Dynamic Optimization of Autocatalytic Esterification in Semi Batch Reactor using Orthogonal Collocation and Control Vector Parameterization Method

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***Abstract*—Catalyzed Esterification of Propionic Anhydride with 2-Butanol is commonly applied in semi batch reactors where the process variables undergo significant changes during the duration of the batch. In this semi batch operation, there is no steady state and thus no constant setpoints around which the key variables can be regulated. Consequently, in this work, dynamic optimization approach is implemented to achieve optimal temperature and feed flowrate trajectories under free and fix interval time that can maximize conversion. Two techniques applied in this work are control vector parameterization (CVP) and orthogonal collocation (OC). From the results, OC produce higher conversion and shorter final time but required slightly larger CPU time as compared to CVP.**

Keywords- Simulation; Dynamic Model; Semi Batch Catalyzed Esterification; Dynamic Optimization

I. INTRODUCTION

The product of esterification of propionic anhydride with 2-butanol is a fragrance and flavors that widely used in food, cosmetic and pharmaceutical industries [1]. The ester is commonly produced in semi batch reactors. In this semi batch process operation, the process variables undergo significant changes during the duration of the batch. There is no steady state and thus no constant setpoints around which the key variables can be regulated. Hence, the major objective in batch operation is not to keep the system at some optimal constant setpoints, but rather to optimize an objective function that expresses the system performance. Optimizing an objective function corresponds to, for example, achieving a desired product quality at the most economical cost, or maximizing the product yield for a given batch time. The optimization is commonly performed in the presence of constraints. In addition to the dynamic system equations acting as constraints, there might be bounds on the inputs as well as constraints. Constraints typically result from safety, performance considerations and operability considerations. Thus, batch optimization problems involve both dynamic and static constraints and fall under the class of dynamic optimization problems [2].

The discretization techniques received major attention and considered as an efficient solution method for dynamic optimization problem. The concept of this approach is to transform the original optimal control problem into a finite dimensional optimization problem, typically a nonlinear programming problem (NLP). Then, the optimal control solution is given by applying a standard NLP solver to directly solve the optimization problem. For this reason, the method is known as a direct method. The transformation of the problem can be made by using discretization technique on either only control variables (control vector parameterization) or both state and control variables (orthogonal collocation) [3].

The optimal trajectories obtained are implemented further for online system. Thus, the computational time required for dynamic optimization technique applied is also an important issue need to be addressed. The feasible technique selected can improve an effectiveness of computation which is compatible for online implementation. In this study, an optimization study of catalyzed Esterification of Propionic Anhydride with 2-Butanol in semi batch is carried out using parameterization (CVP) and orthogonal collocation (OC). Both techniques are evaluated based on the maximum conversion problem under free interval time. Both techniques are compared based on analysis of the optimal trajectories performances obtained and computational time required.

II. MODELING OF CATALYZED ESTERIFICATION

A. Reaction Kinetics

Esterification of propionic anhydride with 2-butanol produce sec-butyl propionate and propionic acid. The process is homogeneous reaction which moderately exothermic with no danger of decomposition reactions. The reaction rate variable is a function of catalyst (strong acid, such as sulphuric acid); exhibits a second-order kinetics when no strong acid is

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present and exhibits a kind of autocatalytic behaviour when sulphuric acid is introduced [4].

In the presence of sulfuric acid, Zalvidar, et al. [5] found that the reaction rate seems to be proportional to the acid concentration; the reaction rate increases with propionic acid concentration and lead to a kind of autocatalytic behavior. However, after reaching a certain concentration, propionic acid has no longer influenced the reaction rate. Since the various theoretical reaction pathways are complex, a model was developed by assuming the existence of two catalysts (cat1, cat2). Meanwhile, the transformation of the initial catalyst was developed by taking into account the acidity function. The esterification reaction scheme under consideration can be written as [5]:

Reaction 1: 2-butanol + propionic anhydride → propionic acid + sec-butyl propionate

Reaction 2: catalyst 1→ catalyst 2

B. Mass Balance of Esterification in Semi Batch Reactor

The mass balances are developed according to the following assumptions: constant reacting heat capacity, effective overall heat transfer coefficient, transport properties of reaction mixture and density are exist; the heat losses with the ambient surroundings are negligible; homogeneous mixing and uniform distribution temperature: no heat accumulation in the reactor wall; no secondary heating effects such as power introduced by stirrer; no pressure effect; 2- butanol stated as limiting reactant. Reaction rate constants follow Arrhenius law.

The expression of the acidity function is [5]:

$$H = -(p_1 C_{cat1} + p_2 C_c)\left(p_3 + \frac{p_4}{T}\right) \tag{1}$$

The mathematical model of semi batch esterification reactor:

$$\frac{dC_A}{dt} = -((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) - \frac{F_0 C_A}{V} \tag{2}$$

$$\frac{dC_B}{dt} = -((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) + \frac{F_o}{V}(C_{B0} - C_B) \tag{3}$$

$$\frac{dC_C}{dt} = \frac{dC_D}{dt} = ((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) - \frac{F_0 C_C}{V} \tag{4}$$

$$\frac{dC_{cat1}}{dt} = -\frac{dC_{cat2}}{dt} = -(k_4 10^{-H} C_{cat1} C_A) - \frac{F_0 C_{cat1}}{V} \tag{5}$$

$$\frac{dV}{dt} = F_o \tag{6}$$

where, C_A,C_B,C_C, C_{cat1}, and C_{cat2} are concentration of 2-butanol, propionic anhydride; propionic acid, sulphuric acid, mono-butyl sulphuric acid, respectively.

Fo , V is the feed rate and volume of solution within reactor. The kinetic parameters values used in this work are depicted from [5].

III. DYNAMIC OPTIMIZATION PROCEDURE

Two discretization methods, i.e. control vector parameterization (CVP) and orthogonal collocation (OC) were applied in this dynamic optimization studies. Both methods were implemented within MATLAB environment. The OC method was implemented by using dynopt code package created by Cizniar et al. [6], where the algorithm had been developed by Cuthrell and Biegler [7]. Whereas, CVP method was implemented by using DOTcvp code package created by Hirmajer et al. [8].

A. Control Vector Parameterization Method

The basis of the CVP method is to parameterize the control trajectories and leave the state trajectories continuous. First, the ODE solver calculates the differential equation. Then, the original problem of dynamic optimization is transformed into the finite dimensional problem (NLP) for execution the static optimizer. Further, a suitable gradient method with a NLP type algorithm is needed. This corresponds to a 'feasible' path approach since the differential equations are satisfied at each step of the optimization. A piecewise-constant or piecewise - polynomial approximation of the inputs is often utilized. The basic procedure is as follows: 1) Parameterize the inputs using a finite number of decision variables (typically piecewise polynomials). The vector of decision variables also includes final time; 2) Choose an initial guess for the decision variables; 3) Integrate the system states to the final time and compute the performance index and the constraints; 4) Use an optimization algorithm (such as steepest descent or Quasi-Newton methods to update the values of the decision variables; Repeat Steps 3-4 until the objective function is minimized.

B. Orthogonal Collocation Method

In this approach, state and control variables are parameterized and the model solution and the optimization problem are solved simultaneously. An orthogonal collocation on finite elements is used to parameterize both state and control variables, and a sequential quadratic programming (SQP) which is used to solve the resulting NLP problems. The gradients of the performance index as well as of the constraints needed in the NLP solver are analytically computed using formal calculus. The basic procedure followed is: 1) Parameterize both inputs and states using a finite number of decision variables (typically piecewise polynomials). The vector of decision variables also includes t_f. 2) Discretize the differential equation in Eq. (2) with their initial conditions for selected time instants, 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) Solve for the optimal set of decision variables by using an NLP code.

C. Optimization Formulation

The reactant, catalyst and product concentrations are considered as states variables. The objective of this problem is to maximize conversion by optimizing feed rate and temperature reactor trajectories. And then, total volume

solution and end limiting reactant concentrations are associated as the inequality constraint. The full process time was discretized with fixed and free 12 piece wise constant interval time. The dynamic optimization problem formulation is shown as:

Problem:

$$\max_{T,F_0} \Im = \frac{C_{A0-}C_A}{C_{A0}}$$

Subject to semi batch dynamic model Eq.2-6

Inequality constraints: $V \leq 2L$; $C_A \leq 0.034M$

Bounds: $0 \leq F_0 \leq 3x\ 10^{-4} L\ s^{-1}$; $303^0K \leq T \leq 343^0K$

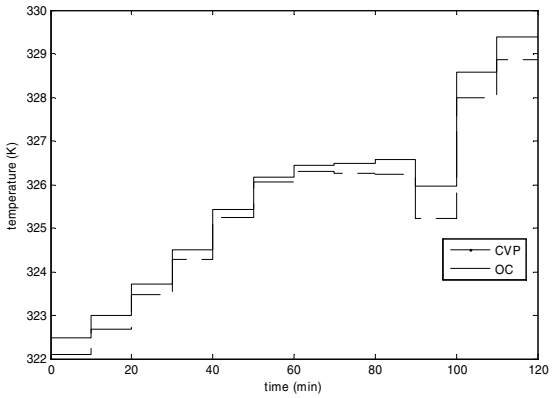
IV. RESULTS AND DISCUSSION

The optimal temperature and feed rate trajectory profiles achieved using CVP and OC for fixed interval and free interval time are shown in Fig.1 and 2, respectively. Dynamic optimization results for CVP and OC which is comprised of switching times and reactor performances such as conversion, final time and CPU simulation time are tabulated in Table.I.

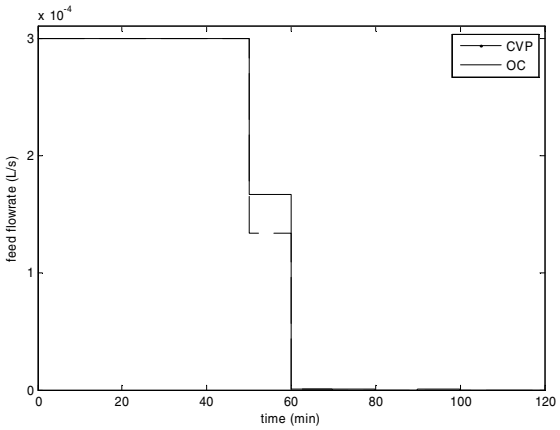
As shown in Table I, the conversion obtained from CVP and OC under fixed interval was 98.8%, 99%, respectively. While, the final time achieved to reach 99% conversion from CVP and OC under free interval was 99 and 96 min, respectively. The OC produce higher conversion and shorter final time due to the discretization of both control and state variables. The approximation of OC using orthogonal collocation on finite element is more accurate to search for the optimal solution Thus; it drove the trajectories to find the optimal solution which caused the increased of conversion and the decrease of final time. However, the CPU simulation time required to complete single batch optimization for OC is longer than CVP. The full discretization of OC increases the order the parameterization and the computation complexity which caused longer the CPU time is required to complete the single optimization.

The conversion achieved from CVP free interval is higher than CVP fixed interval. It is because the CVP free interval executes time element as decision variable. Thus, the accuracy of searching is improved which lead to reach the higher final conversion. It is observed that for free time interval, both CVP and OC resulted to shorter final time than fixed time interval. It is because the former allowed the interval time to be optimized and thus lead to shorter final time. However, the CPU time consumed under free final time is longer than under fixed final time. It is because the interval time has to be optimized and thus increase the order of parameterization. As a result, the computation is more complex and the simulation takes a longer time.

From the result, the difference CPU time of CVP and OC is very small. The shorter CPU time required for CVP due to the discretization only occurs on control variable which can reduce the order complexity of parameterization. However, the iteration system for CVP was required to calculate initial value problem in every step to generate objective function value. The state inequality constraint presented in the CVP problem optimization should transform to new state variables and integrates the violations of this constraint. Furthermore, the objective function in CVP was evaluated by solving an initial value problem of the original ODE system by calculating the sensitivities of all state variables to the decision variables. Unlike CVP, OC does not require the solution of IVPs at every iteration of the NLP and the state inequality constraint applied in process model for OC was bounding directly to the state approximated by Lagrange polynomial. This iteration system and the additional state variables in CVP will lead to longer CPU time. Consequently, small different CPU time for both CVP and OC is obtained.

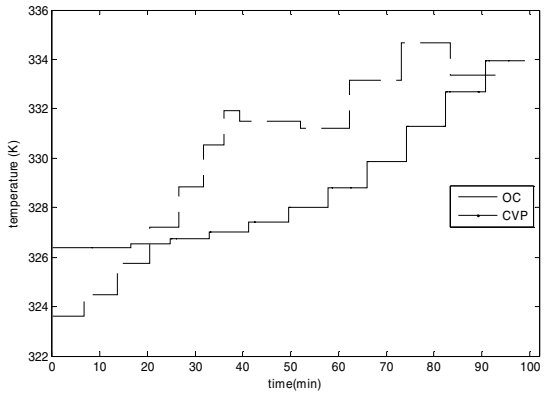


(a) Temperature trajectory

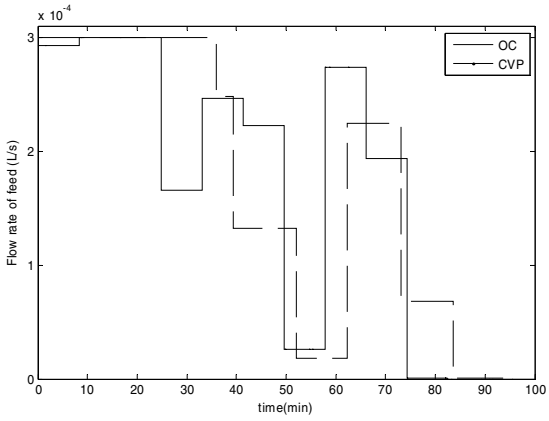


(b) Feed flowrate trajectory

Figure 1. Optimal trajectories generated form CVP and OC under fixed interval time for: a) temperature and (b) feed rate



(a) Temperature trajectory



(a) Feed rate trajectory

Figure 2. Optimal trajectories generated form CVP and OC under free interval time for: a) temperature and (b) feed rate

V. CONCLUSION

Catalyzed Esterification of Propionic Anhydride with 2-Butanol in semi batch is optimized using dynamic optimization techniques. Orthogonal collocation, state and control variables are parameterized and the model solution and the optimization problem are solved simultaneously, and control vector parameterization, parameterize the control trajectories and leave the state trajectories continuous and optimization problem solved sequentially, were implemented to maximize conversion under fixed and free interval time. The results achieved show that the OC lead to higher conversion and shorter final time but slightly longer CPU time as compared to CVP.

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TABLE I. RESULTS SIMULATION OF CVP AND OC TECHNIQUE

Type	conversion	Switching Time (min)	Final time	CPU time
OC (fixed)	99%	Temp:10, 20, 30, 40,50, 60, 70, 80 ,90, 100, 110, 120 Feedrate:50, 60	120	12s
OC (free)	99%	Temp: 8, 14, 22, 27, 32, 35, 38, 41, 53, 62, 72, 83 Feedrate: 36, 38, 52, 62, 72, 84	96 min	42s
CVP (fixed)	98.8%	As same as OC fixed interval	120	10s
CVP (free)	99%	Temp: 18, 25,33, 2, 50, 59, 67, 74, 83, 92 Feedrate: 8, 23, 34, 41, 48, 58, 67, 75, 82	99 min	40s

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