# CHAPTER 2

# MATHEMATICAL MODELING OF A CONTINUOUS STIRRED TANK REACTOR

## 2.1 INTRODUCTION

A Continuous Stirred Tank Reactor (CSTR) is one of the most important unit operations in chemical industries which exhibits highly nonlinear behavior and usually has wide operating ranges. Chemical reactions in a reactor are either exothermic or endothermic and require that energy can either be removed or added to the reactor to maintain a constant temperature. The CSTR is normally run at steady state and is usually operated so as to be quite well mixed. As a result of this quality, the CSTR is generally modeled as having no special variations in concentration, temperature or reaction rate throughout the vessel. Since the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank. Thus the temperature and concentration at the exit are modeled as being the same as those inside the reactor. In systems where mixing is highly nonideal, the well mixed model is inadequate. The following section presents the mathematical modeling of an ideal CSTR and nonideal CSTR.

## 2.2 PROCESS DESCRIPTION (IDEAL CSTR)

The first principles model of the continuous stirred tank reactor and the operating data (given in Table 2.1) as specified in the Pottman and Seborg

(1992) has been used in the simulation studies. Highly nonlinear CSTR is common in chemical and petrochemical plants. In the process considered for the simulation study as shown in Figure 2.1, an irreversible, exothermic chemical reaction $A \rightarrow B$ occurs in constant volume reactor that is cooled by a single coolant stream. A feed material of composition $C_{A0}$ enters the reactor at temperature $T_0$, at a constant volumetric flow rate q. Product is withdrawn from the reactor at the same volumetric flow rate q. The mixing is assumed to be efficient enough to guarantee homogeneity of the liquid content within the reactor.

In a jacketed CSTR the heat is added or removed by virtue of the difference between the jacket fluid and the reactor fluid. Often, the heat transfer fluid is pumped through the agitation nozzles that circulate the fluid through the jacket at a high velocity. The coolant flows at a flow rate of $q_c$ and at a feed temperature $T_{c0}$. The exit temperature of the coolant fluid is $T_c$.
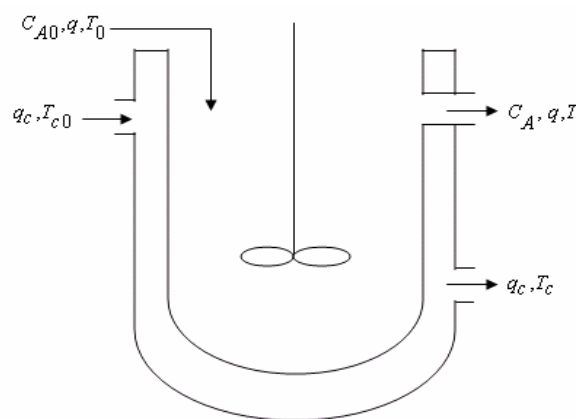


**Figure 2.1 Schematic diagram of a continuous stirred tank reactor**

## 2.3 MATHEMATICAL MODELING

The following assumptions are made to obtain the simplified modeling equations of an ideal CSTR:

a. Perfect mixing in the reactor and jacket

b. Constant volume reactor and jacket

The mathematical model for this process is formulated by carrying out mass and energy balances, and introducing appropriate constitutive equations.

**Reactor Mass Balance**

$$V\frac{dC_A}{dt}=q\left(C_{A0}-C_A\right)-Vr_A \tag{2.1}$$

where, $C_A$ is the product (effluent) concentration of component A in the reactor and $r_A$ is the rate of reaction per unit volume. The Arrhenius expression is normally used for the rate of reaction. A first order reaction results in the following expression

$$r_A=k_o\exp\left(\frac{-E}{RT}\right)C_A \tag{2.2}$$

where, $k_o$ is the reaction rate constant, E is the activation energy, R is the ideal gas constant and T is the reactor temperature on an absolute scale (R, Rankine or K, Kelvin).

**Reactor Energy Balance**

$$V\rho C_p\frac{dT}{dt}=q\rho C_p\left(T_0-T\right)-\left(-\Delta H\right)Vr_A+\rho_c C_{pc}q_c\left[1-\exp\left(\frac{-hA}{q_c\rho_c C_{pc}}\right)\right]\left(T_{c0}-T\right) \tag{2.3}$$

where, $(-\Delta H)$ is the heat of reaction, hA is the heat transfer coefficient, $T_0$ is the feed temperature and $T_{c0}$ is the inlet coolant temperature. From the

equations (2.1) to (2.3), the mass balance and energy balance equations of the CSTR are obtained as follows:

$$\frac{dC_A}{dt} = \frac{q}{V}\left(C_{A0} - C_A\right) - k_o C_A \exp\left(\frac{-E}{RT}\right)$$
(2.4)

$$\frac{dT}{dt} = \frac{q}{V}\left(T_0 - T\right) - \left(\frac{-\Delta H}{\rho C_p}\right) k_o C_A \exp\left(\frac{-E}{RT}\right) + \left(\frac{\rho_c C_{pc}}{\rho C_p V}\right) q_c \left[1 - \exp\left(\frac{-hA}{q_c \rho_c C_{pc}}\right)\right] \left(T_{c0} - T\right)$$
(2.5)

The modeling equations of the CSTR such as equations (2.4) and (2.5) contain nonlinear functions of $T$ and $C_A$. They are coupled and it is not possible to solve one equation independently of the other. For designing the controllers for such a nonlinear process, one of the approaches is to represent the nonlinear system as a family of local linear models. In the following section, state variable models pertaining to the nonlinear equations are derived.

### 2.3.1 State Variable Form of the Equations

Equations (2.4) and (2.5) are represented in the standard state variable form as

$$\frac{dC_A}{dt} = f_1\left(C_A, T\right) = \frac{q}{V}\left(C_{A0} - C_A\right) - k_o C_A \exp\left(\frac{-E}{RT}\right)$$
(2.6)

$$\frac{dT}{dt} = f_2\left(C_A, T\right) = \frac{q}{V}\left(T_0 - T\right) - \left(\frac{-\Delta H}{\rho C_p}\right) k_o C_A \exp\left(\frac{-E}{RT}\right)$$

$$+ \left(\frac{\rho_c C_{pc}}{\rho C_p V}\right) q_c \left[1 - \exp\left(\frac{-hA}{q_c \rho_c C_{pc}}\right)\right] \left(T_{c0} - T\right)$$
(2.7)

## 2.3.2 Linearization

The nonlinear equations are linearized and cast into the state variable form as follows:

$$\dot{\tilde{x}} = A\tilde{x} + B\tilde{u} \tag{2.8}$$

$$\tilde{y} = C\tilde{x} \tag{2.9}$$

where matrices A and B represent the Jacobian matrices corresponding to the nominal values of the state variables and input variables and $\tilde{x}, \tilde{u}$ and $\tilde{y}$ represent the deviation variables. The output matrix is represented as C.

$$\tilde{x} = \begin{bmatrix} \tilde{x}_1 \\ \tilde{x}_2 \end{bmatrix} = \begin{bmatrix} C_A - C_{As} \\ T - T_s \end{bmatrix} \tag{2.10}$$

$$\tilde{y} = \begin{bmatrix} C_A - C_{As} \\ T - T_s \end{bmatrix} \tag{2.11}$$

$$\tilde{u} = \begin{bmatrix} \tilde{u}_1 \\ \tilde{u}_2 \end{bmatrix} = \begin{bmatrix} q - q_s \\ q_c - q_{cs} \end{bmatrix} \tag{2.12}$$

where $C_{As}$, $T_s$, $q_s$, $q_{cs}$ are the steady state values of effluent concentration, reactor temperature, feed flow rate and coolant flow rate respectively.

The Jacobian matrix A is given as,

$$A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} = \begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} \end{bmatrix} \tag{2.13}$$

where

$$A_{11} = -\frac{q}{V} - K_s \qquad (2.14)$$

$$A_{12} = -C_{As}K_s' \qquad (2.15)$$

$$A_{21} = -\left(\frac{\Delta H}{\rho C_p}\right)K_s \qquad (2.16)$$

$$A_{22} = \left(-\frac{q}{V}\right) + \left(\frac{(-\Delta H)C_{As}}{\rho C_p}\right)K_s' + \left(\frac{-\rho_c C_{pc}}{\rho C_p V}\right)q_c + \left(\frac{\rho_c C_{pc}}{\rho C_p V}\right)q_c \exp\left(\frac{-hA}{q_c \rho C_p}\right) \qquad (2.17)$$

where

$$K_s = K_o \exp\left(-\frac{E}{RT_s}\right) \qquad (2.18)$$

$$K_s' = K_o \exp\left(-\frac{E}{RT_s}\right)\left(\frac{E}{RT_s^2}\right) \qquad (2.19)$$

The Jacobian matrix B is given by

$$B = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} = \begin{bmatrix} \dfrac{\partial f_1}{\partial u_1} & \dfrac{\partial f_1}{\partial u_2} \\ \dfrac{\partial f_2}{\partial u_1} & \dfrac{\partial f_2}{\partial u_2} \end{bmatrix} \qquad (2.20)$$

where

$$B_{11} = \frac{(C_{A0} - C_{As})}{V} \qquad (2.21)$$

$$B_{12} = 0 \qquad (2.22)$$

$$B_{21} = \frac{\left(T_0 - T_s\right)}{V} \tag{2.23}$$

$$B_{22} = \frac{\rho_c C_{pc}}{\rho C_p V}\left(T_{c0} - T_s\right)\left\{q_c\left[-\exp\left(\frac{-hA}{q_c \rho_c C_{pc}}\right)\left(\frac{hA}{q_c{}^2 \rho_c C_{pc}}\right)\right] + \left[1 - \exp\left(\frac{-hA}{q_c \rho_c C_{pc}}\right)\right]\right\} \tag{2.24}$$

The output matrix C is given by

$$C = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \tag{2.25}$$

The Steady state operating data are provided in Table 2.1.

**Table 2.1  Steady state operating data**

| Sl. No. | Parameters | Symbols | Values |
|---------|------------|---------|--------|
| 1. | Product concentration | $C_A$ | 0.0882 mol/l |
| 2. | Reactor temperature | T | 441.2 K |
| 3. | Coolant flow rate | $q_c$ | 100 l/min |
| 4. | Feed flow rate | q | 100 l/min |
| 5. | Feed concentration | $C_{A0}$ | 1 mol/l |
| 6. | Feed temperature | $T_0$ | 350 K |
| 7. | Inlet coolant temperature | $T_{c0}$ | 350 K |
| 8. | CSTR volume | V | 100 l |
| 9. | Heat transfer term | hA | $7 \times 10^5$ cal/(min K) |
| 10. | Reaction rate constant | $k_o$ | $7.2 \times 10^{10}$ min$^{-1}$ |
| 11. | Activation energy term | $\dfrac{E}{R}$ | $1 \times 10^4$ K |
| 12. | Heat of reaction | $-\Delta H$ | $-2 \times 10^5$ cal/mol |
| 13. | Liquid densities | $\rho, \rho_c$ | $1 \times 10^3$ g/l |
| 14. | Specific heat | $C_p, C_{pc}$ | 1 cal/(g K) |

The nonlinear CSTR has been linearized at three operating points using the data given in Table 2.1. The operating points for the linear models are presented in Table 2.2. The eigen values, damping factor obtained at the respective operating points are presented in Table 2.3, from which it can be inferred that the process is stable at all the operating points as the eigen values have negative real parts.

**Table 2.2  Steady state operating points for the ideal CSTR**

| Operating point | Feed Flow (l/min) | Coolant Flow (l/min) | Conc (mol/l) | Temp (K) |
|---|---|---|---|---|
| 1 | 103 | 97 | 0.0748 | 445.3 |
| 2 | 100 | 100 | 0.0882 | 441.2 |
| 3 | 97 | 103 | 0.1055 | 436.8 |

**Table 2.3  Eigen values at the three operating points of the ideal CSTR**

| Operating point | Eigen value | Damping factor |
|---|---|---|
| 1 | -3.08±2.85i | 0.733 |
| 2 | -1.98±3.06i | 0.544 |
| 3 | -1.05±2.91i | 0.340 |

The mathematical modeling of the CSTR considering nonideal mixing due to dead space and bypass are discussed in the following section.

## 2.4    PROCESS DESCRIPTION (Nonideal CSTR)

Most of the reactors dealt with in the literature for control purposes are perfectly mixed CSTRs and have been modeled as ideal CSTRs. Unfortunately, in the real world, the behaviour of the real CSTR is very different from that of an ideal CSTR. For an ideal CSTR, it is assumed that

the reactor is well-mixed, meaning that the concentration at different positions of the CSTR are identical throughout the reactor. On the contrary, the mixing in the nonideal CSTR is not uniform, resulting in bypassing and stagnant regions (dead space). In the dead space the fluid does not enter and hence, there is less reactor volume than in the case of perfect operation. Hence, the fluid will pass through the reactor more quickly and as a result the transients in the concentration will decay more rapidly than in the case of perfect operation. Due to bypassing, the flow passing through the reactor will be less than the total volumetric flow rate and as a result; there will be slower decay of the transients in the concentration response than in the case of perfect operation.

### 2.4.1    Nonideal CSTR Modeled Using Bypass and Dead Space

The nonideal CSTR is believed to be modeled as a combination of an ideal CSTR of volume $V_S$, a dead space of volume $V_d$ and a bypass with a volumetric flow rate $q_b$. The diagrammatic representation of the nonideal CSTR and the model as a combination of ideal CSTR with dead space and bypass are shown in Figure 2.2.
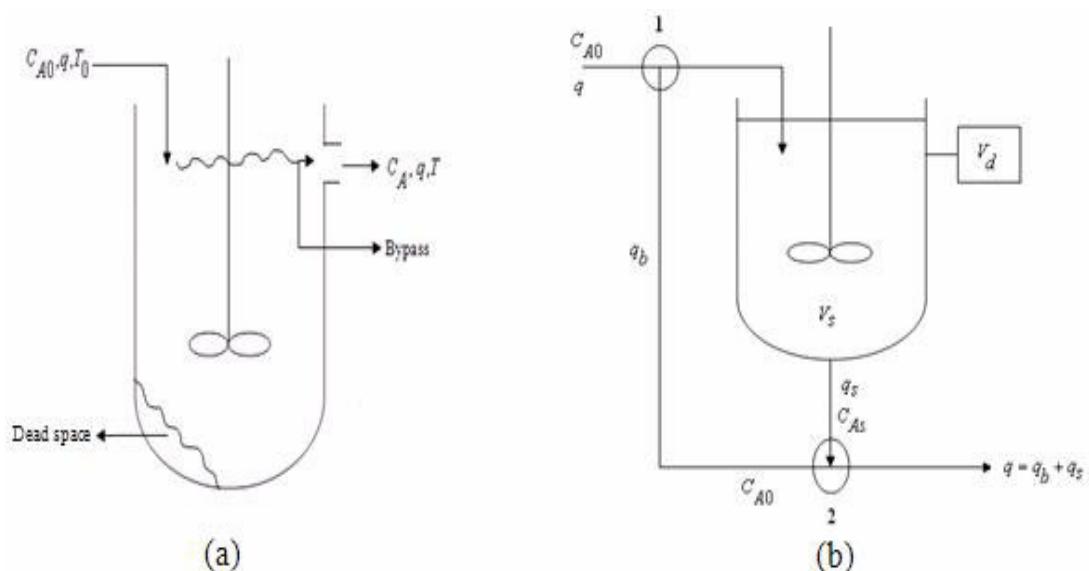
**Figure 2.2  Nonideal CSTR (a) Real system; (b) Model system**

### 2.4.1.1    Bypassing

The space time is calculated as $\tau_{st} = \dfrac{V}{q}$ where, V is the volume of the reactor and q is the total volumetric flow rate. A volumetric flow rate $q_b$ bypasses the reactor while a volumetric flow rate $q_s$ enters the system volume and $q = q_s + q_b$. The reactor system volume $V_s$ is the well mixed portion of the reactor, and the volumetric flow rate entering the system volume is $q_s$. The space time corresponding to the volume $V_s$ and flow rate $q_s$ is calculated as $\tau_s = \dfrac{V_s}{q_s}$. Because some of the fluid bypasses, the flow passing through the system will be less than the total volumetric rate, $q_s < q$ and consequently $\tau_s > \tau_{st}$ resulting in the slow decay of the transient associated with the product concentration $C_A(t)$ than in the case of perfect operation.

### 2.4.1.2    Dead volume (Dead Space)

The total volume of the reactor is $V = V_d + V_s$. As there is a dead volume $V_d$ in which fluid does not enter, there is a less system volume $V_s$ than in the case of perfect operation, $V_s < V$. Consequently the fluid will pass through the reactor with dead volume more quickly than in the case of perfect operation. As a result, the transient associated with the product concentration $C_A(t)$ will decay more rapidly than in the case of perfect operation because there is smaller system volume.

### 2.4.1.3    Solving the model system for $C_A$

Consider the first order reaction $A \rightarrow B$ the bypass stream and the effluent stream are mixed at point 2 in Figure 2.2 (b). From a balance on species A around this point, there results

$$\left[ C_{A0} q_b + C_{As} q_s \right] = \left[ C_A \left( q_b + q_s \right) \right] \tag{2.26}$$

Solving for the concentration of A leaving the reactor,

$$C_A = \frac{q_b C_{A0} + C_{As} q_s}{q_b + q_s} = \frac{q_b C_{A0} + C_{As} q_s}{q}$$

(2.27)

Let $\alpha = \dfrac{V_s}{V}$ and $\beta = \dfrac{q_b}{q}$, Then

$$C_A = \beta C_{A0} + (1-\beta) C_{As}$$

(2.28)

For a first order reaction, a mole balance on $V_s$ gives

$$q_s C_{A0} - q_s C_{As} - K_s C_{As} V_s = 0$$

(2.29)

In terms of $\alpha$ and $\beta$,

$$C_{As} = \frac{C_{A0}(1-\beta)q}{(1-\beta)q + \alpha V K_s}$$

(2.30)

Substituting equations (2.30) into (2.28)   gives the concentration of species A,

$$\frac{C_A}{C_{A0}} = \beta + \frac{(1-\beta)^2}{(1-\beta) + \alpha \tau_{st} K_s}$$

(2.31)

The mass balance of the CSTR as given in equation (2.1), can be modified considering nonideal mixing due to dead space and bypass and is given below:

$$V_s \frac{dC_A}{dt} = q C_{A0} - q C_A - V_s k_o C_{As} \exp\left(\frac{-E}{RT_s}\right)$$

(2.32)

$$\frac{dC_A}{dt} = \frac{q}{V_s}\left(C_{A0}-C_A\right) - k_o C_{As} \exp\left(\frac{-E}{RT_s}\right)$$ (2.33)

Substituting the values of $V_s$, $C_{As}$ and $T_s$ in terms of $\alpha$ and $\beta$ in equation (2.33) gives,

$$\frac{dC_A}{dt} = \frac{q}{\alpha V}\left(C_{A0}-C_A\right) - k_o \exp\left(\frac{-E}{R\left(\frac{T-\beta T_0}{1-\beta}\right)}\right)\left(\frac{C_A-\beta C_{A0}}{1-\beta}\right)$$ (2.34)

$$\frac{dC_A}{dt} = \frac{q}{\alpha V}\left(C_{A0}-C_A\right) - k_o \exp\left(\frac{-E(1-\beta)}{R\left(T-\beta T_0\right)}\right)\left(\frac{C_A-\beta C_{A0}}{1-\beta}\right)$$ (2.35)

The effluent concentration is found by solving the equation (2.35).

The energy balance equation of the CSTR considering the dead space and bypass is given below:

$$V\frac{dT}{dt} = qT_0 - qT - V_s\left(\frac{-\Delta H}{\rho C_p}\right)k_o C_{As}\exp\left(\frac{-E}{RT_s}\right)$$

$$+ \left(\frac{\rho_c C_{pc}}{\rho C_p}\right)q_c\left[1-\exp\left(\frac{-hA}{q_c\rho_c C_{pc}}\right)\right]\left(T_{c0}-T\right)$$ (2.36)

$$\frac{dT}{dt} = \frac{q}{V}\left(T_0-T\right) - \frac{V_s}{V}\left(\frac{-\Delta H}{\rho C_p}\right)k_o C_{As}\exp\left(\frac{-E}{RT_s}\right)$$

$$+ \left(\frac{\rho_c C_{pc}}{\rho C_p V}\right)q_c\left[1-\exp\left(\frac{-hA}{q_c\rho_c C_{pc}}\right)\right]\left(T_{c0}-T\right)$$ (2.37)

Substituting the values of $V_s$, $C_{As}$ and $T_s$ in terms of $\alpha$ and $\beta$ in equation (2.37) gives,

$$\frac{dT}{dt} = \frac{q}{V}(T_0\text{-}T) - \alpha\left(\frac{-\Delta H}{\rho C_p}\right) k_o \exp\left(\frac{-E(1\text{-}\beta)}{R(T\text{-}\beta T_0)}\right)\left(\frac{C_A\text{-}\beta C_{A0}}{1\text{-}\beta}\right)$$

$$+\left(\frac{\rho_c C_{pc}}{\rho C_p V}\right)q_c\left[1\text{-}\exp\left(\frac{-hA}{q_c\rho_c C_{pc}}\right)\right](T_{c0}\text{-}T) \qquad (2.38)$$

The reactor temperature at any operating point is obtained from equation (2.38).

The state space model of the nonideal reactor can be obtained as follows:

$$\frac{dC_A}{dt} = f_1(x_1, x_2) = \frac{q}{\alpha V}(C_{A0}\text{-}C_A) - k_o\exp\left(\frac{-E(1\text{-}\beta)}{R(T\text{-}\beta T_0)}\right)\left(\frac{C_A\text{-}\beta C_{A0}}{1\text{-}\beta}\right) \qquad (2.39)$$

$$\frac{dT}{dt} = f_2(x_1, x_2) = \frac{q}{V}(T_0\text{-}T) - \alpha\left(\frac{-\Delta H}{\rho C_p}\right) k_o\exp\left(\frac{-E(1\text{-}\beta)}{R(T\text{-}\beta T_0)}\right)\left(\frac{C_A\text{-}\beta C_{A0}}{1\text{-}\beta}\right)$$

$$+\left(\frac{\rho_c C_{pc}}{\rho C_p V}\right)q_c\left[1\text{-}\exp\left(\frac{-hA}{q_c\rho_c C_{pc}}\right)\right](T_{c0}\text{-}T) \qquad (2.40)$$

The state space models of the nonideal CSTR can be obtained using the equations (2.39) and (2.40).

The nonideal CSTR has been linearized around three operating regions for two cases.

(a) Considering bypass alone ($\beta$=0.2) and no dead space ($\alpha$=1) (Case-1)

(b) Considering the presence of both bypass (β=0.2) and dead space (α=0.8) (Case-2)

The operating points for the local linear models of the nonideal CSTR for both the cases are presented in Tables 2.4 and 2.5.

**Table 2.4  Steady state operating points for case-1**

**α=1,β=0.2**

| Operating point | Feed flow (l/min) | Coolant flow (l/min) | Effluent Conc (mol/l) | Reactor Temp (K) |
|---|---|---|---|---|
| 1 | 103 | 97 | 0.2442 | 427.9 |
| 2 | 100 | 100 | 0.2512 | 424.9 |
| 3 | 97 | 103 | 0.2598 | 421.8 |

**Table 2.5  Steady state operating points for case-2**

**α=0.8,β=0.2**

| Operating point | Feed flow (l/min) | Coolant flow (l/min) | Effluent Conc (mol/l) | Reactor Temp (K) |
|---|---|---|---|---|
| 1 | 103 | 97 | 0.2598 | 426.3 |
| 2 | 100 | 100 | 0.2706 | 423 |
| 3 | 97 | 103 | 0.2844 | 419.5 |

## 2.5    CONCLUSION

In this section, the first principles model of an exothermic CSTR with a first order chemical reaction is considered for simulation studies. The mathematical model of the CSTR is formulated assuming a constant reactor volume and perfect mixing in the reactor. The inputs to the reactor are the

feed flow and coolant flow. The states are the effluent concentration and the reactor temperature. The outputs are the states. For the design of multivariable controllers, the nonlinear CSTR is represented as a family of local linear models at the three chosen operating points. The mathematical model of the nonideal CSTR is obtained by considering the nonideal mixing due to bypass and dead space. The operating points of the nonideal CSTR are obtained for two cases namely, (1) considering only the bypass and (2) considering both the dead space and the bypass. The local linear models of the nonideal CSTR are obtained for both the cases at the chosen operating points. In the following Chapter, the multivariable control of an ideal CSTR using decentralized and decoupled control schemes using conventional techniques is to be discussed.