End-Point Optimization of Single-Reaction Systems

Jyothy Vemuri, Majura Selekwa, and Srinivas Palanki

Abstract— **Batch and semi-batch processes are of considerable importance in the batch chemical industry. In the face of increased competition, process optimization provides a unified framework for reducing production costs, meeting safety requirements and environmental regulations, improving product quality, reducing product variability, and ease of scale-up [Bonvin, 1988]. In this paper, a numerical optimization approach is developed that utilizes a dynamic model to determine *analytically*, the structure of the optimal solution for a single-reaction system. This approach is tested via simulation of an end-point optimization problem in a batch chemical reactor.**

I. INTRODUCTION

Batch and semi-batch processes are of considerable importance in the chemical industry. A wide variety of specialty chemicals and pharmaceutical products are manufactured in the batch mode. The operation of batch processes typically involves following predefined laboratory *recipes*. 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 [Wiederkehr, 1988]. In the face of increased competition, process optimization provides a unified framework for reducing production costs, meeting safety requirements and environmental regulations, improving product quality, reducing product variability, and ease of scale-up [Bonvin, 1988]. An operating strategy that satisfies all the constraints and leads to optimal production requires the solution of a real-time optimization problem.

The following characteristics were found to be common to a large number of batch industries according to a recent survey conducted by Palanki [2002]:

1) Most of the reactions are liquid phase reactions and while the final product is the result of several synthesis steps, each synthesis step is a new batch operation and typically requires different reactants and solvents and has different batch operating conditions. Some of these steps are done in the same equipment while others are done in different batch equipment.
2) In each batch step, there is one dominant chemical reaction of the type $aA + bB \rightleftharpoons cC + dD$.
3) Most batch chemical reactors are operated at constant temperature and, if semi-batch, at constant feed rate of the reactant(s). The operating temperature and feed rate is determined heuristically, typically by doing a few laboratory experiments.
4) A recipe, which consists of a series of time related steps, is followed in open-loop fashion at the industrial scale batch process.
5) Batch-to-batch variation in product yield and quantity is observed in a number of batch reactors.
6) Some measurements, such as temperature, pH, viscosity and pressure are made online. Furthermore, periodic samples are taken for measuring concentration off-line. However, this data is typically used for determining if the batch is operating properly. This information is not used for making on-line adjustments to the operating strategy.

In this paper, the structure of the optimal solution for an end-point optimization problem in a semi-batch reactor with a single reaction and state/input constraints is analyzed. This analysis is utilized to develop an algorithm that can be utilized to find the optimal solution.

II. PROBLEM FORMULATION

Consider a single liquid-phase reaction of the type

$$aA + bB \rightleftharpoons cC + dD \tag{1}$$

occurring in a jacketed semi-batch reactor. While there may be both reactant and products initially present in the reactor, it is assumed that only the reactant A is fed to the reactor during semi-batch operation. It is also assumed that the jacket dynamics are *fast* and the reactor temperature can be changed quickly via the jacket.

A dynamic model for the semi-batch reactor may be represented as follows:

$$\begin{aligned} \frac{d}{dt}(VC_A) &= -r_A V + FC_{AF} \\ \frac{d}{dt}(VC_B) &= -\frac{b}{a} r_A V \\ \frac{d}{dt}(VC_C) &= \frac{c}{a} r_A V \\ \frac{d}{dt}(VC_D) &= \frac{d}{a} r_A V \\ \frac{d}{dt}(V) &= F \end{aligned} \tag{2}$$

where C_A, C_B, C_C and C_D are the concentrations of species A, B, C and D respectively, V is the reactor volume, F is the volumetric feed rate of species A with a feed concentration of C_{AF}, and r_A is the reaction rate which can be represented by the following function:

$$r_A = g(k_i, C_A, C_B, C_C, C_D) \tag{3}$$

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and the rate constants k_i follow the temperature dependent Arrhenius rate expression:

$$k_i = k_{i0} exp\left(-\frac{E_i}{RT}\right) \tag{4}$$

where T is the reaction temperature, k_{i0} is the frequency factor, E_i is the activation energy and R is the gas constant. The objective is to optimize the following cost function at a final time, t_f, by manipulating the feed rate F and the reaction temperature T:

$$J = \phi(C_A, C_B, C_C, C_D, V)|_{t_f} \tag{5}$$

The input constraints are given by:

$$\begin{array}{rcccl} F_{min} & \leq & F & \leq & F_{max} \\ T_{min} & \leq & T & \leq & T_{max} \end{array} \tag{6}$$

and the state constraints are given by:

$$\begin{array}{rcccl} C_{A,min} & \leq & C_A & \leq & C_{A,max} \\ C_{B,min} & \leq & C_B & \leq & C_{B,max} \\ C_{C,min} & \leq & C_C & \leq & C_{C,max} \\ C_{D,min} & \leq & C_D & \leq & C_{D,max} \\ V_{min} & \leq & V & \leq & V_{max} \end{array} \tag{7}$$

where the subscript min refers to the lower bound and the subscript max refers to the upper bound.

Clearly, the concentrations C_A, C_B, C_C and C_D are not independent and it can be easily shown that:

$$\begin{array}{rcl} C_B & = & \frac{b}{a}C_A + C_{B0}\frac{V_0}{V} - \frac{b}{a}C_{A0}\frac{V_0}{V} - \frac{b}{a}C_{AF} + \frac{b}{a}C_{AF}\frac{V_0}{V} \\ C_C & = & C_{C0}\frac{V_0}{V} + \frac{c}{a}\left(C_{A0}\frac{V_0}{V} - C_A + C_{AF} - C_{AF}\frac{V_0}{V}\right) \\ C_D & = & C_{D0}\frac{V_0}{V} + \frac{d}{a}\left(C_{A0}\frac{V_0}{V} - C_A + C_{AF} - C_{AF}\frac{V_0}{V}\right) \end{array} \tag{8}$$

By defining:

$$\begin{array}{rcl} x_1 & = & C_A V \\ x_2 & = & V \end{array} \tag{9}$$

the end-point optimization problem can we written as:

$$min\ J = \phi(x_1, x_2)|_{t_f} \tag{10}$$

subject to the dynamic constraints:

$$\frac{d}{dt}\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} -r_A^{'} + C_{AF}F \\ F \end{bmatrix} \tag{11}$$

and static constraints:

$$\begin{array}{rcccl} F_{min} & \leq & F & \leq & F_{max} \\ T_{min} & \leq & T & \leq & T_{max} \\ x_{1,min} & \leq & x_1 & \leq & x_{1,max} \\ x_{2,min} & \leq & x_2 & \leq & x_{2,max} \end{array} \tag{12}$$

where $r_A^{'}$ is the reaction rate written in terms of the new variables x_1 and x_2.

III. CLASSICAL SOLUTION STRATEGIES

The end-point optimization problem posed in the previous section is of the following general form:

$$min\ J\ = \Phi(x(t_f)) \tag{13}$$

subject to the process dynamic

$$\begin{array}{rcl} \dot{x} & = & f(x,u) \\ x(0) & = & x_0 \end{array} \tag{14}$$

and state constraints

$$Px - b \leq 0 \tag{15}$$

and input constraints

$$Qu - c \leq 0 \tag{16}$$

where x is the n-vector of system states, u is the m-vector of manipulated inputs, f is a smooth vector function of x and u, b and c are constant vectors of dimension $2n$ and $2m$ respectively which determine the upper and lower bounds of the states and inputs. The matrices P and Q can be determined from the last two and first two equations of eq. (12) respectively.

There are two basic approaches available in the literature to solve the above problem. These are briefly described below.

Solution via Pontryagin's Minimum Principle

By Pontryagin's Minimum Principle (PMP), the optimization problem posed by (13) - (16) is equivalent to the following functional minimization problem [Bryson and Ho, 1975].

$$min\ H = \lambda^T f(x,u) + \mu_1^T(Px - b) + \mu_2^T(Qu - c) \tag{17}$$

where λ is the n-vector of adjoint states described by:

$$\begin{array}{rcl} \frac{d\lambda^T}{dt} & = & -\lambda^T\frac{\partial f}{\partial x} - \mu_1^T P \\ \lambda(t_f) & = & \frac{\partial \phi}{\partial x}|_{t=t_f} \end{array} \tag{18}$$

The lagrange multipliers μ_1 and μ_2 are non-zero when the corresponding constraints are active and are zero otherwise; so $\mu_1^T P = 0$ and $\mu_2^T Q = 0$ always. The first order necessary conditions of optimality are:

$$H_{u_i} = \frac{\partial H}{\partial u_i} = 0 \qquad i = 1, 2, .., m \tag{19}$$

One needs to solve simultaneously eq. (14), (18) and (19) simultaneously to get the optimal inputs. However, one can observe from (14) and (18) that the boundary conditions are split and thus the end-point optimization problem requires the solution of a two point boundary value problem which is computationally expensive to solve.

Solution via Nonlinear Programming

An alternative approach to solving the end-point optimization problem is to discretize the state and input variables. Thus the dynamic equations (14) are reduced to algebraic equations that are satisfied at discrete points. Thus, the optimization problem is reduced to a standard nonlinear programming problem (NLP) that can be solved using standard NLP software [Cuthrell and Biegler, 1989].

The key characteristic of this approach is the fact that the optimization is carried out in the full space of discretized inputs *and* states. So, in general, the differential equations are satisfied only at the *solution* of the optimization problem . This is therefore called an "infeasible path" approach. The basic procedure is as follows [Cuthrell and Biegler, 1989]:

1) Parameterize both the inputs and the states using a finite number of decision variables (typically piecewise polynomials). The vector of decision variables also includes t_f.
2) Discretize the differential equations (2), i.e., the differential equations are satisfied only at a finite number of time instants (typically *via* orthogonal collocation). These two steps transform the dynamic optimization problem into a standard nonlinear program (NLP).
3) Choose an initial guess for the decision variables.
4) Iteratively solve for the optimal set of decision variables using an NLP code.

However, the above procedure typically leads to a large NLP and efficient numerical methods are necessary to solve this problem [Cuthrell and Biegler, 1989].

IV. STRUCTURE OF THE OPTIMAL SOLUTION

The optimal input and state profiles consist of several different intervals. An input or state variable in a given interval is either at its constraint value (minimum or maximum) or it may take a value in the *interior* of its constraint values. Thus, the optimal solution consists of two *types* of intervals: (1) Active constraint interval and (2) Inactive constraint interval.

Knowledge of the solution structure enables one to analyze and estimate the exact solution of the optimization problem, individually within each interval. The following four scenarios may be encountered while analyzing the solution structure with respect to static constraints.

1) *Active input constraint and inactive state constraint*: An interval in which some inputs are on constraints while the states are in the interior of their constraints is very common. The bounded flow rate of feed to a reactor resulting from the valve and piping constraints is an example for active input constraint. When an input constraint is active, that input takes its corresponding constant maximum or minimum value during that interval. Three different cases may occur when the optimal solution falls in this interval:
   - T is active, F is inactive: In this case, $T = T_{min}$ or T_{max} while F stays on the interior of its bounds. Out of the minimum and maximum bounds, the temperature bound that gives better objective function is chosen.
   - T is inactive, F is active: In this case, $F = F_{min}$ or F_{max} while T stays on the interior of its bounds. Out of the minimum and maximum bounds, the flow rate bound that gives better objective function is chosen.
   - Both T and F are active: In this case, $F = F_{min}$ or F_{max} and $T = T_{min}$ or T_{max}. Out of the four minimum and maximum bounds, the combination of flow rate and temperature bounds that gives better objective function is chosen.
2) *Active input constraint and active state constraint*: An interval in which both the inputs and states are active is relatively rare. A maximum allowable feed flow rate (input) resulting in a constant maximum concentration (state) inside the reactor is an example for active input and state constraints. Such constraints are more common in continuous processes. When feasible, both inputs and states are maintained on their corresponding bounds during such as interval. However, it is likely that one constraint may not stay active while maintaining another active constraint. If indeed such an interval is encountered in batch process optimization, the more critical of the two (input and state) active constraints is implemented at the expense of keeping the other inactive, i.e., in compromise-seeking interval. For instance, constraint on temperature is often treated as the more critical constraint compared to a constraint on maximum feed flow rate. When the two constraints coexist, if feasible, the temperature and the flow rate are maintained on the corresponding bounds. If this is infeasible, temperature is maintained on the bound while the flow rate is maintained between the bounds.
3) *Inactive input constraints and active state constraint*: When a state constraint is active, that state takes its corresponding constant maximum or minimum value during that interval. Since the input constraints are inactive, input profiles are so chosen to keep the constrained state on its constraint value. This scenario is commonly encountered in almost all batch processes. It is often required to maintain product concentration (state) at a maximum bound in batch reactors and given the inherent unsteady nature of the processes, a nonlinear feed flow rate (input) may be required to maintain the active state constraint. Thus, the optimization problem for this interval can be posed as a standard regulation problem [Isidori, 1989]. Three different cases may occur when the optimal solution falls in this interval:
   - x_1 is active, x_2 is inactive: In this case, $x_1 = x_{1,min}$ or $x_{1,max}$ while x_2 stays on the interior of its bounds. Out of the minimum and

maximum bounds, the bound that gives better objective function is chosen for x_1. The inputs are optimized to maintain x_1 on the bound.

- x_1 is inactive, x_2 is active: In this case, $x_2 = x_{2,min}$ or $x_{2,max}$ while x_1 stays on the interior of its bounds. Out of the minimum and maximum bounds, the volume bound that gives better objective function is chosen. It can be seen that the optimal flow rate value has to be zero when volume constraint is active. The corresponding optimal temperature will be in the interior of the constraints and can be calculated using the necessary conditions for optimality.
- Both x_1 and x_2 are active: In this case, $x_1 = x_{1,min}$ or $x_{1,max}$ and $x_2 = x_{2,min}$ or $x_{2,max}$. In this situation, both inputs are utilized to keep the two states on their constraint values.

4) Inactive input constraints and inactive state constraints: An interval in which both inputs and states constraints are in the interior of their constraint values is a common scenario encountered in batch processes. Analytical expressions may be evaluated for inputs in terms of states in such intervals as shown in the next section.

V. DEVELOPMENT OF ANALYTICAL EXPRESSIONS

Analytical expressions for the optimal feed rate and the optimal temperature can be derived when these inputs are in the interior of their constraint values. Using the procedure developed in Palanki *et al.*, [1993], it can shown that the optimal feed rate can be determined by the following algebraic expression:

$$x_2 C_{AF} \frac{\partial r_A^{'}}{\partial x_1} + r_A^{'} + x_2 \frac{\partial r_A^{'}}{\partial x_2} = 0 \tag{20}$$

The optimal feed rate takes a value that *constrains* the system states to the surface described by eq. (20). This is a regulator problem that can be solved via standard controller design methods. The optimal temperature profile can be determined by the following algebraic expression:

$$\frac{\partial r_A^{'}}{\partial T} = 0 \tag{21}$$

Since $r_A^{'}$ is an explicit function of T, an algebraic expression that relates the optimal temperature to the system states can be derived.

These expressions can be simplified if the reaction occurring in the reactor is elementary.

Irreversible Elementary Reaction

If the reaction represented by eq. (1) is an irreversible elementary reaction, the reaction rate can be written as follows:

$$r_A = k_0 exp\left(-\frac{E}{RT}\right) C_A^a C_B^b \tag{22}$$

Application of eq. (20) on the reaction rate represented by eq. (22) results in the following surface condition:

$$C_A = \frac{a}{a+b-1} C_{AF} \tag{23}$$

Clearly, there are situations where the above equation results in a physically infeasible situation. For instance when $a = 1$ and $b = 1$, the above condition suggests that the concentration of species A is *equal to* the feed concentration which requires an infinite feed flow rate. This implies that the feed rate has to be on one of its constraint values.

Application of eq. (21) on the reaction rate represented by eq. (22) results in the following expression:

$$\frac{E}{RT^2} k_0 exp\left(-\frac{E}{RT}\right) C_A^a C_B^b = 0 \tag{24}$$

Clearly, there is no finite temperature that can satisfy the above expression and thus the optimal temperature policy for an irreversible elementary reaction is on one of its constraint values.

Reversible Elementary Reaction

If the reaction represented by eq. (1) is a reversible elementary reaction, the reaction rate can be written as follows:

$$r_A = k_{10} exp\left(-\frac{E_1}{RT}\right) C_A^a C_B^b - k_{20} exp\left(-\frac{E_2}{RT}\right) C_C^c C_D^d \tag{25}$$

Application of eq. (20) on the reaction rate represented by eq. (25) results in the following surface condition:

$$\begin{aligned}(a+b-aC_{AF}-1) k_{10} exp\left(-\frac{E_1}{RT}\right) C_A^a C_B^b = \\ (c+d-1) k_{20} exp\left(-\frac{E_2}{RT}\right) C_C^c C_D^d\end{aligned} \tag{26}$$

As in the irreversible case, the above expression provides an expression that can be used to determine if a feed rate in the interior of its constraint values is feasible or not.

Application of eq. (21) on the reaction rate represented by eq. (25) results in the following expression:

$$T = \frac{E_1 - E_2}{R} \frac{1}{ln\left[\frac{k_{10} E_1 C_A^a C_B^b}{k_{20} E_2 C_C^c C_D^d}\right]} \tag{27}$$

This expression provides a nonlinear feedback law that can be implemented in real-time provided state measurements or estimates are available.

VI. DEVELOPMENT OF NUMERICAL ALGORITHM

In the previous sections, it is shown that the optimal solution consists of several intervals. In each interval (input constraint, state constraint, interior to state constraints), it is possible to compute the optimal input vector as a state feedback. To compute the optimal solution, the following numerical approach can be utilized:

1) Guess a sequence of intervals.

2) Using the optimal state feedback laws in each interval, iterate on the switching times between intervals till the objective function cannot be further minimized.
3) Change the sequence of intervals and go to step 2 till there is no further decrease in the objective function.

The above algorithm provides an alternative to the arbitrary parameterization of the inputs and states that is done in the NLP approach [Cuthrell and Biegler, 1989].

VII. ILLUSTRATIVE EXAMPLE

In this section, the methodology described in this work is illustrated via in a simulation example.

Esterification of acetic acid with methanol is a reversible reaction that proceeds as follows:

$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O \quad (28)$$

The reaction rate is given by (Yu *et. al* [2004]):

$$r_A = k_1 C_A C_B - k_2 C_C C_D \quad (29)$$

where $A : CH_3COOH$, $B : CH_3OH$, $C : CH_3COOCH_3$, and $D : H_2O$. The rate constants as a function of temperature are given as follows:

$$\begin{aligned} k_1 &= (1.29 \times 10^4) exp\left(-\frac{44.30}{RT}\right) \\ k_2 &= (8.82 \times 10^3) exp\left(-\frac{50.03}{RT}\right) \end{aligned} \quad (30)$$

The frequency factor has the units of $l/mol/s$ while the activation energy has the units of kJ/mol . The reaction conditions are included in Table 1. The objective of the optimization problem is to find the acetic acid feeding policy that corresponds to the maximum amount of methyl acetate produced inside the reactor.

Parameter	Value	Units
Minimum Temperature (T_{min})	325	K
Maximum Temperature (T_{max})	525	K
Simulation time (t)	6000	s
Frequency factor for forward reaction (k_{10})	$1.29E4$	L/mol.s
Frequency factor for backward reaction (k_{20})	$8.82E3$	L/mol.s
Activation energy for forward reaction (E_1)	$44.3E3$	J/mol
Activation energy for backward reaction (E_2)	$50.03E3$	J/mol
Concentration of acetic acid in feed (C_{AF})	1	mol/L
Initial Reactor volume (V_o)	10	L
Initial concentration of A in the reactor (C_{AO})	0	mol/L
Initial concentration of B in the reactor (C_{BO})	10	mol/L
Initial concentration of C in the reactor (C_{CO})	0	mol/L
Initial concentration of D in the reactor (C_{DO})	0	mol/L
Maximum volumetric flow rate of feed ($F_{o,max}$)	0.5	L/s
Minimum volumetric flow rate of feed ($F_{o,min}$)	0	L/s
Maximum reactor volumete (V_{max})	750	L

Table 1 Reaction Conditions

It is clear from eq. (26) that it is infeasible to have a feed rate in the interior of the constraint values. Thus, the optimal feed rate policy in any given interval of the optimal solution is either at the lower constraint or the upper constraint. Application of eq. (27) indicates that there may be an interval in the optimal solution where the temperature is in the interior of the constraints.

The optimal input and state profiles are shown in figures 1-3.

VIII. CONCLUSIONS

In this paper, the structure of the optimal solution for a single reaction system is analyzed. It is shown that the optimal solution consists of several intervals and it is possible to compute the optimal solution in each interval *analytically*. This analysis can be exploited to develop a numerical algorithm that efficiently finds the optimal solution.

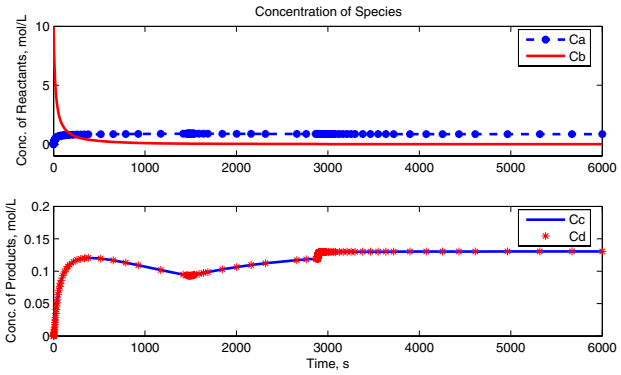

Figure 1 Optimal Concentration Profiles

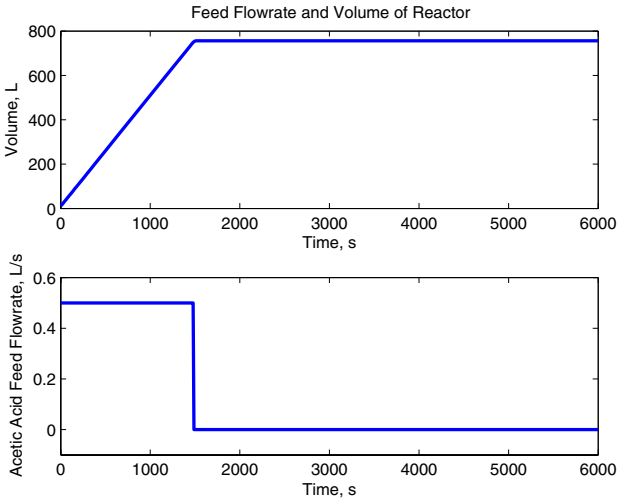

Figure 2 Optimal Feed Rate and Volume Profiles

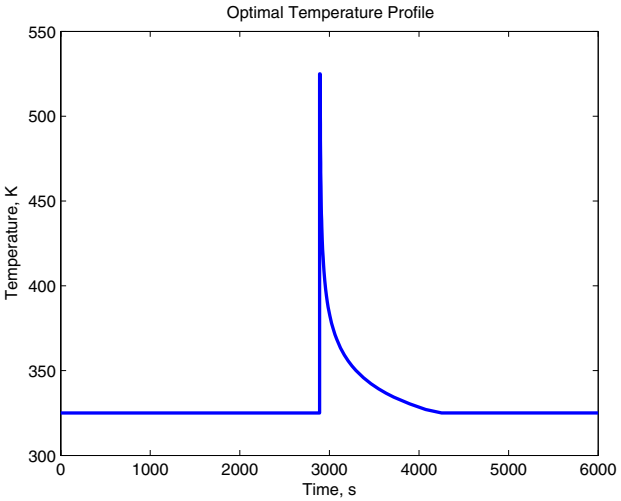

Figure 3 Optimal Temperature Profile

IX. ACKNOWLEDGMENTS

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