OPTIMAL FEED RATE POLICY FOR ISOTHERMAL REACTION SYSTEMS WITH TWO REACTIONS

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Abstract: In the face of growing competition, the optimization of batch processes is a natural choice for reducing production costs, improving product quality, and meeting safety and environmental regulations. To guarantee optimality despite uncertainty, a measurement-based scheme for tracking the active constraints can be used if the optimal solution is determined by the constraints of the optimization problem. If the system under consideration is feedback linearizable, then the optimal solution will necessarily be on constraints. This paper shows that majority of two-reaction systems taking place in isothermal semi-batch reactors belongs to this category. The results are illustrated on several two-reaction systems.

Keywords: Dynamic optimization, Optimal control, Batch chemical processes, Semi-batch reactors, On-line optimization.

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, owing to differences in both equipment and scale, industrial production almost invariably necessitates modifications of these recipes in order to ensure productivity, safety, quality, and satisfaction of operational constraints (Wiederkehr, 1988) for which an optimization approach can be used. The operational decisions such as temperature or feed rate profiles are then determined from the solution to an optimization problem, where the objective is of economic nature and the various technical and operational constraints are considered explicitly.

However, standard model-based optimization techniques are ineffective since the models available in the industry carry a large amount of uncertainty (model errors and disturbances). So, measurement-based optimization methods are of considerable interest (Bonvin *et al.*, 2001). For these methods to be efficient, the optimal solution should be determined by the constraints of the problem (input bounds, state and terminal constraints). In such a case, optimality corresponds to tracking the active path constraints using on-line measurements (Visser *et al.*, 2000), and making the terminal constraints active in a batch-to-batch scheme using off-line measurements (Srinivasan *et al.*, 2000).

This paper addresses the problem of whether or not the solution is determined by constraints so that measurement-based optimization schemes can be applied. Towards this end, the compromises in a terminal-cost optimization problem are classified into two categories: (a) compromises in-

trinsic to the dynamic system, and (b) compromises resulting from the formulation of the optimization problem. The first category corresponds to the input having multiple conflicting influences on the states of the system. Since these influences act against each other, a compromise value of the input (singular arc) needs to be used for the sake of optimality. However, if there are no intrinsic compromises in the system, the optimal input is determined by the path constraints (input bounds and state constraints). The compromises formulated in the optimization problem are achieved by a proper sequencing of the various intervals and, more specifically, by the choice of the switching instants between them.

In this paper, conditions that guarantee the absence of singular arcs in isothermal semi-batch reactors with the feed rate used as manipulated input are presented. These conditions are based on the dynamic model only and not on the formulation of the optimization problem (terminal cost and constraints). If the dynamic system is feedback linearizable, the optimal solution will necessarily be on active constraints. It will be shown that the vast majority of isothermal semi-batch reaction systems with two reactions are indeed feedback linearizable.

The paper is organized as follows. Section 2 briefly reviews the formulation of the optimization problem, the reduction in dimensionality of chemical reaction systems, and the concept of feedback linearizability. Several isothermal semi-batch reaction systems with two reactions are presented and analyzed with respect to feedback linearizability in Section 3. Three examples are provided in Section 4 to illustrate the theoretical developments, and conclusions are drawn in Section 5.

2. PRELIMINARIES

2.1 *Optimization problem*

In most batch chemical processes, the manipulated inputs are flowrates that enter the system equations linearly. Such systems are called control-affine systems. Furthermore, the optimization objective involves meeting certain specifications only at the *end* of the batch. Single input systems will be considered for simplicity. The terminal-cost optimization of a control-affine single input system can be written as:

$$\min_{u(t)} \; J = \phi(x(t_f)) \tag{1}$$

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

$$S(x,u) \le 0, \quad T(x(t_f) \le 0 \tag{3}$$

where J is the scalar performance index to be minimized, x the states with initial conditions x_0, u the scalar input, S the path constraints (which include state constraints and input bounds), T the terminal constraints, f and g smooth vector fields, ϕ a smooth scalar function representing the terminal cost, and t_f the final time which can be either fixed or free.

2.2 *Normal form of chemical reaction systems*

Consider a homogeneous, constant-density, isothermal, semi-batch chemical reaction system comprising S species and R independent reactions (*independent reactions* being those which have both independent stoichiometries *and* independent kinetics (Srinivasan *et al.*, 1998)). The material balance equations and the continuity equation are described by:

$$\begin{array}{ll} \dot{n} = V\,K\,r_n(n,V) + c_{in}\,u & n(0) = n_0 \\ \dot{V} = u & V(0) = V_0 \end{array} \tag{4}$$

where n is the S-dimensional vector of the number of moles, u the inlet volumetric flowrate, V the reactor volume, K the $S \times R$ stoichiometric matrix, r_n the R-dimensional reaction rate vector, c_{in} the molar concentration of the inlet stream, n_0 the initial number of moles, and V_0 the initial volume. The terms $VKr_n(n,V)$ and $c_{in}\,u$ represent the effect of the reactions and the inlet stream on the number of moles, respectively. The molar concentrations are given by $c = n/V$.

Let the rows of the matrix $N \in \mathcal{R}^{S\times(S-R-1)}$ form the null space of $[K\,c_{in}]^T$. Using singular value decomposition (SVD), N can be computed as the matrix of the right singular vectors corresponding to the zero singular values of $[K\,c_{in}]^T$. Let $l \in \mathcal{R}^S$ be the null vector of $[K\,N]^T$. The following transformation,

$$\begin{bmatrix} \xi \\ \bar{\xi} \\ \tilde{\xi} \end{bmatrix} = \begin{bmatrix} K^+ \left(I - \dfrac{c_{in} l^T}{c_{in}^T l} \right) n \\ \dfrac{l^T}{c_{in}^T l} n - V \\ N^T n \end{bmatrix} \tag{5}$$

where the superscript $^+$ denotes the Moore-Penrose pseudo inverse, takes the system (4) to the normal form (Srinivasan *et al.*, 1998):

$$\dot{\xi} = V\,r, \quad \dot{\bar{\xi}} = 0, \quad \dot{\tilde{\xi}} = 0, \quad \text{and} \quad \dot{V} = u. \tag{6}$$

ξ corresponds to the reaction variants, while $\bar{\xi}$ and $\tilde{\xi}$ are the reaction and flow invariants. The invariants can be removed and the reduced system

$$\begin{bmatrix} \dot{\xi} \\ \dot{V} \end{bmatrix} = \begin{bmatrix} V\,r \\ 0 \end{bmatrix} + \begin{bmatrix} 0 \\ 1 \end{bmatrix} u = f(\xi, V) + g\,u \tag{7}$$

of dimension $(R+1)$ is considered for analysis. This model reduction, which uses no information

on the kinetics except for the independence of reactions, eliminates the redundancy in n using information present in the stoichiometric matrix. It is possible that the kinetics are such that the dimension of the space that is controllable from the input is less than $(R+1)$, thereby making a further model reduction possible.

2.3 *Feedback linearizability*

The concept of feedback linearization will be used for characterizing the optimal solution of (1)-(3). A few definitions related to Lie algebra are presented first.

Definition 1. (Nijmeijer and van der Schaft, 1990) Let $a(x)$ and $b(x)$ be vector fields. The Lie bracket $[a, b]$ is defined as:

$$[a, b] = \frac{\partial b}{\partial x} a - \frac{\partial a}{\partial x} b \tag{8}$$

The following notation will be used: $[a, b] = ab$, $[a, [a, b]] = a^2 b$, and $[a, [a^{i-1}, b]] = a^i b$.

Definition 2. The distribution $\mathcal{D} = span\{a_1(x), ..., a_d(x)\}$ is involutive if it is closed under Lie bracketing, i.e., $a_i, a_j \in \mathcal{D} \Rightarrow [a_i, a_j] \in \mathcal{D}$, $\forall i, j$.

Definition 3. (Nijmeijer and van der Schaft, 1990) A control-affine system is feedback linearizable around x_0 if, in the neighborhood of x_0, there exist a transformation $z = T(x)$ and a feedback law $u = p(x) + q(x)v$, $q(x) \neq 0$, such that the new states z and the new input v satisfy the linear differential equation $\dot{z} = Az + Bv$.

The necessary and sufficient conditions for feedback linearizability are stated next.

Theorem 4. (Nijmeijer and van der Schaft, 1990) System (2) is feedback linearizable iff (a) the set of vector fields $\{g, fg, ... f^{d-2}g\}$ is involutive, and (b) the vector fields $\{g, fg, ..., f^{d-1}g\}$) are linearly independent, where d is the dimension of f and g.

Theorem 5. (Benthack, 1997) If System (2) is feedback linearizable, the optimal solution of (1)-(3) is on the boundary of the admissible region.

The reader is referred to (Benthack, 1997; Palanki *et al.*, 1993) for the proof. Intuitively, if the system is feedback linearizable, the system can be transformed into a chain of integrators, implying that the input cannot have multiple conflicting effects on the states of the system. So, the solution is determined by the constraints of the problem for any terminal-cost optimization problem, whatever the cost function and the constraints might be. On the other hand, if the system is not feedback linearizable, depending on the cost function and the constraints, the solution may have intervals where the input is not determined by the constraints (singular intervals). However, it is interesting to note that the condition of feedback linearizability is sufficient, but not necessary, for the optimal solution to be determined by problem constraints, i.e., the system may not be feedback linearizable and yet the optimal solution is on the constraints.

For a system with two reactions ($R = 2$, $d = 3$), involutivity of $\{g, fg\}$ implies that the vectors g, fg, and gfg are linearly dependent. With $f^T = \begin{bmatrix} V r_1 & V r_2 & 0 \end{bmatrix}$ and $g^T = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix}$, the involutivity condition requires:

$$\begin{aligned} \Delta_{inv} &\equiv \det([g,\ fg,\ gfg]) \\ &= \frac{\partial (V r_1)}{\partial V} \frac{\partial^2 (V r_2)}{\partial V^2} - \frac{\partial (V r_2)}{\partial V} \frac{\partial^2 (V r_1)}{\partial V^2} = 0 \end{aligned} \tag{9}$$

The linear independence condition is given by:

$$\Delta_{ind} \equiv \det([g,\ fg,\ f^2 g]) \neq 0 \tag{10}$$

Though the linear independence condition is important for systems with more than two reactions, it plays a minor role when there are only two reactions. Suppose $\Delta_{ind} = 0$ everywhere. Then, the dimension of the space controllable from the input is not $R + 1 = 3$ but 2. In other words, the input sees only one reaction and, thus, no compromise is possible. The kinetics are such that a further model reduction is possible and the reduced system (which has one reaction and two states) is trivially feedback linearizable.

3. A CATALOG OF SYSTEMS WITH TWO REACTIONS

In this section, several isothermal semi-batch reaction systems with two reactions are considered and checked whether or not the system is feedback linearizable. If the two reactions compete from the point of view of the manipulated input, then the system is not feedback linearizable. The competition results in a compromise and, thus, the optimal feeding policy is not necessarily determined by the constraints. The following notations will be used:

- A is the reactant in the reactor at time $t = 0$.
- B is the reactant to be fed.
- C and D are products.
- I_A and I_B are impurities present with A and B, respectively.

Table 1 summarizes the results found for some basic chemical reaction schemes. Most of them gives rise to a feedback linearizable system, for which the optimal feeding policy will necessarily

#	Kinetic model	Description	Δ_{ind}	Δ_{inv}	Feedback linearizable
1	Single reaction	$A+B \overset{k}{\rightarrow} C$	$\Delta_{ind} \neq 0$	-	yes
2	Reversible reaction	$A+B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$	$\Delta_{ind} \neq 0$	-	yes
3	Production of Isomers	$A+B \overset{k_1}{\rightarrow} C$ $A+B \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	-	yes
4	Consecutive series reactions	$A+B \overset{k_1}{\rightarrow} C$ $C \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} = 0$	yes
5	Consecutive parallel reactions	$A+B \overset{k_1}{\rightarrow} C$ $A+C \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} = 0$	yes
6	Consecutive parallel reactions	$A+B \overset{k_1}{\rightarrow} C$ $C+B \overset{k_2}{\rightarrow} D$	$\Delta_{ind} = 0$	$\Delta_{inv} = 0$	yes
7	Reactions with impurity	$A+B \overset{k_1}{\rightarrow} C$ $A+I_B \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} = 0$	yes
8	Reactions with impurity	$A+B \overset{k_1}{\rightarrow} C$ $I_A+B \overset{k_2}{\rightarrow} D$	$\Delta_{ind} = 0$	$\Delta_{inv} = 0$	yes
9	Reactions with impurity	$A+B \overset{k_1}{\rightarrow} C$ $C+I_A \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} = 0$	yes
10	Reactions with impurity	$A+B \overset{k_1}{\rightarrow} C$ $C+I_B \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} = 0$	yes
11	Reactions with decomposition	$A+B \overset{k_1}{\rightarrow} C$ $A \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} = 0$	yes
12	Reactions with decomposition	$A+B \overset{k_1}{\rightarrow} C$ $B \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} \neq 0$	no
13	Parallel reactions ($a \neq 1$)	$A+B \overset{k_1}{\rightarrow} C$ $aA+B \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} \neq 0$	no
14	Parallel reactions ($b \neq 1$)	$A+B \overset{k_1}{\rightarrow} C$ $A+bB \overset{k_2}{\rightarrow} D$	$\Delta_{ind} \neq 0$	$\Delta_{inv} \neq 0$	no

Table 1. Feedback linearizability of isothermal reaction systems (Feed rate of B is manipulated)

be determined by the constraints. In Cases 1-3, there is only one independent reaction and hence there is no intrinsic compromise. If B does not intervene in the second reaction (Cases 4, 5, 7, 9, 10, 11), the absence of compromise is obvious. Interestingly, if B reacts with a product (Case 6) or with an impurity present in the reactor (Case 8), the two reactions are dependent and there is no compromise possible between them. However, compromise solutions are possible if B decomposes (Case 12) or reacts with A in more than one way (Cases 13-14) since, in such a case, the problem of selectivity arises.

4. EXAMPLES

Instead of providing a detailed description of all cases, three examples are considered corresponding to: (1) $\Delta_{ind} \neq 0$, $\Delta_{inv} = 0$, (2) $\Delta_{ind} = 0$, $\Delta_{inv} = 0$, and (3) $\Delta_{ind} \neq 0$, $\Delta_{inv} \neq 0$.

4.1 *Consecutive series reactions: Case 4*

Reaction system: $A+B \overset{k_1}{\rightarrow} C \overset{k_2}{\rightarrow} D$

Kinetics:

$$r_{n_1} = \frac{k_1 n_A n_B}{V^2}, \quad r_{n_2} = \frac{k_2 n_C}{V}$$

Transformations:

$$n \rightarrow \xi : \xi_1 = n_{A0} - n_A, \quad \xi_2 = n_D$$

$$\xi \rightarrow n : \begin{cases} n_A = n_{A0} - \xi_1, \\ n_B = n_{B0} - \xi_1 + c_{B_{in}}(V - V_0) \\ n_C = \xi_1 - \xi_2, \quad n_D = \xi_2 \end{cases}$$

Evaluation of Δ_{ind} and Δ_{inv} using (9)-(10):

$$\Delta_{ind} = \frac{k_1^2 k_2\, c_{B_{in}}}{V^4} n_A^2 \left(n_B - c_{Bin} V\right)$$

$\Delta_{ind} = 0 \Leftrightarrow n_A = 0$ or $n_B = c_{Bin}V$. However, $n_A = 0$ occurs only at the end of the reaction. Likewise, $n_B = c_{Bin}V$ implies $c_B = c_{Bin}$ which is not possible when $n_A \neq 0$. So, $\Delta_{ind} \neq 0$ throughout the chemical reaction.
Here $\Delta_{inv} = 0$. So, the system is feedback linearizable and, for any optimization problem, the solution is determined by the constraints.

Objective: Maximize production of C.
Constraints: Input bounds, constraint on the volume in the reactor.

$$\max_{u(t),t_f} \; J = n_C(t_f)$$

s.t. System dynamics

$$u_{min} \le u \le u_{max}, \quad V(t_f) \le V_{max}$$

Optimal Solution:

- As seen in Figure 1, the input is initially at the upper bound, $u = u_{max}$, in order to increase n_B as quickly as possible and thus maximize the rate of reaction.
- Once the volume reaches V_{max}, the input is set to zero.
- The number of moles of C decreases after a certain time due to the second reaction. So, to maximize n_c, the terminal time t_f is determined such that $\frac{dn_c}{dt}\big|_{t_f} = 0$.

For the numerical values given in Table 2, the optimal cost is $J = 0.40\,\text{mol}$. Note that there is compromise related to the choice of the terminal time but no compromise value for $u(t)$ which is always on either one of the input bounds.

k_1	0.5	l/(mol h)
k_2	0.02	1/h
$c_{B,in}$	5	g/l

u_{min}	0	l/h
u_{max}	0.01	l/h
V_{max}	1	l

n_{A_o}	1	g/l
n_{B_o}	0	g/l
V_o	0.9	l

Table 2. System parameters, operating constraints and initial conditions

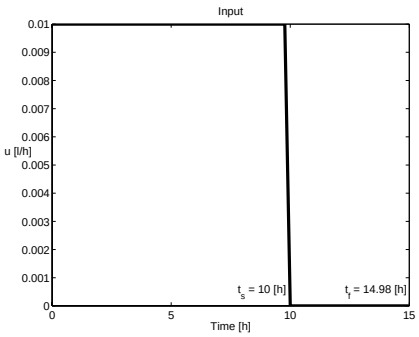

Fig. 1. Optimal feedrate for Example 1

4.2 *Consecutive parallel reactions: Case 6*

Reaction system: $A + B \overset{k_1}{\to} C$, $B + C \overset{k_2}{\to} D$.
Kinetics:

$$r_{n_1} = \frac{k_1 n_A n_B}{V^2}, \quad r_{n_1} = \frac{k_2 n_B n_C}{V^2}$$

Transformations:

$$n \to \xi : \xi_1 = n_{A0} - n_A, \quad \xi_2 = n_D$$

$$\xi \to n : \begin{cases} n_A = n_{A0} - \xi_1 \\ n_B = n_{B0} - \xi_1 - \xi_2 + c_{B_{in}}(V - V_0) \\ n_C = \xi_1 - \xi_2, \quad n_D = \xi_2 \end{cases}$$

Evaluation of Δ_{ind}*:*
Here $\Delta_{ind} = 0$. It can be checked that $n_A^{-(k_2/k_1)}((k_2 - k_1)n_C - k_1 n_A)$ remains constant throughout the reaction. Thus, ξ_2 can be eliminated from the state space and computed algebraically using:

$$\xi_2 = \xi_1 + \frac{k_1}{k_2 - k_1}\left(n_{A,0}^{((k_1-k_2)/k_1)} n_A^{(k_2/k_1)} - n_A\right)$$

So, there is only one independent reaction and the system is feedback linearizable.

Objective: Maximize production of C.
Constraints: Input bounds, constraint on the volume in the reactor, constraint on the maximum number of moles of D.

$$\max_{u(t),t_f} \; J = n_C(t_f)$$

s.t. System dynamics

$$u_{min} \le u \le u_{max}, \quad V(t_f) \le V_{max}$$
$$n_D(t_f) \le n_{D,max} = 0.05\,\text{mol}$$

Optimal solution:

- As seen in Figure 2, the input is initially at the upper bound, $u = u_{max}$.
- For the numerical values considered (Table 2), the constraint $n_D(t_f) \le n_{D,max}$ is more restrictive than $V(t_f) \le V_{max}$. So, the input switches to zero so as to be able to satisfy $n_D(t_f) = n_{D,max}$.
- The number of moles of C decreases after a certain time due to the second reaction. So, to maximize n_c, the terminal time t_f is determined such that $\frac{dn_c}{dt}\big|_{t_f} = 0$.

The optimal cost is $J = 0.33\,\text{mol}$. Here, the compromises that constitute the optimization problem are reflected in the choice of the switching and final times. Despite the fact that B appears in both reactions, there is no compromise value for $u(t)$, and the solution is on the input bounds.

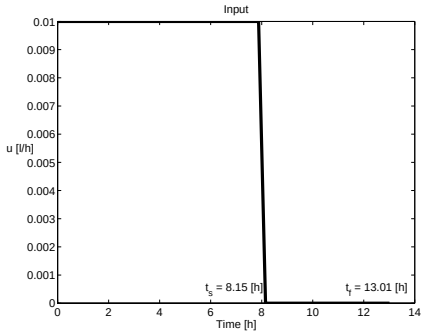

Fig. 2. Optimal feedrate for Example 2

4.3 *Reactions with decomposition: Case 12*

Reaction system: $A + B \overset{k_1}{\to} C$, $B \overset{k_2}{\to} D$.

Kinetics:

$$r_{n_1} = \frac{k_1 n_A n_B}{V^2}, \quad r_{n_1} = \frac{k_2 n_B}{V}$$

Transformations:

$$n \to \xi : \xi_1 = n_{A0} - n_A, \quad \xi_2 = n_D$$
$$\xi \to n : \begin{cases} n_A = n_{A0} - \xi_1 \\ n_B = n_{B0} - \xi_1 - \xi_2 + c_{B_{in}}(V - V_0) \\ n_C = \xi_1, \quad n_D = \xi_2 \end{cases}$$

Evaluation of Δ_{inv}*:*

$$\Delta_{inv} = \frac{2\,k_1 k_2 n_A c_{Bin}(c_{Bin}V - n_B)}{V^5}$$

The system is not feedback linearizable since $\Delta_{inv} \neq 0$. The optimal solution can take values which are not on the constraints (singular) and can be computed as follows:

$$u_{sing} = -\frac{\Delta_{ind}}{\Delta_{inv}} = \frac{n_B(2k_1 n_A c_{Bin}V + 2k_2 c_{Bin}V^2 - k_1 n_A n_B)}{2\,c_{Bin}V(c_{Bin}V - n_B)}$$

Objective: Maximize production of C.
Constraints: Input bounds, constraint on the volume in the reactor, constraint on the maximum number of moles of D, constraint on the final time.

$$\max_{u(t),t_f} \; J = n_C(t_f) \tag{11}$$
$$s.t. \text{ System dynamics}$$
$$u_{min} \le u \le u_{max}, \quad V(t_f) \le V_{max}$$
$$n_D(t_f) \le n_{D,max} = 0.02\,\text{mol}$$
$$t_f \le t_{f,max} = 20\,\text{h}$$

Optimal solution:

- As seen in Figure 3, the input is initially at the upper bound, $u = u_{max}$.
- The compromise between the production of C and D is reached through u_{sing}.
- Since C is not consumed by another reaction, the optimal value of t_f is $t_{f,max}$.

For the numerical values given in Table 2, the optimal cost is $J = 0.41$ mol.

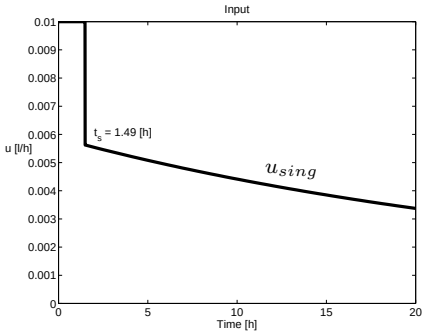

Fig. 3. Optimal feedrate for Example 3

Remark: Even if there is a possibility of a singular arc, its presence or absence in the optimal solution depends on the optimization problem. For example, if the constraint on $n_D(t_f)$ had not been there in (11), the solution will not have any singular arc, i.e., $u = u_{max}$ till $t_s = 10\,\text{h}$ and $u = u_{min}$ for the rest of the batch with $t_f = 20\,\text{h}$.

5. CONCLUSIONS

This paper investigates feedback linearizability of isothermal semi-batch reaction systems, which in turn guarantees that the optimal feed rate policy will be on the constraints of the optimization problem. Reaction systems with a single independent reaction are trivially feedback linearizable. A majority of reaction schemes involving two reactions also belong to this category.

Since for most isothermal two-reaction systems, the optimal feed rate policy is indeed determined by the constraints of the optimization problem, a measurement-based scheme for tracking the active constraints is an interesting alternative to numerical model-based optimization, especially in the presence of uncertainty.

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