Effect of Coolant Flow Rate on the Dynamics of Delayed Recycle Continuous Stirred Tank Reactor

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Abstract

Numerical bifurcation analysis of delayed recycle stream in a continuous stirred tank reactor was studied using DDE-BIFTOOL. A first-order irreversible exothermic reaction \( s_1 \xrightarrow{k_{21}} s_2 \) was considered for analyzing effect of delay on the stability of the delayed recycle system. The non-isothermal CSTR was operated at both infinite and finite coolant inlet flowrates. A constant delay was considered in the recycle stream of CSTR for concentration of reactant, and temperature. DDE-BIFTOOL solver was used for finding dependency of delays on the bifurcation parameters, and its stability characteristics. The bifurcation parameters considered were: (i) fresh feed flowrate, (ii) coolant temperature, and (iii) coolant inlet flowrate. In the absence of delay, the system exhibits the region of dynamic instability for both infinite and finite coolant inlet flowrates. For infinite coolant flowrate, the region of dynamic instability on the reactor temperature was modified as a result of delay by varying either fresh feed flowrate or coolant temperature. The steady-state multiplicity was observed on the coolant temperature by varying fresh feed flowrate at finite coolant inlet flowrate. In the absence of delay, the fold and Hopf bifurcations were observed on the multiple steady-states of coolant temperature. The concentration and temperature delays do not alter substantially the dynamic characteristics of coolant temperature at \( T_{c,in} = 298 \) K. However, delays can alter the region of dynamic instability
for coolant temperature when coolant inlet temperature is higher than 298 K. These are the main result of present work.

Keywords: Kinetics; CSTR; Delay differential Equations; Hopf bifurcation; LMTD; Coolant dynamics.

**Nomenclature**

- $A_{2,1}$: pre-exponential factor, s$^{-1}$
- $c_p$: specific heat capacity of reaction mixture, J kg$^{-1}$ K$^{-1}$
- $c_{p,c}$: specific heat capacity of coolant, J kg$^{-1}$ K$^{-1}$
- $c_{s_1,f}$: initial concentration of reactant $s_1$ in the feed, mol m$^{-3}$
- $c_{s_1}$: concentration of reactant $s_1$, mol m$^{-3}$
- $c_{s_2}$: concentration of product $s_2$, mol m$^{-3}$
- $E_{2,1}$: activation energy of reaction, J mol$^{-1}$
- $I$: identity matrix
- $J$: jacobian matrix with respect to instantaneous state variables
- $J_r$: jacobian matrix with respect to delayed state variables
- $m$: number of delays considered
- $n$: number of state variables
- $Q$: volumetric flow rate, m$^3$s$^{-1}$
- $Q_j$: volumetric flow rate of coolant, m$^3$s$^{-1}$
- $r$: recycle ratio (0 < $r$ < 1)
- $R$: ideal gas constant, 8.314 J mol$^{-1}$ K$^{-1}$
- $s_i$: symbol for reacting species $i$
- $t$: time, s
- $T$: temperature (K)
- $T_c$: coolant temperature (K)
- $T_{c,in}$: coolant inlet temperature (K)
- $T_f$: temperature (K)
\( UA \) overall heat transfer coefficient, J s\(^{-1}\) K\(^{-1}\)

\( V \) volume of reactor, m\(^3\)

\( V_j \) volume of cooling jacket, m\(^3\)

\( z_i \) state variable of index \( i \)

**Greek symbols**

\( \rho \) density of mixture, kg m\(^{-3}\)

\( \rho_c \) density of coolant, kg m\(^{-3}\)

\( \psi \) parameters

\( \tau \) delay, s

\( (-\Delta H) \) heat of reaction, J mol\(^{-1}\)

\( \lambda \) eigenvalue

1. **Introduction**

For the past six decades, the steady state and dynamic characteristics of continuous stirred tank reactor [1-26] (CSTR) as well as reactor-separator-recycle system [27-43] were examined, and innumerable research articles were published on the bifurcation analysis of first-order irreversible exothermic reaction. In 1953, Van Heerden [1] observed the steady-state multiplicity for the first-order irreversible exothermic reaction in a CSTR. Luss and Lapidus [3] presented a method for finding stability characteristics of the state variables in a CSTR. A detailed study on the nonlinear behavior of first-order irreversible exothermic reaction in a recycle CSTR was carried-out by Uppal et al. [5, 6]. They presented the steady-state multiplicity in a parameter space by neglecting delay in the recycle stream. Kubieck et al. [9] studied the existence of isola, and mushroom regions for two inter-connected non-isothermal CSTRs. The chaotic behavior was observed by Mankin and Hudson [10] for two CSTRs connected in series with negligible delays in the recycle stream. Subsequently, many researchers investigated the bifurcation analysis of CSTR by considering various reaction schemes [11-23]. Singularity and
bifurcation theory [14] was applied for finding the performance of first-order exothermic reaction in a CSTR. The chaotic behavior was observed for consecutive first-order irreversible reactions [16,17] in a CSTR through bifurcation analysis.

The nonlinear bifurcation analysis of CSTR-separator-recycle system was investigated by various researchers [27-43]. For example, CSTR-distillation column [30, 31], CSTR-flash-recycle system [34], and so on. Luyben [28] presented the snowball effect in a reactor-separator-recycle system and proposed a control scheme for avoiding snowball effect. Morud and Skogestad [29] observed the instability in a reactor as a result of recycle of mass and energy with large time constant. Singularity and bifurcation theory was applied for determining nonlinear behavior of CSTR-flash recycle system [34]. Bildea et al. [41] observed the large reactor volume prevents the accumulation and infinite recycle of reactant in a reactor-separator-recycle system. Steady-state multiplicity in polymerization reactions was presented by Kiss et al. [42, 43].

Few researchers [44-50] investigated the stability analysis of delayed recycle CSTR. Lehman and coworkers [46-50] studied effect of delay on the stability of first-order exothermic reaction in a CSTR with an assumption of infinite coolant flowrates. They found that a delay in the recycle stream does not alters the dynamic characteristics of the system. A detailed study on the dynamic behavior of first-order irreversible reaction in the delayed CSTR-flash-recycle system was carried-out by Balasubramanian et al. [51-53]. A delay independent stability was determined analytically by controlling the fresh feed flowrate entering into an isothermal CSTR. Furthermore, a delay dependent stability was observed by controlling the effluent flowrate. For non-isothermal CSTR, the switching of stability characteristics from unstable to stable and vice-versa was recognized. Dynamic behavior of CSTR-mechanical separator-recycle system sustaining
first-order irreversible exothermic reaction [54] was studied using DDE-BIFTOOL [55, 56] with an assumption of infinite coolant flowrates. DDE-BIFTOOL [55, 56] is a MATLAB based solver for numerical bifurcation analysis of delay differential equations. New isola regions were found at large delays. Furthermore, the switching of stability characteristics from unstable to stable state, and vice versa was observed for infinite coolant flowrate. Here, dimensionless parameters were considered in the bifurcation analysis.

Uppal et al. [5, 6] presented the bifurcation analysis of delayed recycle CSTR with negligible delays in the recycle stream for first-order irreversible exothermic reaction. Infinite coolant inlet flowrate was assumed for bifurcation analysis, and observed that the system admits fold as well as Hopf bifurcations on the steady-state multiplicity. Likewise, Balasubramanian et al. [51-53] presented the effect of delay on the stability of first-order irreversible exothermic reaction in CSTR-flash-recycle system with an assumption of an infinite coolant inlet flowrate. A delay dependent stability was analytically proved by controlling the effluent flowrate using a flow controller. Previously, researchers studied the bifurcation analysis of first-order irreversible exothermic reaction in a CSTR with an assumption of an infinite coolant flowrate. That is, the exit and inlet coolant temperatures are alike for finding the heat of cooling in a reactor. In the earlier studies, the dynamics of coolant temperature was neglected. The coolant flow rate entering into a reactor must be finite in the realistic situation and reactor temperature of an exothermic reaction must be controlled at a desired value by manipulating the coolant inlet flowrate. Thus, the dynamics of coolant temperature in a reactor should be included in the bifurcation analysis. Various researchers used the dimensionless parameters for bifurcation analysis of delayed recycle systems and the realistic delay values were not included. Therefore,
we decided to use realistic delays up to 180 seconds in the bifurcation analysis for better understanding of its effect on the process variables.

Besides, this article describes a comprehensive numerical bifurcation analysis of first-order exothermic reaction in the CSTR-mechanical separator-recycle system with delays up to 180 s using DDE-BIFTOOL for both infinite and finite coolant inlet flowrates.

2. Model description

In the following, the mass and energy balance equations which describe the steady-state and dynamic performance of the CSTR-mechanical separator-recycle system are presented.

A first-order irreversible exothermic elementary reaction was considered for analyzing the steady-state and dynamic performance of the delayed recycle stream in a reactor. The stoichiometry of elementary reaction [57,58] can be represented as

\[ s_1 \xrightarrow{k_{2,1}} s_2 \] (1)

In Eq. 1, the kinetic constant \( k_{2,1} \) indicates the formation of product \( s_2 \) from reactant \( s_1 \) by virtue of chemical reaction. According to law of mass action kinetics [57,58], the reaction rates for disappearance of reactant \( s_1 \) is

\[ r_i = -k_{2,1}c_i \] (2)

The constitute relationships considered for the nonlinearity of delayed recycle system are: (i) Arrhenius law of kinetics, and (ii) heat of cooling in a jacketed CSTR. According to Arrhenius law, the temperature dependency of kinetic constants can be represented as
\[
k_{2,1} = A_{2,1} \exp \left( -\frac{E_{2,1}}{RT} \right)
\]  

(3)

Fig. 1 illustrates the schematic diagram of CSTR-mechanical separator recycle system. Here, the CSTR was connected with a mechanical separator for the separation of product \( s_2 \) from unconverted reactant \( s_1 \). The latter was recycled back to the reactor. A constant delay was assumed in the recycle stream for both concentration of reactant, and temperature. The non-isothermal operation of the reactor was considered in the bifurcation analysis.

The exothermic heat released by the reaction mixture in a jacketed CSTR during the reaction must be removed by the coolant flow in a jacket. The convective and conductive heat transfer between the cooling jacket and reactor should be included for finding the heat of cooling requirements. Moreover, the logarithmic mean temperature difference between the cooling medium and reaction mixture must be accounted in the heat of cooling calculations. Thus, the formula [59] for finding the heat of cooling in a non-isothermal CSTR is

\[
Q_{cooling} = \frac{UA(T_c - T_{c,in})}{\ln \frac{T - T_{c,in}}{T - T_c}}
\]

(4a)

Various researchers [5-6, 46-50, 51-54] assumed the coolant inlet flowrate was infinite for finding the heat of cooling requirements and Eq. 4a becomes

\[
Q_{cooling} = UA(T - T_c)
\]

(4b)

However, Eq. 4b may not be applicable as a result of finite coolant inlet flowrate entering into a reactor, and is being controlled using a flow controller. In this work, both formulas were used for heat of cooling calculations.
The mole balance equation for the disappearance of reactant in the CSTR is

\[
\frac{dc_i(t)}{dt} = \frac{rQ}{V} c_{s,i} + \frac{(1-r)Q}{V} c_i(t-\tau) - \frac{Q}{V} c_i(t) - A_{2,1}\exp\left(-\frac{E_{2,1}}{RT(t)}\right)c_i(t)
\] (5)

The energy balance equations for the CSTR and cooling jacket are

\[
\frac{dT(t)}{dt} = \frac{rQ}{V} T_f + \frac{(1-r)Q}{V} T(t-\tau) - \frac{Q}{V} T(t) + \frac{(-\Delta H)}{\rho c_p} A_{2,1}\exp\left(-\frac{E_{2,1}}{RT(t)}\right)c_i(t) - \frac{Q_{\text{cooling}}}{V\rho c_p}
\] (6)

\[
\frac{dT_c(t)}{dt} = \frac{Q_j}{V_j} [T_{c,in} - T_c(t)] + \frac{Q_{\text{cooling}}}{V_j \rho c_{p,c}}
\] (7)

At steady states, Eqs. 5-7 become,

\[
0 = \frac{rQ}{V} (c_{s,i} - c_{s,i}) - A_{2,1}\exp\left(-\frac{E_{2,1}}{RT_s}\right)c_{s,i}
\] (8)

\[
0 = \frac{rQ}{V} (T_f - T_s) + \frac{(-\Delta H)}{\rho c_p} A_{2,1}\exp\left(-\frac{E_{2,1}}{RT_s}\right)c_{s,i} - \frac{Q_{\text{cooling}}}{V\rho c_p}
\] (9)

\[
0 = \frac{Q_j}{V_j} [T_{c,in} - T_{c,s}] + \frac{Q_{\text{cooling}}}{V_j \rho c_{p,c}}
\] (10)

In the absence of delay, the following ordinary differential equations describe the time-dependent behavior of the system.

\[
\frac{dc_i(t)}{dt} = \frac{rQ}{V} (c_{s,i} - c_i) - A_{2,1}\exp\left(-\frac{E_{2,1}}{RT}\right)c_i
\] (11)

\[
\frac{dT(t)}{dt} = \frac{rQ}{V} (T_f - T) + \frac{(-\Delta H)}{\rho c_p} A_{2,1}\exp\left(-\frac{E_{2,1}}{RT}\right)c_i - \frac{Q_{\text{cooling}}}{V\rho c_p}
\] (12)
\[
\frac{dT_j}{dt} = \frac{Q_i}{V_j} [T_{c,in} - T_c] + \frac{Q_{cooling}}{V_j \rho_c c_p}
\]

(13)

In the aforementioned model description, the asymptotic values of recycle ratio \( r \) represent the total recycle, and zero recycle of unconverted reactant from the mechanical separator to the CSTR, respectively, at \( r = 0 \) and \( 1 \). A reactor may not be operated under asymptotic recycle ratios. Thus, the recycle ratio \( r \) must be within the range of 0 and 1 for the feasible conversion of reactant.

### 3. Numerical bifurcation analysis

A general form of system of multivariable delay differential equations with constant delays [52, 53, 55, 56] is

\[
\frac{dz_i(t)}{dt} = f[z_i(t), z_i(t - \tau_j), \psi] \quad z_i(t) = z_i,0 \quad \text{for} \quad -\tau_j < t < 0
\]

(14)

In Eq. 14, \( i \) and \( j \) vary from 1 to \( n \) and 1 to \( m \), respectively. The characteristic equation which was used for finding the real parts of roots and further analysis of stability of the steady-states of delay differential equations [55, 56] is

\[
|\lambda I - J - \sum_{j=1}^{m} J_{\tau_j} \exp(-\lambda \tau_j)| = 0
\]

(15)

Bifurcations occur whenever the roots move through the imaginary axis as one or more system parameters are varied. Fold bifurcation does not occur as a result of delayed recycle system cannot be destabilized by a real \( \lambda \) crossing the imaginary axis. Therefore, delays admit Hopf bifurcation in the CSTR-mechanical separator-recycle system as a result of \( \lambda \) is purely imaginary.
DDE-BIFTOOL [55, 56] is a collection of MATLAB based solver for determining numerical bifurcation analysis of delay differential equations. This solver implements the continuation, and stability analysis of steady state solutions as well as fold and Hopf bifurcations. Furthermore, it allows switching from the latter to an emanating branch of periodic solutions. In this work, DDE-BIFTOOL was used for finding the steady-state profiles, real parts of the roots of characteristic equation, and dependency of delays on the bifurcation parameters.

Eqs. 5-7 were numerically solved using MATLAB based dde23 solver [60] for finding the dynamic characteristics of the state variables. The bifurcation diagrams for the state variables were obtained using DDE-BIFTOOL. In the absence of delay, Eqs. 11-13 were numerically solved using MATLAB based ode45 solver for finding time-dependent behavior of the state variables.

4. Results and discussion

The steady-state and dynamic characteristics of CSTR-mechanical separator-recycle system sustaining first-order irreversible exothermic reaction were examined using DDE-BIFTOOL. In the following, numerical bifurcation analysis of delayed recycle CSTR is presented by varying three bifurcation parameters. Table 1 illustrates the system parameters [61-64] used in the bifurcation analysis. Here, the volume of cooling jacket, and coolant inlet flow rate were assumed for finding the steady-state multiplicity on the coolant temperature.

4.1. Infinite coolant inlet flowrate

For the first instance, the fresh feed flowrate \( rQ \) was considered as a bifurcation parameter for stability analysis. The effect of delay on the steady-state and dynamic characteristics of the non-isothermal CSTR was studied by assuming infinite coolant inlet flowrate. Eqs. 4b, 5 and 6
were used in DDE-BIFTOOL for finding the appreciable changes on the region of dynamic instability as a result of delay by varying $rQ$ at a fixed coolant temperature. Here, the coolant dynamics was neglected in the bifurcation analysis. The dependency of delays on $rQ$ at $T_c = 310, 315, 316, 320$ and $326$ K is depicted in Fig. 2. For $T_c < 315$ K, a delay does not affect significantly on the dynamic characteristics of the delayed recycle CSTR. A delay can alter substantially the region of dynamic characteristics when $T_c \geq 315$ K. In particular, the system changes the region of dynamic instability into the stable steady-states, and vice-versa (vide Fig. 2c-e) as a result of delay in the recycle stream. Here, the stable operation of the reactor is possible with small delays if the system is dynamically unstable in the absence of delay. Furthermore, $T_c = 320$ K was selected for finding better insights on the stability characteristics of the delayed recycle system in the absence of coolant dynamics.

Fig. 3 illustrates the bifurcation diagrams for the concentration of reactant, and reactor temperature by varying $rQ$ at $T_c = 320$ K. In the absence of delay, the system exhibits Hopf bifurcation over the range of bifurcation parameter $5.71 \times 10^{-4} \leq rQ \leq 1.13 \times 10^{-3}$ m$^3$s$^{-1}$. Eqs. 4b, 11 and 12 were numerically solved using ode45 solver available in MATLAB for finding the dynamic characteristics of the delayed recycle system. The dynamic simulation plots for the concentration of reactant and reactor temperature at $rQ = 7.15 \times 10^{-4}$, $1.0 \times 10^{-3}$, and $1.12 \times 10^{-3}$ m$^3$s$^{-1}$ are presented in Fig. 1S (vide supporting information). At $T_c = 320$ K, the sustained oscillations of reactant concentration, and temperature were observed.

For better insights on the regions of Hopf bifurcation, the dependency of the real parts of roots of characteristic equation on $rQ$ is depicted in Fig. 4 for various delays. Here, the values are positive over the range of $rQ$ at the delays of 10, 60, 110 and 180 s. These stability characteristics indicate that the system exhibits sustained oscillations on the Hopf bifurcation
regions. The real parts of roots of characteristic equation shown in Fig. 4 can be compared with Fig. 2d for finding the stability characteristics of the boundary. For example, the system exhibits stable steady-states at $\tau = 90$ s in Fig. 2d, and the corresponding real parts of the roots of characteristic equation are negative over the range of $rQ$ as illustrated in Fig. 4d. This result indicates that the critical delay boundary depicted in Fig. 2d is consistent with the stability characteristics of the plots shown in Fig. 4d. For $\tau = 240$, and 300 s, the real parts of roots of characteristic equation on $rQ$ plots are shown in Fig. 2S (vide supporting information). For these delays, the dynamic characteristics are unaltered, and are alike as that of no delay context. The dynamic simulation plots obtained for various delays (20 and 160 s) by numerically solving Eqs 4b, 5, and 6 at $rQ = 1 \times 10^{-3}$ m$^3$s$^{-1}$, and $T_c = 320$ K are shown in Fig. 3S (vide, supporting information). Here, the sustained oscillation of concentration of reactant, and reactor temperature are modified into the state of oscillations.

For the second case, the fresh feed flowrates were fixed at $6.68 \times 10^{-4}$, $1.002 \times 10^{-3}$, and $1.336 \times 10^{-3}$ m$^3$s$^{-1}$ for 60%, 40%, and 20% recycle, respectively. The coolant temperature was considered as a bifurcation parameter over the interval between 300 and 350 K. The bifurcation diagrams obtained by numerically solving Eqs. 4b, 5 and 6 for concentration of reactant, and temperature are depicted in Fig. 5. In the absence of delay, the system exhibits Hopf bifurcation over the range of $316 \leq T_c \leq 327$ K, and $310 \leq T_c \leq 323$ K for 60%, and 40% recycle, respectively. The dependency of delays on $T_c$ for 60% and 40% recycle are illustrated in Fig. 6. Here, the system alters substantially the region of dynamic characteristics from unstable to stable state and vice-versa at 60% recycle. The system exhibits a small stable region on the right-hand side of delay plot at 40% recycle as shown in Fig. 6b. For 20% recycle, an incomplete region of Hopf bifurcation was observed for various delays (10 and 180 s). The real parts of roots of
characteristic equation on $T_c$ plots are depicted in Fig. 4S (vide supporting information). For small recycle, delays do not alter significantly the region of dynamic characteristics. Besides, it was observed that the region of dynamic instability shifted towards low coolant temperature range.

4.2. Finite coolant inlet flowrate

In the following, the bifurcation analysis of the delayed recycle system in the presence of coolant dynamics is described. The coolant inlet flowrate $Q_j$, and temperature $T_{c,in}$ considered for the bifurcation analysis are $4.425 \times 10^{-4}$ m$^3$s$^{-1}$, and 308 K, respectively. Eqs. 4a, 5-7 were used in DDE-BIFTOOL for finding the delay-dependent stability characteristics. The bifurcation diagrams obtained for the concentration of reactant, reactor and coolant temperatures by varying $rQ$ at fixed $Q_j$ and $T_{c,in}$ are shown in Fig. 7. In the absence of delay, the system exhibits the region of dynamic instability for $7.22 \times 10^{-4} \leq rQ \leq 1.08 \times 10^{-3}$ m$^3$s$^{-1}$ as illustrated in Fig. 7d, and multiple steady-states are not observed at $T_{c,in} = 308$ K. The dynamic simulation plots are presented in Fig. 5S (vide supporting information) at $rQ = 8.95 \times 10^{-4}$ m$^3$s$^{-1}$. The dynamic simulation results reveal that the sustained oscillation of coolant temperature in a reactor besides other two state variables. Thus, the dynamics of coolant temperature must be included in bifurcation analysis of the delayed recycle system. The dependency of delays on $rQ$ at fixed $Q_j$ and $T_{c,in}$ is depicted in Fig. 8. Here, the delays on concentration of reactant, and reactor temperature do not alter substantially the region of dynamic characteristics. However, a delay induces a small stable region on the right-hand side of Hopf bifurcation boundary.

Afterwards, an ambient coolant inlet temperature ($T_{c,in} = 298$ K) was considered for analyzing the stability characteristics of the delayed recycle system. Fig. 9 illustrates the bifurcation diagrams for the concentration of reactant, reactor and coolant temperatures by varying $rQ$ at
$Q_j = 4.425 \times 10^{-4} \text{ m}^3\text{s}^{-1}$. In the absence of delay, the system admits multiple steady-states for all three state variables. In particular, the bifurcation analysis reveals that the coolant temperature of the system exhibits steady-state multiplicity. This phenomenon was not observed for an infinite coolant inlet flowrate assumption with the parameters considered. The stability of the steady-states of state variables is depicted in Fig. 9d. Fold bifurcation persists on the middle portion, and an incomplete region of Hopf bifurcation can be found on the lower and upper portions of the profile.

For $T_{c, in} = 308$ K, the system exhibits the region of dynamic instability in the absence of delay (vide Fig. 8a) for the state variables such as concentration of reactant, reactor and coolant temperatures. The concentration and temperature delays in the recycle stream of the reactor do not alter the region of dynamic instability for the range of small delay $0 < \tau < 15$ s as shown in Fig. 8a. For $\tau > 15$ s, the delay alters the right Hopf bifurcation boundary of the system considered. Another Hopf bifurcation region arises near the right Hopf bifurcation boundary when $\tau > 120$ s. Here, the stable operation of the system is possible for the set of parameters. For example, the coolant temperature of the CSTR is stable at $rQ = 1 \text{ m}^3\text{s}^{-1}$ and $90 \text{ s} < \tau < 135$ s. That is, a delay in the recycle stream changes sustained oscillations of the CSTR and coolant temperatures to stable steady-states. The oscillations in the coolant temperature affects the yield of product in a reactor for an exothermic reaction. Ultimately, it increases the possibilities of rise in the reactor temperature as well as the formation of undesired products. Thus, the delayed recycle stream can able to circumvent these problems. For $T_{c, in} = 298$ K, the coolant temperature exhibits multiple steady-states by varying $rQ$ as shown in Fig. 9c. Here, the system does not exhibit a full region of dynamic instability as depicted in Fig. 9d and delay do not alter the dynamic characteristics significantly.
Likewise, the bifurcation diagrams of coolant temperature on $Q_j$ instead of $rQ$ are illustrated in Fig. 10 a, b and c at $T_{c,in} = 293$, 298, and 302 K, respectively. In the absence of delay, the system admits the multiple steady-states for the state variables considered Fold and Hopf bifurcations were observed on the multiple steady-states of the state variables. For all three coolant temperatures, the incomplete regions of Hopf bifurcation were found on the upper and lower portion of the profiles. However, a broader Hopf bifurcation region was observed on the steady-state profile at $T_{c,in} = 302$ K as illustrated in Fig. 10e and f. A region of fold bifurcation was found on the middle portion of the curve and was not induced by delay. Here, a delay on the recycle stream of the CSTR do not alter substantially the dynamic characteristics as a result of steady-state multiplicity on the coolant temperature.

In this work, the effect of delay in the recycle stream of CSTR was analyzed using DDE-BIFTOOL for both infinite and finite coolant inlet flowrates at $0 \leq \tau \leq 180$ s. In the absence of coolant dynamics, the concentration and temperature delays in the recycle stream substantially alter the dynamic characteristics (vide Figs. 2 and 6) with the set of parameters used. However, the system exhibits different behaviors for the finite coolant flowrates. The coolant temperature in the delayed recycle CSTR exhibits sustained oscillations in addition to the oscillations in the other two state variables. These oscillations can be either minimized or circumvented to a stable operation (vide Fig. 8) for certain concentration and temperature delays in the recycle stream when $T_{c,in} > 298$ K. However, a delay does not alter the stability characteristics of the coolant temperature in the jacketed CSTR at $T_{c,in} = 298$ K. Lehman et al. [50] analytically proved that a delay in the recycle stream of CSTR does not alter the dynamic characteristics of the system for infinite coolant flowrate. In the present work, the logarithmic mean temperature difference was considered for finding dependency of delays on the coolant temperature using DDE-BIFTOOL.
Besides, the bifurcation analysis results presented at $T_{c,in} = 298$ K are consistent with the results of Lehman et al. [50].

5. Conclusion

A comprehensive bifurcation analysis of first-order irreversible exothermic elementary reaction in a CSTR-mechanical separator-recycle system was presented using DDE-BIFTOOL. For infinite coolant inlet flowrate, the system changes the region of Hopf bifurcation as a result of delay by varying either fresh feed flowrate or coolant temperature. In particular, the stable steady-states were observed on the parameter space for some delays. On contrary, fold and Hopf bifurcations exist for finite coolant inlet flowrate entering into the CSTR. Steady-state multiplicity was observed on the coolant temperature besides the reactor temperature and concentration of reactant. Delays do not induce fold bifurcation on the system considered. The heat of cooling based on logarithmic mean temperature difference between coolant and reaction mixture is not influenced significantly by temperature delays in the recycle stream. Thus, delays do not alter substantially the dynamic characteristics at finite coolant inlet flowrate into the CSTR.

Besides, the bifurcation analysis results presented here provide guidelines for analyzing effect of delay on the dynamic characteristics of fluid catalytic cracking unit, CSTRs connected in series, and other process engineering systems. The input delays on fresh feed as well as coolant, and effect of flow controller for controlling coolant inlet flowrate based on coolant and reactor temperatures are not included here. These are beyond the scope of present work.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at
References

[60] Shampine LF, Thompson S. Mathematics Department, Southern Methodist University, Dallas, TX, 75275.


Fig. 1. Schematic diagram of CSTR-mechanical separator-recycle system.
Fig. 2. Dependency of delays on $rQ$ at fixed $T_c$. The unit for $rQ$ is m$^3$s$^{-1}$. (a) $T_c = 310$ K, (b) $T_c = 315$ K, (c) $T_c = 316$ K, (d) $T_c = 320$ K, and (e) $T_c = 326$ K.
**Fig. 3.** Bifurcation diagrams of the system at $T_c = 320$ K. Solid line: stable steady-states, and dashed line: unstable steady states (Hopf bifurcation). (a) reactant concentration, and (b) temperature.
Fig. 4. Real parts of roots of characteristic equation versus $rQ$ for various delays at $T_c = 320$ K (Hopf bifurcation regions). (a) $\tau = 0$ s, (b) $\tau = 10$ s, (c) $\tau = 60$ s, (d) $\tau = 90$ s, (e) $\tau = 110$ s, and (f) $\tau = 180$ s. The unit for $rQ$ is m$^3$s$^{-1}$.
Fig. 5. Bifurcation diagrams of the system at fixed $rQ$. Solid line: stable steady-states, and dashed line: unstable steady states (Hopf bifurcation). (a and b) $rQ = 6.68 \times 10^{-4} \text{ m}^3 \text{s}^{-1}$, and (c and d) $rQ = 1.002 \times 10^{-3} \text{ m}^3 \text{s}^{-1}$.
Fig. 6. Dependency of delays on \( T_c \) at fixed \( rQ \). (a) \( rQ = 6.68 \times 10^{-4} \text{ m}^3\text{s}^{-1} \), and (b) \( rQ = 1.002 \times 10^{-3} \text{ m}^3\text{s}^{-1} \).
Fig. 7. Bifurcation diagrams of the system at $T_{c,in} = 308$ K, $\tau = 0$ s, and $Q_j = 4.425 \times 10^{-4}$ m$^3$/s$^{-1}$. Solid line: stable steady-states, and dashed line: unstable steady states (Hopf bifurcation). (a) concentration of reactant, (b) reactor temperature, and (c) coolant temperature. (d) Real parts of roots of characteristic equation plot by varying $rQ$. 
Fig. 8. (a) Dependency of delays on $rQ$ at fixed $Q_j$ and $T_{c,in}$, and (b) Real parts of roots of characteristic equation versus $rQ$ plot. $\tau = 130 \text{ s}$, $Q_j = 4.425 \times 10^{-4} \text{ m}^3\text{s}^{-1}$, and $T_{c,in} = 308 \text{ K}$. The unit of $rQ$ is m$^3$s$^{-1}$. 
Fig. 9. (a-c) Bifurcation diagrams obtained using DDE-BIFTOOL at $Q_j = 4.425 \times 10^{-4}$ m$^3$s$^{-1}$, and $T_{c,in} = 298$ K. (d) Real parts of roots of characteristic equation versus $rQ$ plot. (a) concentration of reactant, (b) reactor temperature, and (c) coolant temperature. The unit of $rQ$ is m$^3$s$^{-1}$.
Fig. 10. (a, c and e) Steady-state coolant temperature as a function of coolant inlet flow rate. (b, d and f) Real parts of roots of characteristic equation versus $Q_j$ plots. $rQ = 1.12 \times 10^{-3}$ m$^3$s$^{-1}$, and $\tau = 10$ s. (a and b) $T_{c,\text{in}} = 293$ K, (c and d) $T_{c,\text{in}} = 298$ K, and (e and f) $T_{c,\text{in}} = 302$ K. The unit of $Q_j$ is m$^3$s$^{-1}$. 
Table 1 Parameters considered in the numerical bifurcation analysis using DDE-BIFTOOL.

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<th>parameter</th>
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<th>unit</th>
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<td>volume of cooling jacket</td>
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<td>specific heat of coolant</td>
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<td>J kg$^{-1}$K$^{-1}$</td>
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</table>
Graphical Abstract

![Graphical Abstract Image]

- $T_c$ (K)
- $rQ$ (m$^3$s$^{-1}$)
- $t$ (s)

Unstable regime indicated.