = \frac{\partial^2 r_s V}{\partial V \partial \xi_i} = 0$, which gives $\mathcal{C} = 0$ and $\mathcal{W} = \left(\frac{\partial r_d V}{\partial V}\right)^2 \frac{\partial r_s V}{\partial \xi_d}$. The choice $a_d = (0, 1)$ forces the term $\left(1 - \alpha_d + b_d \frac{c_{B_{in}}}{c_B}\right) = \left(1 - a_d + b_d \left(\frac{c_{B_{in}}}{c_B} - 1\right)\right)$ to be positive. Hence, $\frac{\partial r_d V}{\partial V} > 0$ and, from $\lambda_d \frac{\partial r_d V}{\partial V} = 0$, it follows that $\lambda_d = 0$ for all t . This implies $\dot{\lambda}_d = 0$, which together with (17) leads to either $\lambda_s = 0$ or $\frac{\partial r_s V}{\partial \xi_d} = 0$. If $\lambda_s = 0$, it follows from (27) that $\frac{d^2 H_F}{dt^2} = 0$ irrespective of the choice of F . If $\frac{\partial r_s V}{\partial \xi_d} = 0$, $\mathcal{W} = 0$ and, in this case too, $\frac{d^2 H_F}{dt^2} = 0$ follows irrespective of the choice of F . This means that F has no effect on H , which contradicts the assumption that the optimal feed rate can be determined from $H_F = 0$ and its time derivatives.
- (2) *Scenario II: The two reactions are second order, with the desired and side reactions being first- and zeroth-order with respect to the added species, i.e. $\alpha_d = \alpha_s = 2$, $b_d = 1$, $b_s = 0$.* Furthermore, A and C do not react with each other in the side reaction. For this scenario, it can be worked out using (28)-(33) that $\mathcal{C} = 0$ and

$$\mathcal{W} = -\frac{V c_{B_{in}}}{c_B^2} \left(c_B r_s^2 \frac{\partial r_d}{\partial \xi_s} - (c_{B_{in}} - c_B) r_d^2 \frac{\partial r_s}{\partial \xi_d} + \frac{r_d^2 r_s}{V} \right) \quad (34)$$

$\mathcal{W} \neq 0$ implies $\frac{d^2 H_F}{dt^2} \neq 0$, which contradicts (25) derived from the necessary conditions of optimality. It will be shown next that $\mathcal{W} = 0$ also leads to a contradiction. For this scenario, $\frac{\partial r_d}{\partial \xi_s} = -a_s \frac{r_d}{c_A V}$ and $\frac{\partial r_s}{\partial \xi_d} = -a_s \frac{r_s}{c_A V} + c_s \gamma \frac{r_s}{c_C V}$. Thus, $\mathcal{W} = 0$ implies:

$$a_s c_B r_s - (c_{B_{in}} - c_B) (a_s - c_s \gamma \frac{c_A}{c_C}) r_d - c_A r_d = 0 \quad (35)$$

Various cases for a_s need to be considered:

- $a_s = 0$: If $c_s = 0$, Condition (35) gives $r_d = 0$, which is inconsistent with the assumption that the reaction rates are strictly positive. For $c_s = 1$ or 2 , Condition (35) reduces to $c_C = c_s \gamma (c_{B_{in}} - c_B)$. Differentiating it with respect to time leads to $(c_s - 1) \gamma r_d + c_s r_s = 0$. Due to the positivity of r_d and r_s , the above condition is inconsistent with the assumptions.
 - $a_s = 1$: Since by definition of Scenario II, $a_s c_s = 0$, it follows that $c_s = 0$. Also, for the side reaction to be second order, $x_s = 1$ (or $d_s = 1$; in which case the proof is similar with X replaced by D). Differentiating (35) with respect to time gives $(c_{B_{in}} - c_B + c_A)(c_A + c_B) c_X r_d^2 + ((c_{B_{in}} - 2c_B + c_A) c_B c_X r_d r_s - c_B^2 (c_A + c_X) r_s^2) = 0$. Solving this along with (35) for c_A and c_B gives $c_A = 0$ or $c_B = 0$. This implies that the reaction rates are zero, which is inconsistent with the assumptions.
 - $a_s = 2$: It follows from $\alpha_s = 2$ that $c_s = 0$ and $x_s = 0$. Differentiating (35) with respect to time gives $(2c_{B_{in}}(c_A + c_B) + c_A^2 - 2c_B^2) r_d^2 + (c_A - 6c_B + 2c_{B_{in}}) c_B r_d r_s - 4c_B^2 r_s^2 = 0$. Solving this along with (35) for c_A and c_B gives $c_A = 2c_{B_{in}} \frac{2k_s - k_d}{k_d}$, and $c_B = 4k_s c_{B_{in}} \frac{k_d - k_s}{k_d^2}$. The fact that c_A is constant implies $r_d + 2r_s = 0$, which is inconsistent with the assumptions.
- (3) *Scenario III: The two reactions are of the same order and involve the added species in a similar way, i.e. $\alpha_d = \alpha_s$ and $b_d = b_s$.* Furthermore, A and C do not react with each other in the side reaction. Equation (30) implies $\frac{\partial r_i V}{\partial V} = r_i \kappa$, with κ a scalar factor independent of i . Then, (24) gives $\lambda_d r_d + \lambda_s r_s = 0$. This, together with $\lambda_V = 0$, gives $H = \lambda_d r_d V + \lambda_s r_s V + \lambda_V F = 0$ irrespective of the choice of F . This means that F has no effect on H , which contradicts the assumption that the optimal input can be determined from $H_F = 0$ and its time derivatives.

Thus, it has been shown by contradiction that, for the scenarios presented in Table 1, the solution is necessarily determined by the constraints of the optimization problem. \square

Interpretation:

Though the proof of the theorem is quite involved, the results can be interpreted fairly intuitively.

- First, the basic tradeoff introduced by a variation of F is discussed. The feed rate has two opposing effects on each reaction rate.

For example, feeding more B increases c_B and thereby also r_d . On the other hand, c_A is decreased due to dilution, thus decreasing r_d .

Mathematically, these two effects can be analyzed as follows: The input F has no direct effect on ξ_i as r_i does not depend explicitly on F . However, upon considering $\ddot{\xi}_i$, it is seen that F influences the reaction system in two ways: (i) through n_B weighted by b_i , and (ii) through V weighted by the reaction order α_i . Hence the importance of b_i and α_i in Table 1.

Since F influences each of the two reactions in two ways, it can have four different effects on the reaction system. If these four effects do not oppose each other, there is no need for F to look for a compromise, and the optimal solution will necessarily be on the boundary of the feasible region.

- Next, the opposing effects *within a reaction* are analyzed. Consider the reaction rate r_d . The influence of F on $\ddot{\xi}_d$ is through $\frac{\partial r_d V}{\partial V} = r_d b_d \left(\frac{c_{B_{in}} - c_B}{c_B} \right) + r_d(1 - a_d)$. Here, the first term that depicts the influence of F through the increase of c_B is always positive, while the effect of dilution (second term) can change sign as a function of a_d . So, in order to avoid compensation between the two terms, the effect of dilution on the reaction rate should not be negative, i.e. the stoichiometric coefficient a_d should not exceed 1.

There is no competition between the opposing effects of F within the side reaction if either $b_s = 0$ (Scenario I, II) or $a_s \leq 1$ (Scenario III).

- The competition *between the two reactions* is now considered. In Scenario I, the influence of F on $\ddot{\xi}_s$ is eliminated. With $\alpha_s = 1$, the effect of dilution does not exist. In addition, if $b_s = 0$, then $\ddot{\xi}_s$ is independent of F .

In Scenario II, only the dilution effect exists in $\ddot{\xi}_s$ since $b_s = 0$. For the dilution to have a similar effect on both reactions, the orders have to be the same, $\alpha_s = \alpha_d$. The condition $b_d = 1$ can be shown to arise from matching the third time derivatives $\xi_d^{(3)}$ and $\xi_s^{(3)}$. However, since this part is quite technical, it is not discussed here.

The four effects exist in Scenario III. In order for them not to compete, they need to be ‘similar’, i.e. $\alpha_s = \alpha_d$ and $b_s = b_d$.

- Finally, the condition $a_s c_s = 0$ can be explained as follows: As mentioned above, to prevent the two reactions from competing for the feed of B , they should be ‘similar’, i.e. agree with respect to the total reaction order or the order of B . This does not only

impose restrictions on α_s and b_s , but also prevents A and C from reacting together in the side reaction. For example, if given the desired reaction $A + B \rightarrow C$, the product C reacts further with A as in $A + C \rightarrow D$, this is stoichiometrically (but not necessarily kinetically) equivalent to a side reaction of the form $2A + B \rightarrow D$, which may give rise to a compromise.

Remarks:

- (1) Since Theorem 2 and its proof involve only the *dynamic model*, it applies irrespective of the objective function and constraints of the optimization problem.
- (2) Theorem 2 states that, for certain scenarios, the optimal feed-rate profile is guaranteed to be determined by the boundary of the feasible region. Though not included here, it has also been proven that for *all* the other cases, there exists the possibility for the optimal solution to lie inside the feasible region. However, as in the case of the temperature, a guarantee for the existence of a sensitivity-seeking feed rate requires more information regarding the optimization problem (objective function as well as state and path constraints).
- (3) If the feed contains several reacting species, Theorem 2 can still be applied upon considering one reacting species at a time and independently of the other reactants that are added.

Catalogue of two-reaction systems

Next, several semi-batch reaction systems involving two reactions are analyzed with respect to the scenarios of Table 1. Instead of using a superstructure where some of the coefficients can be zero, all coefficients will be restricted to be positive in order to emphasize the structure of the reaction schemes.

For some generic two-reaction schemes, Table 2 summarizes the conditions for which the optimal feed rate of B is on the boundary of the feasible region. The 15 reaction schemes can be classified in 5 groups according to the type of conditions that guarantee that the optimal feed rate will be determined by the constraints of the optimization problem:

- (1) *Group 1:* The side reaction is first order and does not involve B (Case i).
- (2) *Group 2:* The side reaction does not involve B but a single other species. There are two possibilities for a constraint-seeking solution: either the side reaction is first order or both reactions are second order (Cases ii-iv).

Group	Case	Description	Conditions \rightarrow Scenario
1	i	$b_d B \xrightleftharpoons[k_s]{k_d} c_s C$	$c_s = 1 \rightarrow \text{I}$
2	ii	$a_d A + b_d B \xrightleftharpoons[k_s]{k_d} c_s C$	$a_d, c_s = 1 \rightarrow \text{I}$ $a_d, b_d = 1, c_s = 2 \rightarrow \text{II}$
	iii	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $c_s C \xrightarrow{k_s} \delta D$	$a_d, c_s = 1 \rightarrow \text{I}$ $a_d, b_d = 1, c_s = 2 \rightarrow \text{II}$
	iv	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $a_s A \xrightarrow{k_s} \delta D$	$a_d, a_s = 1 \rightarrow \text{I}$ $a_d, b_d = 1, a_s = 2 \rightarrow \text{II}$
3	v	$a_d A + b_d B \xrightleftharpoons[k_s]{k_d} a_s A$	$a_d, b_d = 1, a_s = 2 \rightarrow \text{II}$
	vi	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $c_s C + x_s X \xrightarrow{k_s} \delta D$	$a_d, b_d, c_s, x_s = 1 \rightarrow \text{II}$
	vii	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $c_s C + d_s D \xrightarrow{k_s} \delta D$	$a_d, b_d, c_s, d_s = 1 \rightarrow \text{II}$
	viii	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $a_s A + x_s X \xrightarrow{k_s} \delta D$	$a_d, b_d, a_s, x_s = 1 \rightarrow \text{II}$
	ix	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $a_s A + d_s D \xrightarrow{k_s} \delta D$	$a_d, b_d, a_s, d_s = 1 \rightarrow \text{II}$
4	x	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $a_s A + b_s B \xrightarrow{k_s} \delta D$	$a_d, a_s = 1, b_d = b_s \rightarrow \text{III}$
	xi	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $x_s X + b_s B \xrightarrow{k_s} \delta D$	$a_d, x_s = 1, b_d = b_s \rightarrow \text{III}$
	xii	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $c_s C + b_s B \xrightarrow{k_s} \delta D$	$a_d, c_s = 1, b_d = b_s \rightarrow \text{III}$
5	xiii	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $b_s B \xrightarrow{k_s} \delta D$	-
	xiv	$b_d B \xrightarrow{k_d} \gamma C$ $a_s A + c_s C \xrightarrow{k_s} \delta D$	-
	xv	$a_d A + b_d B \xrightarrow{k_d} \gamma C$ $a_s A + c_s C \xrightarrow{k_s} \delta D$	-

Table 2. Catalogue of two-reaction systems with the conditions for which the optimal feed rate of B is determined by constraints and the corresponding scenarios of Table 1.

- (3) *Group 3*: The two reactions are second order with the desired reaction being first order in B and the side reaction involving neither B nor A and C together (Cases v-ix).
- (4) *Group 4*: B is active in the two reactions that involved two species and are of the same order. In addition, all the species reacting with B contribute one order to the kinetic law (Cases x-xii).
- (5) *Group 5*: B is active (directly, or indirectly via C) in the two reactions that either are of different orders or see B with different orders (Cases xiii-xv). These are the only cases without conditions for which the optimal feed rate is on the boundary of the feasible region.

A few remarks are appropriate at this point. In the case of reversible reactions (Cases i, ii and v), there is only one *independent* reaction and thus no expected compromise. However, with a reaction order with respect to A larger than 1, the feed rate

could create a compromise between an increase of the concentration of B and a decrease of that of A due to the effect of dilution.

If B is not involved in the side reaction (Cases i-ix), the absence of a basic compromise is obvious since the two reactions do not compete for the manipulated input. However, here too, the dilution effect plays a role for reaction orders with respect to A larger than 1.

Interestingly, if B reacts with the main reactant (Case x), a secondary reactant (Case xi) or a product (Case xii) and the two reactions have similar orders, there exists no compromise between them. However, a sensitivity-seeking solution is possible if the two reactions are dissimilar in total order or in the order with respect to B (Case xiii-xv).

5. EXAMPLES

This section presents the optimal solution for several qualitatively different examples. The emphasis will be on using the theoretical results of Sections 3 and 4 to predict whether or not the optimal solution will be determined by the constraints of the optimization problem. Then, the optimal solution will be calculated numerically and the various intervals interpreted in terms of constraint- or sensitivity-seeking arcs. The following three examples will be considered:

- (1) *Optimal temperature profile for a reversible reaction in a batch reactor.* There is a single manipulated variable, T . The type of solution will depend on the relative values of E_s and E_d .
- (2) *Optimal feed rate in the presence of a decomposition reaction in an isothermal reactor.* There is also a single manipulated variable, F . With the chosen reaction scheme, there is no guarantee that the solution be determined by constraints, and a sensitivity-seeking arc will be computed in the particular optimization problem.
- (3) *Optimal temperature and feed-rate profiles for a series reaction.* There are two inputs, T and F . With respect to the feed rate, the series reaction does not offer the possibility of a sensitivity-seeking interval. For the temperature, however, a sensitivity-seeking arc may result for $E_s > E_d$. This example will also illustrate the couplings that take place between the various inputs.

5.1 Example 1: Optimal temperature profile for a reversible reaction

Reaction system: $A + B \xrightleftharpoons[k_s]{k_d} C$.

Objective: Maximize the amount of C at a given final time.

Constraints: Bounds on temperature.

Manipulated variable: Reactor temperature.

Kinetics:

$$r_d = \frac{k_{d0} e^{-\frac{E_d}{RT}} n_A n_B}{V^2}, \quad r_s = \frac{k_{s0} e^{-\frac{E_s}{RT}} n_C}{V}$$

Reaction extents:

$$n_A = n_{A0} - \xi_d + \xi_s$$

$$n_B = n_{B0} - \xi_d + \xi_s$$

$$n_C = n_{C0} + \xi_d - \xi_s$$

Optimization problem:

k_{d0}	4	1/mol h	T_{min} 20 °C	
k_{s0}	800	1/h		T_{max} 50 °C
E_d	6×10^3	J/mol		
E_s	20×10^3	J/mol		
R	8.31	J/mol K		
			t_f 1 h	
	n_{A0}	3 mol		
	n_{B0}	2 mol		
	n_{C0}	0.5 mol		
	V	1 l		

Table 3. Model parameters, operating constraints and initial conditions for Example 1

$$\begin{aligned} \max_{T(t)} J &= n_C(t_f) & (36) \\ \text{s.t. } \dot{\xi} &= r(\xi, T)V & \xi(0) = 0 \\ T_{min} &\leq T(t) \leq T_{max} \end{aligned}$$

Optimal solution: The numerical values of the model parameters, constraints and initial conditions are given in Table 3. A sensitivity-seeking solution is possible since the side reaction reduces the objective function and $E_s > E_d$. The compromise between the production and consumption of C is reached through a sensitivity-seeking arc, T_{sens} , that can be computed using (23). T_{sens} is initially large to speed up the forward reaction and decreases with time in order to reduce the backward reaction. The optimal solution computed numerically is given in Figure 2. It consists of three arcs as explained below:

- Initially, since $T_{sens} > T_{max}$, T_{max} is used.
- Once $T_{sens} = T_{max}$, T_{sens} is used.
- Upon reaching T_{min} , T_{min} is used.

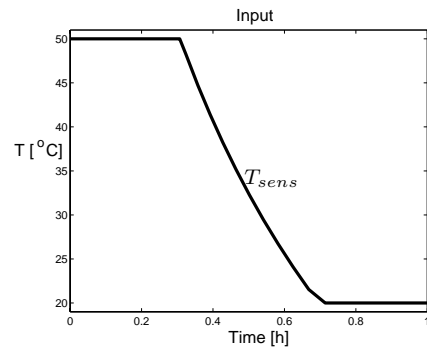


Fig. 2. Optimal temperature profile for Example 1

Remark: For $E_d > E_s$, the differential selectivity $\frac{r_d}{r_s}$ increases with temperature. Thus, from both a productivity and a selectivity viewpoint, it is recommended to increase the temperature. The optimal temperature profile will then be determined by T_{max} .

5.2 Example 2: Optimal feed rate in the presence of a decomposition side reaction

Reaction system: $A + B \xrightarrow{k_d} C$, $B \xrightarrow{k_s} D$.

Objective: Maximize the amount of C at a given final time.

Constraints: Input bounds, constraint on the volume in the reactor, constraint on the amount of D at final time.

Manipulated variable: Feed rate of B .

Kinetics:

$$r_d = \frac{k_d n_A n_B}{V^2}, \quad r_s = \frac{k_s n_B}{V}$$

k_d	0.5	l/mol h	F_{min}	0	l/h	n_{A_0}	1	mol
k_s	0.02	1/h	F_{max}	0.01	l/h	n_{B_0}	0	mol
$c_{B_{in}}$	5	g/l	V_{max}	1	l	n_{C_0}	0	mol
			$n_{D_{max}}$	0.02	mol	n_{D_0}	0	mol
			t_f	20	h	V_0	0.9	l

Table 4. Model parameters, operating constraints and initial conditions for Example 2

Reaction extents:

$$\begin{aligned} n_A &= n_{A_0} - \xi_d \\ n_B &= n_{B_0} - \xi_d - \xi_s + c_{B_{in}}(V - V_0) \\ n_C &= n_{C_0} + \xi_d \\ n_D &= n_{D_0} + \xi_s \end{aligned}$$

Optimization problem:

$$\begin{aligned} \max_{F(t)} \quad & J = n_C(t_f) \\ \text{s.t.} \quad & \text{system dynamics (10)} \\ & F_{min} \leq F \leq F_{max} \\ & V(t_f) \leq V_{max} \\ & n_D(t_f) \leq n_{D_{max}} \end{aligned} \quad (37)$$

Optimal solution: The reaction scheme corresponds to Case xv of Table 2, for which there exists no condition guaranteeing that the optimal solution is determined by constraints. Thus, there is the possibility of the sensitivity-seeking arc F_{sens} . For the parameter values of Table 4, the optimal solution obtained numerically is given in Figure 3. It consists of two arcs as explained below:

- The input is initially at the upper bound, $F = F_{max}$.
- The compromise between the production of C and D is implemented through F_{sens} , which can be computed as $\frac{W}{C}$ from (27):

$$F_{sens} = \frac{n_B(2k_d n_A c_{B_{in}} V + 2k_s c_{B_{in}} V^2 - k_d n_A n_B)}{2c_{B_{in}} V(c_{B_{in}} V - n_B)}$$

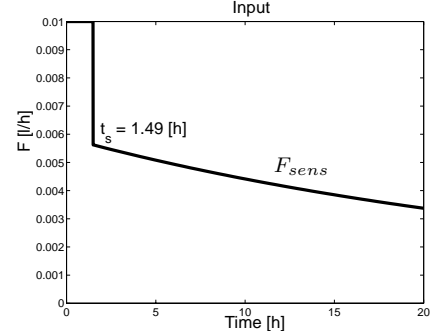


Fig. 3. Optimal feed rate for Example 2

Remark: Even when the possibility of a sensitivity-seeking arc exists, the presence or absence of this arc in the solution depends on the formulation of the optimization problem. For example, if the constraint on $n_D(t_f)$ had not been there in (37), the solution would not have contained the arc F_{sens} , i.e. $F = F_{max}$ until the reactor is full at $t_s = 10$ h and $F = F_{min} = 0$ for the rest of the batch.

5.3 Optimal temperature and feed-rate profiles for a series reaction

Reaction system: $A + B \rightarrow C \rightarrow D$.

Objective: Maximize the amount of C at a given final time.

Constraints: Bounds on feed rate and reactor temperature, constraint on the heat rate produced by the reactions, constraint on the volume in the reactor.

Manipulated variables: Feed rate of B and reactor temperature.

Comments: The reactor temperature is assumed to be a manipulated variable though, in practice, either the flowrate or the temperature in the cooling jacket is manipulated. Hence, the heat balance equation for the reactor is neglected. However, to guarantee heat removal even in the worst scenario, a bound on the heat rate produced by the reactions, $q_{rx}(t) \leq q_{rx_{max}}$, is imposed as an additional constraint.

Kinetics:

$$r_d = \frac{k_{d_0} e^{-\frac{E_d}{RT}} n_A n_B}{V^2}, \quad r_s = \frac{k_{s_0} e^{-\frac{E_s}{RT}} n_C}{V}$$

Reaction extents:

k_{d_o}	4	l/mol h	F_{min}	0	l/h
k_{s_o}	800	1/h	F_{max}	1	l/h
E_d	6×10^3	J/mol	T_{min}	20	°C
E_s	20×10^3	J/mol	T_{max}	50	°C
R	8.31	J/mol K	V_{max}	1.1	l
ΔH_d	-3×10^4	J/mol	$q_{rx_{max}}$	1.5×10^5	J/h
ΔH_s	-10^4	J/mol	t_f	0.5	h
$c_{B_{in}}$	20	mol/l			
n_{A_o}	10	mol			
n_{B_o}	1.1685	mol			
n_{C_o}	0	mol			
n_{D_o}	0	mol			
V_o	1	l			

Table 5. Model parameters, operating constraints and initial conditions for Example 3

$$n_A = n_{A0} - \xi_d \quad (38)$$

$$n_B = n_{B0} - \xi_d + c_{B_{in}}(V - V_0) \quad (39)$$

$$n_C = n_{C0} + \xi_d - \xi_s \quad (40)$$

$$n_D = n_{D0} + \xi_s \quad (41)$$

Optimization problem:

$$\max_{F(t), T(t)} J = n_C(t_f) \quad (42)$$

s.t. system dynamics (10)

$$F_{min} \leq F(t) \leq F_{max}$$

$$T_{min} \leq T(t) \leq T_{max}$$

$$(-\Delta H_d) \frac{k_d n_A n_B}{V} + (-\Delta H_s) k_s n_C \leq q_{rx_{max}}$$

$$V(t_f) \leq V_{max}$$

Specific choice of experimental conditions: Let the initial conditions be chosen such that as much B as possible is charged initially in the reactor while still meeting the heat removal constraint. Thus, n_{B_o} is chosen to verify $(-\Delta H_d) \frac{k_d n_{A_o} n_{B_o}}{V_o} + (-\Delta H_s) k_s n_{C_o} = q_{rx_{max}}$.

Optimal solution: The numerical values of the model parameters, constraints and initial conditions are given in Table 5. A sensitivity-seeking temperature profile is possible since the side reaction reduces the objective function and $E_s > E_d$. Furthermore, the reaction scheme corresponds to Case iii of Table 2 with $a_d = c_s = 1$ (Scenario I), which guarantees that the feed rate is determined by constraints. The optimal inputs computed numerically are given in Figure 4. Each input consists of two arcs, F_{path} and F_{min} for the feed rate, and T_{max} and T_{sens} for the temperature:

- Since the initial condition c_{B_o} verifies $q_{rx}(0) = q_{rx_{max}}$, the feed rate F_{path} is applied to keep that path constraint active.
- Once the volume constraint is attained, the feed rate is set to $F_{min} = 0$.

- The temperature starts at its upper bound T_{max} to favor the desired reaction.
- Later, the temperature switches to T_{sens} to take advantage of the temperature-dependent compromise between the production and consumption of C .

When the temperature goes inside the feasible region, there is a discontinuity in the feed rate due to the coupling between the two inputs. Similarly, when the feed rate switches to zero to satisfy the volume constraint, there is a discontinuity in the rate of change of the temperature.

6. CONCLUSIONS

For non-isothermal, semi-batch systems with two reactions, this paper has proposed conditions under which the optimal temperature and feed-rate policies are determined by the constraints of the optimization problem. The optimal temperature profile is necessarily determined by an active path constraint if the desired reaction has a larger activation energy than the side reaction (which is often the case) or if the side reaction tends to improve the objective function (rarely the case). Otherwise, the optimal temperature profile can also be inside the feasible region. With respect to the optimal feed-rate profile, it has been shown that, for the majority of two-reaction systems, it is determined by active path constraints.

When the optimal policies are determined by constraints, a measurement-based scheme for tracking the active constraints is an interesting alternative to numerical model-based optimization, especially in the presence of uncertainty (Bonvin *et al.*, 2002).

The results presented in this paper are based on two core assumptions: (i) power-law kinetics and (ii) systems with two reactions. Power-law kinetics are monotonic, and maximizing the reaction rate corresponds to increasing the concentrations of the reacting species as much as possible. However, if the kinetics are not monotonic, e.g. if there is inhibition, then the maximum reaction rate occurs at some intermediate concentration and the optimal solution is not necessarily determined by constraints.

The second assumption of two reactions is quite important. Though the basic tools (first- and second-order conditions of optimality and their time derivatives) can still be used for systems with more than two reactions, the analytical developments get involved. The conditions to guarantee the solution on the boundary of the feasible region get extremely complicated, thus questioning the utility of such results. So, in the authors' opinion,

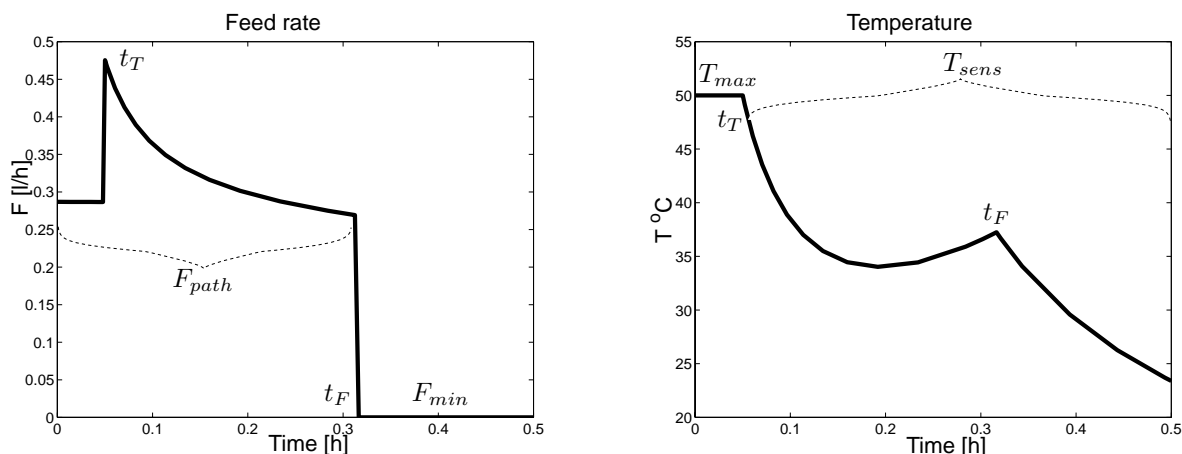


Fig. 4. Optimal feed rate and temperature profiles for Example 3

there is little hope for a general analytical theory for reaction systems with more than two reactions, while they can still be solved in a case-by-case basis using standard numerical optimization tools.

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