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Optimal operation policies in batch reactors

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Abstract

Optimal operation policies in batch reactors are obtained using dynamic optimisation technique. Two different types of optimisation problems, namely, *maximum conversion* and *minimum time problems* are formulated and solved and optimal operation policies in terms of reactor temperature or coolant flow rate are obtained. A path constraint on the reactor temperature is imposed for safe reactor operation and an endpoint constraint on undesired waste production (by-product) is imposed to minimise environmental impact.

Two different types of models are considered within the optimisation framework. The shortcut model allows determination of optimal reactor temperature profile to be used for detailed design of the reactor. The detailed model allows optimising operating conditions for an already designed batch reactors. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Batch reactor; Model; Optimal operation; Dynamic optimisation; Path constraint

1. Introduction

1.1. Batch reactor

Batch reactor is an essential unit operation in almost all batch-processing industries. It is used for small-scale operation; for testing new processes that have not been fully developed; for the manufacture of expensive products and for processes that are difficult to convert to continuous operations [1]. In a batch reactor, there is no inflow or outflow of reactants or products while the reaction is being carried out. The reactants are initially charged into a vessel, are well mixed and are left to react for a certain period. The resultant mixture is then discharged. This is an inherently unsteady-state operation, where composition and temperature change with time; however, the common assumption is that at any instant the composition and temperature throughout the reactor is uniform.

Batch production is usually carried out in standard types of equipment that can easily be adapted and if necessary reconfigured to produce many other different products. This type of reactor can achieve high conversion with long batch time but may require high operating cost per unit production. It is particularly suitable for products such as pharmaceuticals, polymers, biotechnological or other fine chemicals products for which annual requirement can be manufactured in a few days or a few batches in an existing plant. Batch reactors are also used when there are many processing steps in chemical process, when isolation is required for reasons of sterility or safety and when materials involved are difficult to handle [2].

Batch processes offer some of the most interesting and challenging problems in modelling and control because of their inherent dynamic nature. Therefore, modelling of batch reactors results in differential and algebraic equations (DAEs) and optimisation of such reactors requires the use of dynamic optimisation technique. The control of a batch reactor in a simple case consists of charging the reactor, controlling the reactor temperature within a safe limit to meet some processing criterion, and shutting down and emptying the reactor. For an exothermic reaction, heat may be required to obtain the desired reaction temperature, and then cooling is used to maintain the proper reaction temperature.

The aim of fine chemical industries is to produce high quality and purity product, in general small amounts with a control of polluting waste materials and losses of raw material. Therefore, an optimisation of batch operating conditions such as temperature, operating time, etc. is the more efficient approach to obtain a maximum yield in a minimum time or minimum cost, as well as to reach the specific final conditions of the product in terms of quality and quantity. Therefore, operating batch reactors efficiently and economically is very important as far as overall profitability is concerned. Because of the necessity to answer to strict constraints and objectives, the optimisation problems encountered in fine chemical industries are very complex.

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Nomenclature

A_i	inside area
A_o	outside area
C_i	concentration of component i (kmol/m^3)
C_p	specific heat of reactant
$C_{p\mathrm{m}}$	specific heat of metal
$C_{p\mathrm{J}}$	specific heat of coolant
E_j	activation energy for reaction j
F_J	coolant flow rate (m^3/h)
$\Delta H_{\mathrm{r}j}$	enthalpy of reaction for reaction j
k_j	reaction rate constant for reaction j
Q_J	amount of heat transferred to coolant (J/h)
Q_m	amount of heat transferred to metal (J/h)
r_j	reaction rate of reaction j
R	universal gas constant
t	time (h)
T	temperature of the reaction mixture (K)
T_J	temperature of coolant (K)
T_J0	inlet temperature of coolant (K)
T_m	temperature of the reactor metal (K)
U_i	inside heat transfer coefficient
U_o	outside heat transfer coefficient
V	volume of reactor contents (m^3)
V_J	volume of coolant (m^3)
V_m	volume of reactor metal (m^3)

Greek letters

ν_{ji}	stoichiometric coefficient of component i in reaction j
ρ_m	density of metal
ρ_J	density of coolant

1.2. Dynamic optimisation of batch reactors

The dynamic optimisation (optimal control) of batch reactors has received major attention since the early works of Denbigh [3]. The objective was to determine the optimum temperature profiles for cases where there are competing side reactions, so that an increase in yield (productivity, profit, etc.) may be obtained using the optimal profiles.

In this work, two optimisation problems are considered:

P1: Maximum conversion problem — is the operation time is fixed a priori.

P2: Minimum time problem — is the conversion is fixed a priori.

Logsdon [4] considered the optimisation problem P1 for a consecutive reaction scheme. Their objective was to find an optimal temperature (control variable) profile that maximises the conversion of the desired product at a fixed reaction time. They solved this problem using two-point collocation method. Later Logsdon and Biegler [5], solved the same optimisation problem but with a relaxed simultaneous approach that leads to faster solution.

Luus [6] also considered the optimisation problem P1 for a consecutive reaction and used iterative dynamic programming (IDP) for the solution of the problem. Reactor temperature profile was chosen as the control variable which was optimised in order to maximise the conversion. He considered piecewise constant temperature profile but with fixed switching time and claimed to achieve higher conversion and shorter computational time to solve the optimisation problem compared to the methods used by other researchers.

Garcia et al. [7] also considered the optimisation problem P1 for a consecutive parallel reaction scheme. They converted the dynamic optimisation (optimal control) problem into an NLP problem and solved by generalised reduced gradient method coupled with golden search technique. They used 5 or 10 time intervals to discretise the temperature profile and with fixed (equally spaced) switching time. They concluded that there is no significant change in the temperature profile when a more accurate level of discretisation (more than five intervals) is used. In every plant the capacities of heating and cooling are limited and that is why the optimal temperature profiles numerically calculated are not often experimentally feasible. For this reason, Garcia et al. introduced the constraints limiting the rate of cooling and heating in the batch reactor problem which are expressed in terms of maximal or minimal temperature.

1.3. This work

Most of the works mentioned above were primarily concerned with the development of numerical method for the optimisation of dynamic systems and have used batch reactor as an example to demonstrate the accuracy and efficiency of the methods. Therefore, all of them concentrated on one of the optimisation problem mentioned earlier. Due to this reason also, an analysis on the effect of constraints to the objective function and to the other operating parameters are left unexplained. The intention of this paper is not to develop new numerical methods for dynamic optimisation but to formulate optimisation problems for batch reactors with design, operation and environmental constraints and to select a suitable and efficient method from existent techniques to solve such problems. Also, the aim is to study the effect of waste and/or temperature constraints (at the final time or at any time throughout the batch time) on the optimal operation policies and on the objectives (maximum conversion and minimum time) of the optimisation problems.

In this work, we consider a typical consecutive reaction scheme in batch reactors. We formulated two types of optimisation problems. In order to operate the reactor safely, we impose a path constraint on the system to make sure that the reactor temperature throughout the processing period does not go beyond a certain temperature.

Each waste or by product of the reaction has a certain value (threshold value) before it can be discharged to the environment. So in this work, rather than producing the waste and treating it at the end, we put a limit on the waste production. The resulting optimisation problem thus not only has path constraint but also has end point constraints which results to complex optimisation problem. The reaction temperature is the key variable which governs (controls) the batch reactor operation. Most of the previous researchers considered the reactor temperature directly as the control variable. They assumed that the optimal temperature profiles obtained from the solution of the optimisation problems can always be achieved. This assumption does not require consideration of some of the design parameters (such as the reactor volume), operating parameters (such as the reactor jacket temperature) and energy balance in the model. Therefore, in most cases the models used by previous researchers were simple (one such model is presented with a case study in this work) and required only mass balance and kinetic information.

However, in practice, the reactor temperature is affected by the external heating or cooling depending whether the reaction is endothermic or exothermic. Therefore, for optimising the operation of existing batch reactors (with fixed design in terms of reactor volume, jacket configuration, maximum limits to coolant (or heating media) flow), it is more desirable to manipulate coolant flow (or heating) to maintain a safe reactor temperature. The reactor model should therefore include both mass and energy balances together with the design parameters. It is to be noted that the simple model is useful at the preliminary design stage, where the required optimal temperature profile can be used as a guide to determine the size of the reactor, jacket and to configure the cooling or heating requirement.

In this work we considered both a simple and a detailed models. For the optimisation of batch reactors using a simple model we used temperature as control variable (to compare the results with those in the literature). However, for optimisation with the detailed model, we choose the coolant flow rate as the control variable. Control vector parameterisation (CVP) technique is used in both cases to pose the dynamic optimisation problems as an NLP problem which are solved using a SQP-based optimisation technique.

2. Modelling of batch reactor

The batch reactor models are based on the assumptions of perfect mixing and ideal liquid mixture behaviour. It is applied only for liquid phase.

2.1. Simple model

Mass balance:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \sum_{j=1}^{n} r_j \nu_{ji} \quad \forall i \tag{S1}$$

Reaction rates:

$$r_j = k_j \prod_{i=1}^{m} C_i^{\beta_{ij}} \quad \forall j \tag{S2}$$

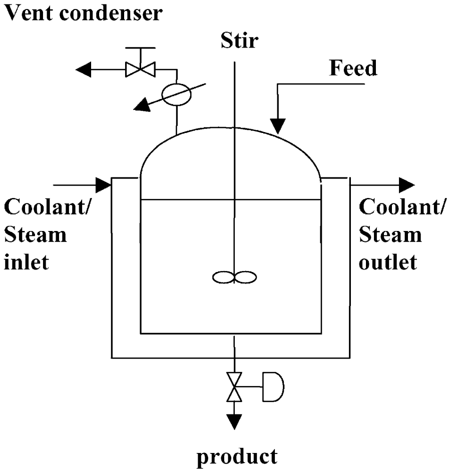

Fig. 1. Schematic diagram of a jacketed batch reactor.

Reaction rate constants:

$$k_j = k_{j0} \exp\left(-\frac{E_j}{RT}\right) \quad \forall j \tag{S3}$$

2.2. Detailed model

Fig. 1 shows a schematic diagram of a jacketed batch reactor.

2.2.1. Jacketed reactor

Mass balance:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \sum_{j=1}^{n} r_j \nu_{ji} \quad \forall i \tag{D1}$$

Reaction rates:

$$r_j = k_j \prod_{i=1}^{m} C_i^{\beta_{ij}} \quad \forall j \tag{D2}$$

Reaction rate constants:

$$k_j = k_{j0} \exp\left(-\frac{E_j}{RT}\right) \quad \forall j \tag{D3}$$

Energy balance:

$$\text{reactor}: \quad \frac{\mathrm{d}T}{\mathrm{d}t} = \frac{Q_\mathrm{r} - Q_\mathrm{m}}{C_p V \rho} \tag{D4}$$

$$\text{reactor wall (metal)}: \quad \frac{\mathrm{d}T_\mathrm{m}}{\mathrm{d}t} = \frac{Q_\mathrm{m} - Q_\mathrm{J}}{C_{p\mathrm{m}} V_\mathrm{m} \rho_\mathrm{m}} \tag{D5}$$

$$\text{jacket}: \quad \frac{\mathrm{d}T_\mathrm{J}}{\mathrm{d}t} = \frac{F_\mathrm{J}}{V_\mathrm{J}}(T_\mathrm{J0} - T_\mathrm{J}) + \frac{Q_\mathrm{J}}{C_{p\mathrm{J}} V_\mathrm{J} \rho_\mathrm{J}} \tag{D6}$$

Heat of reaction:

$$Q_\mathrm{r} = \sum_{j=1}^{n} r_j (-\Delta H_{\mathrm{r}j}) V \tag{D7}$$

Heat transfer via external cooling system:

$$Q_\mathrm{m} = U_\mathrm{i} A_\mathrm{i} (T - T_\mathrm{m}) \tag{D8}$$

$$Q_\mathrm{J} = U_\mathrm{o} A_\mathrm{o} (T_\mathrm{m} - T_\mathrm{J}) \tag{D9}$$

The simple or the detailed model results to DAEs and can be written in compact form as

$$f(t, \underline{x}'(t), \underline{x}(t), \underline{u}(t), \underline{v}) = 0$$

where t is the independent variable (time), $\underline{x}(t)$ the set of all state variables, $\underline{x}'(t)$ denotes the derivatives of $\underline{x}(t)$ with respect to time, $\underline{u}(t)$ the vector of control variables and $\underline{v}$ is a vector of time invariant parameters (design variables).

3. Optimisation problem formulation in batch reactors

The optimisation problems mentioned in the introduction section, can be detailed as follows.

3.1. P1—maximum conversion problem

The problem can be described as

Given	the fixed volume of the reactor and the batch time;
Optimise	the coolant flow rate or temperature profile;
So as to maximise	the conversion of the desired product;
Subject to	constraints on the waste product and bounds on the reactor temperature, bounds on the coolant flow rate.

Mathematically, the optimisation problem can be written as

$$\max_{T(t) \text{ or } F_\mathrm{J}(t)} X$$

s.t.

$$f(t, \underline{x}'(t), \underline{x}(t), \underline{u}(t), \underline{v}) = 0 \quad \text{(model)}$$

$$t_\mathrm{f} = t_\mathrm{f}^*$$

$$T_\mathrm{L} \le T \le T_\mathrm{U} \text{ or } F_\mathrm{JL} \le F_\mathrm{J} \le F_\mathrm{JU}$$

$$W \le W^*$$

where X is the conversion of the limiting reactant to the desired product, T is the reactor temperature, F_J is the coolant flow, t_f is the batch time, W is the waste, T_L and T_U are the lower and upper bounds of the reactor temperature, F_JL and F_JU are the lower and upper bounds of the coolant flow, t_f^* is the fixed batch time and W^* is the threshold limit for the waste.

3.2. P2—minimum time problem

The problem can be described as

Given	the fixed volume of the reactor and the conversion to the desired product;
Optimise	the coolant flow rate or temperature profile;
So as to minimise	the batch time;
Subject to	constraints on the waste product and bounds on the reactor temperature, bounds on the coolant flow rate.

Mathematically, the optimisation problem can be written as

$$\min_{T(t) \text{ or } F_\mathrm{J}(t)} t_\mathrm{f}$$

s.t.

$$f(t, \underline{x}'(t), \underline{x}(t), \underline{u}(t), \underline{v}) = 0 \quad \text{(model)}$$

$$X = X^*$$

$$T_\mathrm{L} \le T \le T_\mathrm{U} \text{ or } F_\mathrm{JL} \le F_\mathrm{J} \le F_\mathrm{JU}$$

$$W \le W^*$$

where X^* is the fixed conversion and t_f is the batch time.

It is to be noted again that most of the previous researchers optimised reactor temperature profile and therefore used simple model (similar to case study 1) and did not consider environmental and or path constraints.

Throughout this work conversion to the desired product refers to ‘net conversion’ to the desired product and excludes conversion of the desired product to by-products.

4. Solution methods for dynamic optimisation problems

The transient behaviour of many chemical engineering systems is described by DAEs (as can be seen from the models presented in the previous section). The optimisation of such systems has received significant attention over the past decade [5,8]. A number of different solution approaches to dynamic optimisation problems for systems described by ordinary differential equations (ODEs) or DAEs have been proposed in the literature. One such approach involves the use of dynamic programming techniques [6,9].

A second class of solution is based on the solution of the necessary optimality conditions expressed as a two-point boundary value problem. These methods include the quasi-linearisation approach proposed by Miele [10] and the use of multiple shooting algorithms as well as other shooting algorithms such as that proposed by Dixon and Bartholomew-Biggs [11].

In the last two decades, two main solution methodologies have emerged to convert the dynamic optimisation problem into a finite dimensional NLP problem through the discretisation of all variables [12]. Initial work was based on the finite difference approximation to the system constraint but later a global orthogonal collocation, orthogonal collocation on finite elements [13] and stochastic algorithms which transform the original optimal control problem into an NLP problem using a control parameterisation approach [14] were also used. The key characteristic of the complete discretisation approach outlined above is the fact that the optimisation is carried out in the full space of discretised variables, and the discretised constraints are in general, satisfied at the solution of the optimisation problem only. This is therefore often called an “infeasible path” approach.

An alternative approach is to carry out the optimisation in the space of the decision (optimisation) variables only. In this case, it is necessary to discretise only the control variable $\underline{u}(t)$ (control vector parameterisation (CVP)) and values of the other decision variables. It is then possible to integrate the underlying DAE system using standard integration algorithms so as to evaluate the objective function and other constraints that have to be satisfied by the solution. This method [8,12,15] corresponds to a “feasible path” approach since the DAEs are satisfied at each step of the optimisation algorithm. In addition to the smaller size of the optimisation problem, this approach has the advantage of efficiently controlling the discretisation error by adjusting the size and order of the integration steps using well-established ODE/DAE integration techniques. Also the number of such steps need not be known in advance, nor does it have to be constant during the course of the optimisation.

The main attraction of the CVP technique is its ability to handle large systems without the need to solve excessively large optimisation problem. Besides that, it is able to solve the minimum time optimisation problem (P2), which cannot be ignored in the daily practice. It is also proved that CVP methods are significantly faster compared to IDP method [16].

Due to several advantages above and due to continuously been used by the previous researchers (since last two decades), in this work we choose the CVP method in batch reactor optimisation problems. We used a sequential model solution and optimisation strategy which is commonly known as feasible path approach. In this approach, the process variables are partitioned into dependent and independent variables (decision variables), and for each choice of the decision variables, the simulator is used to converge the process equations (DAEs). Therefore, the method includes two levels, the first level performs the simulation to converge all the equality constraints and to satisfy the inequality constraints and the second level performs the optimisation. The resulting optimisation problem is thus an unconstrained non-linear optimisation problem or a constrained optimisation problem with simple bounds on the associated decision variables plus any interior or terminal point constraints. Since each search point is feasible, if the process is terminated at the optimisation level before reaching a solution, the terminating point is still feasible and may be acceptable as a practical, although sub-optimal, solution of the problem. This method has been used by many researchers in the past [8,15,17].

Cuthrell and Biegler [18] used a sequential quadratic programming approach to solve the non-linear optimisation problem. Eaton and Rawlings [19] used orthogonal collocation on finite elements to include the differential equation constraints and the successive quadratic programming (SQP) was employed to solve the resulting non-linear program. In this work, SQP-based optimisation technique developed by Chen [20], is used to solve the problem. This method has been applied to a wide range of steady state and dynamic processes in the past and found to be very efficient.

5. Path constraints in batch reactors

When a certain process variable (e.g. the reactor temperature) cannot exceed a given limit for the entire processing period, the process is said to have a path constraint. There are two kinds of path constraints: equality and inequality path constraints. When the concerned process variable is always on the limit, the process is said to have an equality path constraint. In all other situations, the process is said to have an inequality path constraint. Bryson and Ho [21] introduced an integral penalty terms in objective function to be minimised in order to treat the equality path constraint. To avoid the numerical difficulties which may be caused by the use of the penalty term, an alternative approach that involves the conversion of the path constraint to an equivalent end point constraint was introduced by Sargent and Sullivan [22]. A common characteristic of all these techniques is that the penalty terms or end point constraints introduced have zero gradients with respect to the optimisation parameters at the solution. This, in turn may result in a reduced convergence rate near the solution, and as noted by Goh and Teo [23], the success of such techniques depends very strongly on the line-search merit function used by the optimisation algorithm.

Most of the established approaches for dealing with inequality path constraints are similar to the techniques for handling equality path constraints. Thus, they rely on defining a measure of the constraint violation over the entire horizon and then penalising it in the objective function, or forcing it directly to zero through an end point constraint. Here we consider an integral expression to provide a single measure of the violation of an inequality path constraint over the entire time horizon of interest and then replace such constraint by a single end point constraint.

To illustrate this idea, consider a typical reactor temperature profile in Fig. 2. $T_{\max}$ shows the maximum allowable reactor temperature for a safe operation. In order to make sure that the reactor temperature, T does not go above $T_{\max}$ at any time, a path constraint on T is imposed in the optimisation problem.

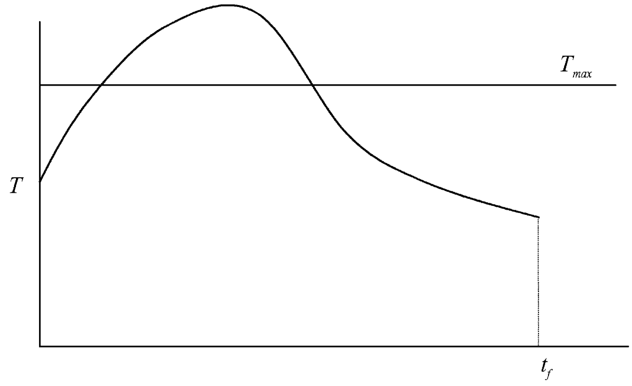

Fig. 2. Typical reactor temperature profile.

In Fig. 2, the reactor operates without any control on the reactor temperature, and therefore T goes above the limit $T_{\max}$ during the batch. At any time during the batch, this violation of safe operation V can be defined as

$$V = \begin{cases} (T(t) - T_{\max})^2 & \text{if } T > T_{\max} \\ 0 & \text{if } T < T_{\max} \end{cases}$$

A typical plot of V versus batch time, t is shown in Fig. 3.

The total accumulated violation over the entire period can be written as

$$V_{\mathrm{T}} = \int_{t=0}^{t_{\mathrm{f}}} V(t)\,\mathrm{d}t$$

Therefore,

$$\frac{\mathrm{d}V_{\mathrm{T}}}{\mathrm{d}t} = V(t) = (T(t) - T_{\max})^2 \qquad (1)$$

In this work, Eq. (1) is added to the model equations presented earlier. Also the following additional terminal constraint is added in each of the optimisation formulation presented earlier:

$$0 \leq V_{\mathrm{T}} \text{ at } t_{\mathrm{f}} \leq \varepsilon \qquad (2)$$

where ε is a very small finite positive number. The above constraint will ensure that $T(t)$ will always be $\leq T_{\max}$.

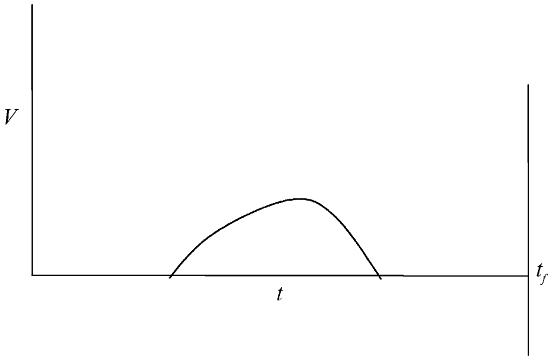

Fig. 3. Violation during the reaction process.

However, it is to be noted that for a given bounds on the optimisation variables (e.g. the coolant flow rate), the numerical value of the end point constraint V_{T} at the final time t_{f} can be very large (can be as high as 10^5) or very low (close to zero) compared to other constraints (e.g. environmental, conversion, etc.) (usually less than 10) in the optimisation problem (P1, P2). During the solution of the optimisation problem this can result to a high overall constraint violation and can lead to an oscillatory behaviour in the optimisation variables (e.g. coolant flow rate), hitting either the lower or the upper bounds. This may result to a failure of the optimisation problem or to a sub-optimal solution or a very large number of iteration. The use of narrow bounds in the optimisation variables in many cases may not satisfy $V_{\mathrm{T}} \leq \varepsilon$ at t_{f} and other constraint bounds. Therefore, scaling of the optimisation variables as well as constraints may be necessary.

In the past, V_{T} has always been evaluated at the final time t_{f} (at the end of the process). However, in this work (instead of using narrow bounds or scaling the variables or constraints) we propose that the total batch time t_{f} be divided into a finite number of intervals n with t_j as the length of each interval (as is done in CVP method). At the junction of each interval (called '*path-interval*') Eq. (2) is satisfied. This results to a series of n dynamic optimisation problems solved sequentially. The final state of any optimisation problem $j-1$ becomes the initial state of the optimisation problem j. The optimisation problem P1 for any time interval j can be written as

$$\mathrm{P1}(j): \quad \max_{F_{\mathrm{J}}(t)} \text{conversion}(X_j)$$

s.t.

$$f(t, \underline{x}'(t), \underline{x}(t), \underline{u}(t), \underline{v}) = 0 \quad \text{(model)}$$

$$F_{\mathrm{JL}} \leq F_{\mathrm{J}} \leq F_{\mathrm{JU}}$$

$$T \leq T_{\mathrm{U}} \quad \text{(path constraint)}$$

$$x_0^j = x_{\mathrm{f}}^{j-1}$$

$$t_j = t_j^* = \frac{t_{\mathrm{f}}^*}{n}$$

$$V_{\mathrm{T}} \leq 0 \text{ at } t = t_j$$

Note each *path-interval* t_j can be subdivided and CVP technique can be applied for the control (optimisation) variables. Maximisation of conversion in each *path-interval* will ensure maximum conversion at the final time ($X_{\text{total}} = \sum_{j=1}^{n} X_j$). The case study presented later shows the merits of this approach over the *single-path-interval* method.

The optimisation problem P2 for any time interval j can be written as

$$\mathrm{P2}(j): \quad \min_{F_{\mathrm{J}}(t)} t_j$$

s.t.

$$f(t, \underline{x}'(t), \underline{x}(t), \underline{u}(t), \underline{v}) = 0 \quad \text{(model)}$$

$$F_{\mathrm{JL}} \le F_{\mathrm{J}} \le F_{\mathrm{JU}}$$

$$T \le T_{\mathrm{U}} \quad \text{(path constraint)}$$

$$x_0^j = x_{\mathrm{f}}^{j-1}$$

$$X_j = X_j^* = \mathrm{f}\,(X^*, n)$$

$$V_{\mathrm{T}} \le 0 \text{ at } t = t_j$$

As shown earlier, the minimum time formulation (optimisation problem P2) requires fixed product conversion, say X^*. We can assume that in *multi-path-interval* optimisation formulation, the desired conversion at the end of each *path-interval* t_j is $X^* = X_j{}^*/n$ (assuming linear conversion profile over time). Alternatively, we can choose X_j^* so that $X^* = \sum_{j=1}^{n} X_j^*$. The total minimum batch time, $t_{\min} = \sum_{j=1}^{n} t_j$.

6. Case studies

6.1. Case study 1

The reaction scheme considered by Luus [6] is chosen in this study which is

$$\mathrm{A} \overset{k_{\mathrm{A}}}{\rightarrow} \mathrm{B} \overset{k_{\mathrm{B}}}{\rightarrow} \mathrm{C}$$

where B is the desired product. Both temperature and batch time will influence the selectivity and conversion (yield) of the desired product. The general reaction scheme shown above is of a considerable practical importance in a number of chemical processing operations, such as the oxidation of HCs or the chlorination of aromatics.

6.1.1. Model equations

We use the simple model involving only mass balance and reaction kinetics. The conversion to B from A follows a second-order reaction rate while conversion to C from B follows a first-order reaction rate. The reactor volume is assumed constant.

6.1.1.1. Component A. From Eq. (S1) with $\nu_{\mathrm{A1}} = -1$, we have mass balance as follows:

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = -r_{\mathrm{A}} \tag{S4}$$

From Eq. (S2) with $\beta_{\mathrm{A1}} = 2$, we have reaction rate as follows:

$$r_{\mathrm{A}} = k_1 C_{\mathrm{A}}^2 \tag{S5}$$

Combining Eqs. (S4) and (S5), we have

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = -k_1 C_{\mathrm{A}}^2 \tag{S6}$$

6.1.1.2. Component B. Similar to the above, we have

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = k_1 C_{\mathrm{A}}^2 - k_2 C_{\mathrm{B}} \tag{S7}$$

where reaction rate constants are as follows:

$$k_1 = 4000 \exp\left(-\frac{2500}{T}\right) \tag{S8}$$

$$k_2 = 6.2 \times 10^5 \exp\left(-\frac{5000}{T}\right) \tag{S9}$$

The final set of model equations is from Eqs. (S6)–(S9) which do not contain any design parameters (e.g. reactor volume, reactor jacket cooling/heating configuration, etc.).

As discussed before, this type of model can be used at the design stage to find optimal reactor temperature profile to achieve the target performance of the reactor. This temperature profile can then be used for detailed design of the reactor including controller design [24].

There are eight variables in Eqs. (S6)–(S9) and they are $\mathrm{d}C_{\mathrm{A}}/\mathrm{d}t$, $\mathrm{d}C_{\mathrm{B}}/\mathrm{d}t$, k_1, k_2, C_{A}, C_{B}, T and t. Therefore, the degree of freedom is given by

$$\begin{aligned}\text{d.f.} &= \text{total number of variables} - \text{total number of equations}\\ &= 8 - 4 = 4\end{aligned}$$

Note C_{A} and C_{B} are differential variables of the model equations. So initial value at $t = 0$ must be given. For this case study $C_{\mathrm{A}}(0) = 1$ and $C_{\mathrm{B}}(0) = 0$. Here t is the independent variable of the model equations. T is used as the control (optimisation) variable and therefore it is relaxed from the specification set and optimised.

Here the optimisation problem is solved with two different target performances.

6.1.2. Maximum conversion problem (problem P1)

The objective is to maximise the conversion of the desired product B while optimising the reactor temperature profile within a safe bounds on the temperature.

A fixed batch time of 1 h, as used by Luus [6] is used here to compare the results. The reactor temperature is optimised within the bounds: $298 \le T \le 398$ K (same as used by Luus). It is assumed that the optimum temperature profile is obtainable by controlling external heating/cooling (not shown in the reactor description or in the model) and therefore path constraints given by Eqs. (1) and (2) are not included in the optimisation problem. A number of runs are presented. Up to eight time intervals is considered within the total batch operation time. In each interval, the temperature as well as the length of the interval are optimised. The total number of optimisation variables varies from case to case (15 variables for Run 4). The results are summarised in Table 1.

Table 1 shows that by using one time interval, the conversion achieved after 1 h ($t_{\mathrm{f}} = 1$ h) of reaction is $C_{\mathrm{B}} = 0.60595$. This value is about 1% lower than the value $C_{\mathrm{B}} = 0.61079$ reported by Luus [6]. When three time intervals are

Table 1
Summary of the results (problem P1)

Run	Optimum Temperature Profile	Max Conv, C_B
1	Temperature, K: 335.34 Switching time, hr: $t = 0$, 1.0	0.60595
2	Temperature, K: 338.58, 331.59 Switching time, hr: $t = 0$, 0.46, 1.0	0.60748
3	Temperature, K: 356.59, 334.44, 327.00 Switching time, hr: $t = 0$, 0.15, 0.58, 1.0	0.60948
4	Temperature, K: 352.2, 342.5, 339.8, 337.7, 335.7, 333.5, 332.5, 328.2 $t = 0$, 0.14, 0.24, 0.26, 0.30, 0.36, 0.51, 0.68, 1.0 Switching time, hr	0.60960

used a conversion of $C_B = 0.60948$ is achieved which is much closer to the value reported by Luus (the difference is only about 0.2%). However, the important point is that the minimum length of the time interval is of the order of 10 min in our case which will allow even a manual control. Luus had used 100 piecewise constant time intervals to approximate a continuous temperature profile meaning that every 36 s the temperature has to be switched to the next optimum value by the controller. This will require a very sophisticated controller and may not be possible to implement practically (will demand capital investment to change to this type of controller).

However, it is also shown in Table 1 that when the number of intervals is increased to 8, the optimum results achieved are better but manual control can be difficult to achieve. Beginning with a larger value the optimal reactor temperature gradually decreases with batch time. Luus [6] also has reported similar trend in the optimal temperature profile.

6.1.3. Minimum time problem (problem P2)

The objective is to minimise the batch time for a given conversion to B while optimising the reactor temperature profile within a physical and safe bounds on the temperature. Several runs were carried out but with different fixed conversion. The bounds on the temperature are same as before. For runs 1–3 we considered one time interval which is minimised. Run 4 is presented with three intervals when switching times are optimised while minimising the final time. The optimal temperature profiles, conversion and the minimum batch time are presented in Table 2 for all runs.

Table 2 shows it that the minimum batch time increases with the increase in conversion to the desired product which is obvious. This type of operation may become unavoidable if the reactant is very expensive or if we need to fulfil a strict requirement of conversion to the desired product in the downstream process.

At low desired conversion to B (Run 1), there is little room for more B to convert to C. So operating at higher temperature although increases the rate constants (k_1, k_2), the desired conversion to B is achieved quicker although it produces more C. At high desired conversion to B (compare Runs 2–4 to Run 1), there is more room for B to convert to C. Therefore, to keep the rate constants lower, the reactor needs to be operated at lower temperature (Runs 2–4) compared to Run 1. This consequently requires higher minimum batch time.

Table 2
Summary of the results (problem P2)

Run	Optimum Temperature Profile	Conv to *B* (Fixed)	Min Time	Conv to *C*
1	Temperature, K: 332.10 Switching time, hr: $t = 0$, 1.19	0.62	1.19	0.0987
2	Temperature, K: 320.25 Switching time, hr: $t = 0$, 1.71	0.65	1.71	0.0856
3	Temperature, K: 328.23 Switching time, hr: $t = 0$, 3.28	0.70	3.28	0.0782
4	Temperature, K: 316.19, 321.13, 298.03 Switching time, hr: $t = 0$, 0.13, 0.26, 4.30	0.72	4.30	0.0832

6.2. *Case study 2*

In this example also a consecutive reaction scheme is considered. However, the batch reactor system is described using a detailed model consisting mass and energy balances and detailed design parameters of the reactor (as presented in Section 2).

The reaction type is same as case study 1 which is

$$\mathrm{A}\xrightarrow{k_1}\mathrm{B}\xrightarrow{k_2}\mathrm{C}$$

where A is the raw material, B the desired product and C is the waste or by-product.

However, the conversion to B from A and conversion C from B follow a first-order reaction rate.

6.2.1. *Models equations*

Simple manipulations of Eqs. (D1) and (D2) results in the following:

$$\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} = -k_1 C_\mathrm{A} \qquad \text{(D10)}$$

$$\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t} = k_1 C_\mathrm{A} - k_2 C_\mathrm{B} \qquad \text{(D11)}$$

$$\frac{\mathrm{d}C_\mathrm{C}}{\mathrm{d}t} = k_2 C_\mathrm{B} \qquad \text{(D12)}$$

From Eqs. (D3)–(D9), we have

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{Q_\mathrm{r} - Q_\mathrm{m}}{C_p V \rho} \qquad \text{(D13)}$$

$$\frac{\mathrm{d}T_\mathrm{m}}{\mathrm{d}t} = \frac{Q_\mathrm{m} - Q_\mathrm{J}}{C_{p\mathrm{m}} V_\mathrm{m} \rho_\mathrm{m}} \qquad \text{(D14)}$$

$$\frac{\mathrm{d}T_\mathrm{J}}{\mathrm{d}t} = \frac{F_\mathrm{J}}{V_\mathrm{J}}(T_\mathrm{J0} - T_\mathrm{J}) + \frac{Q_\mathrm{J}}{C_{p\mathrm{J}} V_\mathrm{J} \rho_\mathrm{J}} \qquad \text{(D15)}$$

$$Q_\mathrm{r} = -\Delta H_1 (k_1 C_\mathrm{A} V) - \Delta H_2 (k_2 C_\mathrm{B} V) \qquad \text{(D16)}$$

$$Q_\mathrm{m} = U_\mathrm{i} A_\mathrm{i} (T - T_\mathrm{m}) \qquad \text{(D17)}$$

$$Q_\mathrm{J} = U_\mathrm{o} A_\mathrm{o} (T_\mathrm{m} - T_\mathrm{J}) \qquad \text{(D18)}$$

$$k_1 = k_{10} \exp\left(-\frac{E_1}{RT}\right) \qquad \text{(D19)}$$

$$k_2 = k_{20} \exp\left(-\frac{E_2}{RT}\right) \qquad \text{(D20)}$$

Total number of variables in Eqs. (D10)–(D20) is 40. They are $\mathrm{d}C_\mathrm{A}/\mathrm{d}t$, $\mathrm{d}C_\mathrm{B}/\mathrm{d}t$, $\mathrm{d}C_\mathrm{C}/\mathrm{d}t$, $\mathrm{d}T/\mathrm{d}t$, $\mathrm{d}T_\mathrm{m}/\mathrm{d}t$, $\mathrm{d}T_\mathrm{J}/\mathrm{d}t$, k_1, k_2, Q_r, Q_m, Q_J, C_A, C_B, C_C, T, T_m, T_J, ΔH_1, ΔH_2, ρ, ρ_m, ρ_J, C_p, $C_{p\mathrm{m}}$, $C_{p\mathrm{J}}$, V, V_m, V_J, E_1, E_2, F_J, T_J0, R, k_{10}, k_{20}, U_i, U_o, A_i, A_o, t.

$$\begin{aligned}\text{d.f.} &= \text{total number of variables} - \text{total number of equations}\\ &= 40 - 11 = 29\end{aligned}$$

Table 3
Constant parameters used in the model

$\Delta H_1 = -6.50\mathrm{E}8$ J/kmol	$\Delta H_2 = -1.20\mathrm{E}8$ J/kmol	$\rho = 800$ kg/m^3
$\rho_\mathrm{m} = 8200$ kg/m^3	$\rho_\mathrm{J} = 1000$ kg/m^3	$C_p = 4200$ J/kg K
$C_{p\mathrm{m}} = 500$ J/kg K	$C_{p\mathrm{J}} = 4200$ J/kg K	$E_1 = 3.49\mathrm{E}7$ J/kmol
$E_2 = 4.65\mathrm{E}7$ J/kmol	$V = 1.23$ m^3	$V_\mathrm{m} = 0.27$ m^3
$V_\mathrm{J} = 0.53$ m^3	$k_{10} = 4.38\mathrm{E}4$ h^{-1}	$k_{20} = 3.94\mathrm{E}5$ h^{-1}
$R = 8314$ J/kmol K	$U_\mathrm{i} = 7.0\mathrm{E}6$ J/h K m^2	$U_\mathrm{o} = 8.18\mathrm{E}6$ J/h K m^2
$A_\mathrm{i} = 5.25$ m^2	$A_\mathrm{o} = 5.25$ m^2	$T_\mathrm{J0} = 298$ K

6.2.2. *Specifications*

The number of parameters is 21. They are ΔH_1, ΔH_2, ρ, ρ_m, ρ_J, C_p, $C_{p\mathrm{m}}$, $C_{p\mathrm{J}}$, V, V_m, V_J, E_1, E_2, T_J0, R, k_{10}, k_{20}, U_i, U_o, A_i, A_o. Independent variable $= 1 = t$. Initial value at time $t = 0$ for all the differential variables (C_A, C_B, C_C, T, T_m, T_J) to be specified is 6.

The above specifications count to 28 variables. In this work F_J (coolant flow) is relaxed from the specifications and is optimised.

It is assumed that the system is preheated to 350 K before the actual process starts and the jacket is full with water at room temperature. The initial value of C_A, C_B and C_C are 0.975, 0.025 and 0.0, respectively. The initial value of T, T_m and T_J are 350, 373 and 300 K, respectively.

Here we solve both optimisation problems P1 (maximum conversion problem) and P2 (minimum time problem). The constant parameters of the model are given in Table 3.

6.2.3. *Maximum conversion problem (problem P1)*

In this reaction, an end point constraint for the reactant temperature ($T \leq 320$ K) is imposed to guarantee that the products are at or below certain desired temperature. The total batch time is 3.5 h and the number of control intervals is 4. Coolant flow is bounded between 0 m^3/h (valve fully closed) and 9 m^3/h (valve fully open). The end point constraint for the waste (product C) is set at 0.10.

Five different runs have been presented for the maximum conversion problem (problem P1 or P1(j)). Run 1 is with an end point constraint on the reactor temperature only. Run 2 is with end point constraints on the reactor temperature and on the waste (product C). Run 3 has been solved with path (*one-path-interval*) and end point constraints on the reactor temperature and an end point constraint on the waste. Runs 4 and 5 are solved with path and end point constraints on the reactor temperature. However, Run 4 deals with *one-path-interval* on T and Run 5 deals with *two-path-interval* on T. For Runs 3–5 the reactor temperature must not exceed 370 K at any time (path constraint).

The results for all runs are summarised in Table 4 in terms of conversion to B (desired product) and C (waste). Table 4 shows that, a higher conversion to B is achieved in Run 1 compared to that of Run 2. This can be explained as: the rate of production of C depends on both the kinetic constant k_2 and the amount of B present at any time. Also since k_2 is much larger than k_1, near the end of the reaction process, the

Table 4
Summary of the results—maximum conversion problem

Run	Type of problem	Conversion to B	Conversion to C (waste)
1	With end point constraint on *T*	0.6462	0.1659
2	With end point constraint on *T* and waste	0.6249	0.1000
3	With path and end point constraint on *T* and end point constraint on waste	0.6253	0.0991
4	With path and end point constraint on *T* (*one-path-interval*)	0.6253	0.0991
5	With path and end point constraint on *T* (*two-path-interval*)	0.6401	0.1161

rate of production of B is slower than the rate of production of C. Therefore, the only way to satisfy the constraint on the waste production is by producing less B. Production of more B will produce more C for the type of reaction considered here (Run 1, Table 4).

Run 3 results in a further reduction in conversion of B due to added path constraint on the reactor temperature. It signifies that in order operate the system safely, a decrease in the amount of product has to be tolerated. For Runs 1–3 the optimal coolant flow profile and the reactor temperature profile are shown in Figs. 4–6. Figs. 4 and 5 clearly show that although in both runs end point constraints on the reactor temperature are satisfied, the maximum reactor temperature goes beyond the safe limit (370 K), to produce more B (as it is favoured at higher temperature). For Run 3, path constraint is satisfied (Fig. 6) and therefore results in low conversion of B compared to Runs 1 and 2. Also it is interesting to note that Run 1 demands higher reactor temperature as the batch proceeds to favour more conversion to B while Run 2 demands lower reactor temperature to produce less waste C. These temperature demands are fulfilled by lower and higher coolant flow rate (Figs. 4 and 5), respectively.

For Run 3 the reactor is run with a higher coolant flow (compared to Runs 1 and 2) for a long time (longer than Runs 1 and 2) to ensure that the path constraint is satisfied (Fig. 6). Near the end of the batch, the reactor is run with even higher coolant flow to ensure that the end point constraints on temperature as well as on the waste are satisfied.

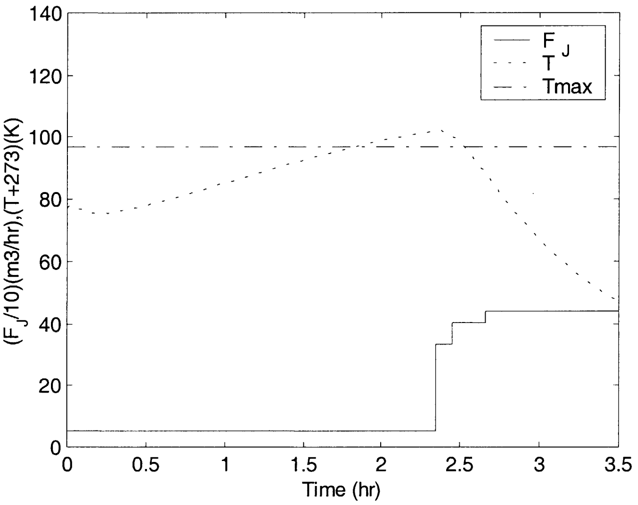

Fig. 5. Case study 2 — Run 2 (problem P1).

Run 4 uses *one-path-interval* of 3.5 h which is the same as the total batch time. While Run 5 uses *two-path-interval*, the length of each interval being 1.75 h. Run 4 uses four control intervals (Fig. 7) within the *path-interval* while Run 5 uses two control intervals within each *path-interval* (Fig. 8). For

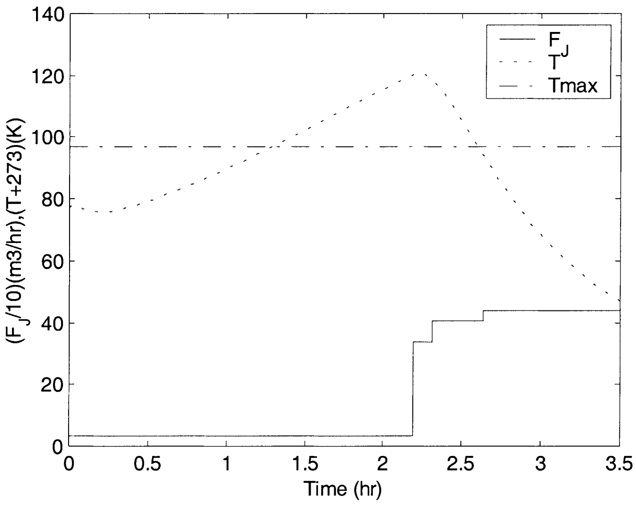

Fig. 4. Case study 2 — Run 1 (problem P1).

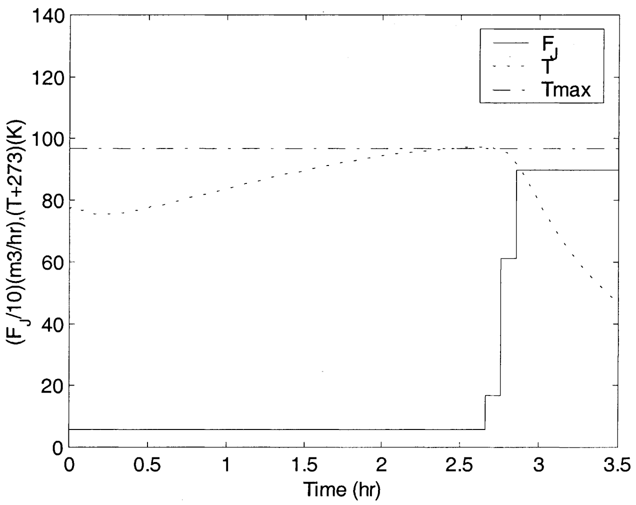

Fig. 6. Case study 2 — Run 3 (problem P1).

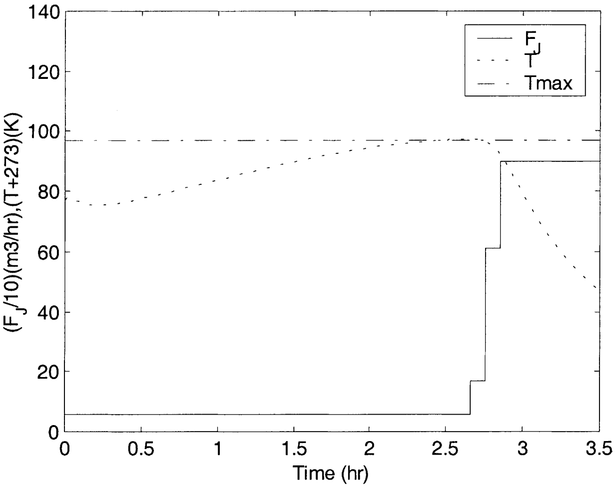

Fig. 7. Case study 2 — Run 4 (problem P1).

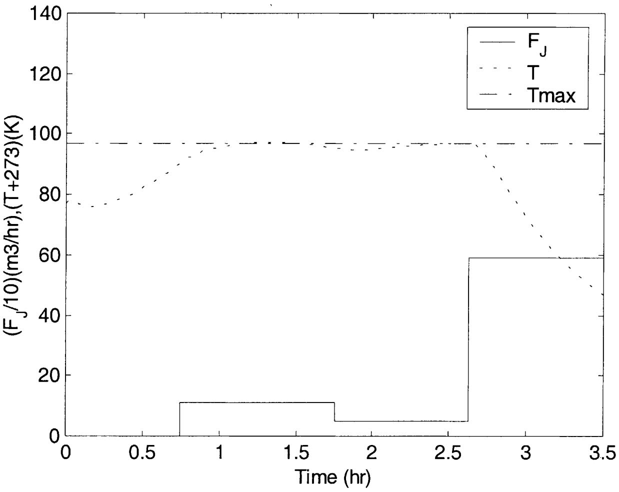

Fig. 8. Case study 2 — Run 5 (problem P1).

Run 5, the optimisation problem is solved sequentially. In the first part (in *path-interval* 1) the problem is solved without the end point constraint on T and in the second part (in *path-interval* 2) the problem is solved using both the path constraint and end point constraints. This strategy results to higher conversion to B in Run 5 (2.4% higher) compared to that in Run 4. This is because the reactor in Run 5 could be operated at higher temperature (low coolant flow) compared to that in Run 4 for a longer period, which results to higher conversion of B at any time during the operation (Fig. 9).

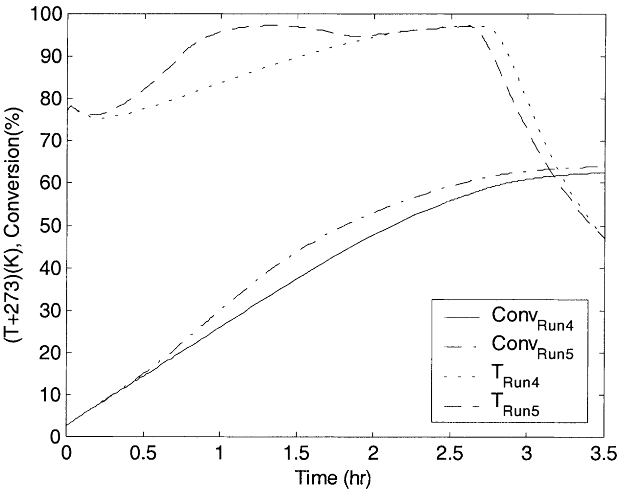

Fig. 9. Case study 2 — Runs 4 and 5 (problem P1).

It is to be noted that in Table 4 the conversion obtained for Runs 3 and 4 is similar. The reason behind is, in Run 4 the value of the waste being produced is in the range of the waste constraint imposed in Run 3. The production of B and C cannot be increased in order to fulfil the path constraint on the reactor temperature.

6.2.4. Minimum time problem (problem P2 or P2(j))

Here, we rerun Runs 1, 4 and 5 of Table 4 but with a fixed conversion of B at 0.600. The bounds on the coolant flow rate are same as before. For Run 5, in *path-interval* 1, the desired conversion of B to achieve is 0.350 and the problem is solved using only the path constraint. For *path-interval* 2, the problem is solved using both the path and end point constraints. As before, four control intervals are used in Runs 1 and 4 and two control intervals are used in each *path-interval* in Run 5. Each run has therefore four control intervals which is optimised while minimising the final time. Results are summarised in Table 5 and Figs. 10–13.

From Table 5, it is found that the time needed to get the same conversion (0.600) while under a path constraint (Runs 4 and 5) is longer compared to the run without the path constraint (Run 1). This is because in Run 1 the reactor temperature goes above the safe limit $T_{\max}$ and achieve the desired conversion quicker (Fig. 10). However, the batch time needed with *two-path-interval* (Run 5, Table 5) is lower compared to that of Run 4 (Table 5) which was expected. For Run 5 in the first *path-interval* (0–1.15 h), there was no end point constraint and the reactor temperature could go higher

Table 5
Summary of the results—minimum time problem

Run	Type of problem	Conversion to B	Conversion to C (waste)	Final time (h)
1	With end point constraint on T	0.600	0.1071	2.46
4	With path and end point constraint on T (*one-path-interval*)	0.600	0.0809	3.21
5	With path and end point constraint on T (*two-path-interval*)	0.600	0.0845	2.91

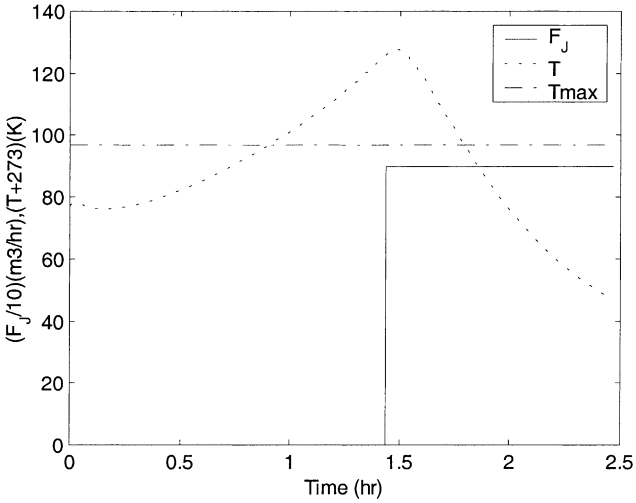

Fig. 10. Case study 2 — Run 1 (problem P2).

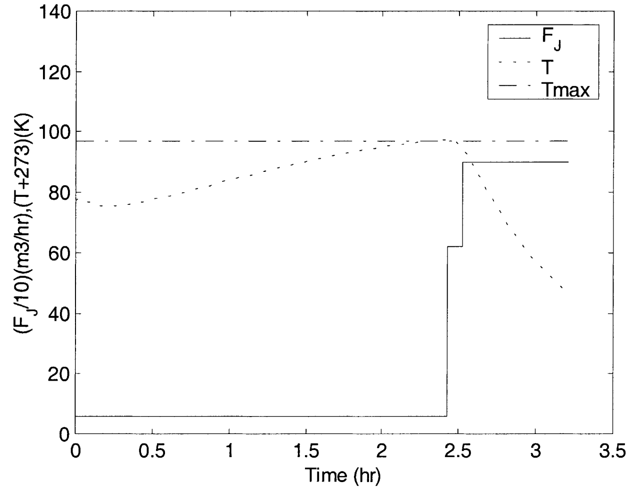

Fig. 11. Case study 2 — Run 4 (problem P2).

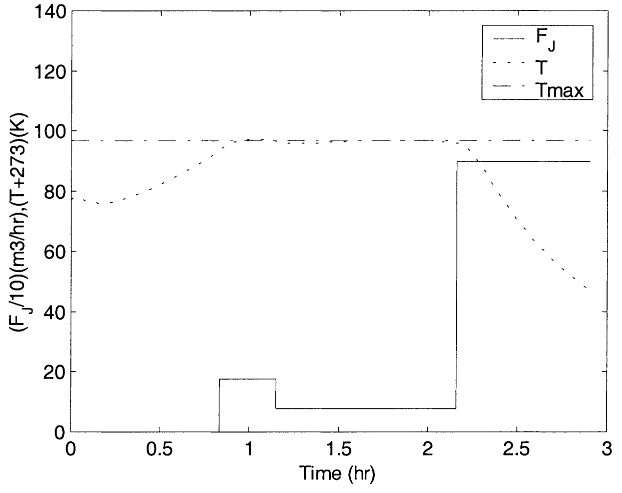

Fig. 12. Case study 2 — Run 5 (problem P2).

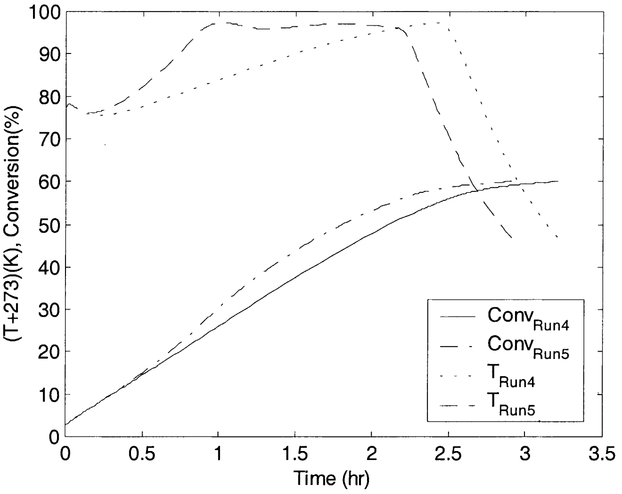

Fig. 13. Case study 2 — Runs 4 and 5 (problem P2).

than that of Run 4 at any time during the batch producing more B quicker (Fig. 13). For the second *path-interval* (1.15–2.91 h), the reactor temperature for Run 5 was higher than that of Run 4 for a considerable period thus producing more B quicker. In all runs, the coolant flow hits its upper bound at the end of the processes to satisfy the end point constraint.

7. Conclusions

Optimal operation policies in batch reactors were obtained using dynamic optimisation techniques. Optimisation problems for two different types of performance measures (maximum conversion and minimum batch time) were formulated and the solutions of such problems were presented using typical examples. Two types of batch reactor models were used in the optimisation framework. The effects of waste and/or temperature constraints (at the final time or at any time throughout the batch time) on the optimal operation policies and on the objectives (maximum conversion and minimum time) of the optimisation problems were also studied.

The shortcut model (consisting of only mass balance and reaction kinetics) allows determination of the optimal reactor temperature profiles to achieve a desired performance (case study 1). The optimal temperature profiles can then be used as a basis for the detailed design of the reactor (i.e. reactor volume, heating/cooling configuration, etc.). Case study 1 also provided the comparison of the results with those from a published literature.

The detailed model (consisting of mass and energy balances, reaction kinetics and cooling/heating configuration) allows determination of the best operating conditions (e.g. cooling/heating profile) of already designed (existing) reactors to achieve a desired performance within the safe operating as well as environmental constraints (case study 2).

Coolant flow has been used as the control variable and safe reactor operation is achieved by introducing a path constraint on the reactor temperature in the optimisation framework. The path constraint has been translated to an equivalent end point constraint by adding an extra differential equation to the model equations.

Also, *multi-path-interval* path constraint optimisation problem formulations have been proposed for the two types of optimisation problems. This approach allowed reactor operation at high temperature (more close to the safe temperature limit) for a longer period compared to the traditional *one-path-interval* method and resulted in better performance of the reactor. Case study 2 (Tables 4 and 5) showed the advantages of such approach in terms of the product conversion and batch time. Also comparison of Runs 1 and 2 with those of Runs 3 and 4 in Table 4 shows the importance of imposing path constraint in the optimisation problem formulation.

Once the optimal operation policies are obtained, these can be implemented by designing appropriate controllers [24].

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