Journal of Cybernetics and Informatics

published by

Slovak Society for Cybernetics and Informatics

Volume 9, 2010

DYNAMIC OPTIMIZATION OF A HYBRID SYSTEM: EMULSION POLYMERIZATION REACTION

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Abstract: This work deals with the problem of dynamic optimization of an emulsion polymerization reaction in batch reactor. This process can be described as a hybrid system, i.e. dynamic system with both continuous and discrete character. We obtain optimal trajectories of control variable using control vector parameterization (CVP) method. This method translates infinite dynamic optimization problem into finite non–linear programming (NLP) problem. The NLP computation requires gradient information which we provide using method of adjoint variables.

Keywords: Dynamic Optimization, Hybrid Systems, Emulsion Polymerization

1. INTRODUCTION

Hybrid models provide better dynamic information of physical phenomena occurring in processes in real world than classical continuous models. As an example of hybrid system we treat emulsion copolymerization reaction of styrene and α–methylstyrene in batch reactor.

Emulsion polymerization refers to a unique process employed for some radical chain polymerizations. It involves the polymerization of monomers in the form of emulsions (Odian, 2004). This process has several distinct advantages. The physical state of the emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerization. The product of an emulsion polymerization, referred to as latex, can in many instances be used directly without further separations (Odian, 2004).

Approach used to find an optimal control of a plant or process is termed optimal control or dynamic optimization. It encompasses several techniques, which can be divided in two broad frameworks, variational methods and discretization methods. In variational methods, a classical calculus of variations together with Pontryagin's maximum principle (Pontryagin et al, 1964) is applied. These methods address the dynamic optimization problem in its original infinite dimensional form. A big advantage of this is that we are looking for exact solution to problem without any transformations. But it can be disadvantageous in case of more complex systems. Then a discretization plays an important role, since original infinite dimensional problem can be in principle transformed to non–linear programming (NLP) problem. And there are plenty of solvers capable to solve NLP problems.

There also exist a number of methods which can be utilized to generate discretization grid of variables participating in dynamic optimization problem. Sequential discretization and full

discretization are two classes of these methods. Full discretization represents an approach which takes advantage of states and control discretization (Tsang et al., 1975). Second class, sequential discretization, is based on control discretization. Sequential discretization is usually achieved via control parameterization, (Brusch et al., 1973) in which the control variable profiles are approximated by a sum of basis functions with a finite set of real parameters. These parameters then become the decision variables in a dynamic embedded NLP. Function evaluations are provided to this NLP via numerical solution of a fully determined initial value problem (IVP), which is given by fixing the control profiles. This method possesses the advantages of yielding a relatively small NLP and exploiting the robustness and efficiency of modern IVP and sensitivity solvers.

2. PROCESS MODEL

Like in previous works (Gentric et al., 1999), our goal is to produce polymer of prescribed terminal quantity and quality in minimum time. Quantity condition is represented by final conversion of monomer (styrene and α–methylstyrene) and quality condition is described by the final value of number–average molecular weight, weight–average molecular weight or polydispersity index of polymer. Control variable is reactor jacket inlet temperature. Overall process model involves kinetic model, molecular weight distribution model, and reactor temperature dynamics model. It is described by seven first–order non–linear ordinary differential equations (ODEs) which right hand sides are varying according to one of the three stages of the process.
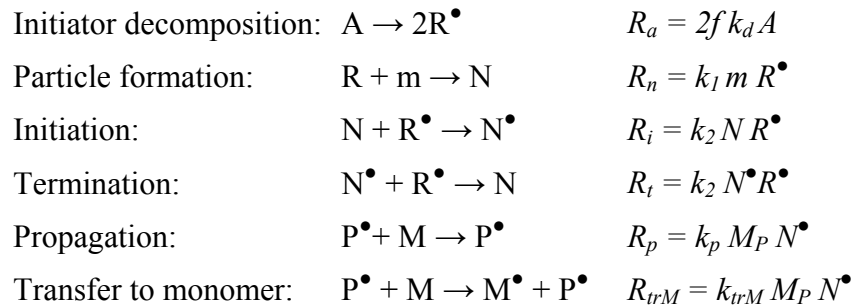
Kinetic Mechanism

The three stages of the process are as follows:

1. In the first stage, free radicals are produced in the aqueous phase by initiator decomposition. They are captured by the micelles swollen with monomer. The polymerization begins in these micelles. This stage, corresponding to particle heterogeneous nucleation (the polymerization rate is increasing), stops when all of the micelles have disappeared.

2. Particle growth occurs during the second stage. Monomer diffuses rapidly from monomer droplets toward the particles, which are saturated with monomer as long as monomer droplets exist. This stage ceases when all of the monomer droplets have disappeared (the polymerization rate is constant).

3. The third and final stage is characterized by the decrease of the monomer concentration in particles; also the polymerization rate is decreasing.

The following assumptions are used in the modeling of the kinetic process:

Styrene and α–methylstyrene are both hydrophobic monomers; thus, only micellar nucleation is taken into account. Because of this hydrophobic character, the reactions of propagation, transfer to monomer, termination in the aqueous phase, and radical desorption are neglected. Termination in particles is considered to be very rapid compared to radical entry into particles; thus, it can be assumed that no more than one radical is present in each polymer particle (zero–one system). This allows us to write $P_j^\bullet = N^\bullet$, where variable $P_j^\bullet$ represents number of activated polymers of chain length j and $N^\bullet$ represents number of active particles. The maximum conversion rate considered is generally around 65%, so that gelation has not yet occurred. Thus, the gel effect is not included in the model to avoid unnecessary complexity. Coagulation is assumed to be negligible.

The kinetic mechanism is then written as follows:

Initiator decomposition: $A \rightarrow 2R^{\bullet}$ $R_a = 2f\,k_d\,A$

Particle formation: $R + m \rightarrow N$ $R_n = k_1\,m\,R^{\bullet}$

Initiation: $N + R^{\bullet} \rightarrow N^{\bullet}$ $R_i = k_2\,N\,R^{\bullet}$

Termination: $N^{\bullet} + R^{\bullet} \rightarrow N$ $R_t = k_2\,N^{\bullet}R^{\bullet}$

Propagation: $P^{\bullet} + M \rightarrow P^{\bullet}$ $R_p = k_p\,M_P\,N^{\bullet}$

Transfer to monomer: $P^{\bullet} + M \rightarrow M^{\bullet} + P^{\bullet}$ $R_{trM} = k_{trM}\,M_P\,N^{\bullet}$

Here A means initiator concentration, $R^{\bullet}$ stands for initiator radical concentration, m represents number of micelles per unit volume, M is global monomer concentration and finally f is initiator efficiency. Variables R and k differing by index of partial reaction of kinetic mechanism denote reaction rates and reaction kinetic coefficients.

Kinetic Model

Only the global monomer concentration is described. The depropagation is taken into account by including in the propagation rate constant a factor depending on the α–methylstyrene molar fraction in the initial charge

$$k_p = k_p^{'} \exp(-a.f_{MS}) \tag{1}$$

where a is a constant, f_{MS} is molar fraction of α–methylstyrene at the beginning of a reaction and $k_p^{'}$ is the propagation rate constant for styrene homopolymerization. The quasi–stationary state approximation allows calculating the initiator radicals' concentration

$$R^{\bullet} = \frac{R_a}{k_1 m + k_2 N_p} \tag{2}$$

where $N_p = N + N^{\bullet}$ is overall number of polymer particles. Then the rate of particles formation may be written

$$\dot{N}_p = k_1 m \frac{R_a N_A}{k_1 m + k_2 N_p} \tag{3}$$

Here N_A stands for Avogadro's number. Like (Harada et al., 1972), we introduce the factor which is similar to effectiveness for the particles relative to the micelles in collecting an initiator radical

$$\varepsilon = \frac{k_2 S N_A}{k_1 m} \tag{4}$$

The rate of particle formation is now expressed by

$$\dot{N}_p = k_1 m \frac{R_a N_A}{1 + \dfrac{\varepsilon N_p}{S N_A}} \tag{5}$$

With the classical hypothesis that the emulsifier molecules are adsorbed in a monomolecular layer on the polymer particles surface, the emulsifier concentration may be written

$$S = S_0 - k_v (X M_0)^{2/3} N_p^{1/3} \tag{6}$$

where S_0 denotes initial emulsifier concentration, M_0 means initial monomer concentration,

X signifies monomer conversion and

$$k_v = \left[\frac{36\pi M_M}{\omega_P^2 (a_s N_A)^3 \rho_P^2} \right]^{1/3} \tag{7}$$

where M_M denotes monomer molecular weight, ω_P means polymer weight fraction in particles, variable a_s represents surface area occupied by an emulsifier molecule and ρ_P stands here for polymer particle density. The rate of monomer consumption is expressed according to

$$\dot{M} = -R_p = -k_p M_p \frac{N_p}{N_A} \bar{n} \tag{8}$$

with average number of radicals per particle $\bar{n} = 0.5$, and monomer concentration in particles M_p which can be expressed as

$$M_p = M_{pc} = \frac{(1-X_c)\rho_M}{[(1-X_c) + X_c \rho_M/\rho_P] M_M} \qquad X \le X_c$$

$$M_p = \frac{(1-X)\rho_M}{[(1-X) + X\rho_M/\rho_P] M_M} \qquad X > X_c \tag{9}$$

here constant M_{pc} denotes critical monomer concentration in particles, X_c stands for critical monomer conversion and ρ_M represents monomer density.

Molecular Weight Distribution Model

Besides it is important to evaluate the polymer properties. They are linked to the polymer structure and can be described in terms of average molecular characteristics (number– and weight–average molecular weights, polydispersity index, etc.). The used approach is an extension of the tendency model (Villermaux et al., 1984) to emulsion polymerization. According to the kinetic mechanism, the rates of production of the zeroth, first and second order moments of the molecular weight distribution may be written as

$$\dot{Q}_0 = R_t + R_{trM}$$
$$\dot{Q}_1 = L(R_t + R_{trM})$$
$$\dot{Q}_2 = 2L^2 (R_t + R_{trM}) \tag{10}$$

where

$$R_t = \frac{R_a \bar{n} N_p}{N_p + \dfrac{S}{\varepsilon}}$$

$$R_{trM} = k_{trM} M_p \frac{N_p}{N_A} \bar{n} \tag{11}$$

$$L = \frac{R_p}{R_t + R_{trM}}$$

Variable L denotes kinetic chain length. Once these moments are known, the number– and weight–average molecular weight ($\overline{M}_n$ and $\overline{M}_w$) and polydispersity index (I_p) can be calculated

$$\overline{M}_n = M_M \frac{Q_1}{Q_0} \qquad \overline{M}_w = M_M \frac{Q_2}{Q_1} \qquad I_p = \frac{\overline{M}_w}{\overline{M}_n} \tag{12}$$

Reactor Temperature Dynamics Model

In order to achieve temperature control, it is necessary to describe the reactor temperature dynamics. The reaction takes place in a glass stirred tank reactor. Heat control is realized thanks to a cooling fluid circulating in a jacket at constant flow rate. The inlet temperature of the cooling fluid is controllable. Energy balances on the jacket and the reactor contents give the following equations for the reactor and jacket temperature dynamics

$$\dot{T} = -\frac{V\Delta H}{m_r C_p}R_p + \frac{UA}{m_r C_p}(T_j - T)$$

$$\dot{T}_j = \frac{F_j}{V_j}(T_{j,in} - T_j) - \frac{UA}{\rho_j V_j C_{p,j}}(T_j - T)$$

$$(13)$$

where V and V_j are reactor contents volume and reactor cooling jacket volume respectively, ΔH means polymerization reaction enthalpy, term $m_r C_p$ represents reactor total heat capacity, constant U means heat–transfer coefficient, A is cooling surface, variables F_j, ρ_j and $C_{p,j}$ signify cooling fluid flow rate, cooling fluid density and cooling fluid heat capacity respectively. All the kinetic coefficients are calculated according to Arrhenius law

$$k_i = k_{i,0}\exp(-E_j / RT)$$

$$(14)$$

Hybrid Representation of the Process Model

Majority of this section uses notation introduced by (Feehery, 1998). Dealing with the hybrid systems of ODEs means dealing with a system of a form

$$\text{mode } S_i \quad \dot{x}^{(i)} = f^{(i)}(x^{(i)}, u^{(i)}, p, t) \qquad \forall t \in \left[t_0^{(i)}, t_f^{(i)}\right], S_i \in \bigcup_{k=1}^{n_k} S_k$$

$$(15)$$

where $x^{(i)} \in \Re^{n_x^{(i)}}, u^{(i)} \in \Re^{n_u^{(i)}}$ and $p \in \Re^{n_p}$. Function $f^{(i)}$ is such that $f^{(i)} : \Re^{n_x^{(i)}} \times \Re^{n_u^{(i)}} \times \Re^{n_p} \times$

$\Re \to \Re^{n_x^{(i)}}$. Switching from one stage (mode S_k) to another (mode S_j) occurs when a unique transition condition $L_j^{(k)}(\dot{x}^{(j)}, x^{(j)}, u^{(j)}, p, t), S_j \in P^{(k)}$ is satisfied. Set $P^{(k)}$ contains all possible successive stages of mode S_k. Transition function $T_j^{(k)}(\dot{x}^{(k)}, x^{(k)}, u^{(k)}, \dot{x}^{(j)}, x^{(j)}, u^{(j)}, p, t)$ determines possible discontinuity in variables participating in model. There is a special case of transition function defined at mode initial time $t = t_0^{(k)}$ where

$$T_j^{(0)}(\dot{x}^{(k)}, x^{(k)}, u^{(k)}, p, t) = 0 \Rightarrow x^{(k)}(t_0^{(k)}) = x_0^{(k)}$$

$$(16)$$

Hence that model represented by equations (5), (8), (10) and (13) is strongly non–linear and hybrid as well (Salhi et al., 2004). Its hybrid character can be expressed as follows

$$\text{mode } S_i \quad \dot{x}^{(i)} = f^{(i)}(x^{(i)}, u, p) \qquad \forall t \in \left[t_0^{(i)}, t_f^{(i)}\right], S_i \in \{S_1, S_2, S_3\}$$

$$(17)$$

where states vector is defined as

$$x^T = \left[M, N_p, Q_0, Q_1, Q_2, T, T_j\right]$$

$$(18)$$

In our case switching between stages passes in order known in advance. So we can define transition conditions as

$$L_2^{(1)}(\dot{x}^{(1)}, x^{(1)}, u, p, t) = 0 \Rightarrow N_p(t) = N_p^{st}$$

$$L_3^{(2)}(\dot{x}^{(2)}, x^{(2)}, u, p, t) = 0 \Rightarrow X(t) = X_c$$

$$(19)$$

where constant $N_p{}^{st}$ represents constant number of particles dependent on temperature and initial load in reactor. Note that due to known sequence of stages we can write

$$t_0 = t_0^{(1)} \quad t_f^{(1)} = t_0^{(2)} \quad t_f^{(2)} = t_0^{(3)} \quad t_f^{(3)} = t_f \tag{20}$$

Transition functions finally can be defined as

$$
\begin{aligned}
T_1^{(0)}(\dot{x}^{(1)}, x^{(1)}, u, p, t) &= 0 \Rightarrow x^{(1)}(t_0^{(1)}) = x_0^{(1)} \\
T_2^{(1)}(\dot{x}^{(1)}, x^{(1)}, u^{(1)}, \dot{x}^{(2)}, x^{(2)}, u, p, t) &= 0 \Rightarrow x^{(2)}(t_0^{(2)}) = x^{(1)}(t_f^{(1)}) \\
T_3^{(2)}(\dot{x}^{(2)}, x^{(2)}, u^{(2)}, \dot{x}^{(3)}, x^{(3)}, u, p, t) &= 0 \Rightarrow x^{(3)}(t_0^{(3)}) = x^{(2)}(t_f^{(2)})
\end{aligned}
\tag{21}
$$

The rest of this section forms conditions for particular stages of the process. As it was told before, in process second and third stage number of particles stays constant which says that $\dot{N}_p^{(2)} = \dot{N}_p^{(3)} = 0$. In the third stage, calculation of variable M_p changes (see equations (9)). This changes also right hand sides of equations (8), (10) and (13) where M_p is present implicitly.

3. PROCESS OPTIMIZATION

We obtain optimal trajectories of control variable using control vector parameterization (CVP) method. This method translates infinite dynamic optimization problem into finite non–linear programming (NLP) problem. The NLP computation requires gradient information which we provide using method of adjoint variables.

Our objective is to compute such a control *u(t)* of the system that will drive system to desired terminal state (some state values are prescribed at final time) at minimum time possible. We can define our optimization problem as

$$
\begin{aligned}
\min_{u(t), p} &\int_{t_0}^{t_f} dt = t_f - t_0 \\
s.t. \quad &\dot{x}^{(i)} = f^{(i)}(x^{(i)}, u, p) \quad \forall t \in \left[t_0^{(i)}, t_f^{(i)}\right], S_i \in \{S_1, S_2, S_3\} \\
&x^{(1)}(t_0^{(1)}) = x_0^{(1)} \\
&h(x^{(3)}(t_f), u(t_f), p, t_f) = 0 \\
&u(t) \in [u^L(t), u^U(t)] \\
&p \in [p^L, p^U]
\end{aligned}
\tag{22}
$$

where initial state vector is defined as

$$\left(x_0^{(1)}\right)^T = [M_0, 0, 0, 0, 0, T_0, T_{j,0}] \tag{23}$$

where M_0 is amount of monomer (styrene and α–methylstyrene) input to reactor and T_0 and $T_{j,0}$ are variables which represent initial reactor and cooling jacket temperature. These are parameters *p* to be optimized. Lower and upper bounds imposed on parameters as well as on controls are signified by superscripts *L* and *U* respectively. Terminal state of the reaction is characterized both by quantity and quality terminal conditions, *h(x(t_f),u(t_f),p,t_f)*. Quantity terminal condition means that we desire final conversion of monomer to be

$$X_f = X(t_f) = 1 - \frac{M(t_f)}{M_0} \tag{24}$$

Quality terminal condition is represented by final value of number–average molecular weight, weight–average molecular weight or polydispersity index of polymer and can be computed by equations (12). The optimized control *u(t)* is reactor cooling jacket inlet temperature $T_{j,in}(t)$.

Optimization Method

Equations (21) state that studied system is continuous and the same goes for the adjoint variables. Optimality conditions derived from application of Pontryagin's maximum principle (Pontryagin et al., 1964) can be then summarized as

$$\frac{\partial H^{(i)}}{\partial u} = 0$$

$$\dot{\lambda}^{(i)}(t) = -\frac{\partial H^{(i)}}{\partial x^{(i)T}} \qquad S_i \in \{S_1, S_2, S_3\} \tag{25}$$

$$\lambda^{(3)}(t_f) = \frac{\partial G}{\partial x^{(3)T}}\bigg|_{t=t_f}$$

where

$$H^{(i)}(x^{(i)}(t), \lambda^{(i)}(t), u(t), p, t) = F(x^{(i)}(t), u(t), p, t) + \lambda^{(i)T}(t) f(x^{(i)}(t), u(t), p, t) \tag{26}$$

is Hamiltonian function and λ is vector of adjoint variables and G is the non–integral part of objective function. We employ CVP method to solve dynamic optimization problem. In first step, control trajectory $u(t)$ is discretized to final number of intervals with constant control u_j, where $j = \{1, \ldots, n_u\}$ indicates control interval number.

The performance index is evaluated by solving an initial value problem (IVP) of the original ODE system, and gradients of the performance index as well as the constraints with respect to the parameters (p and approximations of $u(t)$) can be obtained by solving either the adjoint equations or the sensitivity equations.

Computing Gradients

Accurate gradients calculation is one of the most challenging steps in solving the NLP problem which was derived from original problem (22) using piecewise–constant control u_j applied on specified instant of time $\Delta t_j = t_j - t_{j-1}$. Gradients of objective function J can be computed such that

$$\frac{\partial J}{\partial t_f} = H^{(3)}(t_f^-) + \frac{\partial G}{\partial t_f}$$

$$\frac{\partial J}{\partial t_j} = H^{(i)}(t_j^-) - H^{(i)}(t_j^+) + \frac{\partial G}{\partial t_j} \quad \forall j \in \{1, \ldots, n_u - 1\}, S_i \in \{S_1, S_2, S_3\}$$

$$\frac{\partial J}{\partial p} = \frac{\partial G}{\partial p} - J_p(t_0) + \lambda^{(1)T}(t_0^+) \frac{\partial x_0^{(1)}}{\partial p} \tag{27}$$

$$\frac{\partial J}{\partial u_j} = J_u(t_{j-1}) - J_u(t_j) \quad \forall j \in \{1, \ldots, n_u\}$$

where

$$\dot{J}_u = \frac{\partial H^{(i)}}{\partial u}$$

$$\qquad S_i \in \{S_1, S_2, S_3\} \tag{28}$$

$$\dot{J}_p = \frac{\partial H^{(i)}}{\partial p}$$

Constraint functions can be expressed in form of optimization criterion (Salhi et al., 2004), so that constraint gradients can be found in similar manner like presented in equations (27).

Optimization Algorithm

We employ the procedure which can be described in following steps:

Step 1: Perform initial guess for values of u_j, Δt_j and p.

Step 2: Integrate system forward in time.

Step 3: Evaluate objective function and constraint functions.

Step 4: Integrate system of adjoint equations backward in time.

Step 5: Calculate gradients.

Step 6: Use NLP solver to obtain new values of variables u_j, Δt_j and p.

Step 7: If the optimality conditions are satisfied then quit. Else, go to Step 2.

4. RESULTS AND DISCUSION

Optimization algorithm proposed in Section 3 is implemented using MATLAB and its NLP solver *fmincon* which solves constrained non–linear programming problems. Integration is performed using *ode45* integrator where 4th order Runge–Kutta numerical integration method is implemented. Optimization problem is solved for different control discretization scenarios. Obtained results are summarized in following table:

Table 1: Comparison of different control strategies for desired terminal state: $X_f = 0.7$, $\overline{M}_n = 2 \times 10^3$

n_u	$J[s]$	X_f	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-6}$	I_p
1	5340	0.7	2.0	4.3	2.13
2	5234	0.7	2.0	4.4	2.20
3	4950	0.7	2.0	4.8	2.38
4	4859	0.7	2.0	5.7	2.87
5	4673	0.7	2.0	5.8	2.87
6	4609	0.7	2.0	5.8	2.87
7	4550	0.7	2.0	6.0	3.01
8	4539	0.7	2.0	6.3	3.13
9	4502	0.7	2.0	6.3	3.13
10	4445	0.7	2.0	6.4	3.18

where variable n_u represents the number of control segments considered. It can be seen that by the rising number of control segments not only the optimization criterion is lowering its value (as expected) but also an overall quality of polymer produced rises (this can be seen in last two columns of the Table 1). Graphically, the results can be represented in Figure 1 where the control trajectories of selected control scenario with 10 control segments as well as reactor temperature trajectories are depicted. Using of multistart method (i.e. starting optimization algorithm from multiple different starting points) showed that optimization problem appears to have multiple local minima.
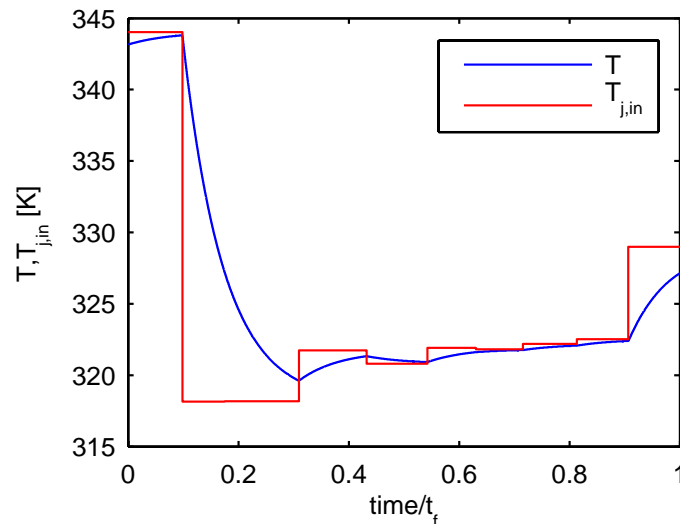
Figure 1: Optimal control ($T_{j,in}$) trajectory for $n_u=10$

5. CONCLUSIONS

We discuss process of copolymerization of styrene and α–methylstyrene. In previous sections we

- model this process

- give hybrid representation of process model

- optimize the process such to produce desired quality polymer in minimum time amount

As the computations suggest there might exist more than one solution to our problem because when the optimization algorithm is launched from different initial point (a multistart method) a different solution is reported at the end of an algorithm run. This suggests that our optimization problem possesses multiple (local) minima. Further this tells that to find an optimal point we should utilize another approach (global optimization) to achieve guarantee of global optimality of control variable profiles. This will be the goal for future works, beside practical implementation of optimal control to real process.

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