Periodic operation of tubular reactors for autocatalytic reactions with input multiplicity

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The performance of an isothermal tubular reactor for the two models of a autocatalytic reaction, one considering a cubic autocatalytic reaction (A \( \rightarrow \) 2B \( \rightarrow \) 3B) and the second considering successive bimolecular reactions (A \( \rightarrow \) X, X \( \rightarrow \) B \( \rightarrow \) 3B), is analyzed. The two models are shown to have input multiplicity behaviour. Though the conventional steady-state operation gives an identical yield of product B for both the reactions under certain parameters values, the input multiplicity behaviour (yield vs residence time) is different for the two reactions. Further, the effect of feed concentration cycling on the average yield of B is compared under input multiplicity.

Feed concentration cycling of a variety of nonlinear processes has been shown to give a superior time-averaged performance over conventional steady-state operation\(^1\)\(^-\)\(^4\). The reports on feed concentration cycling are, however, limited to simple reactions\(^5\)\(^-\)\(^11\). A simulation study has been applied on the concentration cycling of a plug flow reactor for a homogeneous liquid phase autocatalytic reactions of both quadratic (A \( \rightarrow \) B \( \rightarrow \) 2B) and cubic (A \( \rightarrow \) 2B \( \rightarrow \) 3B) forms\(^12\). It has been shown that both forms of autocatalytic reactions give similar behaviour under periodic operation. It has also been reported that the steady-state reactor equations for successive bimolecular reactions (A \( \rightarrow \) X, X \( \rightarrow \) B \( \rightarrow \) 3B) reduce to the equations of a cubic reaction (A \( \rightarrow \) 2B \( \rightarrow \) 3B) when the two parameters \( \xi = k_2a_0/k_{-2} \) and \( \kappa = k_2a_0/k_{-2} \), arising in system equations for the bimolecular reaction, tend to zero\(^13\). Examples of autocatalytic reactions are found in the acid catalyzed hydrolysis of various esters and similar compounds\(^14\) and in various biochemical processes such as the conversion of trypsojen into trypsin with trypsin autocatalyzing the reactions\(^15\) and in industrial wastewater treatment by activated sludge process.

In the present study the performance of an isothermal tubular reactor for the two models of the autocatalytic reactions particularly under feed concentration cycling is theoretically evaluated. Certain nonlinear processes like tubular reactor for consecutive reaction shows input multiplicity behaviour. That is, under steady-state operation, more than one value of an input variable (more than one value of flow rate) give identical yields of product. Input multiplicity arises due to the presence of competing effects in the process or due to recycle structure\(^16\). It has been shown that the concentration cycling of an isothermal tubular reactor for consecutive reactions (A \( \rightarrow \) B \( \rightarrow \) C) gives different behaviour of average yield under input multiplicity\(^17\). The objective of the present work is to analyze also the input multiplicity behaviour of the cubic and successive bimolecular autocatalytic reactions under steady state and under feed concentration cycling.

**Model Equations for Tubular Reactors**

The first model for the autocatalytic reaction is the two variable one given by

\[
A + 2B \rightarrow 3B \quad r = -k_1ab \quad \ldots (1)
\]

The second model considers a 3 variables scheme with consecutive second order reactions:

\[
A + B \rightarrow X \quad r = -k_2ab + k_{-2}x \quad \ldots (2)
\]

\[
X + B \rightarrow 3B \quad r = -k_3xb \quad \ldots (3)
\]

The decay of autocatalyst B is considered as\(^13\)

\[
B \rightarrow C \quad R = -k_4b \quad \ldots (4)
\]

Here \( a, b \) and \( x \) are the concentration of the species A, B and X, respectively. For an isothermal, homogeneous autocatalytic reaction of successive bimolecular type in a plug flow reactor, the

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steady-state dimensionless model equations are given by\textsuperscript{13,18}

\[
\frac{1}{q}\frac{d\alpha}{dZ} = -[\alpha\beta - (\xi/\kappa)]/\varepsilon \quad \ldots (5)
\]

\[
\frac{1}{q}\frac{d\beta}{dZ} = -[\alpha\beta - (\xi/\kappa)]/\varepsilon + (2\beta\xi/\kappa) - (\beta/\phi) \quad \ldots (6)
\]

\[
\frac{1}{q}\frac{d\xi}{dZ} = [\alpha\beta - (\xi/\kappa)]/\varepsilon - (\beta\xi/\kappa) \quad \ldots (7)
\]

at \(Z=0\), \(\alpha = \alpha_0, \beta = \beta_i \quad \ldots (11)\)

These equations clearly reduce to the original model equations for a cubic rate form [for Eq. (1)] in the limit both \(\varepsilon \to 0\) and \(\kappa \to 0\).

The steady-state equations are solved numerically by standard subroutine implementing Gear method and the yield of B versus \((1/q)\) is plotted as shown in Figs 1 and 2, respectively, for 2 and 3 variables models. It is interesting to note that for \((1/q) = 0.06993\) the two variable model and for \((1/q) = 0.06667\) the three variable model both give identical yield of B \((Y = 0.43)\). Both the models show input multiplicity in yield of B versus \((1/q)\). The values of \((1/q)\) at which identical yield of B (for example \(Y = 0.43\)) is obtained for two variable model are 0.06993 and 0.12048. Whereas for the three variables model to give the same yield of B (for example \(Y = 0.43\)), the values of \((1/q)\) required are 0.06667 and 0.09434. Figs 1 and 2 show that for a given yield of B, the range of \((1/q)\) over which input multiplicity behaviour occurs is also distinctly different for the two models. Since the variable \(q\) contains \(LU\) and \(a_0\), the input multiplicity can be considered as identical yield of B under two values of the residence time or base value of concentration.

**Periodic Operation**

The periodic operation considered here is the one in which the steady-state condition is chosen arbitrarily and the mean value of the feed cyclic input is the same as that steady-state input\textsuperscript{19}. Then the time-averaged performance of the process under periodic operation is compared with that obtained under steady-state operation. In the present work this type of periodic operation is considered. The periodic forcing function is a rectangular pulse in the inlet concentration of both \(\alpha_f\) and \(\beta_f\) as shown in Fig. 3 where \(\alpha_f\) and \(\beta_f\) are the dimensionless amplitude of the inlet concentration pulse and \(\gamma\) is the cyclic split (i.e. pulse width expressed as a fraction of the dimensionless period). The condition of \(\gamma = 1\) represents the usual steady-state operation and that of \(\gamma < 1\) represents the periodic operation. If the dimensionless steady-state input is fixed as \(C_A\) and \(C_B\), then the following expressions can be obtained by averaging the inlet pulse over the period of oscillation, \(\tau\)

\[
\alpha_i = C_A/\gamma; \beta_i = C_B/\gamma \quad \ldots (12)
\]

To evaluate the average yield of B under periodic operation, the transient equation of the tubular reactors [including accumulation terms in the left side of equations, Eqs (5)-(7)] should be con-

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**Fig. 1**—Yield of B versus \((1/q)\) under steady-state operation for two variable model. \(C_A = 0.8, C_B = 0.2, \phi = 20.0\). For the yield of B = 0.43, the values of \((1/q)\) are 0.06993 and 0.12048.

**Fig. 2**—Yield of B versus \((1/q)\) under steady-state operation for three variable model. \(C_A = 0.8, C_B = 0.2, \phi = 20.0, \varepsilon = 0.1, \kappa = 0.1\). For the yield of B = 0.43, the values of \((1/q)\) are 0.06667 and 0.09434.
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Fig. 3—Inlet feed concentration of reactants A and B. --- periodic operation; --- steady-state operation

Fig. 4—Average yield of B under periodic operation. 1—two variable model, \((1/q)=0.12048\). 2—three variable model, \((1/q)=0.09434\)

Fig. 5—Average yield of B under periodic operation. 1—two variable model, \((1/q)=0.06993\). 2—three variable model, \((1/q)=0.06667\)

considered. However, for isothermal homogeneous plug flow reactors, the average yield can be obtained by solving the steady-state equations \([Eqs. (5)-(7)]\) for two levels of inlet concentrations separately and getting the average of these yields\(^7\).

Steady-states of two different outputs for two different inputs, i.e., one for Eq. (12) and another for \(a_i=0\) and \(\beta_i=0\) are mixed to get the average exit state given as

\[
(\beta)_{\text{out}} = \gamma(\beta)_{z=1}
\]

where \((\beta)_{z=1}\) is the output for the input \(a_i\) and \(\beta_i\) as per Eq. (12). The average yield is given by

\[
Y = (\beta)_{\text{out}} - C_B
\]

\[
= \gamma(\beta)_{z=1} - C_B
\]

Fig. 4 shows the results of evaluation of the average yield of B of the three variable scheme \([\varepsilon=0.1, \kappa=0.1, \text{in Eqs. (9) and (10)}]\) and comparison of the behaviour of the two systems for \((1/q)=0.12048\) for two variable model and \((1/q)=0.09434\) for three variable model. Though at conventional steady-state both the models give identical average yield, the average yield under periodic operation shows distinctly different behaviour. Two variable model gives larger improvement in the average yield. The average yield versus \(\gamma\) behaviour for the two models, \((1/q)=0.06993\) for two variable model and \((1/q)=0.06667\) for three variable model, is shown in Fig. 5. The average yield of B decreases under concentration cycling. There is no significant difference in the average yield under concentration cycling between the two model.

From the responses in Figs 4 and 5, it is found that the difference in the two model occurs only at the larger value of \((1/q)\). This may be due to the narrow range of \((1/q)\) for the three variables model. The parameter \(q\) contains the kinetic constants of the corresponding reaction scheme, \((L/U)\) and \(a_i\). The narrow range of \((1/q)\) is mainly due to the values of the kinetic constants since the values of \((L/U)\) and \(a_i\) are same for the situation.

Conclusion

For certain operating conditions, both the cubic autocatalytic reaction and the successive bimolecular reactions give identical yield under steady-state operation of an isothermal tubular reactor. However, the input multiplicity behaviour of the reactor is different for these reaction models. The average yield of product is higher for two variable model particularly at the larger value of the parameter \((1/q)\) under feed concentration cycling. For the smaller value out of the input multiplicity in \((1/q)\), there is a continuous decrease in the average yield for both the models under feed concentration cycling.

Nomenclature

- \(A, B\) = reactant and autocatalyst, respectively
- \(a\) = concentration of reactant A, \(\text{g mol cm}^{-3}\)
- \(a_i\) = base value of concentration to which dimensionless concentration is obtained, \(\text{g mol cm}^{-3}\)
- \(b\) = concentration of product B, \(\text{g mol cm}^{-3}\)
- \(C_A, C_B\) = dimensionless feed concentration of reactant A and B, respectively, at conventional steady-state operation.
\[ k_1 = \text{reaction rate constant for Eq. (1), } \text{g mole}^{-1} \text{cm}^{-2} \text{sec}^{-1} \]
\[ k_2 = \text{forward reaction rate constant for Eq. (2), } \text{g mole}^{-1} \text{cm}^{-1} \text{sec}^{-1} \]
\[ k_{-2} = \text{backward reaction rate constant for Eq. (2), } \text{sec}^{-1} \]
\[ k_4 = \text{reaction rate constant for the reaction } b + X \rightarrow 3B, \]
\[ k_{3} = \text{decay reaction rate, sec}^{-1} \]
\[ L = \text{reactor length, cm} \]
\[ q = k_{12} u L / U = \left( k_2 k_{-2} / k_4 \right) a u / U \]
\[ U = \text{velocity of the fluid, cm sec}^{-1} \]
\[ X = \text{intermediate product} \]
\[ x = \text{concentration of intermediate product, g mole cm}^{-3} \]
\[ Y = \text{average yield of B} \]
\[ Z = \text{normalized distance, } z / L \]
\[ z = \text{reactor axial distance, cm} \]

Greek Letters
\[ \alpha = a / a_0, \text{ dimensionless concentration of reactant A} \]
\[ \beta = b / a_0, \text{ dimensionless concentration of product B} \]
\[ \epsilon = k_{12} / k_{-2} \]
\[ \gamma = \text{pulse width expressed as a fraction of the dimensionless period, } \tau \]
\[ \xi = x / a_0, \text{ dimensionless concentration of the intermediate product} \]
\[ \phi = k_{12} u / k_{-2} = (k_2 k_{-2} / k_4) u / k_4 \]
\[ \kappa = k_2 a_0 / k_{-2} \]

Subscript
\[ f = \text{feed} \]

References