Dynamic Multi-Objective Optimization of Autocatalytic Esterification in Semi Batch by Using Control Vector Parameterization (CVP) and Non-Dominated Sorting Genetic Algorithm (NSGA-II)

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Abstract. Catalyzed Esterification of sec-butyl propionate in semi batch reactor prefers to be solved by dynamic-nonlinear programming (NLP) based optimization for determining optimal temperature and feed flowrate trajectories. In this autocatalytic esterification process, there are contrary objective functions, i.e. maximum productivity and minimum process time. Simultaneous optimization of these objectives yields in a dynamic multi-objective optimization (DMOO) problem, which is characterized by a set of multiple solutions, known as non-dominated or Pareto solutions. In this work, a control vector parameterization (CVP) and non-dominated sorting genetic algorithm (NSGA-II) approach were used to generate the Pareto solutions for two objectives: maximize conversion and minimize process time. Each point of Pareto solutions consists of different optimal temperature reactor and feed rate profiles, which lead to a variation combination of conversion and process time. These solutions give multiple alternatives in evaluating the trade-offs and selecting the most suitable operating policy.

Keywords: Dynamic optimization; Multi-objective optimization; Autocatalytic esterification

1. Introduction

The esterification process is an important process in the food, cosmetic and pharmaceutical which is mainly used for flavors and fragrance components in products. Moreover, ester products also have wide applications in areas such as pesticides and herbicides, metal extraction agents, synthetic lubricants, polymerization aids for acrylic acid esters, insect attractants, repellants and photographic applications [1]. In industry, the ester is a specialty chemical product and commonly produced in batch processes which are typically applied to yield high productivity and selectivity [2]. The ester (sec-butyl propionate) can be produced by catalyzed reaction between propionic anhydride and 2-butanol [3].

The model based optimization for the generating of the optimum operating variable of semi batch esterification reactor is an efficient tool for decision-makers to determine the optimal solution many with minimal operating cost and experimental trials [4]. Mathematical modeling of esterification in semi batch process operating under transient conditions involves mixed systems of ordinary
differential equations (ODE) and differential algebraic equations (DAE) that are subject to technical constraints. Dynamic optimization is able to give the optimum solutions for the best trajectories of feed flow rate and temperature which leads to the maximization of productivity and efficiency[5].

The available literature on the dynamic optimization of the esterification reaction between propionic anhydride and 2-butanol for sec-butyl propionate production was carried out by solving single objective optimization problems [6]. Actually, contradictory objective functions have been found in this esterification process, i.e. maximum conversion and minimum process time which generates various combinations of optimum process variables. The optimum results from the single-objective optimization problem cannot interpret the correlation between conflicting objective functions, and unable to provide a combination set of optimal trajectories. It is infeasible to determine a unique solution which is the optimal solution for the entire objectives altogether. Thus, it is suggested that application of a multi-objective optimization MOO approach for the improving optimal policy can offer a better way for predicting performance trade-offs emerging due to opposite actions of operating objectives for the esterification process. Notwithstanding this, the application of multi-objective optimization to the esterification for sec-butyl propionate production has been unexplored. The investigation of dynamic MOO in autocatalytic esterification can fill the gap of optimization study for semi batch esterification process.

The objective of this paper is to solve the multi-objective optimization problem in esterification process the esterification reaction between propionic anhydride and 2-butanol. The aim of this optimization problem is to determine the optimal feed flowrate and temperature profiles to optimize the objective functions which are minimization process time and maximization conversion.

2. Process modeling of autocatalytic esterification in semi batch reactor

Reaction between propionic anhydride and 2-butanol yields sec-butyl propionate and propionic acid. In the presence of sulfuric acid as catalyst, the reaction rate is effected by the acid concentration proportionally which influence to autocatalytic behavior [3]. The reaction mechanism was represented as the existence of two catalysts (cat1, cat2). The catalyst transformation was expressed by the acidity function. The kinetics of autocatalytic esterification reaction was described as [3]:

Main reaction : 2-butanol + propionic anhydride → propionic acid + sec-butyl propionate
Catalyst transformation: catalyst 1 (sulphuric acid) → catalyst 2 (mono-butyl sulphuric acid)

Reaction rate constants were calculated by the Arrhenius law. The approximation of the acidity function was modeled as [3]:

\[ H = -(p_1 C_{cat1} + p_2 C_c) \left( p_3 + \frac{p_4}{T} \right) \]  \hspace{1cm} (1)

The dynamic trend of the concentrations in the autocatalytic esterification reaction can be stated by deriving the mass balances equations which were taken into account in the dynamic optimization task. The mass balances for semi batch autocatalytic esterification reactor [7] are represented by Equations (2-6) as shown below:

\[ \frac{dC_A}{dt} = -((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) - \frac{F_0 C_A}{V} \]  \hspace{1cm} (2)

\[ \frac{dC_B}{dt} = -((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) + \frac{F_o}{V} (C_{b0} - C_B) \]  \hspace{1cm} (3)

\[ \frac{dC_c}{dt} = \frac{dC_{cat}}{dt} = ((k_1 + k_2 C_{cat1}) C_A C_B + k_3 C_{cat2} C_B) - \frac{F_o C_c}{V} \]  \hspace{1cm} (4)

\[ \frac{dC_{cat1}}{dt} = -\frac{dC_{cat2}}{dt} = -(k_4 10^{-H} C_{cat1} C_A) - \frac{F_0 C_{cat1}}{V} \]  \hspace{1cm} (5)

\[ \frac{dV}{dt} = F_o \]  \hspace{1cm} (6)
where $C_A$, $C_B$, $C_C$, $C_{cat1}$, and $C_{cat2}$ are the concentration of 2-butanol, propionic anhydride; propionic acid, sulphuric acid and mono-butyl sulphuric acid, respectively. $F_0$, $V$ and $T$ are the feed rate, the volume of solution and temperature within reactor. The initial value of $C_A$, $C_B$, $C_C$, $C_D$, $C_{cat1}$, $C_{cat2}$ and $V_j$ is 3.4M, 0M, 0M, 0M, 1.02 x 10^{-2}M, 0M and 1L, respectively. The information about reaction kinetics of this esterification which includes the data of parameters was adopted from Zaldivar et al. [3] as listed in Table 1.

Table 1. Kinetic parameter equations [3]

| Subscript $i$ | $k_{ri}$ | $E_{ai}$ (J mol^{-1}) | Parameter $p_i$ |
|---------------|---------|-----------------|-----------------|
| 1             | 5.36178x 10^7 L mol^{-1} s^{-1} | 80,478.64 | 2.002x 10^{-1} |
| 2             | 2.8074x 10^{10} L^2 mol^{-2} s^{-1} | 79,159.5 | 3.205 x 10^{-2} |
| 3             | 3.9480x 10^{10} L mol^{-1} s^{-1} | 69,974.6 | -21.3754 |
| 4             | 1.4031x 10^{8} L mol^{-1} s^{-1} | 76,6172.2 | 12706 |

3. Dynamic multi-objective optimization techniques

The dynamic optimization method implemented in this study was control vector parameterization, CVP. The control vector parameterization (CVP) method was using AMIGO2 package within MATLAB environment developed by Balsa-Canto et al [8]. The AMIGO2’s algorithm of CVP approach was adopted from Vassiliadis et al.’s [9] work.

The main characteristic of the CVP method is a discretization of the control trajectories and an initial value problem (IVP) solver of the state trajectories continuous. The basic step of CVP method is described as follows: First step, the ODE solver computes the IVP of the differential equations. Second step, the transformation of dynamic optimization problem into the finite dimensional nonlinear problem (NLP) is executed by control variables discretization. Then, a NLP solver, such as Sequential Quadratic Programming or Quasi-Newton methods is applied to update the values of the decision variable as the differential equations are satisfied at each step of the optimization. Finally, the search direction of NLP solver is terminated as the objective function is minimized or maximized.

3.1. Multi-objective optimization (MOO) technique

The optimal solution for MOOs which is characterized as a multiple optimal solutions, forms a set of solutions defined as Pareto-optimal solutions. A set is said to be a non-dominated set or Pareto-optimal set if it is not dominated by any other solution that belongs to the solution set. The Pareto-optimal set is the best optimal solution for all objective functions if there is no improvement of a given objective without degenerating the value of another objective. Elitist Non-dominated Sorting GA or NSGA-II was one of widely used MOO procedures which were developed by Deb et al [10]. The NSGA-II implemented three features, i.e., elitist principle, explicit diversity preserving mechanism and non-dominated emphasizing. Here, the individuals in a population underwent non-dominated sorting, and ranks are given to individual according to this kind of sorting. A crowding distance which represents the neighbourhood density of a solution, was implemented in selection step. The non-dominated individuals from the combined population which consisted of the parent and child population, were augmented to the next generation by applying elitism principle. The next step included off-springs generating from the selected population using crossover and mutation operators. Finally, the present off-springs and population were sorted dependent upon the non-domination and only the best individuals with the number of the population size (P).

3.2. Problem optimization formulation
The controls (decision) variables were piece wise constant of temperature reactor and feed flowrate. The reactant, catalyst and product concentrations were considered as states variables which were expressed as mass balance of selected operation mode. The catalyzed esterification process equations are applied as a shortcut-process model. It involves only the mass balance equations (2–6). This type of model generates optimum operating conditions, i.e. optimal trajectories of reactor temperature and feed flowrate, which is used to achieve the target performance of the reactor. The upper and lower bounds implemented were the minimum and maximum capacity of the temperature reactor considered (303K- 343K) and the flowrate of the pumps (0-5x 10^4 L/s), respectively. The overall process time consisted of six intervals time \( \Delta t \) which treated as free final time. Therefore, the length of interval time, \( \Delta t \), was also be optimized which bounded in the range 10min-30min. 

The bi-objective functions were to maximize the conversion and to minimize process time. It is assumed that the objective function is of the form min function (to minimize). To maximize 

\[
\frac{C_{A0}V_0 - C_{A}V}{C_{A0}V}
\]

, the max function is expressed as min 

\[
\frac{C_{A0}V_0 - C_{A}V}{C_{A0}V}
\]

. The inequality constraint was volume solution accumulated in the final time, 2L. The dynamic optimization problem is expressed mathematically as:

\[
\min_{T(t),F_o(t)} \varphi_1 = -\left(\frac{C_{A0}V_0 - C_{A}V}{C_{A0}V}\right)
\]

\[
\min_{T(t),F_o(t),\Delta t} \varphi_2 = t_f
\]

Subject to:

- \( Mdx/dt = f(x(t),u(t),p,t) \) (model equation);
- \( 0 \leq F_0 \leq 5 \times 10^{-4} \text{L/s} \)
- \( 303 \text{K} \leq T \leq 343 \text{K} \)
- \( 10 \text{min} \leq \Delta t \leq 30 \text{min} \) (Lower and upper bounds)
- \( V \leq 2 \text{L} \) (Final inequality constraint)

4. Results and discussion

The Pareto-optimal front selected, i.e. NSGA-II, which is exhibited in Figure 1, comprises of three zones. The lower end of the Pareto-optimal front (zone I) was signified by relatively short process time and lower conversion. Meanwhile, the upper end of the Pareto-optimal front (zone III) was signified by relatively long process time and high conversion. The intermediate zone (zone II) which was placed between zone I and zone II, was indicated as medium process time and conversion.
Each point of the Pareto-optimal front in Figure 2 was correlated with different feed flowrate and temperature profiles. The non-dominated points A, B and C which was located at zone I, zone II and zone III, respectively, had different trend trajectories, as shown in succession of Figures 2-4. Dynamic optimization results for non-dominated points A, B and C which is comprised of two distinct ED performances such as process time and conversion, are tabulated in Table 2.

| Non-dominated point | Point A | Point B | Point C |
|---------------------|---------|---------|---------|
| Process time, min   | 45.00   | 49.47   | 66.88   |
| Conversion          | 0.989   | 0.997   | 0.999   |

As shown in Table 2, the process time for non-dominated points A, B and C were 45min, 49.47min and 66.88min, respectively. While the conversion achieved for non-dominated points A, B and C were 0.989, 0.997 and 0.999, successively. The control variable that has a significant impact on process time and conversion is temperature. Since the reaction rates for the reactant, the catalyst and the product increased significantly with an increase in temperature [7]. Therefore, the different temperature profiles produces variation amount of process time and conversion as shown in Fig. 2b, 3b and 4b. The point A produced the smallest conversion and process time due to lowest value of the optimal temperature trajectory obtained, and vice versa for the point C.

The optimal profiles of temperature (Fig. 2b-4b) and feed flowrate (Figure 2a-4a) had opposite trend, but had complementary effect for supporting reaction rate. As temperature profile situated in lower value, the feed flowrate trajectory equilibrated to maintain reaction rate by increasing the value of feed flowrate. This is because a higher feed flowrate of propionic anhydride can promote the autocatalytic mechanism, which enhances the conversion rate, consequently.
Figure 2. Optimal trajectories in point A
Figure 3. Optimal trajectories in point B

(a) Feed flowrate

(b) Temperature
The application of a PF obtained is associated with the capacity of decision maker. The different optimal trajectories obtained along PF assists the decision maker to select the best trade off and to find the most adequate operating condition for the esterification process. The PF of NSGA-II obtained obviously provides many alternatives to the decision maker to apply the optimal trajectories based on practical and feasible consideration.

**Conclusion**

Autocatlytic esterification process in semi batch reactor typically has many performance objectives some of which conflicts with each other.. The elitist non-dominated sorting genetic algorithm or NSGA-II approaches have been applied to obtain the Pareto-optimal solutions for constrained multi objective optimization problems that are related to the process time and conversion . Each point of Pareto front has different optimal feed flowrate and temperature trajectories which lead
to variation amount of process time and conversion. The information within Pareto-optimal front can provide the decision-maker observe the trade-offs between different objectives, and determine a suitable optimal trajectories for the process. The final outcome of this study is that the optimal temperature trajectory from the selected trade-off becomes as pre-determined set point. It is tracked afterward by controller in online application.

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