SIMULATION OF WASTE GENERATION DURING START-UP OF AN INTERCONNECTED PROCESS NETWORK

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ABSTRACT

During start-up, an interconnected process network, e.g., a network of chemical reactors, often generates an appreciable amount of product or products that do not meet the specifications and thus should be regarded as waste to be treated or reprocessed. Moreover, if a hazardous or toxic component is contained in the product, its accumulation may be such that it poses a high environmental or health risk. Naturally, it is desirable that this accumulation be minimized. To devise an optimal start-up strategy for the process requires an understanding of its transient behavior for various modes of start-up.

For illustration, the start-up characteristics of a system comprising three continuous stirred tank reactors (CSTR's) connected in series are examined in this work through computer simulation. Specifically, the transient characteristics of a numerical example are considered under three modes of the start-up, i.e., series, batch and parallel; in addition, the rates at which the waste or off-spec product accumulated and the total amount of this waste are evaluated. The example involves the simultaneous and sequential reactions of the 1.5th and 2nd orders under isothermal conditions.

KEY WORDS

start-up, process network, hazardous waste

INTRODUCTION

Start-up is almost always one of the most crucial steps in the successful operation of a process plant or system in the light of its safety or risk implications. Often, it may take many days for a large interconnected process to attain the normal or steady-state operating conditions, thereby giving rise to generation and accumulation of inordinately large amounts of off-spec products requiring further processing and treatment. Naturally, it is highly desirable that such generation and accumulation be minimized. To devise an optimal start-up strategy or strategies for accomplishing this requires us first to understand the process' transient behavior for various modes of start-up.

Mason and Piret [1] investigated start-up of three different systems of continuous stirred tank reactors (CSTR's) connected in series. The first contained reactors identical in size; the second consisted of reactors of different volumes; and the third comprised combinations thereof. Nevertheless, consideration was given only to single, simultaneous, consecutive and reversible reactions of the first order. Analytical solutions have been obtained for the concentration changes occurring during start-up. The reactors were assumed to be operated under isothermal conditions collectively or individually. In their subsequent study, Mason and Piret [2] experimentally studied to verify some of the analytical solutions obtained with the hydrolysis of acetic anhydride in water solution. The experimental system, consisting of five equal-volume CSTR's-in-series under isothermal conditions, were started up according to six different modes. These modes included batch, series and
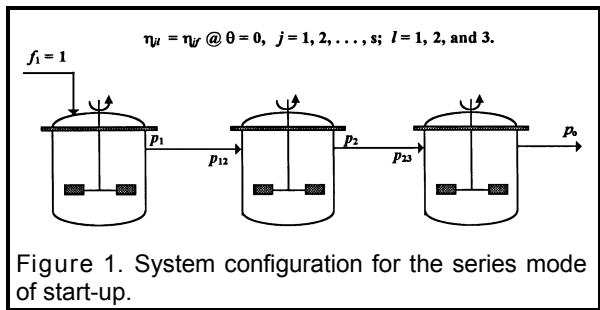
$$\eta_{jl} = \eta_{ljf} @ \theta = 0, \quad j = 1, 2, \dots, s; \quad l = 1, 2, \text{ and } 3.$$

Figure 1. System configuration for the series mode of start-up.

$$\eta_{jl} = \eta_{ljf} @ \theta = 0, \quad j = 1, 2, \dots, s; \quad l = 1, 2, \text{ and } 3.$$

Figure 2. System configuration for the batch mode of start-up.

parallel modes, with and without reaction taking place during the filling of reactors.

Phillips et al. [3, 4] have proposed adaptive control strategies for the start-up of a flu-idized sand bath. In their strategies, a self-tuning control approach determines the switching time on-line. Westerholt et al. [5] have adopted the bang-bang (time-optimal) algorithm for start-up control of a process. The algorithm was verified experimentally by controlling the temperature during start-up of a laboratory-scale batch extruder, sandbath and dummy cracking reactor. Moreover, the algorithm was demonstrated by simulating the start-up control of a single batch reactor with an exothermic reaction.

None of the available publications have dealt with the accumulation of off-spec or undesirable products, be they hazardous or toxic. Such products almost always pose environmental or health risks, thus requiring further processing and treatment, which can be costly.

In this work the start-up characteristics of a system comprising three CSTR's con-nected in series are examined through computer simulation. The example involves the simultaneous and sequential reactions of the 1.5th and 2nd orders under isother-mal conditions.

START-UP MODES

A system of CSTR's-in-series can be started up in a variety of ways or modes. This study considers three modes, i.e., se-ries, batch and parallel, combinations of
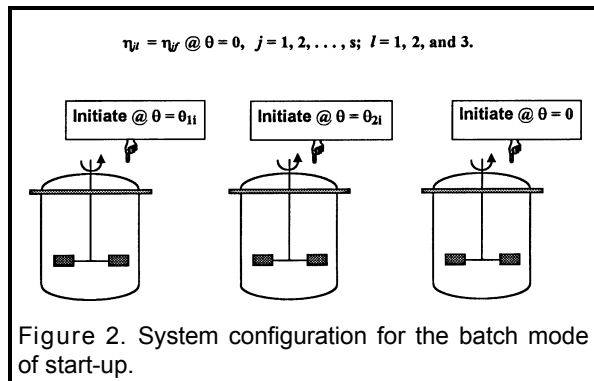
which leads to various other modes. In this study, the dynamics of the transportation lines and that of pumping devices are as-sumed to have negligible effects on the system. It is also assumed that all the reac-tors are initially filled with reactants and the steady-state values of the state variables are known a priori.

The product is accumulated until all the state variables reach their respective steady states, i.e., until the start-up time is reached. Nevertheless, in general, all the state variables of a multivariable system do not simultaneously reach their respective steady states. Thus, the system is consid-ered to be in a steady state when all state variables reach their respective steady-state values. The start-up mode of opera-tion is abruptly changed to the mode pre-vailing under normal operating conditions, i.e., series mode in the present work, when the specified state variable (SSV) reaches its steady-state value, i.e., when the switching time is reached. The SSV is the variable selected to determine the switch-ing time; selecting it is essential prior to ini-tiating the start-up operation. The moment at which the start-up operation is affected, i.e., the initiation time, may vary from reac-tor to reactor. The accumulated product during the start-up, which does not meet product specification, i.e., to be off-spec, is processed for recycling or treated as waste.
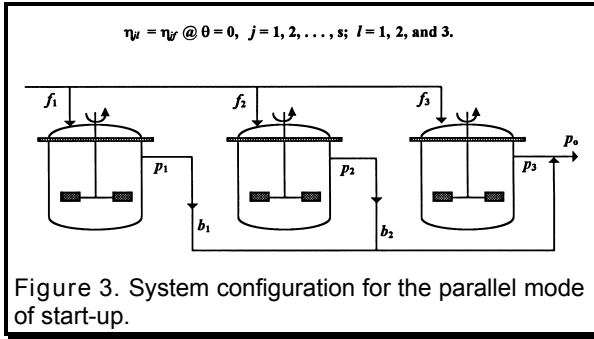
Figure 3. System configuration for the parallel mode of start-up.

Figure 4. Generalized system configuration encompassing the three modes of start-up.

Series

This appears to be the simplest mode of starting up a system of CSTR's-in-series. The feed is introduced into the first reactor at a steady-state flow rate, and the system is operated in series and continuously from the outset as illustrated in Figure 1. It is worth noting that the switching time is at the initiation of start-up operation for this mode.

Batch

Figure 2 shows this mode of start-up in which each reactor is separately operated in batch. The operation is initiated from the last reactor backward in such a way that the steady-state values of the SSV are reached simultaneously in all the reactors. At this instant, the system is placed in series by introducing the feed in the first reactor and opening all the passages between the reactors.

Parallel

In this mode, all reactors are placed in parallel at the outset of operation, and the exit flow streams from them are bypassed for accumulation during start up; see Figure 3. The feed is divided among all the reactors so that the respective steady-state values of the SSV are achieved simultaneously. If this is not possible because of the material balance constraints, e.g., the total feed rate is equal to the steady-state feed rate, the following modifications are made.
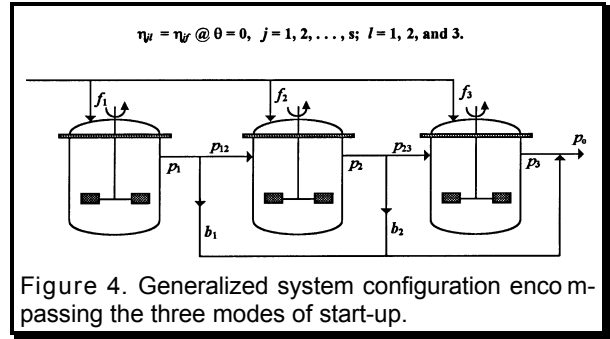
The third reactor is operated in batch at the outset of the operation, and the feed is divided between the first and second reactors. To achieve the respective steady-state values of the SSV simultaneously in all the reactors, the initiation time of the parallel operation in the first two reactors is delayed accordingly, as will be elaborated later. When the respective steady-state values of the SSV are reached, the system is switched to operate in series by discontinuing the feed of the second and/or third reactors, and by opening all the passages between the reactors as done in the batch mode.

GENERAL START-UP MODEL

The general configuration encompassing all the start-up modes described in the preceding section is illustrated in Figure 4 where f_l is the feed rate to the l-th reactor; p_l, the exit flow rate from the l-th reactor; p_{lm}, the inlet flow rate from the exit of the l-th reactor to the m-th reactor; p_o, the outlet flow rate from the exit of the system; and b_l, the bypass rate from the exit of the l-th reactor to the end of the system. All these flow rates are dimensionless; they represent the fractions of the steady-state volumetric feed rate.

The general start-up model for a system of three CSTR's-in-series is derived based on the following assumptions.

- The reactors are identical in size.

- The reaction mixture is micromixed.

- The content of the reactor is liquid.

- The reaction mixture has the constant physical properties.

- The heat of reaction is constant.

- The work required for stirring the contents of the reactors is negligibly small.

- The dynamics of the transportation lines and pumping devices can be neglected.

The mass and energy balance equations in terms of the dimensionless variables may be written as follows:

$$\frac{d\lambda_1}{d\theta} = f_1\lambda_f - p_1\lambda_1 + \tau\sum_{i=1}^{R}\gamma_{ik} \cdot r_{ik}^* \qquad (1)$$

$$\frac{d\lambda_2}{d\theta} = f_2\lambda_f + p_{12}\lambda_1 - p_2\lambda_2 + \tau\sum_{i=1}^{R}\gamma_{ik} \cdot r_{ik}^* \qquad (2)$$

$$\frac{d\lambda_3}{d\theta} = f_3\lambda_f + p_{23}\lambda_2 - p_3\lambda_3 + \tau\sum_{i=1}^{R}\gamma_{ik} \cdot r_{ik}^* \qquad (3)$$

$$\frac{d\eta_{j1}}{d\theta} = f_1\eta_{jf} - p_1\eta_{j1} + \tau\sum_{i=1}^{R}\nu_{ij}\frac{r_{ik}^*}{\nu_{ik}} \qquad (4)$$

$$\frac{d\eta_{j2}}{d\theta} = f_2\eta_{jf} + p_{12}\eta_{j1} - p_2\eta_{j2} + \tau\sum_{i=1}^{R}\nu_{ij}\frac{r_{ik}^*}{\nu_{ik}} \qquad (5)$$

$$\frac{d\eta_{j3}}{d\theta} = f_3\eta_{jf} + p_{23}\eta_{j2} - p_3\eta_{j3} + \tau\sum_{i=1}^{R}\nu_{ij}\frac{r_{ik}^*}{\nu_{ik}} \qquad (6)$$

$$N_j^* = \int_0^{\theta_s}[b_1\eta_{j1} + b_2\eta_{j2} + p_3\eta_{j3}]d\theta \qquad (7)$$

$$V^* = \int_0^{\theta_s}[b_1 + b_2 + p_3]d\theta \qquad (8)$$

The dimensionless variables in the above equations are defined as follows:

$$\theta = \frac{t}{\tau} \qquad (9)$$

$$\lambda_l = \frac{T_l c_P \rho_f}{(-\Delta H_1)C_{af}} \qquad (10)$$

$$\eta_{jl} = \frac{C_{jl}}{C_{af}} \qquad (11)$$

$$\gamma_{ik} = \frac{(-\Delta H_{ik})}{(-\Delta H_1)} \qquad (12)$$

$$r_{ik}^* = (C_{af})^{n_i-1}r_{ik}(\eta_j, \lambda), \quad j = 1, 2,..., s \qquad (13)$$

$$V^* = V_{off\text{-}spec}/V_R \qquad (14)$$

$$N_j^* = N_j/(V_R \cdot C_{af}) \qquad (15)$$

In these expressions, τ is the space time based on the steady-state feed rate; θ, the dimensionless time; λ_l, the dimensionless temperature of the l-th reactor; c_P, the mean specific heat of the feed in kcal/kg·K; ρ_f, the density of the feed in kg/m^3; C_{af}, the concentration of the limiting reactant in the feed in kmol/m^3; C_{jl}, the concentration of species j in the l-th reactor in kmol/m^3; ΔH_{ik}, the molar heat of reaction i in kcal/kmol of species k reacted; γ_{ik}, the dimensionless heat of reaction i; η_{jf}, the dimensionless feed concentration of species j; η_{jl}, the dimensionless concentration of species j in the l-th reactor; n_i, the overall order of reaction i; r_{ik}, the known rate of reaction of species k in reaction i; s, the total number of species participating in the reactions; ν_{ij}, the stoichiometric coefficient of species j in the i-th reaction; θ_s, the dimensionless start-up time; N_j^*, the dimensionless amount of species j accumulated in the off-spec product; and V^*, the total dimensionless volume of the off-spec product.

SIMULATION

Simulations have been carried out for various complex reaction systems under isothermal as well as nonisothermal conditions in the present work. For lack of space, however, only a single example involving reactions occurring under isothermal condi-
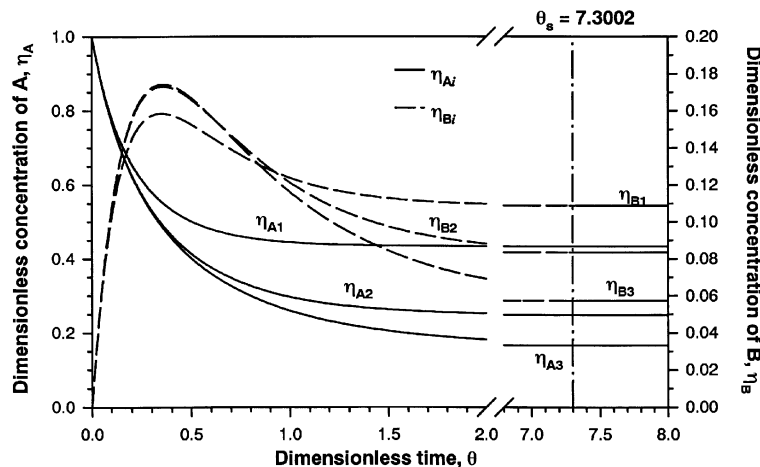
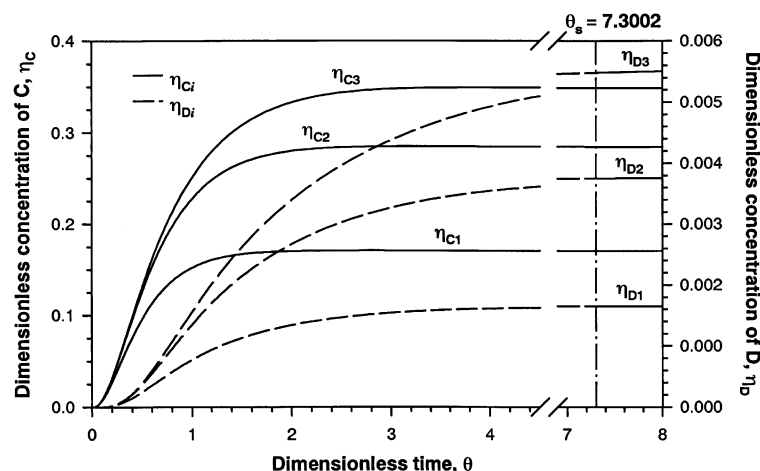Figure 5a. Transient behavior of the system during the series mode of start-up: concentrations of A and B.

Figure 5b. Transient behavior of the system during the series mode of start-up: concentrations of C and D.

tions is presented here; under such condi-tions Equations 1 through 3 can be neglected for the simulations.

Simulation is initiated at $\theta = 0$; however, as stated earlier, the dimensionless initiation time of an individual reactor, θ_{li}, may not be identical. The simulation is continued until the dimensionless switching time, θ_c, as indicated by the SSV, is reached with the start-up mode of operation; after θ_c, the simulation is continued until θ_s is reached with the normal mode of operation. Nevertheless, it is not a trivial matter to identify the SSV because all the state variables of a multivariable system do not simultaneously reach their final steady states as mentioned

earlier. Judicious trade-off must be made among the state variables in identifying or selecting the SSV through repeated preliminary simulations.

The attainment of θ_s is identified when all state variables reach the steady states as stated earlier. Theoretically, however, it is impossible for a state variable to reach completely the final steady state in a finite period of time in a micromixed CSTR. For practical purposes, therefore, the steady state can be assumed to be virtually attained when the SSV traverses 99% of the difference between its initial state and final
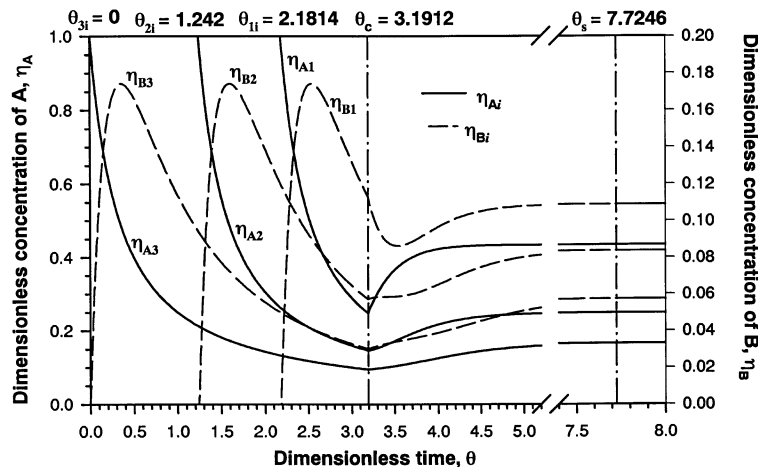
Figure 6a. Transient behavior of the system during the batch mode of start-up: concentrations of A and B.
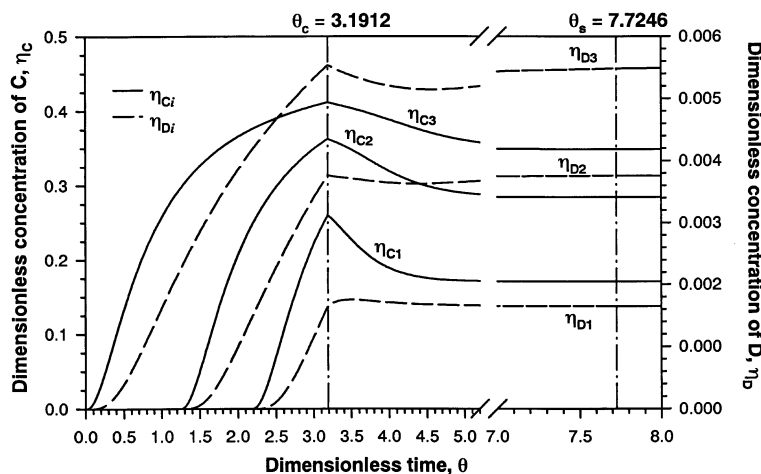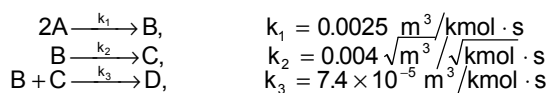

Figure 6b. Transient behavior of the system during the batch mode of start-up: concentrations of C and D.

steady state (see, e.g., Seborg et al. [6]; Fogler [7]).

Specifically, the example considers an isothermal liquid-phase system in which the following irreversible reactions take place;

$$2A \xrightarrow{k_1} B, \qquad k_1 = 0.0025 \ m^3/kmol \cdot s$$
$$B \xrightarrow{k_2} C, \qquad k_2 = 0.004 \ \sqrt{m^3}/\sqrt{kmol} \cdot s$$
$$B + C \xrightarrow{k_3} D, \qquad k_3 = 7.4 \times 10^{-5} \ m^3/kmol \cdot s$$

where A is the reactant; B, the intermediate product; C, the main product; and D, the toxic byproduct. Other pertinent parameters of the system are as follows:

$$V_R = 1.2 \ m^3 \ ; \ \upsilon_f = 0.001 \ m^3/s \ ;$$
$$V_R / \upsilon_f = \tau = 1200 \ s \ ; \ C_{Af} = 1.0 \ Kmol / m^3$$

The initial conditions specified are

$$\eta_{Af} = 1.0; \ \eta_{Bf} = 0; \ \eta_{Cf} = 0; \ \eta_{Df} = 0 \qquad (16)$$

The SSV for the present example, selected after the preliminary simulations, is the concentration of D which is the state variable reaching its steady-state value last or having the longest rise time.

The governing equations for this example have been numerically solved on a personal computer by the second and third order Runge-Kutta formula (see, e.g., Ral-
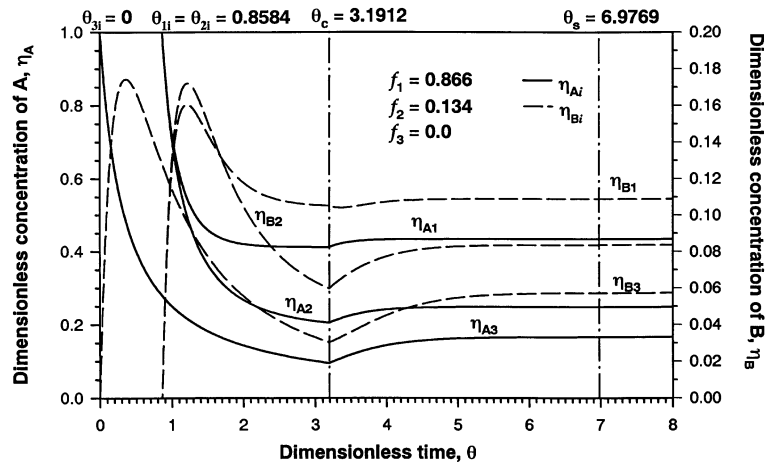
Figure 7a. Transient behavior of the system during the parallel mode of start-up: concentration of A and B.
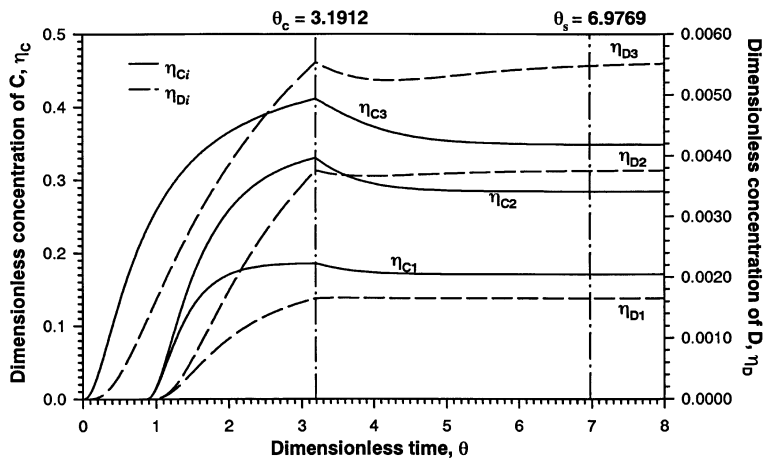

Figure 7b. Transient behavior of the system during the parallel mode of start-up: concentrations of C and D.

ston [8]) for the three modes of start-up, i.e., series, batch and parallel.

RESULTS AND DISCUSSION

The results of simulation are depicted in Figures 5 through 7 in terms of the dimensionless concentrations of the reactant and products as functions of the dimensionless time, θ, with the concentration of D selected as the SSV. The dimensionless concentrations of A and B in the I-th reactor, i.e., η_{Al} and η_{Bl}, are plotted in Figures 5a, 6a and 7a; and those of C and D, i.e., η_{Cl} and η_{Dl} in Figures 5b, 6b and 7b for the three modes of start-up. The total amounts of the product accumulated during the three modes of start-up as well as the start-up times are summarized in Figure 8. The figure also exhibits the cumulative amounts of A, B, C and D, i.e., N_A^*, N_B^*, N_C^* and N_D^*, respectively, for the three modes of start-up. Note that Figure 8 is presented in terms of the dimensionless quantities.

Naturally, $\theta_{li} = 0$ and $\theta_c = 0$ for the series mode of start-up; moreover, Figures 5a and 5b collectively indicate that $\theta_s = 7.3002$. The total dimensionless cumulative volume of the off-spec product, V^*, is 7.3002 as expected, and the dimensionless amount of the toxic component in the off-spec product, i.e., N_D^*, is 0.0292 for this mode of start-up; see Figure 8.
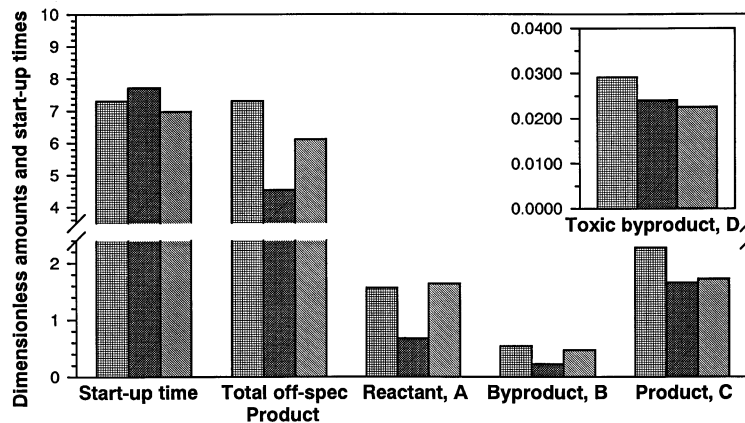
Figure 8. Start-up times and amounts of the off-spec product and individual components accumulated during start-up: modes of start-up; ▦ series, ▨ batch, ▨ parallel.

To determine θ_{li}'s for the batch mode of start-up, the dimensionless times at which the SSV in individual reactors reach their steady-state values have been determined first through preliminary simulations. The resultant times are 1.0098, 1.9492 and 3.1912 for the first, second and third reactors, respectively. Thus, the values of θ_{li} can be obtained as follows:

$$\theta_{3i} = 0; \; \theta_{2i} = 3.1912 - 1.9492 = 1.2420;$$
$$\text{and } \theta_{1i} = 3.1912 - 1.0098 = 2.1814$$

The values of SSV in these reactors reach their steady-state levels in the order of the first, second and third reactors. The start-up operation, therefore, must be initiated in the reverse order, i.e., in the order of the third, second and first reactors; see Figure 6a. This implies that the value of θ_c for the batch mode is also 3.1912. At this instant, the mode of operation is transformed into series; however, as shown in Figures 6a and 6b, the system reaches the steady state at $\theta = 7.7246$, which is the value of θ_s. The corresponding value of V^* is 4.5334, and that of N_D^* is 0.0241; see Figure 8.

For the parallel mode of start-up, the feed is to be distributed among the three reactors so that the values of SSV simultaneously reach their respective steady-state levels in all the reactors. In other words, the

dimensionless feed distribution among the three reactors, f_1, f_2 and f_3, need to be identified by solving Equations 4 through 6 for various combinations of f_i's so that η_{D1}, η_{D2} and η_{D3} simultaneously attain the dimensionless steady-state values, η_{D1s}, η_{D2s} and η_{D3s}, respectively. The values of f_i's must sum to 1.0 because of the material balance constraint; moreover, for the system involving three reactors and four chemical species, Equations 4 through 6 give rise to a set of 12 nonlinear simultaneous ordinary differential equations. Obviously, therefore, analytical solution of this set of equations is impossible; in fact, even numerical solution is at best extremely difficult, if not impossible.

To circumvent the difficulty mentioned above, sequential solution has been attempted by initially assuming f_3 at its minimum value of 0. The values of f_1 and f_2 that render η_{D1} and η_{D2} to simultaneously reach their steady-state values are identified to be 0.8660 and 0.1340, respectively. The corresponding θ, η_{D1} and η_{D2} are 2.3328, 0.00165 and 0.00376, respectively. Nevertheless, with $f_3 = 0$, η_{D3} does not attain its steady-state value until θ is 3.1912, which is already greater than 2.3328; any permissible change of f_3 from 0, i.e., an increase of f_3, magnifies the difference between these two numbers, thereby appar-

ently indicating that the parallel distribution of the feed to all the reactors are impossible for attaining the steady-state values of the SSV for the system under consideration. Consequently, the batch operation is initiated in the third reactor at the outset of the start-up operation, i.e., at $\theta = 0$. It is continued until η_{D3} reaches its steady-state value at $\theta = 3.1912$. Meanwhile, the parallel feeding to the first two reactors is initiated at θ of $3.1912 - 2.3328 = 0.8584$, which is the extent of delay in starting the parallel operation of the first two reactors. As a result, the values of SSV in all the reactors reach their respective steady-state levels when θ is 3.1912, i.e., $\theta_c = 3.1912$; see Figures 7a and 7b. At this instant, the mode of operation is switched to the series. The resultant value of θ_s is 6.9769, and the corresponding values of V^* and N_D^* are 6.1185 and 0.0226, respectively, for this mode of start-up; see Figure 8.

To evaluate their efficacy, various facets of the three modes of start-up are compared in Table 1. These facets include the complexities of the operational procedure and system configuration, θ_c, θ_s, V^* and N_D^*. The last three items are also depicted in Figure 8.

CONCLUDING REMARKS

The most basic modes of starting up an interconnected process network appear to be the series, batch and parallel modes.

The characteristics and efficacy of these modes of start-up have been explored through numerical simulation. The specific example given involves a set of complex reactions taking place in a system comprising three CSTR's connected in series under isothermal conditions.

The results of simulation indicate that from the standpoint of operation, the series mode is optimal or least complex while the batch mode is most complex; from the standpoint of system configuration, the series mode is again optimal or least complex while the parallel mode is least desirable; the batch mode requires the shortest start-up time while the parallel mode, the longest; during start-up, the batch mode generates the least amount of the off-spec product while the series mode, the largest; and also during start-up, the parallel mode produces the smallest amount of the toxic component while the series mode produces the largest amount.

The observations and results of this work are system specific in terms of the reactions and network configuration; they also depend on the specific state variable selected as the indicator for switching from the start-up mode to the steady-state mode. In other words, care should be exercised in generalizing these observations and results. Moreover, nonisothermal operation should be considered because temperature can be manipulated to facilitate start-up; this is currently under investi-

Modes of start-up	Complexity of the procedure[a]	Complexity of the configuration[a]	θ_c [b]		θ_s [b]		V^* [b]		N_D^* [b]	
			rank	(value)	rank	(value)	rank	(value)	rank	(value)
Series	1	1	1	(0.0)	2	(7.3002)	3	(7.3002)	3	(0.0292)
Batch	3	2	2	(3.1912)	1	(6.9769)	1	(4.5334)	2	(0.0241)
Parallel	2	3	3	(3.1912)	3	(7.7246)	2	(6.1185)	1	(0.0226)

(a) ranked in ascending order with 1 being the least complex
(b) ranked in ascending order with 1 being the minimum

Table 1. Comparison of the three modes of start-up.

gation.

In starting up a network system in practice, the dynamics of transportation lines and that of pumping devices need to be taken into account, in addition to the consideration of cost. Whenever possible, such cost should be arrived at through multiobjective optimization by trading off among the multitude of significant factors including the start-up time, cumulative amounts of the off-spec product and the toxic component, and the operational and configurational complexities.

ACKNOWLEDGMENTS

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