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Short Communication

Performance improvement of a chemical reactor by non-linear natural oscillations

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Abstract

The dynamic behaviour of two coupled continuous stirred tank reactors in sequence is studied when the first reactor is being operated under limit cycle regimes producing self-sustained natural oscillations. The periodic output from the first reactor is then used as a forced input into the second reactor. It has been observed and demonstrated through stability analysis and computation that the overall performance of the system can be greatly enhanced in terms of time-averaged conversion by employing the above-mentioned operation strategy. This new concept of coupling free and forced oscillation does not require any additional external energy and can have significant implications beyond the chemical systems and possibly for various biological systems as limit cycles occur much more frequently in biological processes than in chemical processes.

Keywords: Stirred-tank reactors; Chemical oscillator; Dynamic simulation; Modelling; Reactor

1. Introduction

Most chemical processes operate at steady state. However, numerous investigations [1–13], both theoretical and experimental studies, have shown that periodic operation of chemical reactors in some cases leads to improved conversion. Most of these investigations studied the possibility of enhancing the performance of a chemical reactor by inducing periodic forced oscillations in the feed compositions, feed flow rate or reaction temperature. Most of the work on periodic and aperiodic (chaotic) oscillations has focused on understanding the fascinating and exotic behaviors of the system. It appears that little effort has been made until now to improve reactor performance through natural oscillations.

In this paper, the dynamic behaviour of two coupled non-isothermal continuous stirred tank reactors (CSTRs) is studied. A novel operation strategy that involves the use of self-generated oscillation to improve the overall performance is proposed and applied to a model reactor system. Parameters are chosen so that the basic state of the first reactor is oscillatory. In this work, it has been shown that, when the periodic output from the first reactor is used as a forced input into the second reactor, there is a distinct possibility of improvement in overall performance of the reactor over the steady state performance of a single CSTR of equal volume. The most significant criterion of this operation strategy lies in the fact that the performance enhancement of the overall system is achieved through natural oscillation rather than forced oscillation. In experimental studies and in eventual application to industrial processes this system is advantageous to previous work in that no additional external energy is required to generate this situation.

2. The system

We seek to observe any enhancement in conversion that can be obtained by employing an operation strategy of creating natural oscillations in the first of the two non-isothermal CSTR in sequence with a single first-order chemical reaction as a model system (Fig. 1). Unlike the steady states, there are no direct analytical methods for investigation of limit cycles; the methods of bifurcation theory of dynamic systems [14] should be applied for a systematic study. We will examine the bifurcation diagrams describing the influence of changes in the residence time on the conversion in a CSTR. It is assumed that the chemical reaction is irreversible

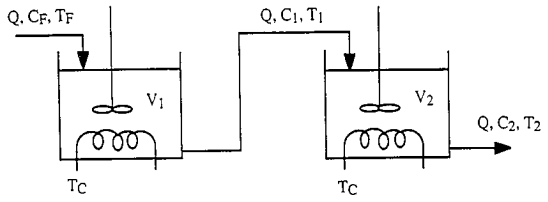

Fig. 1. Schematic diagram of two CSTRs in series.

so that species A simply converts to species B. No recycling is considered, and the system is non-isothermal owing to the exothermic nature of the reaction. It is assumed that the fluid properties are constant and that the activation energy is large so that the rate constant of the reaction follows the Arrhenius type of temperature dependence. The mathematical model representing this system consists of four equations, two in each reactor. The system equations in dimensionless form can be written as follows: for reactor 1,

$$\frac{dX_1}{dt'} = F_1(X_1, Y_1, \mathbf{P}) = 1 - X_1[1 + \alpha_1 E(Y_1)] \quad (1)$$

$$\frac{dY_1}{dt'} = F_2(X_1, Y_1, \mathbf{P}) = -(1+\mu_1)Y_1 + \alpha_1\beta_1 X_1 E(Y_1) \quad (2)$$

for reactor 2,

$$\frac{dX_2}{dt'} = F_3(\mathbf{X}, \mathbf{Y}, \mathbf{P}) = \frac{V_1}{V_2}\{X_1 - [1+\alpha_2 E(Y_2)]X_2\} \quad (3)$$

$$\frac{dY_2}{dt'} = F_4(\mathbf{X}, \mathbf{Y}, \mathbf{P}) = \frac{V_1}{V_2}\left[(Y_1 - Y_F)^*\left(\frac{T_{R1}}{T_{R2}}\right)^2 - (1+\mu_2)Y_2 + \alpha_2\beta_2 X_2 E(Y_2)\right] \quad (4)$$

The initial conditions are:

$X_i(0) = X_{i0}$, $Y_i(0) = Y_{i0}$, $i = 1, 2$

where

$$E(Y_i) = \exp\left(\frac{Y_i\gamma_i}{Y_i + \gamma_i}\right)$$

and the dimensionless variables used are

$$X_i = \frac{C_i}{C_F}, \quad Y_i = \frac{T_i - T_{Ri}}{T_{Ri}}\gamma_i,$$

$$\gamma_i = \frac{E}{RT_{Ri}}, \quad \mu_i = \frac{U_i A_C}{Q\rho C_p}, \quad t = \frac{Qt'}{V_1}$$

$$\alpha_i = \frac{V_i k_0}{Q}\exp(-\gamma_i),$$

$$\beta_i = \frac{(-\Delta H)C_F\gamma_i}{\rho C_p T_{Ri}}, \quad Y_F = \frac{T_F - T_{R1}}{T_{R1}}\gamma_1$$

The reference temperature was defined as

$$T_{Ri} = \frac{T_F + \mu_i T_{Ci}}{(1+\mu_i)}, \quad i = 1, 2$$

To analyse the dynamic behaviour in the CSTR, we have to study the steady states as a function of the system parameters. Steady states are the time-invariant solutions of the equation

$$\frac{d\mathbf{Z}}{dt} = \mathbf{F}(\mathbf{Z}, \mathbf{P}), \quad \mathbf{Z}(0) = \mathbf{Z}_0 \quad (5)$$

satisfying

$$\mathbf{F}(\mathbf{Z}, \mathbf{P}) = 0 \quad (6)$$

where

$\mathbf{Z}^T = \{Z_1, Z_2, Z_3, Z_4\} = \{X_1, Y_1, X_2, Y_2\}$

$\mathbf{F}^T = \{F_1, F_2, F_3, F_4\}$

and $\mathbf{P}$ is a vector of system parameters:

$\mathbf{P}\ \{\alpha_1, \beta_1, \mu_1, \gamma_1, \alpha_2, \beta_2, \mu_2, \gamma_2\}$

The steady state solution obtained by solving Eq. (6) can then be given by

$$X_{1S} = \frac{1}{1+\alpha_1 E(Y_1)} \quad (7)$$

$$Y_{1S} = \frac{\alpha_1\beta_1 E(Y_{1S})}{(1+\mu_1)[1+\alpha_1 E(Y_{1S})]} \quad (8)$$

$$X_{2S} = \frac{1}{[1+\alpha_1 E(Y_{1S})][1+\alpha_2 E(Y_{2S})]} \quad (9)$$

$$Y_{2S} = \frac{1}{(1+\mu_2)} \times \left[Y_1 - Y_F + \frac{\alpha_2\beta_2 E(Y_{2S})}{[1+\alpha_1 E(Y_{1S})][1+\alpha_2 E(Y_{2S})]}\right] \quad (10)$$

Since there is no recycle, the operation of the first reactor is totally independent of the second reactor. Therefore, all the information in the literature on the single-reactor problem applies to the first reactor. Uppal et al. [15] described the necessary conditions for a multiple steady state to exist for the present model system as

$$B_i = \frac{\beta_i}{1+\mu_i} \geqslant 4 \quad (11)$$

For simplicity, we will apply our concept only for cases where $B_i < 4$, so that a unique steady state exists.

From the physical nature of the system as defined by the dimensionless parameter, the concentration can never fall below zero or rise above the feed concen-

tration. The minimum temperature possible will be either the freed or the coolant temperature, whichever is the lower, and the maximum temperature that can be attained by the system can be shown by a similar argument to that given by Douglas and Rippin [1] to be B_i:

$0<X_i<1$ and smaller of Y_C or $Y_F<Y_i<B_i$

For the first reactor, the locus (X_S, Y_S) of steady state conditions can be obtained from the solution of the equation

$$G(Y_1, \alpha_1; B_1, \gamma_1)=B_1\alpha_1E(Y_1)-Y_1[1+\alpha_1E(Y_1)] \quad (12)$$

By equating $G=0$, Eq. (12) can be rearranged to

$$\alpha_1=\frac{Y_1}{(B_1-Y_1)E(Y_1)} \quad (13)$$

Eq. (13) and Eq. (7) can now be used to plot conversion in the first reactor for various Damkohler numbers α or residence times V_1/Q, or for different values of the volume V_1 of the first reactor for fixed Q.

An interesting phenomenon that has been extensively studied and observed both theoretically and experimentally is the occurrence of periodic oscillations in a CSTR [14]. The situation arises when one or more of the system's bifurcation parameters change continuously and a given steady state solution bifurcates to a limit cycle. We intend generating limit cycles in the first reactor to achieve overall performance improvement, so we need to know conditions under which a stable limit cycle exists in a single CSTR. The problem of the existence and stability of limit cycles has been attacked in number of different ways. When the modelling equations (Eqs. (1)–(4)) are linearized around the steady state, these sets of linearized equations can be represented by

$$\frac{d\mathbf{Z}}{dt}=\mathbf{AZ} \quad (14)$$

The local stability is determined by the sign of the real part of the eigenvalues of **A**. Since the Jacobian of the two CSTRs in series is just the product of the Jacobians of each, the necessary and sufficient conditions for the steady state to be asymptotically stable are just that the traces should be negative (dynamic condition) and two determinants positive (slope condition). Svoronos [16] has shown that the slope condition, det $\mathbf{A}>0$, is satisfied for all steady states in the region of a unique steady state, the region of our interest, for all values of the Damkohler number. The point where tr $\mathbf{A}=0$ defines the onset of instability. Svoronos [16] has also shown that the system described by Eq. (14) has periodic solutions (with X_S and Y_S as centre) when det $\mathbf{A}>0$ and tr $\mathbf{A}=0$.

For the first reactor, the condition for the existence of a limit cycle then can be obtained by equating tr $\mathbf{A}=0$, i.e.

$$\frac{\partial F_1}{\partial X_1}+\frac{\partial F_2}{\partial Y_1}=0 \quad (15)$$

where

$$\frac{\partial F_1}{\partial X_1}=-[1+\alpha_1E(Y_1)]$$

$$\frac{\partial F_2}{\partial Y_1}=-(1+\mu_1)+\alpha_1\beta_1X_1E(Y_1)\frac{\gamma_1^2}{(\gamma_1+Y_1)^2}$$

Simplifying the equation tr $\mathbf{A}=0$ gives the locus of conditions for which limit cycles exist in the first reactor:

$$X_1=\frac{2+\mu_1+\alpha_1E(Y_1)}{\alpha_1\beta_1E(Y_1)}\frac{(\gamma_1+Y_1)^2}{\gamma_1^2} \quad (16)$$

Eq. (16) together with Eq. (13) can now be used to plot conversion in the first reactor for various values of the Damkohler number α_1 or for different volumes V_1 of the first reactor when limit cycles exist.

3. Application of bifurcation theory

The steady state behaviour of Eq. (12) has been thoroughly studied by Uppal et al. [15]. We are only interested to find the parameter space for which improvement in conversion over steady state can be obtained by creating limit cycles. The enhancement in conversion can be visualized best by plotting Eqs. (7), (13) and (16) for different values of β_1, γ_1, μ_1 and B_1. Steady state conversion and conversion when limit cycles exist in the first reactor have been plotted against Damkohler number α_1 for a typical set of parameter values β_1, γ_1, μ_1 and B_1 in Fig. 2. From the figure it can be seen that conversion increases with α_1. This is expected as with increase in α_1 residence time of reactant also increases. Fig. 2 also shows that conversion attained

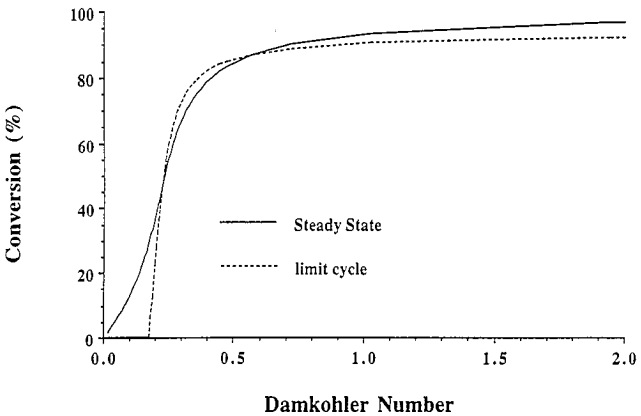

Fig. 2. Steady state conversion and conversion when limit cycles exist in the first reactor against Damkohler number for $\beta=18.0$, $\gamma=40.0$, $\mu=5.0$ and $B=3.0$.

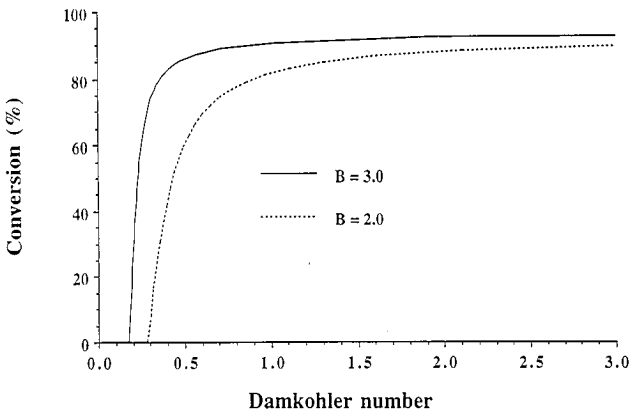

Fig. 3. Conversion when limit cycles exist in the first reactor for two different values of B against Damkohler number for $\gamma=40.0$ and $\mu=5.0$.

in the first reactor when limit cycles exist is higher than the steady state value for α_1 between 0.227 and 0.621. In Fig. 3, conversion in the first reactor when limit cycle exists is plotted for two different values of $B_1 \equiv \beta_1/(1+\mu_1)$ for fixed values of μ_1 and γ_1. Conversion attained for higher values of B_1 is much larger than when B_1 is smaller. Figs. 2 and 3 also show that limit cycles do not exist in the reactor if α_1 is less than a particular value. A close scrutiny of Figs. 2 and 3 reveals that improvement in conversion is more pronounced for some range of values of α_1 when B_1 and γ_1 are large and when μ_1 is kept small.

The system parameters can now be set in the first reactor from the knowledge of the parameter space for which limit cycles exist producing free oscillations. The free oscillation from the first reactor then causes forced oscillation to occur in the second reactor, resulting in possible overall performance improvement.

4. Numerical methods

Commercial software Trax (Exeter software, version 1.2) is used for viewing pictures of phase space of dynamical systems for Eqs. (1)–(4) and investigating their dynamic properties and characteristics. From the pictures of phase space obtained from Trax, we identified a limit cycle in the first of the series of two CSTRs. Numerical solutions of Eqs. (1)–(4) are then obtained by using the numerical software package LSODE (DSS/2, Differential Systems Simulator, version 2, library routine), an initial value integrator program for stiff ordinary differential equation (ODEs). For better accuracy of the average value, a numerical program is written which first evaluates the maximum and minimum values of dimensionless concentration X_2 with time, compares the successive values of maximum (or minimum) to find out that a limit cycle has been established, and then calculates the time-average value of overall conversion from the first maximum (or minimum) where the limit cycle is established to the last maximum (or minimum) by using numerical integration techniques of combination of Simpson's one-third and three-eighths method. The steady state solutions X_{is} and Y_{is} are obtained by solving Eqs. (7)–(10) by the Newton–Raphson method.

5. Illustrative examples

In order to find the improvement in overall performance of CSTR's in series through oscillations, two specific problems were investigated.

5.1. Case 1

A first-order irreversible exothermic chemical reaction in a non-isothermal CSTR is considered. The parameters and operation variables used for the numerical calculations in this case are taken from Douglas and Rippin [1]. For the set of values, the dimensionless parameters are as follows:

$\mu_1, \mu_2=5.0;\ \gamma_1, \gamma_2=35.332;$

$\beta_1, \beta_2=15.547;\ B_1, B_2=2.59$

For the first reactor, steady state conversion (from Eqs. (13) and (7)) and conversion for conditions when limit cycles exist (Eq. (16)) have been plotted against different volumes of the reactor in Fig. 4. For the above set of parameter values, B_1 is less than 4 ($B_1=2.59$), and therefore we are in region I of Uppal et al. [15] where only a single stable steady state exists for all values of the Damkohler number α_1. From the figure it can be seen that steady state conversion increases with the volume of reactor. This is expected as with increase in residence time higher conversion is attained. Fig. 4 also shows that for a volume of the reactor less than

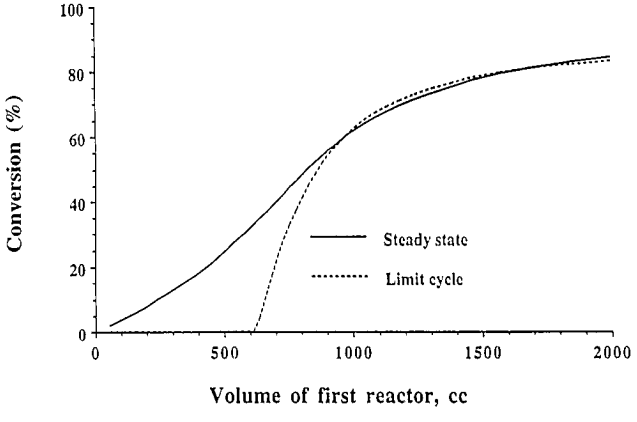

Fig. 4. Steady state conversion and conversion when limit cycles exist against volume of first reactor for case 1. Parameter values are $\beta=15.547$, $\gamma=35.332$, $\mu=5.0$ and $B=2.59$.

615 cm³ limit cycles do not exist, whereas for a volume of the reactor greater than 940 cm³ and less than 1660 cm³ the conversion obtained when limit cycles exist is greater than the steady state conversion. The steady state conversion is higher for volumes of the reactor greater than 1660 cm³. In Fig. 5, overall average conversion and overall steady state conversion obtained from two CSTRs (of total volume 2000 cm³) connected in series are plotted against different volumes of the first reactor. From the figure it can be seen that, for the set of parameter values used, no limit cycle exists if the smaller reactor is placed first in the sequence of two CSTRs. However, by placing an equal-size or larger reactor first in the sequence, limit cycles exist in the overall system and the overall average conversion obtained is always higher than the steady state conversion for the same total volume of two reactors or of a single reactor of equal volume. This improvement is attained only for volumes of reactor 1 between 1000 cm³ and 1600 cm³. Fig. 5 also reveals that, for 940 cm³ $< V_1 <$ 1660 cm³, the maximum conversion attained by steady state is 86.09% for $V_1 = 1477.3$ cm³ whereas maximum conversion when limit cycles exist is 86.55% for $V_1 = 1100$ cm³. However, the maximum percentage increase in overall conversion when limit cycles exist compared with the steady state operation is only 1.34% when V_1 is 1000 cm³.

5.2. Case 2

The parameters and operation variables used for the numerical calculations in this case are representative of an industrial oxo reactor given in a recent paper by Vleeschhouwer and Garton [17]. The oxo reaction converts olefins and synthesis gas to aldehydes, the main product, which partially converts to oxo alcohol. In the neighbourhood of the steady operating state the overall oxo reaction is described by A→B, where A is a single pseudocomponent olefin and B represents aldehyde. At a fixed concentration of catalyst and synthesis gas the reaction is first order and irreversible. The parameters used are the following:

$k_0 = 6.1 \times 10^7$ s^{-1}; $E = 91\,454$ J mol^{-1}; $-\Delta H = 159\,000$ J mol^{-1}; $\rho = 650$ kg m^{-3}; $C_P = 2400$ J kg^{-1} K^{-1}; $U_1A_C = U_2A_C = 75\,000$ W K^{-1}; $T_F = 303$ K; $T_{C1} = T_{C2} = 445$ K; $C_F = 5076.5$ mol m^{-3}; $Q = 0.004\,923$ m^3 s^{-1}

For the above set of values, the dimensionless parameters are as follows:

$\mu_1, \mu_2 = 9.766$; $\gamma_1, \gamma_2 = 25.474$;

$\beta_1, \beta_2 = 30.524$; $B_1, B_2 = 2.8353$

Steady state conversion and conversion for conditions when limit cycles exist have been plotted against different volumes of the first reactor in Fig. 6. For the above set of parameter values, B_1 is less than 4 ($B_1 = 2.8353$), and therefore we are in region I of Uppal et al. [15]. From the figure it can be seen that for volumes of the reactor less than 1.72 m³ limit cycles do not exist, whereas for volumes of the reactor greater than 2.25 m³ the conversion obtained when limit cycles exist is greater than the steady state conversion. In Fig. 7,

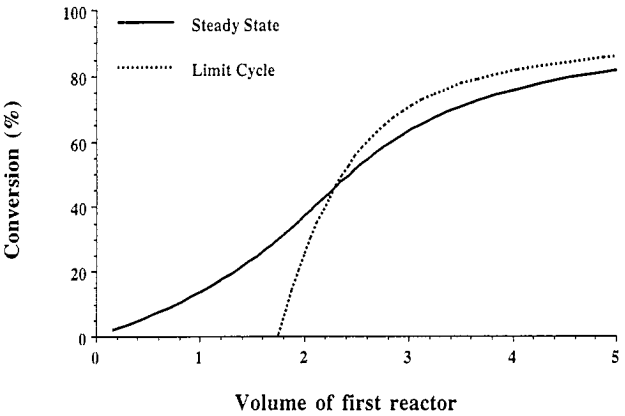

Fig. 6. Analysis of an industrial oxo reactor (case 2).

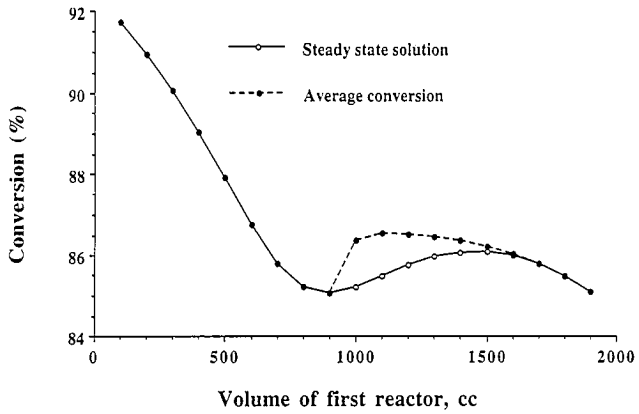

Fig. 5. Overall conversion (steady state and average) attained for two CSTRs in series for case 1. Total volume of two reactors is 2000 cm³.

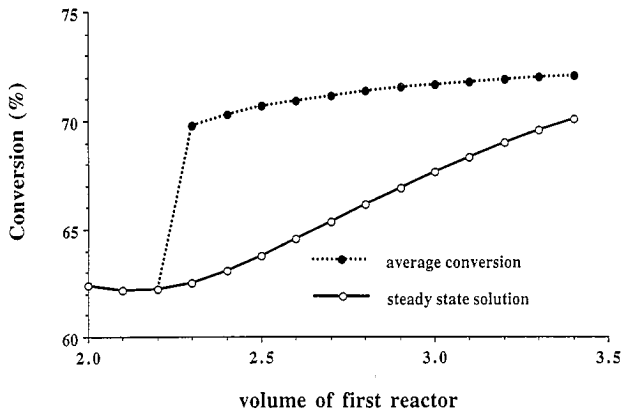

Fig. 7. Comparison of overall conversion obtained when limit cycles exist with steady state solution for case 2. Total volume of two reactors is 3.5 m³.

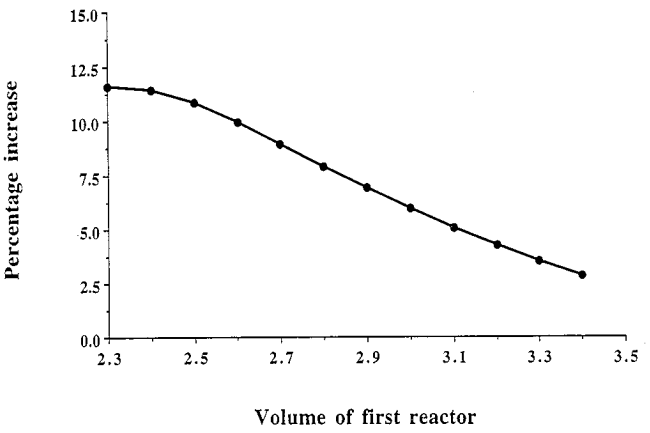

Fig. 8. Percentage increase in overall conversion when limit cycles exist compared with the steady state solution for case 2.

overall average conversion and overall steady state conversion obtained from two CSTRs (of total volume 3.5 m^3) connected in series are plotted against the volume of the first reactor. From the figure it can be observed that, for the set of parameter values used, no limit cycle exists if the smaller reactor is placed first in the sequence of two CSTRs. However, by placing the larger reactor first in the sequence, a limit cycle exists in the overall system and the overall average conversion obtained is always higher than the steady state conversion for the same total volume of two reactors. Fig. 8 shows the percentage increase in overall conversion when limit cycles exist compared with the steady state operation. From the figure it can be seen that an increase in conversion of up to 11.6% can be achieved from this system.

6. Conclusions

The novel operation strategy proposed in this paper can improve overall reactor performance under certain operating conditions when applied to a completely deterministic model system of two reactors in series, with one reactor serving as a forcing system for the other. In experimental and in eventual application to industrial processes this system is advantageous compared with previous work in that no external forcing is required to generate this situation. The improved performance is accomplished at no additional costs, an attractive proposition to the cost-conscious processing industry.

The dynamic behaviour for a first-order exothermic chemical reaction occurring in two continuous flow stirred tank reactors connected in series is considered. Parameter regions for which limit cycles exist in the first reactor are determined and it is found that increased conversion can be obtained for some range of values of the Damkholer number. We have also demonstrated that, when the second reactor is forced by the stable limit cycle of the first reactor, an increase in overall conversion is achieved from the system of two reactors in series. We considered two examples representing two different chemical systems. In one case we found out that the increase in conversion is not significant, whereas for the other case the increase in overall conversion is significantly higher than the overall conversion attained if the reactors are operated at steady states or if a single reactor of the same total volume is operated at steady state.

Even though the analysis of the mathematical model considered in this paper describes a first-order exothermic irreversible reaction, it represents nevertheless a broad range of physical systems for chemical reactors and is very rich in the variety of dynamical behaviours that can occur. The mathematical treatment can be easily extended for other cases. However, it is possible that additional new complexities may arise when it is extended to other systems.

The process concept involving oscillations appears to be more applicable to biological systems which have a penchant for periodicity [18]. From the production of alcohol from glucose by *Saccharomyces cerevisiae* [19] to waste water treatment process by the activated sludge method [20] to more complex plant cell culture [21] the existence of natural oscillation and Hopf bifurcation is well known. Moreover, it has been well recognized that in many bioprocesses a system of two CSTRs connected in series is superior to one reactor of equal volume. However, little effort has been made to use natural oscillation to improve the performance of bioreactors.

The controversial question of whether dynamic operation of a chemical reactor under oscillatory conditions is economically beneficial or not over the steady state result is not answered completely in this paper. However, we should emphasize that oscillations have been reported for systems in all areas of non-linear dynamics, and our system is by no means an exception. Therefore, as an engineer, one should be prepared to utilize these situations for economic benefits, or at least should know how to avoid them in practice.

Appendix A: Nomenclature

A_C	heat transfer area
B	$\beta/(1+\mu)$
C	concentration
C_p	specific heat
E	activation energy
$E(Y)$	$\exp[\gamma Y/(\gamma+Y)]$
F	function

G steady state function
ΔH heat of reaction
k_0 Arrhenius pre-exponential factor
P system parameter
Q volumetric flow rate
R universal gas constant
t' time
t dimensionless time
T temperature
U heat transfer coefficient
V volume of reactor
X dimensionless concentration
Y dimensionless temperature
Z state variable

Greek letters

α Damkohler number
β dimensionless adiabatic temperature rise
γ dimensionless activation energy
μ dimensionless heat transfer coefficient
ρ density

Subscripts and superscripts

1 reactor 1
2 reactor 2
C coolant
F feed
i reactor i
i_0 initial condition
R_i reference value for reactor i
S steady state

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