Use of a Novel Algorithm to Determine Cyclic Steady State in a Controlled-Cycled Stirred Tank Reactor

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A simple algorithm originally proposed by Choong, Paterson and Scott (2002) was tested on a model of an isothermal controlled-cycled stirred tank reactor with substrate inhibition kinetics, $\left(r = \dfrac{-kC}{1+KC} \right)$. In previous work, this reacting system had been shown to exhibit steady-state multiplicity. The transition period of this system to the stable steady state is sometimes characterized by very slow change followed by a very rapid convergence to the stable steady state. Tests of the Choong-Paterson-Scott algorithm showed that the feature, which prevents premature termination of the calculations prior to reaching the true steady state, is very useful for this system. However, tests of the stopping criterion showed that the other feature of reducing the computing time was not realized in this system.

Keywords: Choong-Paterson-Scott algorithm, controlled-cycled stirred tank reactor, cyclic processes, cyclic steady state, multiplicity, *and* rational stopping criterion.

INTRODUCTION

Many chemical processes are operated cyclically. In such systems, the process is started with a pre-determined set of initial conditions and then allowed to go through one cycle after which the output from the initial cycle determines the initial conditions for the succeeding cycle. In many cases, simulating such systems involve solving a number of ordinary differential equations (ODE's) or partial differential equations (PDE's) thousands of times before the so-called "cyclic steady state" is achieved.

Ideally, a cyclic steady state is achieved when

$$\overline{y}_{n+1} - \overline{y}_n = 0 \qquad (1)$$

where $\overline{y}_{n+1}$ and $\overline{y}_n$ are the vectors of state variables at corresponding portions of the cycle at cycles n and n+1 respectively. Verbally, we say that "cyclic steady state" has been achieved when the output form succeeding cycles are identical.

While condition (1) may be intuitively obvious, it is impossible to achieve. Hence, a common criterion for achieving cyclic steady state is used to

$$\overline{y}_{n+1} - \overline{y}_n \le \varepsilon \qquad (2)$$

where ε is a previously selected small number.

The transient behaviors of these systems are often characterized by either very slow or extremely rapid transitions to steady state.

Hence, the use of condition (2) may sometimes result in a premature termination of the simulations before the time cyclic steady state is achieved. To address this concern, Choong, Paterson and Scott (2002) proposed a rational stopping criterion for determining when the cyclic steady state has been achieved.

THE RATIONAL STOPPING CRITERION

In this section, the essential fixtures and equations of the Choong, Paterson and Scott (2002) algorithm are discussed. The reader is referred to the original paper for a more extensive discussion. (The author has taken the liberty of modifying the original notation slightly to aid in clarity.)

The Choong Paterson and Scott algorithm has two features, which may make it useful for the simulation of cyclic processes. First, it provides an unambiguous criterion for determining when cyclic steady state has been achieved. Second, the algorithm may result in savings in computer time as the algorithm provides for a prediction of the values of the state variables at cyclic steady state.

To achieve these two features, the algorithm numbers use of the behavior of the difference in the values of the state variables in two succeeding cycle. In a system with a single state-variable, the difference between successive cycles (the "advance") may be represented as:

$$\Delta y_n \equiv |y_n - y_{n-1}| \tag{3}$$

If the advances are plotted vs. number of cycles in a semi log plot, the slope k_n at the n-th cycle is expressed as

$$k_n = \ln \Delta y_n - \ln \Delta y_{n-1} \tag{4}$$

A quasi-linear region is said to have been identified when

$$\frac{k_n - k_{n-1}}{k_n} < 0.1 \tag{5}$$

and

$$k_n < 0 \tag{6}$$

When these conditions are met, $k_n = k$ can be said to be almost constant and a prediction for cyclic steady state can be derived such that

$$y_\infty = y_n + \Delta y_n \frac{\exp(k)}{1 - \exp(k)} \tag{7}$$

where y_∞ is the prediction of the final cyclic steady state. An extension of this derivation will provide a criterion such that the simulation can be stopped when

$$\Delta y_n \le 0.49 \times 10^{-\delta} \left[\frac{1 - e^k}{e^k} \right] \tag{8}$$

where δ is the number of significant figures required in the final product or outcome.

THE CONTROLLED-CYCLED STIRRED TANK REACTOR

The operation of the first stage of a controlled-cycled stirred tank reactor is similar to that of a batch reactor. However, in succeeding stages, not all of the reacting mixture is emptied. A fraction is allowed to remain behind. The next stage is then started with a mixture of the fraction that remains behind and a fresh batch of feed. The operation of a CCTR is diagrammed in Figure 1.
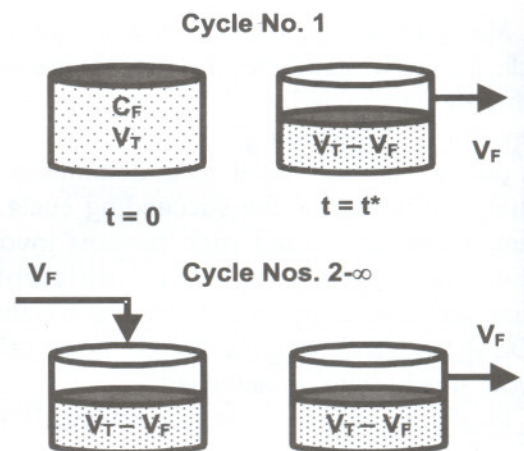

Figure 1. Operation of a Controlled-Cycled Stirred Tank Reactor

N. B. Le (1982) created some simple models of a CCTR including that of an exothermic first-order reaction occurring in a diabatic CCTR. In her work, N. B. Le (1982) found some very complex behavior including very long-period oscillations and "chaotic" behavior. An isothermal CCTR, while simpler, can also be shown to exhibit some fairly complex behavior. In this situation, only a mass-balance needs to be derived. The mass- balance for the n-th batch of a CCTR is similar to that of any other batch reactor:

$$\frac{dC_n}{dt} = r(C_n) \qquad (9)$$

subject to the initial condition $C_n = C_n(0)$ where C_n is the concentration of the n-th batch after start-up and $r(C_n)$ is the reaction rate.

The CCTR differs from a batch reactor in that the initial condition for a particular batch is derived from the previous batch. Defining $C_n(t^*)$ as the concentration in the reactor at the time the reaction is stopped, t*, the initial concentration in the (n+1)-st batch can then be obtained via the mass balance.

$$V_T C_{n+1}(0) = V_R C_n(t^*) + V_F C_F \qquad (10)$$

where V_T is the total reactor volume, V_R is the amount of reacting fluid allowed to remain and V_F is the amount of feed fed into the reactor at the beginning of each cycle and C_F is the feed concentration.

When simple first-order and second-order reactions are conducted in a CCTR, the steady state has been shown to be always unique and stable (Razon, 1988). However, it has been shown that when a reaction represented by substrate-inhibition kinetics

$$r(C_n) = \frac{-kC_n}{1 + KC_n} \qquad (11)$$

is conducted in a CCTR, steady state multiplicity may be possible (Razon, 1988).

In this system, the conversion for the n-th batch,

$$X_n(t) = \frac{C_F - C_n(t)}{C_F} \qquad 0 \le X_n(t) \le 1 \qquad (12)$$

can be computed numerically from the implicit non-linear algebraic equation.

$$\ln\left|\frac{f - X_{n+1}(0)}{f[1 - X_n(0)]}\right| + K^*\left[X_n(0) - \frac{X_{n+1}(0)}{f}\right] + Da = 0 \qquad (13)$$

where $K^* = KC_F$, $f = \dfrac{V_R}{V_T}$, $Da = kt^*$

The behavior of this system is complicated by the fact that equation (13) becomes undefined if at any time $X_n(0) = 1$. In this case,

$$X_{n+1}(0) = f \qquad (14)$$

and the succeeding batch is defined instead by

$$\ln\left|\frac{f - X_{n+2}(0)}{f(1 - f)}\right| + K^*\left[f - \frac{X_{n+2}(0)}{f}\right] + Da = 0 \qquad (15)$$

With these model equations, some simple numerical simulations can be done. Depending on the initial condition and the results from the previous batch, either equation (13) or the combination of equations (14) and (15) are solved successively, using the secant method, to determine the conversion at each cycle.

Some results are demonstrated in Figure 2. It can be seen in curve (a) that the transient state of such reactor is sometimes characterized by very long induction period followed by a rapid convergence onto the steady state. Hence, the system makes a good test for the usefulness of the Choong, Paterson and Scott algorithm.

NUMERICAL SIMULATIONS—TRIALS OF THE CHOONG-PATERSON-SCOTT ALGORITHM

Effectiveness of the Choong-Paterson-Scott algorithm was tested by comparing it to the
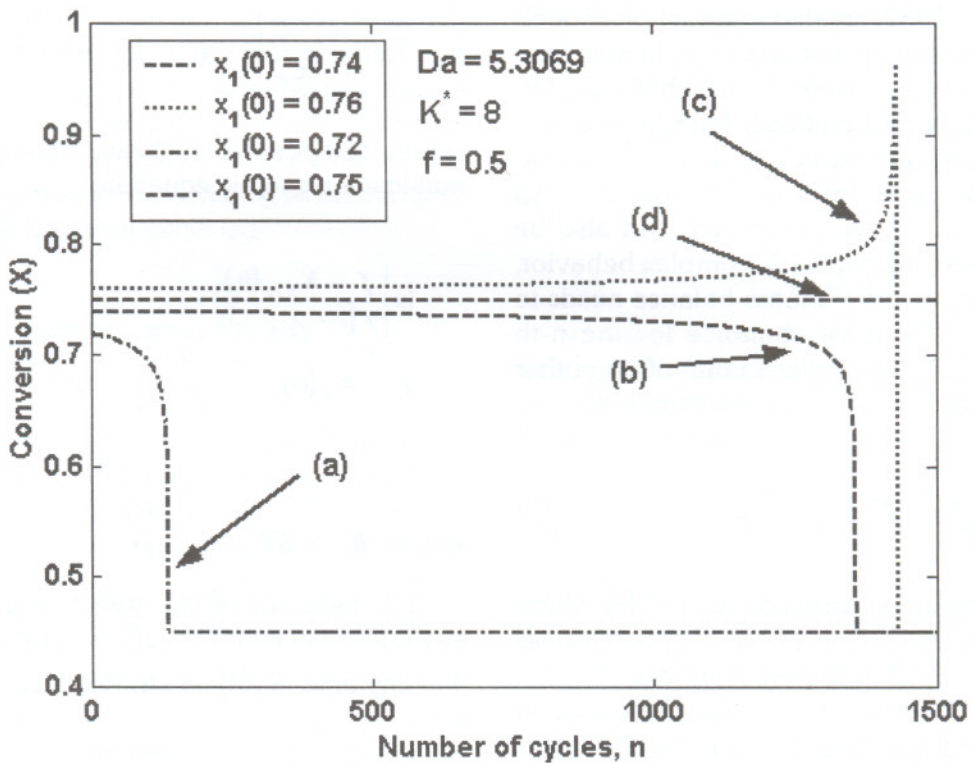
Figure 2. Conversion vs. Number of Cycles for Four Different Initial Conditions

Effectiveness of the simple stopping criterion represented by Eq. (2). Effectiveness of each can then be judged according to the following criteria:

1. What value is predicted by the algorithm to be the steady-state value?
2. At which cycle does each stopping criterion predict the value of the steady-state?

A comparison can then be made to the true steady-state value for each set of parameters.

Comparisons were made using a set of parameters where it is predicted that the system will exhibit multiple steady states (*Razon, 1988*). *The chosen parameters were* $Da = 6 - \ln(2)$, $f=0.5$ and $K^*= 8$. At this set of parameters, steady states are predicted at

$$\overline{X}_\infty = [0.45008034\ ,0.75,1.04991966\ ].$$

Direct simulations in previous work have shown that the first steady state is stable and that the middle one is unstable (Razon, 1988). The third steady state is physically impossible. Treatment of the third steady state is discussed below.

Three initial conditions were chosen which could be considered typical examples of the variety of behavior that is usually observed in this system. At an initial condition $X_1(0) = 0.72$, a short, rapid transition to steady state is observed. This is illustrated in curve (a) of Figure 2. The second type [curve (b) in Figure 2] is one, which starts with a very long induction period, followed by a rapid transition to steady state. The third initial condition illustrates behavior that is rather unusual and may be unique to this system. In this case, the system makes a slow approach to a high conversion, until it reaches a predicted conversion of greater than 100% [curve (c) in Figure 2]. Since this is not possible, the system should be simulated by Equation (14) and (15) instead of Equation (13). Because of this, a lower value of $X_n = f = 0.5$ is immediately predicted in the next cycle and the system once again goes to the lower steady state. Curve (d) in Figure 2 shows the behavior when the initial condition is set exactly at $x_1(0) = 0.75$, the value of the unstable steady state. Curve (d) was drawn only to show the location of the unstable steady state.

Table 1 shows the results from applying the Choong-Paterson-Scott Algorithm [Equation (7)] to these situations. A comparison is made to the simple criterion represented by Equation (2). In the simulations summarized in Table 1, a desired accuracy of three significant figures was chosen. Hence, in applying Equation (7), a value of ä = 3 was used. In applying Equation (2), a value of å = 0.49 x 10 $^{-3}$ was used. The "true" value is 0.45008034, the lower steady state.

The comparison in Table 1 shows the obvious advantage of using Equation (7). If Equation (2) is used, the simulation is stopped far too early and hence the simulation would have been stopped after only two cycles. Equation (7), in conjunction with the other criteria set by the Choong-Paterson-Scott algorithm, predicts the value of the steady state to a reasonable accuracy. The slow transition from the initial condition, which could be deceiving, was accurately determined to be merely a transition.

The rapid transition to steady state, however, causes Equation (7) to predict a steady state only after a large number of cycles. In fact, it consistently predicts that the computations should be stopped only eight cycles before accuracy to 6 significant figures is achieved. Hence, we do not get much savings in computing time.

A few other trials not reported here, showed results consistent with the results summarized in Table 1.

CONCLUSIONS

The Choong-Paterson-Scott algorithm provides a simple-to-implement and accurate means of determining the attainment of cyclic steady state. Simulations with a controlled-cycled stirred tank reactor showed that the algorithm accurately detected a slow transition. Steady state was correctly predicted to occur later in the transition. Therefore, it provides a simple, effective and conservative criterion for determining cyclic steady-state. The other possible benefit, reduced computing time, was however not achieved, as the Choong-Paterson-Scott did not make a prediction until a considerable number of cycles had been simulated.

Further tests of the Choong-Paterson-Scott algorithm can be done on systems that are more complex. More work can also perhaps be done on developing algorithms of this type.

NOTATION

Roman Letters

C_F	concentration of the feed for each batch.
C_n	concentration of the reactant for the n-th cycle
Da	Damkohler number, kt*
f	fraction of the reacting mixture removed at the end of the cycle, V_F/V_T
k	rate constant
k_n	slope of a semi log plot of advances vs. number of cycles

Table 1. Performance of Stopping Criteria

Initial Condition $X_1(0)$	Equation (7)			Equation (2)			Cycle number when convergence to 6 s.f. is detected
	Predicted value of steady-state $X_?$	Deviation from "true" value	Cycle number when stopped	Predicted value of steady-state $X_?$	Deviation from "true" value	Cycle number when stopped	
0.74	0.46969323	2.33%	1360	0.7399964	64.4%	2	1368
0.76	0.46578914	3.49%	1434	0.7600035	68.8%	2	1442
0.72	0.46060825	2.34%	138	0.7198985	60.0%	2	146

K	equilibrium constant
n	cycle number
t	time
t^*	time when the reaction for the n-th batch is stopped
V_T	total volume of reactant
V_R	volume of reacting fluid allowed to remain
V_F	volume of reactant fed into each batch
$X_n(t)$	conversion of reactant at time t for the n-th batch.
y_n	generic state variable, determined at the n-th cycle
Y_n	predicted value of the steady state (n = ")

Greek Letters

d	number of significant figures required in the final product
$å$	an arbitrarily chosen small number

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