Bifurcation Analysis in Cubic Autocatalytic Reactions with Time Delay

By

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11951

Dissertation submitted in partial fulfillment of
the requirements for the
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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr Periyasamy Balasubramanian)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPTEMBER 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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KAMARUL JAZMI HAZWAN B KAMARUL ARIFFIN

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First and foremost, I give thanks and praise to God for His guidance and blessings throughout the entire course of my Final Year Project.

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My acknowledgement would be incomplete without giving credit to Universiti Teknologi PETRONAS, especially Chemical Engineering Department which has equipped students with essential skills for self-learning.

Finally, I would like to thank my family. They have been a wonderful source of encouragement and joy to me and also not to forget the fellow colleagues. Their help was tremendous gift to me. May God bless all of us and only He, the Almighty could repay all my debts to them.

Abstract

The purpose of this interim report is to provide an overview of the author's Final Year Project. The author would like to study the effect of delay on the stability of recycle stream of Continuously Stirred Tank Reactor (CSTR) sustaining cubic autocatalytic reactions with time delay. The reactor is operated under isothermal condition. The reaction system is governed by the delay differential equations. The dynamic behavior of the cubic autocatalytic reaction system with time delay is investigated using DDE23 solver which is available in MATLAB. In the absence of delay, the system is dynamically unstable with the set of model parameters. It has been observed that the dynamic characteristic changes as a result of delay in the recycle stream of a CSTR.

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CHAPTER 1

1 INTRODUCTION

1.1 Background of Study

Continuous Stirred Tank Reactor (CSTR) is a common ideal reactor type in chemical reaction engineering. In an ideal mixed reactor, the exit stream composition is identical to the composition of the material inside the reactor, which is a function of residence time. For a CSTR with a recycle stream, the exit stream of the reactor is sent through separation process. Portions of the output composition which are the feed are recycled into the CSTR by travelling through pipes. The benefits of the recycle reactor are it increases the overall conversion of the reactor and also reduces the overall inventory of the process. Several researchers have discussed the stability of a recycle CSTR but the effect of delay in the recycle stream was neglected. It is highly unrealistic although this assumption makes theoretical analysis simpler. This is because the process of recycle in which the output is separated from the input and travel through pipes after separation often requires a great deal of time and will introduce a delay into the model.

Bifurcation analysis is the mathematical study of changes in the qualitative structure such as the integral curves of a family of vector fields. A bifurcation occurs when a small smooth change made to the parameter value of a system causes a sudden qualitative change in its behavior. Bifurcation analysis provides the solutions for the differential equations and it can occur in both continuous and also discrete systems.

In this Final Year Project, the author would like to investigate the behavior of two differential equations, which are Ordinary Differential Equation (ODE) and also Delay Differential Equation (DDE). Both of these differential equations can be used to analyze and solve the stability of the system. The difference between these two differential equations is the presence of delay (τ) in the equation. For ODE, the concentration of reacting species is function of time only, while for DDE, the concentration of reacting species is function of time (t), as well

as delay time (τ). Thus, if there is delay present in the system, the performance of the system will be governed by DDE and if there is no delay, it will be governed by ODE.

1.2 Problem Statement

In this Final Year Project, the author considers the cubic autocatalytic reactions to model the system and is governed by the delay differential equations. Parkash Badola et al. (1990) have obtained the solutions to the delay differential equations by using semiimplicit Runge-Kutta method with a variable step size algorithm and cubic spline interpolation. Thus, in this present work, the author would like to study the dynamic behavior of cubic autocatalytic reactions in a sustaining recycle CSTR with time delay using DDE23 software available in MATLAB. Besides that, the bifurcation analysis is not performed yet in the literature for cubic autocatalytic reactions with time delay.

The stoichiometry of the cubic autocatalytic reactions can be represented as

$$A + 2B \xrightarrow{k_1} 3B \qquad (1)$$

$$B \xrightarrow{k_2} C \qquad (2)$$

Where

k_1 = kinetic constant for the cubic autocatalytic reaction
k_2 = kinetic constant for the decay reaction

The first reaction is cubic autocatalytic reaction and the second reaction is a further decay of desired product B.

1.3 Objectives

The objectives of the present thesis report are given below.

- To study the steady state and dynamic behavior of the cubic autocatalytic reactions without time delay in the recycle stream of a CSTR.
- To study the dynamic behavior of the cubic autocatalytic reactions with time delay in the recycle stream of a CSTR.
- To compare the results from cubic autocatalytic reactions with the first order monomolecular irreversible reaction.

1.4 Scope of Study

In this project, the main focus is to study the effect of time delay in the recycle stream of CSTR on the stability of the system. Cubic autocatalytic reaction is considered to model the system and is governed by the delay differential equations. In order to solve the delay differential equations, the model equations must be developed from the first principles of conservation of mass. The stability of the system can be analyzed by looking at the graph of conversion, x versus time, t. The present of oscillation in the graph shows that the system is not stable, while a straight horizontal line in the graph shows that the system is stable.

CHAPTER 2

2 LITERATURE REVIEW

As stated in the background, several researchers have studied the stability of a CSTR and the effects of a recycle stream. Uppal et al. (1973) have analyzed the dynamic behavior of CSTR. They have studied the types of dynamic behavior possible for a single first order reaction carried out in a CSTR. Based on their research, the dynamic behaviors are classified according to values of the parameters and plots in parameter space used to define the various possibilities. They have used the first method of Liapunov, a local method to obtain the stability of the steady states. While for the dynamic behavior, they used the results of Poore on the direction and stability of branches of periodic orbits which bifurcate from certain steady states. However, the effect of delay on the stability of recycle stream was neglected.

Recently, Balasubramanian et al. (2010) studied numerical bifurcation of delayed recycle stream in a CSTR. Using DDE-BIFTOOL, the stability analysis was carried out to study the effect of delay in recycle stream of the CSTR. A first order irreversible elementary reaction was considered. Based on their research, in the absence of delay, the recycle isothermal CSTR is stable for all the values of recycle ratio, r and Da. As a result of delay, the system exhibits delay independent stability for all the values of r and Da. For non-isothermal operation of CSTR, the system is dynamically unstable in the absence of delay. The system parameters considered by them are; $B = 11$, $\beta = 3$ and $0.283 \leq Da \leq 0.405$.

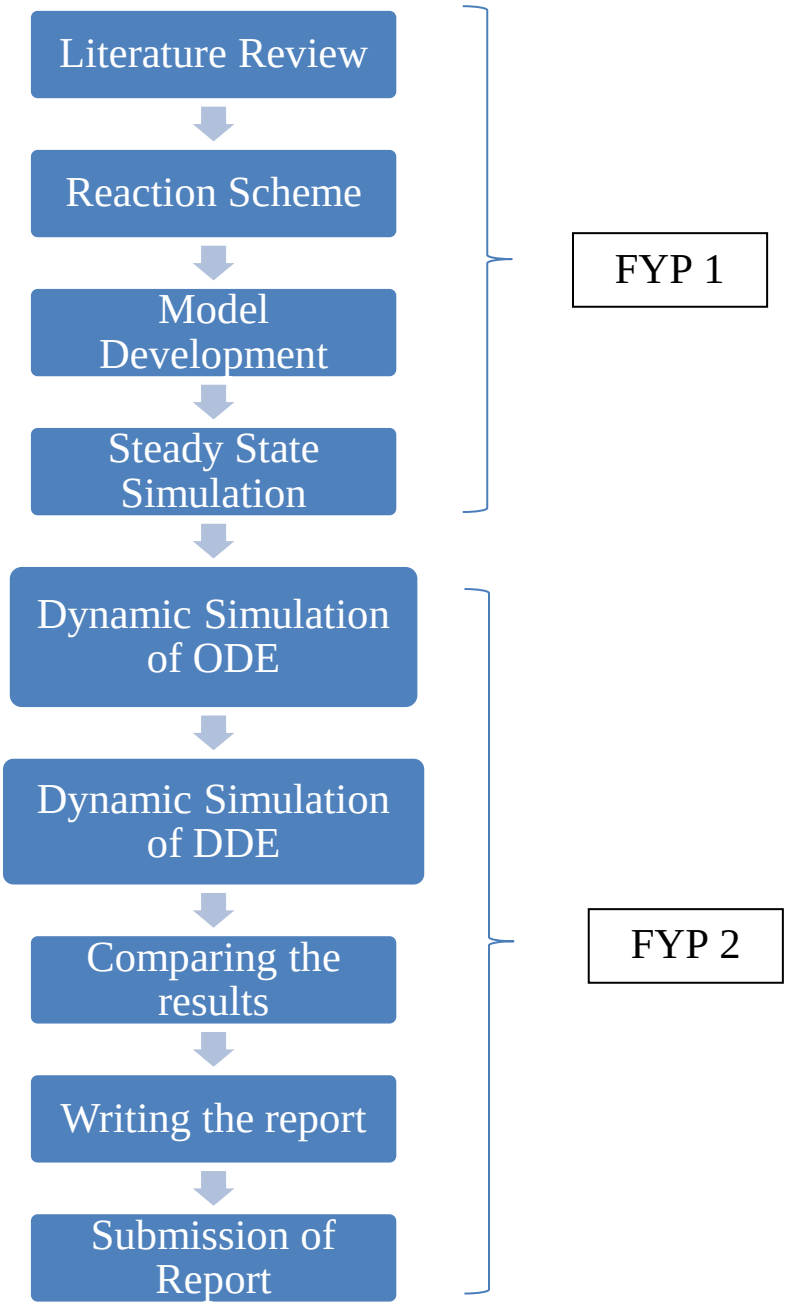
Parkash Badola et al. (1990) have analyzed the bursting solutions for cubic autocatalysis in a CSTR with recycle and time delay. The solutions to the delay differential equations were obtained by using semiimplicit Runge-Kutta method and a cubic spline interpolation. With parameter values corresponding to $\alpha = 0.0166$, $\beta = 0.11$ and $\gamma = 0.0008658$ and in the absence of recycling, the system has three unstable steady states. They had investigated that a simple model of cubic autocatalytic reaction in CSTR in the presence of recycling and time delay in order to show the existence of bursting solutions in certain regions of parameter space.

CHAPTER 3

3 METHODOLOGY

3.1 Project Methodology

The outline of the methodology for the project work is given below.



3.2 Gantt Chart

No	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic															
2	Literature review and survey															
3	To understand the reaction scheme															
4	Model Development															
5	Steady State Simulation															
6	Dynamic Simulation of ODE															
7	Dynamic Simulation of DDE															
9	Comparing the results															
10	Submission of Interim Report															

Mid Semester Break

Expected Completion

3.3 Model Development

Cubic Autocatalytic Reactions

The schematic diagram of the CSTR with recycle stream is depicted in Figure 1.

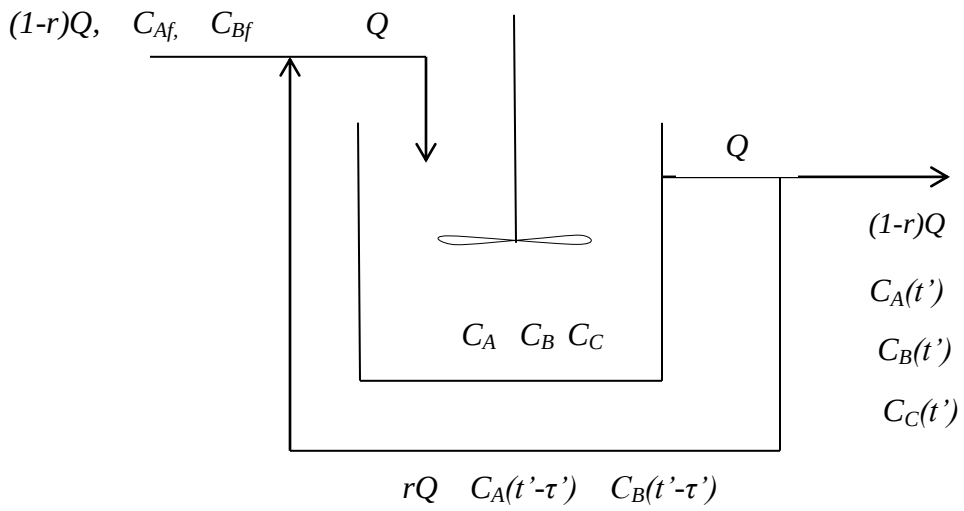


Figure 1 Schematic Diagram for CSTR with recycle stream

Where

Q = Volumetric flow rate
r = Recycle ratio
C_{Af} = Initial concentration of A
C_{Bf} = Initial concentration of B
C_i = Concentration of species i in the reactor (i = A, B and C)
t' = Actual time
τ' = Actual delay time

Cubic autocatalytic reaction with product decay was considered in this work. The stoichiometry for cubic autocatalytic reactions is given by:

$$A + 2B \xrightarrow{k_1} 3B$$

$$B \xrightarrow{k_2} C$$

The mass balance equation for the reactant *A* and product *B* are developed from the law of conservation of mass. It states that the mass of an isolated system will remain constant over time in which:

Mass accumulation = Mass input – Mass output ± Rate of reaction

The molar concentration of reactant *A* and product *B* are governed by the delay differential equations and are given by:

$$V\frac{dC_{\mathrm{A}}}{dt'} = (1-r)QC_{\mathrm{Af}} + rQC_{\mathrm{A}}(t'-\tau') - QC_{\mathrm{A}} - k_1C_{\mathrm{A}}C_{\mathrm{B}}{}^2V$$

$$V\frac{dC_{\mathrm{B}}}{dt'} = (1-r)QC_{\mathrm{Bf}} + rQC_{\mathrm{B}}(t'-\tau') - QC_{\mathrm{B}} + k_1C_{\mathrm{A}}C_{\mathrm{B}}{}^2V - k_2C_{\mathrm{B}}V$$

Where

Q = volumetric flow rate (m^3s^{-1})
C_{Af} = feed concentration of reactant *A*
C_{Bf} = feed concentration of reactant *B*
C_A = concentration of reactant *A*
C_B = concentration of reactant *B*
V = reactor volume (m^3)
k_1 = kinetic constant for reaction 1
k_2 = kinetic constant for reaction 2

The dimensionless form of mass balance equations for reactant *A* and product *B* are given below.

$$\frac{dx}{dt} = r\gamma x(t-\tau) - \gamma x + (1-x)y^2$$

$$\frac{dy}{dt} = (1-r)\gamma\beta - \gamma y + r\gamma y(t-\tau) + (1-x)y^2 - \alpha y$$

The dimensionless parameters are

$$\gamma = \frac{Q}{Vk{C_{\mathrm{A,f}}}^2}$$

$$\beta = \frac{C_{\mathrm{B,f}}}{C_{\mathrm{A,f}}}$$

$$\alpha = \frac{k_2}{k_1{C_{\mathrm{A,f}}}^2}$$

$$t = k{C_{\mathrm{A,f}}}^2 t'$$

$$x = \frac{C_{\mathrm{A,f}} - C_{\mathrm{A}}}{C_{\mathrm{A,f}}}$$

$$y = \frac{C_{\mathrm{B}}}{C_{\mathrm{A,f}}}$$

In the absence of delay, the behavior of the system is governed by the ordinary differential equation. They are:

$$\frac{dx}{dt} = \gamma x(r-1) + (1-x)y^2$$

$$\frac{dy}{dt} = (1-r)\gamma\beta + \gamma y(r-1) + (1-x)y^2 - \alpha y$$

The author used the dimensionless forms of mass balance equation for reactant *A* and product *B* to run the steady state simulation, dynamic simulation of ordinary differential equation and also dynamic simulation of delay differential equation.

First Order Monomolecular Irreversible Reaction

As stated in the objectives part, the author would like to compare the results of simulation of cubic autocatalytic reactions with the first order monomolecular irreversible reaction. The effect of delay on the stability of delayed recycle stream in CSTR of first order irreversible elementary reaction has been studied by Balasubramanian et al. (2010). Thus, the author used the results from [3] to compare with the simulation of cubic autocatalytic reactions.

The stoichiometry for first order irreversible reaction is given by:

$$A \xrightarrow{k_1} B$$

Based on Balasubramanian et al. (2010), the dimensionless form of mass and energy balance equations are given by

$$\frac{dx(t)}{dt} = -\frac{1}{r}x(t) + \left(\frac{1}{r} - 1\right)x(t-\tau) + Da\big(1 - x(t)\big)\exp\big(\theta(t)\big)$$

$$\frac{d\theta(t)}{dt} = -\left(\frac{1}{r} + \beta\right)\theta(t) + \left(\frac{1}{r} - 1\right)\theta(t-\tau) + BDa(1 - x(t))\exp(\theta(t))$$

The dimensionless parameters are defined as:

$$t = \frac{t'rQ}{V}$$

$$Da = k^{\circ}_{2,1}\exp\left(\frac{-E_{2,1}}{RT_{\mathrm{f}}}\right)\frac{V}{rQ}$$

$$\beta = \frac{UA}{\rho C_{\mathrm{p}} rQ}$$

$$\theta = \left(\frac{E_{2,1}}{RT_{\mathrm{f}}^2}\right)(T - T_{\mathrm{f}})$$

$$B = \left(\frac{-\Delta H}{\rho C_{\mathrm{p}}}\right)\frac{E_{2,1}}{RT_{\mathrm{f}}^2}c_{\mathrm{s1,f}}$$

CHAPTER 4

4 RESULTS AND DISCUSSION

4.1 Steady State Simulation for Cubic Autocatalytic Reactions

The parameters [Badola et al. 1991] considered for determining the dynamic behavior of the system are: $\alpha = 0.0166$, $\beta = 0.11$, and $\gamma_{wr} = 0.0008658$. At steady state, the behaviors of the system are governed by the nonlinear algebraic equation and are given by:

$$0 = \gamma x(r-1) + (1-x)y^2$$
$$0 = (1-r)\gamma\beta + \gamma y(r-1) + (1-x)y^2 - \alpha y$$

Also, delay does not alter the steady state characteristics. By using MATLAB, the steady state simulation was performed and is shown in Figure 2.

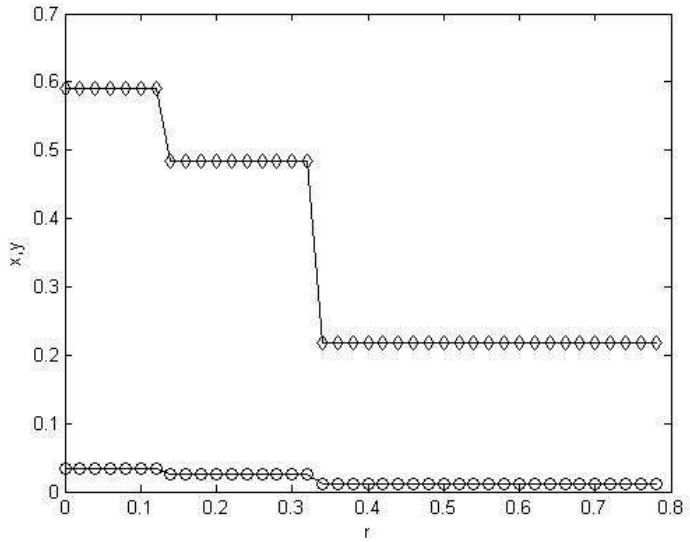


Figure 2 Steady state simulation for the cubic autocatalytic reactions

The conversion of reactant *A* and the formation of product *B* as a function of recycle ratio are shown in Figure 2. Here, we observed that the conversion of reactant decreases with an increase in the recycle ratio. The conversion is constant at about 0.6 when the recycle ratio lies between 0

and 0.15. Then the conversion decreases and is constant to 0.5 when the recycle ratio lies in the range of 0.15 to 0.3. When the recycle ratio is beyond 0.3, the conversion is constant at 0.2.

4.2 Dynamic Behavior of Cubic Autocatalytic Reactions

For the dynamic simulation of cubic autocatalytic reactions, the author considers three cases which are, no delay in the system which means that $\tau=0$, recycle ratio, $r=0.2$ and $\tau=1080$. The following differential equations were solved using DDE 23 solver which available in MATLAB.

$$\frac{dx}{dt} = r\gamma x(t-\tau) - \gamma x + (1-x)y^2$$

$$\frac{dy}{dt} = (1-r)\gamma\beta - \gamma y + r\gamma y(t-\tau) + (1-x)y^2 - \alpha y$$

By using MATLAB, the dynamic behavior of cubic autocatalytic reactions is performed and the results are shown below.

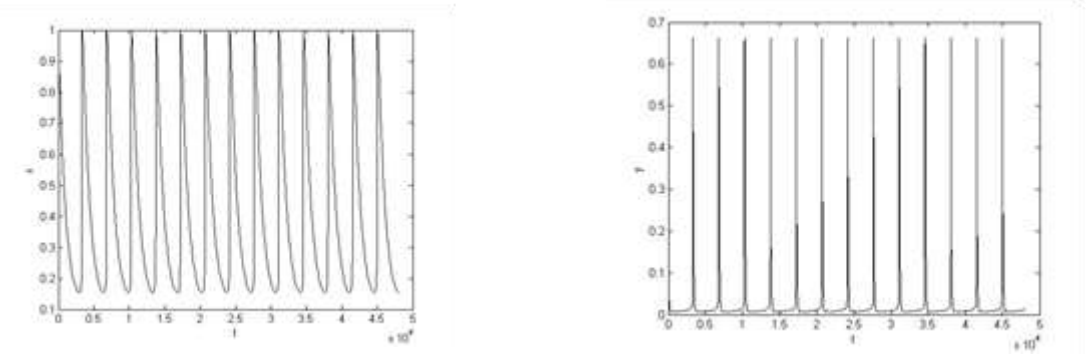
Case 1

For the first instance, the dynamic behavior of the cubic autocatalytic reaction system is studied without considering delay in the recycle stream of the CSTR. Dynamic simulation was performed by considering three different values of *r*. That is; *r* = 0, 0.2 and 0.5. ODE 45 solver is used to solve ordinary differential equations. The dynamic simulation plots were shown in Figures 3-5.

When $\tau = 0$

(a) (b)

Figure 3 Dynamic simulation when *r*=0. (a)reactant A (b)product B



(a) (b)

Figure 4 Dynamic simulation when *r*=0.2. (a)reactant A (b)product B

(a) (b)

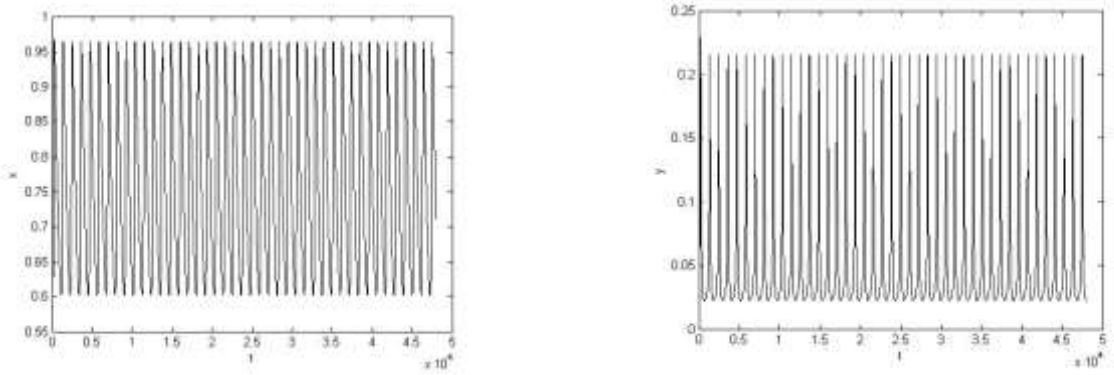
Figure 5 Dynamic simulation when *r*=0.5. (a)reactant A (b)product B

In the absence of delay, the system is dynamically unstable for $0 \leq r \leq 1$. For the conversion of the reactant, the oscillation of the amplitude range from 0.15 to 1 while for the formation of product, the value range from 0 to 0.65.

Case 2

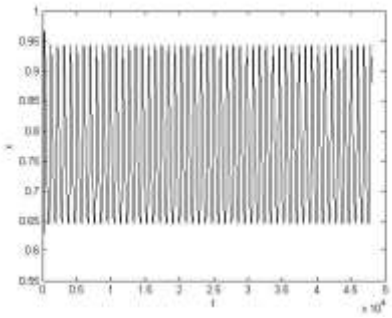
In the second case study, the recycle ratio is fixed at r = 0.2 and effect of delay on the dynamic behavior of the system was investigated. The dynamic simulation plot for the delay differential equation at τ = 100, 500, 750, 1000 and 1080 were shown in Figures 6-10, respectively.

When *r = 0.2*

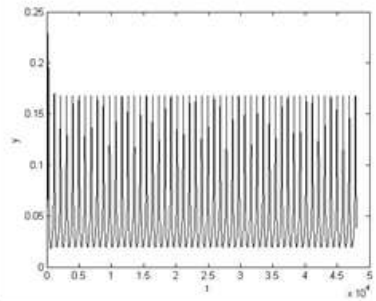


(a) (b)

Figure 6 Dynamic simulation when τ=100. (a)reactant A (b)product B

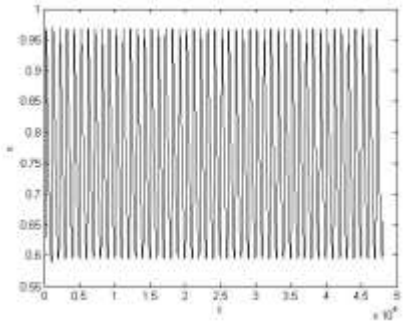


(a)

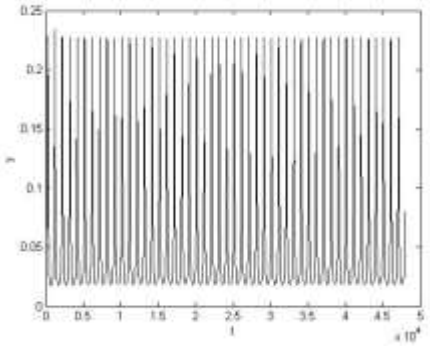


(b)

Figure 7 Dynamic simulation when τ=500. (a)reactant A (b)product B

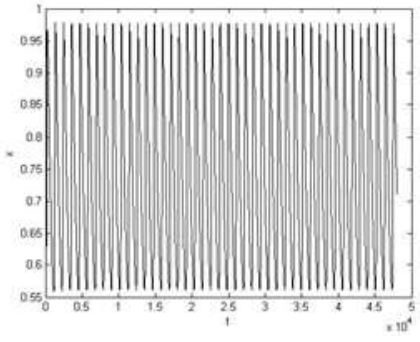


(a)

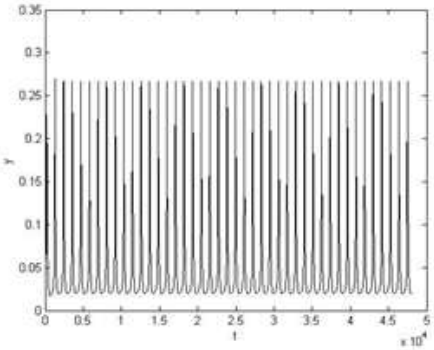


(b)

Figure 8 Dynamic simulation when τ=750. (a)reactant A (b)product B

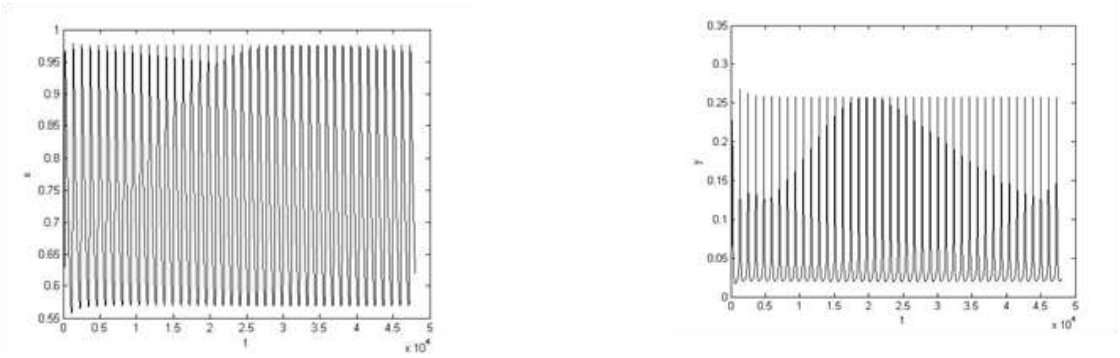


(a)



(b)

Figure 9 Dynamic simulation when τ=1000. (a)reactant A (b)product B



(a) (b)

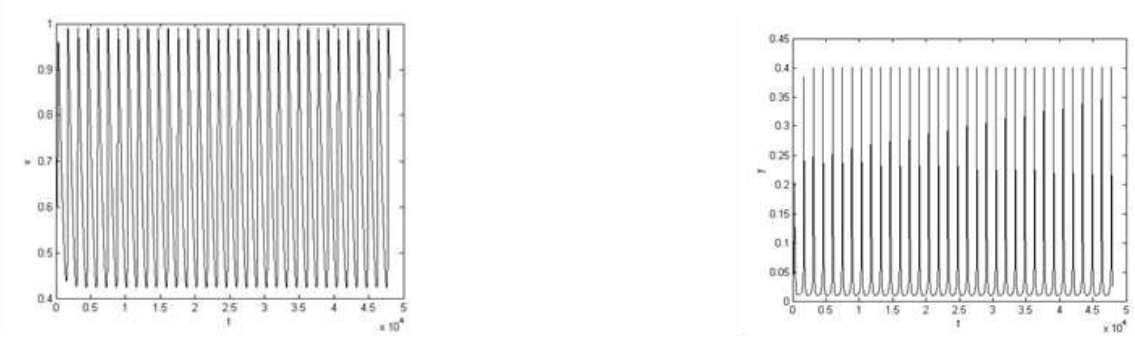
Figure 10 Dynamic simulation when τ=1080. (a)reactant A (b)product B

For the second case of dynamic simulation, the author fixed the value of recycle ratio to 0.2 and manipulated the value of the delay. As a result of delay, the system changes the dynamic characteristics. The amplitude of the oscillation is reduced as delay is introduced in the system. Besides of that, it was observed that the amplitude of oscillation changes as a result of concentration delay in the recycle stream of CSTR. As the value of the delay increases, the amplitude of the oscillation also increases.

Case 3

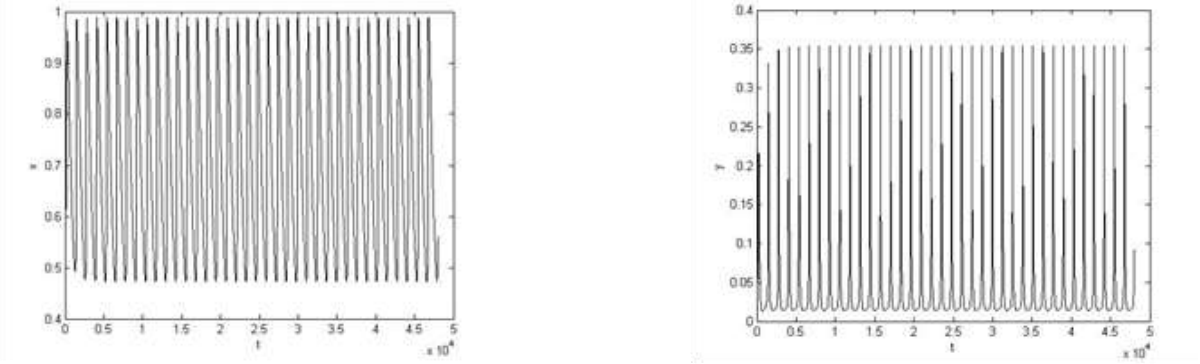
For the third case study, the author fixed the value of τ = 1080 and effect of delay on the dynamic behavior of the system was investigated. The dynamic simulation plot for the delay differential equation at r = 0.1, 0.15, 0.2, 0.25 and 0.3 were shown in Figures 11-15 respectively.

When τ = *1080*



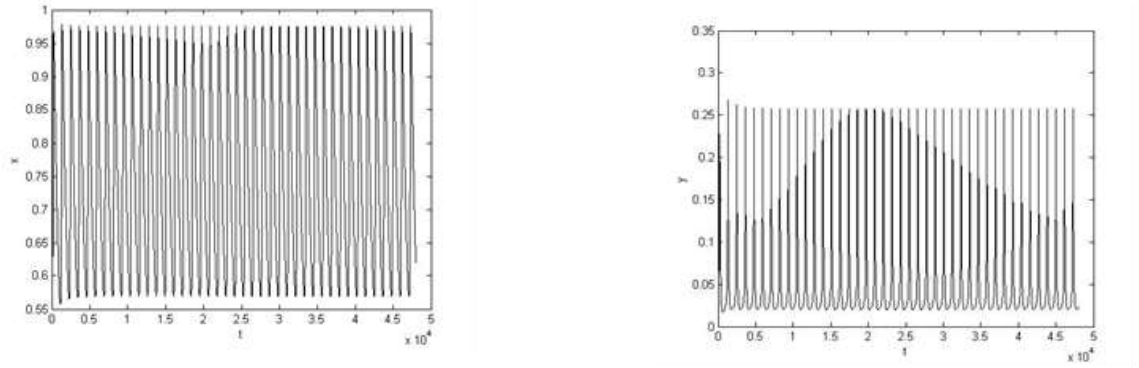
(a) (b)

Figure 11 Dynamic simulation when *r*=0.1. (a)reactant A (b)product B



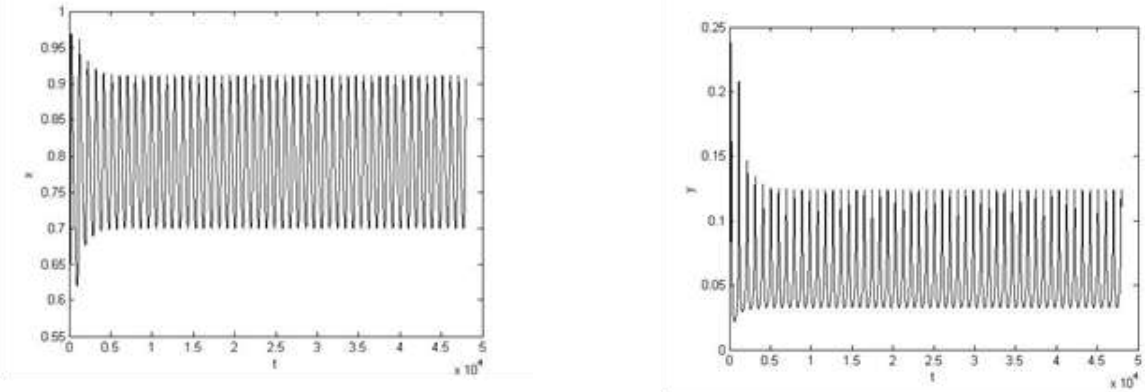
(a) (b)

Figure 12 Dynamic simulation when *r*=0.15. (a)reactant A (b)product B



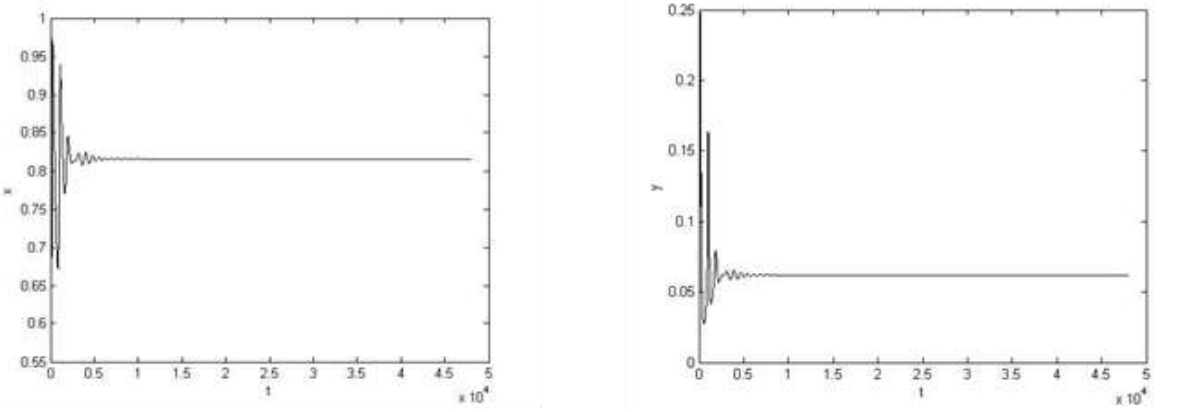
(a) (b)

Figure 13 Dynamic simulation when *r*=0.2. (a)reactant A (b)product B



(a) (b)

Figure 14 Dynamic simulation when *r*=0.25. (a)reactant A (b)product B



(a) (b)

Figure 15 Dynamic simulation when *r*=0.3. (a)reactant A (b)product B

For the third case of dynamic simulation, the author fixed the value of the delay at 1080 and manipulated the value of the recycle ratio. As a result of large delay, the system switches from unstable state to stable state. It was observed that, as the value of *r* increases, the amplitude become shorter and finally at *r*=0.3, the system achieved its stable state.

Parkash Badola et al. (1990) had also done the simulation for cubic autocatalytic reaction using the same value of delay which is 1080. They varied the value of *r* from 0.1 to 0.6. The dynamic simulation performed shows that the system is oscillating for $0.1 \leq r \leq 0.6$. Thus, in their case, as a result of large delay, the system is dynamically unstable for $0.1 \leq r \leq 0.6$. But in this work, the results show that the system is stable for value of $r \geq 0.3$.

4.3 Steady State Simulation for First Order Monomolecular Irreversible Reaction

The parameters value [2] considered by Balasubramanian et al. (2010) for determining the dynamic behavior of the system are: B = 11 and β = 3. At steady state, the behaviors of the system are governed by the nonlinear algebraic equation and are given by:

$$0 = -x + Da(1 - x)\exp(\theta)$$
$$0 = -(1 + \beta)\theta + B(Da)(1 - x)\exp(\theta)$$

As we can see from the equations, recycle ratio, r does not alter the steady state characteristics. By using MATLAB, the steady state simulation was performed and is shown in Figure 16.

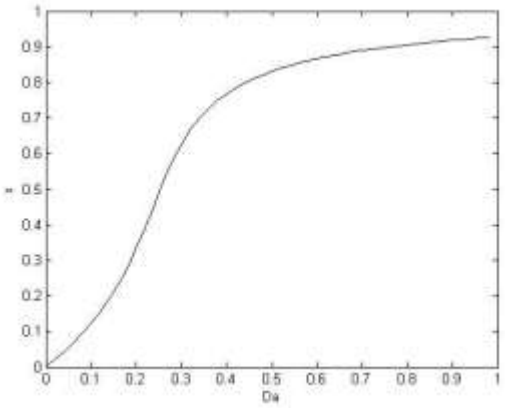


Figure 16 Bifurcation diagram for the first order irreversible reaction

Figure 16 shows the conversion of reactant as a function of Damkohler number, *Da*. Balasubramanian et al. [3] stated that, the system is dynamically unstable for non-isothermal operation of the CSTR with the system parameters considered: $0.283 \leq Da \leq 0.405$.

4.4 Dynamic Behavior of First Order Monomolecular Irreversible Reaction

In order to compare the results of cubic autocatalytic reactions with the first order irreversible reaction, the author also consider the same three cases of cubic reactions in the first order reaction. This section will present the results of the dynamic behavior of first order irreversible reaction when τ = 0, recycle ratio, r = 0.8, τ = 0.2 (small delay) and τ = 3 (large delay).

The following differential equations were solved using DDE 23 solver which available in MATLAB.

$$\frac{dx(t)}{dt} = -\frac{1}{r}x(t) + \left(\frac{1}{r} - 1\right)x(t-\tau) + Da\big(1 - x(t)\big)\exp\big(\theta(t)\big)$$

$$\frac{d\theta(t)}{dt} = -\left(\frac{1}{r} + \beta\right)\theta(t) + \left(\frac{1}{r} - 1\right)\theta(t-\tau) + BDa(1 - x(t))\exp(\theta(t))$$

By using MATLAB, the dynamic behavior of first order irreversible reaction is performed and the results [3] are shown below.

Case 1

For the first case, the dynamic behavior of the first order reaction system is studied without considering the delay in the recycle stream of CSTR. Based on [3], the dynamic simulation was performed at three different values of *Da*. That is; *Da* = 0.283, 0.35 and 0.4. As there is no delay, the performance of the system is governed by ordinary differential equation, thus ODE 15s solver is used to solve the differential equation. The dynamic simulation plots were shown in Figures 17-19.

When $\tau = 0$

(a) (b)

Figure 17 Dynamic simulation when *Da*=0.283

(a) (b)

Figure 18 Dynamic simulation when *Da*=0.35

(a) (b)

Figure 19 Dynamic simulation when *Da*=0.4

Based on the three graphs above, we can observe oscillation in each of the graph. The present of oscillation in the three graphs above show that the system is dynamically unstable. Thus, in the absence of delay, the system is dynamically unstable for $0.283 \leq Da \leq 0.405$.

Case 2

In the second case, the recycle ratio is fixed at r = 0.8. The value of r in the first order reaction is equal to (1 - r) in cubic autocatalytic reaction. As we fixed the value of r = 0.2 in cubic autocatalytic reaction, thus we set the value of r = 0.8 in this case. The effect of delay on the dynamic behavior of the system was investigated as we varied the value of τ =0.2 and 2. Figures 20-21 shows the dynamic simulation plot.

When r = 0.8

(a) (b)

Figure 20 Dynamic simulation when τ=0.2

(a) (b)

Figure 21 Dynamic simulation when τ=2

For the second case, the author fixed the value of recycle ratio to 0.8 and manipulated the value of delay. In the presence of delay, the system still dynamically unstable as there is oscillation in the graph.

Case 3

For the third case study, the author fixed the value of $\tau = 0.2$. This value represents the small delay in the system. The dynamic simulation plot for the delay differential equation at r = 0.8 is shown in Figure 22.

When τ = 0.2

(a) (b)

Figure 22 Dynamic simulation when *r*=0.8

The graphs above show the dynamic behavior of first order reaction when small delay is introduced in the system. In [3], they had done the plot on dependency of critical delay on *Da* for small delay and are shown in Figure 23.

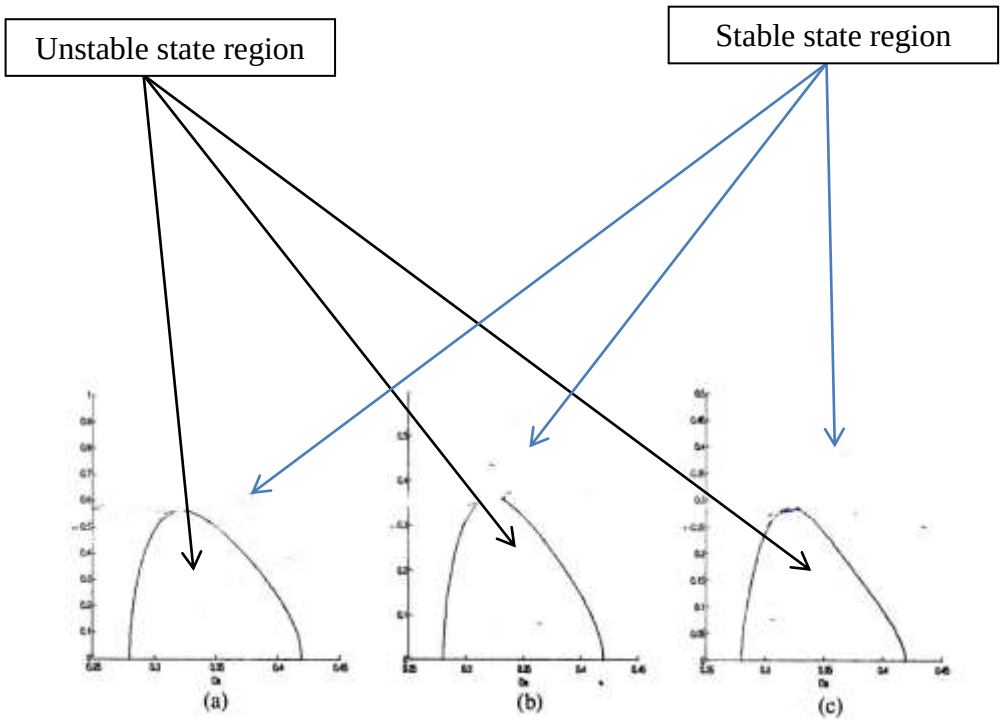


Figure 23 Dependency of critical delay on *Da* for small delay (τ=0.2)

(a) r = 0.75(25% recycle), (b) r =0.5(50% recycle) (c) r = 0.25(75% recycle)

Figure 23 show the system operates at three different value of recycle which are 25% recycle, 50% recycle and also 75% recycle. The system is dynamically unstable inside the isola regions and stable outside the isola region. The system changes it dynamic characteristic from unstable state to stable state as the value of τ increases. The region of dynamic instabilities vanishes quickly by varying the recycle rate from 25% to 75%. Thus, for small delays, the system attains stable steady state for all the three recycle ratios [3].

Case 4

In the fourth case, the author fixed the value of $\tau = 2$. This value represents the large delay in the system. Figure 24 below show the dynamic simulation plot when value of *r* is set at 0.8.

When $\tau = 2$

(a) (b)

Figure 24 Dynamic simulation when *r* = 0.8

The graphs above show the dynamic behavior of first order reaction when large delay is introduced in the system. In [3], they had done the plot on dependency of critical delay on *Da* for large delay and are shown in Figure 25.

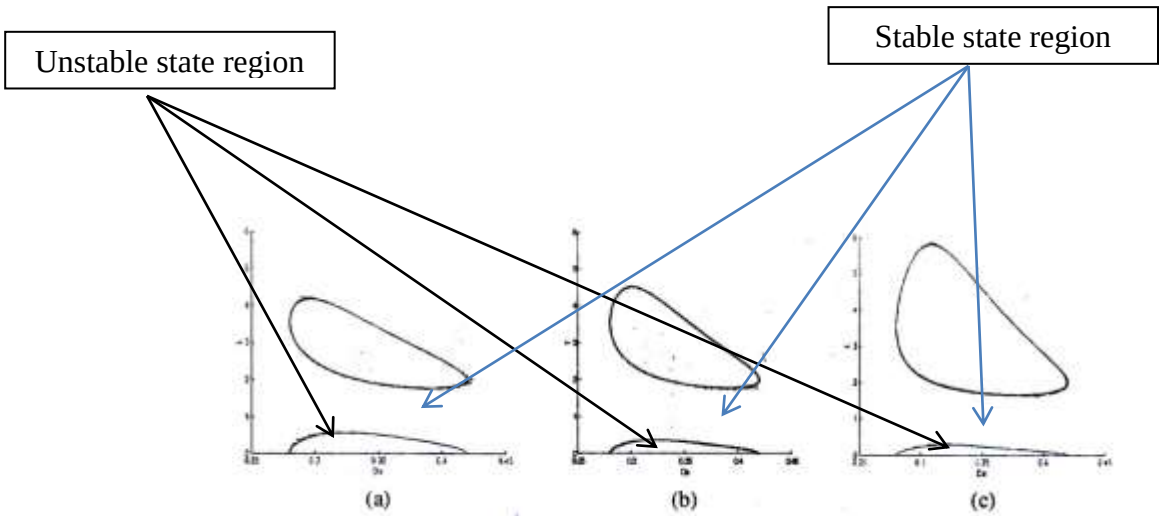


Figure 25 Dependency of critical delay on Da for large delay (τ=2)

Figure 25 a, b, c are set at three different values of recycle rate which are 25%, 50% and also 75% respectively. Inside the isola region, the system is dynamically unstable. It has been observed that there are two isola regions (unstable state region) for large delays, compared to small delays. Thus, as a result of large delay, the stability of the system switches from unstable state to stable state and vice-versa. As the recycle rate is increase from 25% to 75%, the region of isola also increases [3].

4.5 Comparison between Cubic Autocatalytic Reactions and First Order Monomolecular Irreversible Reaction

For steady state simulation, recycle ratio effect the behavior of the system in cubic autocatalytic reaction. As shown in Figure 2, as the recycle ratio increases, the conversion of the reactant decreases. The conversion of the reactant is high at 0.6 when the recycle ratio is in the range of 0 to 0.15. The conversion is at the lowest value which is 0.2 when the recycle ratio is in the range 0.35 to 0.8.

While in the first order reaction, recycle ratio does not affect the behavior of the system. Based on Figure 16 which is the bifurcation diagram for first order reaction, it is a function of conversion of reactant versus *Da*. The bifurcation analysis [3] shows that the system is dynamically unstable when the value of *Da* is in the range of 0.283 to 0.405.

The dynamic simulation performed for both reactions are dynamic simulation of ODE and also dynamic simulation of DDE. In dynamic simulation of ODE, delay is not present in the system. For cubic autocatalytic reactions, when there is no delay, the system is dynamically unstable. Figures 3-5 show that the system oscillates and have very high amplitude. Although the value of r is varied, the system still oscillates. Thus, in the absence of delay, the system is dynamically unstable for $0 \leq r \leq 1$.

Figures 17-19 show the simulation of ODE for first order irreversible reaction. In this case, value of *Da* is set at three different values, which are 0.283, 0.35 and also 0.4. The graphs show oscillation at these three values of *Da* thus indicating that, the system is dynamically unstable in the absence of delay.

For simulation of DDE, in cubic autocatalytic reactions, the value or *r* is fixed at 0.2 and the value of τ are varied at 5 different values which are 100, 500, 750, 1000 and 1080 and is shown in Figures 6-10 respectively. For this case, it has been observed that the amplitude of oscillation is reduced compared to Figures 3-5 as a result of delay. The system is still dynamically unstable as the system oscillates and is shown in the graphs. The author also observed that as the value of τ increases, the amplitude of oscillation also increases.

In the first order reaction, the value of *r* is fixed at 0.8 and the value of τ are varied at two different values which are $\tau = 0.2$ which represents the small delay and $\tau = 2$ which represent the large delay. Based on [3], the system changes from unstable state to stable state for small delay. The region of unstable state also disappears quickly as the value of recycle rate increases from 25% to 75%. For the value of large delay, the system switches from unstable state to stable state and vice versa. Figure 25 show that there are two unstable state regions in the graph of critical delay versus *Da*. The region of unstable state also increases when the recycle rate increases.

For cubic autocatalytic reactions, the author also did the simulation for large delay. In this case, the value of τ is set at 1080 and the values of recycle ratio are varied at 0.1, 0.15, 0.2, 0.25 and 0.3 and are shown in Figures 11-15 respectively. In this case, the system switches from unstable state to stable state as a result of large delay. The amplitude of oscillation decreases as the value of *r* increases. Finally, at *r*=0.3, the graph shows a horizontal line which indicates the system achieved its stable state.

CHAPTER 5

5 CONCLUSION

The effects of delay on the stability of recycle CSTR for cubic autocatalytic reactions have been studied by using the DDE 23 solver which available in MATLAB. In the absence of delay, the system is dynamically unstable for all values of recycle ratio. For the first order monomolecular irreversible reaction, the system is dynamically unstable for $0.283 \leq Da \leq 0.405$ in the absence of delay.

As a result for large delay in cubic autocatalytic reactions, the system switches from unstable state to stable state. As the value of recycle ratio increases, the amplitude of oscillation decreases and finally it shows a horizontal line. In first order irreversible reaction, the system switches from unstable state to stable state and vice versa as a result of large delay. The region of unstable state also increases as the value of recycle rate increases.

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