# CHAPTER 6

# MODELING OF THE ACETYLENE HYDROGENATION PROCESS

## 6.1 Introduction

In this chapter, the modeling of the acetylene hydrogenation reactors is presented. The first part is the step for finding the suitable structure of model of an acetylene hydrogenation process that was described in the chapter 5. The process is comprised of three fixed-bed reactors, pre-heated system, and two inter-cooler systems. The developed model is the semiempirical model. The kinetic background of an acetylene hydrogenation process is used to develop the kinetic model for all reactions that occur in the reactors. The actual data from the industrial plant is used to find out the rate constant parameter values and used to check the performance and accuracy of the model.

## 6.2 Dynamic model equations

The mathematical model of an acetylene hydrogenation process is derived from the set of physical and chemical equations of the process such as: material and energy balance equations, reaction rate equations, and catalyst activity equations. The set of equations can be separated in three sections as follow

### 6.2.1 Reactors model

A catalytic fixed-bed adiabatic reactor can be approximated by a series of continuous stirred tank reactors ( CSTR ) system as Figure 6.1. Due to the structure and performance of the N series of CSTRs stay between the ideal plug flow reactor and the ideal CSTR, and the real industrial reactor is not an ideal reactor, thus, the structure of the model that suitable is pointed out in the N series of CSTRs structure.
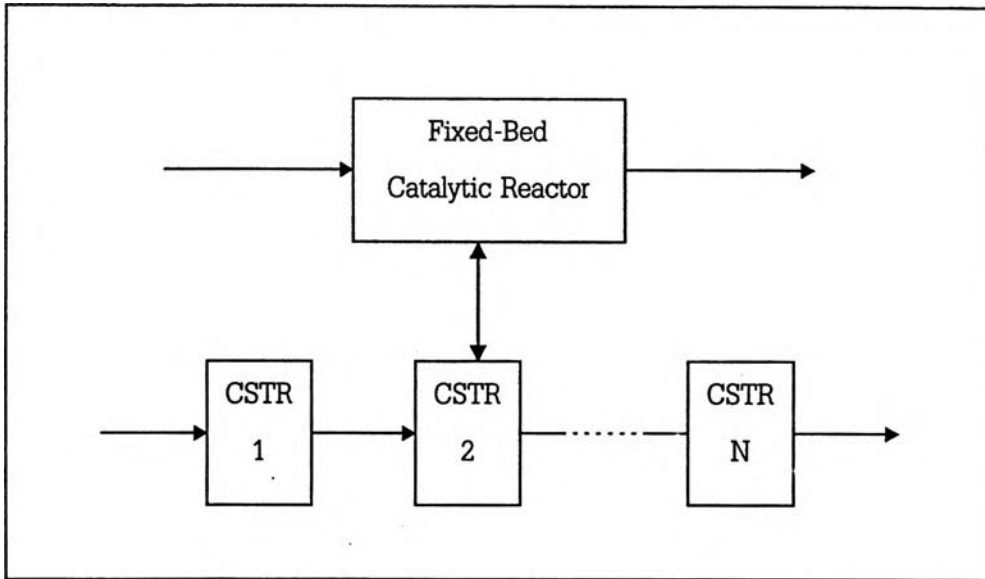
**Figure 6.1** Similar-comparing between fixed-bed catalytic reactor

and N number of CSTRs

The material and energy balances of the process can be derived from the material and energy balances equations of CSTR and can be given by the following equations :

a). Material balances : for i = 1, 2, ..., N, j = i-1

I. $C_2H_2$ mole balance :

$$Vr\frac{dC_{Ac\,i}}{dt} = F_j C_{Ac\,j} - F_i C_{Ac\,i} - R_{Ac_i} Vr \qquad (6.1)$$

II. $C_2H_4$ mole balance :

$$Vr\frac{dC_{Eth\,i}}{dt} = F_j C_{Eth\,j} - F_i C_{Eth\,i} + (R_{Ac_i} - R_{Eth_i}) Vr \qquad (6.2)$$

III. MA mole balance :

$$Vr\frac{dC_{MA\,i}}{dt} = F_j C_{MA\,j} - F_i C_{MA\,i} - R_{MA_i} Vr \qquad (6.3)$$

IV. PD mole balance :

$$Vr\frac{dC_{PD\,i}}{dt} = F_j C_{PD\,j} - F_i C_{PD\,i} - R_{PD_i} Vr \qquad (6.4)$$

V. $H_2$ mole balance :

$$Vr\frac{dC_{H2\,i}}{dt} = F_j C_{H2\,j} - F_i C_{H2\,i} - (R_{Ac_i} + R_{Eth_i} + R_{MA_i} + R_{PD_i}) Vr \qquad (6.5)$$

VI.   CO mole balance :

$$Vr\frac{dC_{CO_i}}{dt} = F_j C_{CO_j} - F_i C_{CO_i} - R_{CO_i} Vr \tag{6.6}$$

VII.   $C_2H_6$ mole balance :

$$Vr\frac{dC_{Ei}}{dt} = F_j C_{Ej} - F_i C_{Ei} + R_{Eth_i} Vr \tag{6.7}$$

VIII.   $C_3H_6$ mole balance :

$$Vr\frac{dC_{Pri}}{dt} = F_j C_{Prj} - F_i C_{Pri} + (R_{MA_i} + R_{PD_i})Vr \tag{6.8}$$

IX.   $CH_4$ mole balance :

$$Vr\frac{dC_{Mei}}{dt} = F_j C_{Mej} - F_i C_{Mei} \tag{6.9}$$

X.   BD and others mole balance :

$$Vr\frac{dC_{BDi}}{dt} = F_j C_{BDj} - F_i C_{BDi} \tag{6.10}$$

b). Energy balances : for i = 1, 2, ..., N, j = i-1

$$M_i C_m \frac{dT_i}{dt} = D_j F_j Cp_j T_j - D_i F_i Cp_i T_i$$
$$+ (R_{Ac_i} Hr_{Ac} + R_{Eth_i} Hr_{Eth} + R_{MA_i} Hr_{MA} + R_{PD_i} Hr_{PD})Vr - Q \tag{6.11}$$

Where

   i    = i th stage

   $F_i$   = outlet volumetric flow rate of the feed at i th stage, $M^3$/hr

   $C_{Ac}$ = acetylene concentration, mol/$M^3$

   $C_{Eth}$ = ethylene concentration, mol/$M^3$

   $C_{H2}$ = hydrogen concentration, mol/$M^3$

   $C_{MA}$ = methyl acetylene concentration, mol/$M^3$

   $C_{PD}$ = propadiene concentration, mol/$M^3$

   $C_{CO}$ = carbonmonoxide concentration, mol/$M^3$

   $C_E$  = ethane concentration, mol/$M^3$

   $C_{Pr}$ = propylene concentration, mol/$M^3$

   $C_{Me}$ = methane concentration, mol/$M^3$

$C_{BD}$ = butadiene concentration, mol/M$^3$

$Vr$ = volume of one CSTR stage, M$^3$

$R_{Ac}$ = rate of acetylene hydrogenation

$R_{Eth}$ = rate of ethylene hydrogenation

$R_{MA}$ = rate of methyl acetylene hydrogenation

$R_{PD}$ = rate of propadiene hydrogenation

$R_{CO}$ = adsorption rate of carbonmonoxide

$T$ = temperature

$Hr_{Ac}$ = heat of acetylene hydrogenation

$Hr_{Eth}$ = heat of ethylene hydrogenation

$Hr_{MA}$ = heat of methyl acetylene hydrogenation

$Hr_{PD}$ = heat of propadiene hydrogenation

$M_i$ = mass of reacting system at i th stage including catalyst

$Cp$ = heat capacity of feed stream

$C_m$ = heat capacity of the reacting system including catalyst

$D$ = fluid density

$Q_i$ = heat loss at i[th] stage

First set of the reaction rate equations are obtained form the kinetic models that is presented in the Dynamics and Control of Industrial Front-End Acetylene converter paper (Schbib *et. al.*, 1994) as the following :

c). Reaction rate equation

Acetylene(Ac) hydrogenation reaction

$$Rate_{Ac} = k_{Ac}C_{Ac}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3 \qquad (6.12)$$

Ethylene(Eth) hydrogenation reaction

$$Rate_{Eth} = k_{Eth}C_{Eth}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3 \qquad (6.13)$$

Methyl acetylene(MA) hydrogenation reaction

$$Rate_{MA} = k_{MA}C_{MA}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3 \qquad (6.14)$$

Propadiene(PD) hydrogenation reaction

$$Rate_{PD} = k_{PD}C_{PD}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3 \qquad (6.15)$$

Carbonmonoxide adsorption rate equation(physical adsorption)

$$Rate_{CO} = k_{CO}C_{CO}$$ (6.16)

Where

$K_{Ac}$ = adsorption equilibrium constant of acetylene

$K_{Eth}$ = adsorption equilibrium constant of ethylene

$K_{H2}$ = adsorption equilibrium constant of hydrogen

$K_{CO}$ = adsorption equilibrium constant of carbonmonoxide

$k$ = reaction rate constant

$C_{Ac}$ = acetylene concentration

$C_{Eth}$ = ethylene concentration

$C_{H2}$ = hydrogen concentration

$C_{MA}$ = methyl acetylene concentration

$C_{Pd}$ = propadiene concentration

**Table 6.1** Equilibrium constant values for the rate equation(Schbib et. al., 1996)

(form Kinetics of Front-End Acetylene Hydrogenation in Ethylene Production)

| $K$ (m$^3$/kmol) | log($A$) | $E$ (kcal/gmol) |
|---|---|---|
| $K_{H2}$ | 20.2 | 21.22 |
| $K_{CO}$ | 13.6 | 9.95 |
| $K_{eth}$ | 0.26 | 0.005 |
| $K_{ac}$ | -16 | 0.001 |

Where

$A$ = pre-exponential factor in Arrhenius expression

$E$ = activation energy in Arrhenius expression

Reaction rate constant equation

$$k = f(T, \theta)$$

arrhenius expression :

$$k = \theta * A * EXP(-E/RT)$$ (6.17)

Where

$\theta$   = catalyst activity

$T$   = temperature

$R$   = gas constant

The catalyst activity can be written as :

$\theta$   = $\dfrac{\text{(present conversion rate of the reactants)}}{\text{(conversion rate of the reactants with fresh catalyst)}}$   (6.18)

$\theta$   = $x_j / x_{Fj}$     ; $j = Ac$     (6.19)

$\theta$   = $1/[1+K_{deac}\Sigma(green\ oil)]$     (6.20)

Note :   The green oil is the polymer specie of acetylene and it is the catalyst poison. The amount of the generated green oil is relatively with the amount of the inlet acetylene. Thus, $\Sigma$(green oil) can instead by $\Sigma$(acetylene) (Michael *et. al.*, 1991)

$\therefore$     $\theta$   = $1/[1+K_{deac}\Sigma(acetylene)]$     (6.21)

Note :   catalyst deactivition phenomenon occursonly on the sites responsible for the hydrogenation of acetylene (Michael *et. al.*, 1991)

such that the rate equations can be rewritten as :

Acetylene(Ac) hydrogenation reaction

$Rate_{Ac} = \theta A_{Ac}EXP(-E_{Ac}/RT)C_{Ac}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3$     (6.22)

Ethylene(Eth) hydrogenation reaction

$Rate_{Eth} = A_{Eth}EXP(-E_{Eth}/RT)C_{Eth}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3$     (6.23)

Methyl acetylene(MA) hydrogenation reaction

$Rate_{MA} = A_{MA}EXP(-E_{MA}/RT)C_{MA}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3$     (6.24)

Propadiene(PD) hydrogenation reaction

$Rate_{PD} = A_{PD}Exp(-E_{PD}/RT)C_{PD}C_{H2}/(1+(K_{H2}C_{H2})^{0.5}+K_{CO}C_{CO}+K_{Ac}C_{Ac}+K_{Eth}C_{Eth})^3$     (6.25)

### 6.2.2 Shell and tube heat exchanger model

A type of heat exchanger used in this model is that of the shell and tube arrangement. One fluid flow on the inside of the tubes, while the other fluid is forced through the shell and over the outside of the tubes.

The heat transfer equation is

$$Q = U * Area * \left( \frac{\left( \left( Tin_h - Tout_c \right) - \left( Tout_h - Tin_c \right) \right)}{\ln \left( \left( Tin_h - Tout_c \right) / \left( Tout_h - Tin_c \right) \right)} \right) \qquad (6.26)$$

The energy balance equation are

for hot stream :

$$V_h * D_h *(Cp_{ave})_h * \frac{dTout_h}{dt} = M_h *(Cp_{ave})_h *(Tin_h - Tout_h) - Q \qquad (6.27)$$

for cool stream :

$$V_c * D_c *(Cp_{ave})_c * \frac{dTout_c}{dt} = M_c *(Cp_{ave})_c *(Tin_c - Tout_c) + Q \qquad (6.28)$$

### 6.3 Stages of CSTR system

In this section, how to obtain the suitable series of CSTRs that used to approximate the fixed-bed reactor is described. The first kinetic model that is described by equations (6.12), (6.13), (6.14), and (6.15) as the reaction rate equations is used to find out the best value of N. Before to do that, the four reaction rate constant values are estimated though the actual plant data about thirty points (3 Feb 97 - 4 Mar 97) that is completely reconciled.

The estimation program is written on SPEEDUP in estimation mode. The program estimates the rate constant values by minimizing the errors between the predicted output and the actual data by adjusts the value of the rate constants of the five reaction rate equations in the dynamic run. The objective function of the estimation program can be written as

$$Min_{k} \sum_{i=1}^{NDYN} \sum_{j=1}^{NT_i} \sum_{l=1}^{NM_{lj}} w_{lji}^2 \left( z_i^{(l)}(t_{lj}) - \hat{z}_{lji} \right)^2 + \sum_{l=1}^{NSS} \sum_{i=1}^{NM_l} w_{li}^2 \left( z_i^{(l)} - \hat{z}_{li} \right)^2 \quad (6.29)$$

where

|        |                                                          |
|--------|----------------------------------------------------------|
| $z$    | = the actual output data                                 |
| $\hat{z}$ | = the predicted output                                |
| NDYN   | = the number of the dynamic run                          |
| NSS    | = the number of the steady state run                     |
| NT     | = the number of the time step of the actual input-output data |
| NM     | = the number of the output variables                     |
| $w$    | = the weight fraction                                    |

The input data of the program is the actual data from the industrial plant as follow

-All input and output components concentration

-The inlet and outlet temperature

-Total mass flow and molecular weight

-Pressure

The results of the estimated values are shown in Table 6.2 .

**Table 6.2** Reaction rate constants for Ac, Eth, MA and PD

hydrogenation reaction rate equations.

| Rate constant | value |
|---------------|-------|
| $k_{Ac}$ | 8.06761E14 |
| $k_{Eth}$ | 4.92318E13 |
| $k_{MA}$ | 8.37989E14 |
| $k_{PD}$ | 1.86762E18 |

Then the proper number of CSTR system can be found by simulate this model with the different number of CSRT (N). The N versus in five levels as N = 8, 12, 16, 20, and 24 stages. The results of the simulations are compared with the actual data. The important variables that are used to consider for the best value of N are the temperature profile of each bed, the outlet acetylene concentration of each bed, and the computation time.

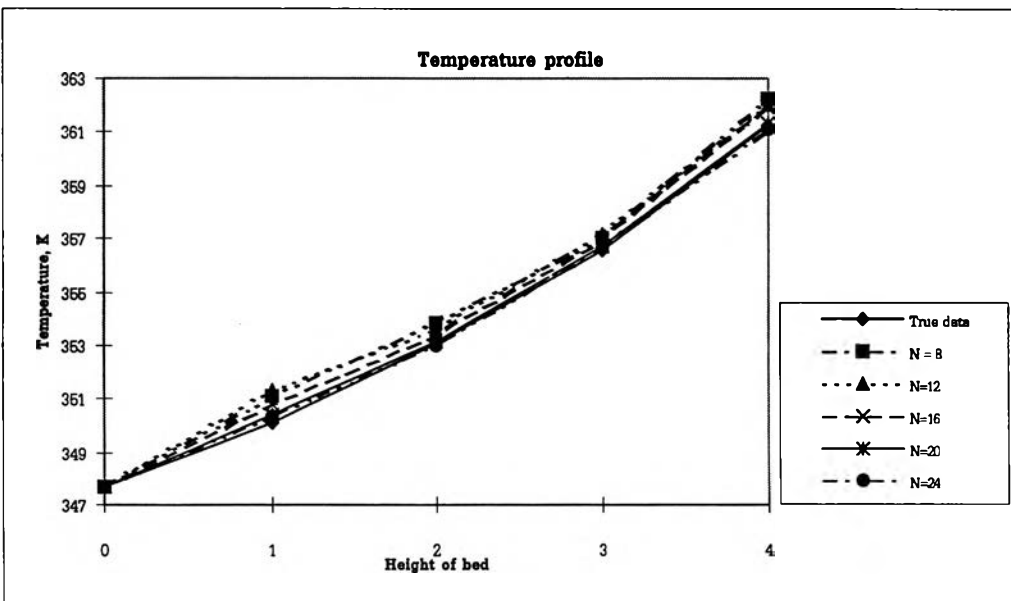**Table 6.3** Calculation time for solving the simulation program.

| N stages of CSTR | Time (cp seconds) |
|:---:|:---:|
| N=8 | 5.07 |
| N=12 | 8.34 |
| N=16 | 13.9 |
| N=20 | 23.35 |
| N=24 | 39.41 |
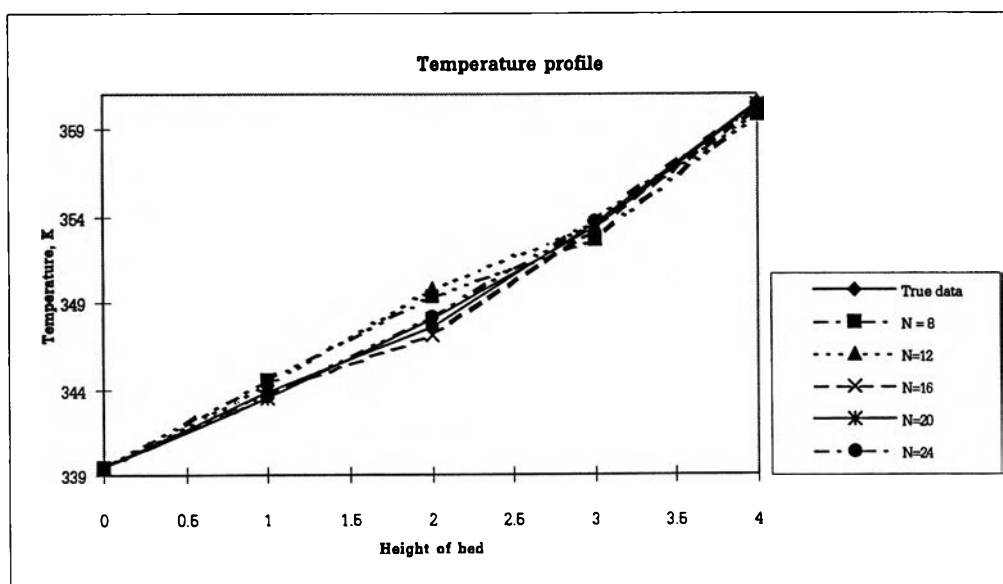


**Figure 6.2** Temperature profile in the reactor I that compose with N=8, N=12, N=16, N=20 and N=24 stages of CSTR.
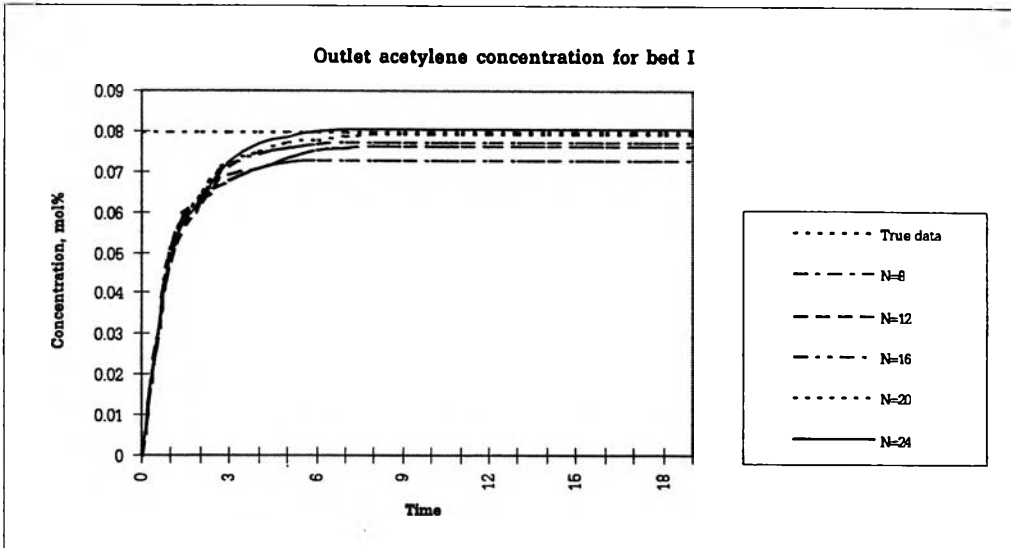
**Figure 6.3** Outlet acetylene concentration for the reactor I that compose with

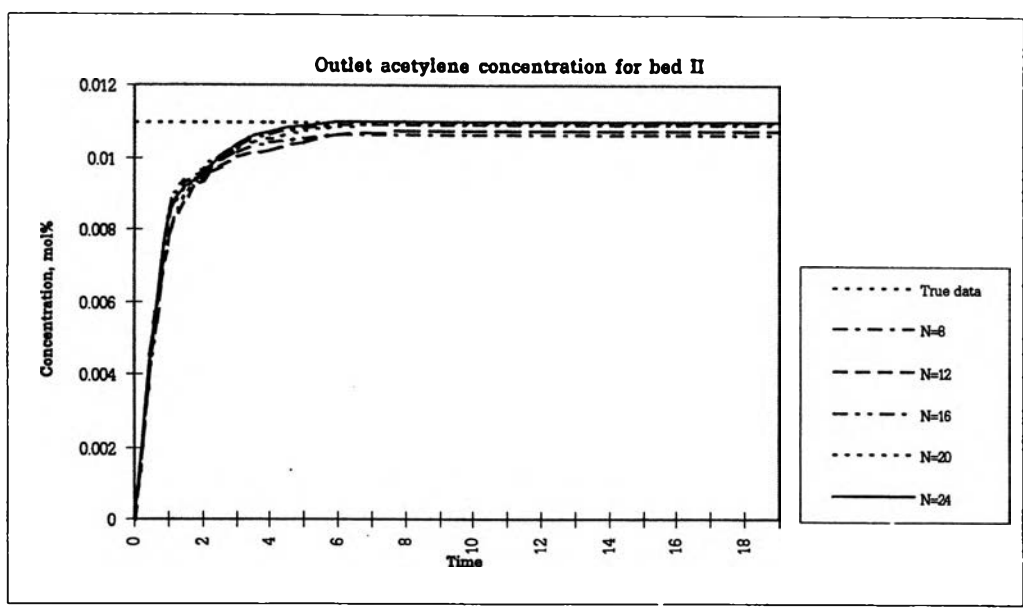N=8, N=12, N=16, N=20 and N=24 stages of CSTR.



**Figure 6.4** Temperature profile in the reactor II that compose with N=8,

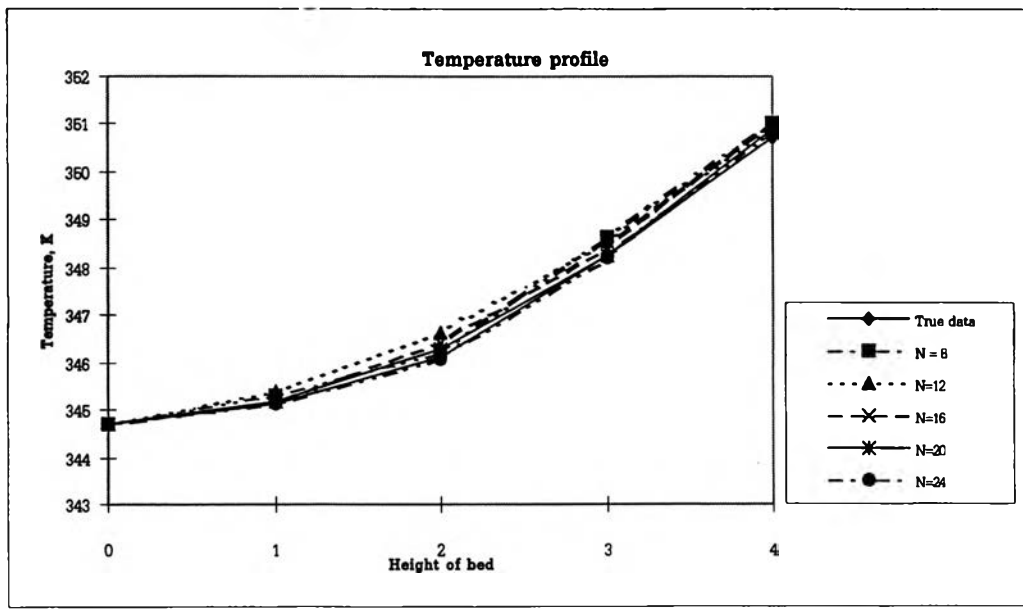N=12, N=16, N=20 and N=24 stages of CSTR.

**Figure 6.5** Outlet acetylene concentration for the reactor II that compose with N=8, N=12, N=16, N=20 and N=24 stages of CSTR.
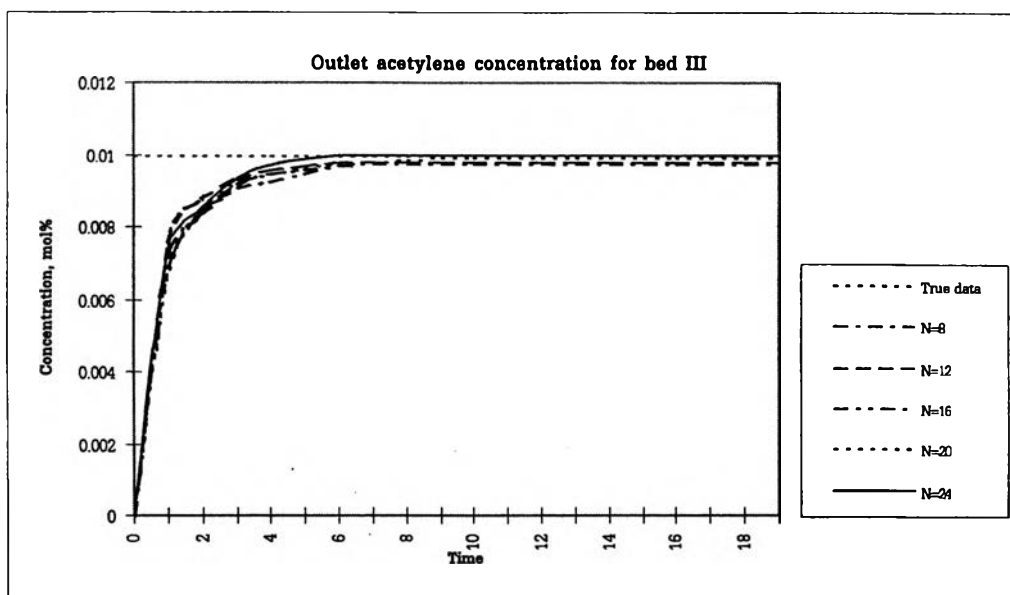


**Figure 6.6** Temperature profile in the reactor III that compose with N=8, N=12, N=16, N=20 and N=24 stages of CSTR.

**Figure 6.7** Outlet acetylene concentration for the reactor III that compose with

N=8, N=12, N=16, N=20 and N=24 stages of CSTR.

Figure 6.2 - 6.7 show the effect of number N stages of CSTR to the perform of the model. Figure 6.2, 6.4, and 6.6 show the comparison of the predicted temperature profile of each different N model with the actual temperature profile of the each bed reactor.

Figure 6.3, 6.5, and 6.7 show the comparison of the predicted outlet acetylene concentration of each different N model with the actual outlet acetylene concentration of the each bed reactor.

All figures indicate that, increasing in N values makes the simulation temperature profile and outlet acetylene concentration value close to the real temperature profile and real outlet acetylene concentration value. And from Table 6.3, the calculation time is increased when the N value increases. At N=20 and N=24, the result of simulation (temperature profile and outlet acetylene concentration value) of both models are nearly similar and give the best agreement with the actual temperature profile and the actual outlet acetylene concentration.

In the other hand, as show in Table 6.3, the average calculation time of the model for each the N value are shown. If the N value increases, the calculation time of the model also increases. The both of model with N = 20 and N=24 give the best agreement of the predicted results with the actual data but the calculation time of the model with N=24 is greater than the model with N=20. For the real work in an industry, the calculation time or speed of calculation is important. Thus, the model with 20 stages of CSTR is selected for the fixed-bed catalytic acetylene hydrogenation reactor model.

## 6.4 The proper reaction rate equations for an acetylene hydrogenation process

In this section, how to get the suitable kinetic model that used to approximate the real reaction is described. The new set of kinetic models are developed by using the background knowledge and the concept of Langmuir-Hinshelwood kinetics that is described in chapter 5. With the different assumptions, the twelve set of kinetic models are developed and used to demonstrate the kinetic model for the each simulation model. For example : MODEL V

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MODEL V

The assumption :

   1. The rate limiting step is a surface rate of reaction.

   The rate of reaction are :

$$-r_{Ac} = k_{Ac}\theta_{Ac}\theta_{H2}$$

$$-r_{Eth} = k_{Eth}\theta_{Eth}\theta_{H2}$$

$$-r_{MA} = k_{MA}\theta_{MA}\theta_{H2}$$

$$-r_{PD} = k_{PD}\theta_{PD}\theta_{H2}$$

   2. The hydrogen breaks into free atom.

   3. The product dose not be adsorbed on the catalytic surface.

   4. The catalyst activity equation is

$$activity = 1/(1+K_{activity}\Sigma Ac)$$

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Use the Langmuir-Hinshelwood kinetics concept will obtain

$$\theta_{Ac} = K_{Ac}C_{Ac}(1-\Sigma\theta)$$

$$\theta_{Eth} = K_{Eth}C_{Eth}(1-\Sigma\theta)$$

$$\theta_{H2} = (K_{H2}C_{H2})^{0.5}(1-\Sigma\theta)$$

$$\theta_{MA} = K_{MA}C_{MA}(1-\Sigma\theta)$$

$$\theta_{PD} = K_{PD}C_{PD}(1-\Sigma\theta)$$

$$\theta_{CO} = K_{CO}C_{CO}(1-\Sigma\theta)$$

$$\Sigma\theta = \theta_{Ac}+\theta_{Eth}+\theta_{H2}+\theta_{MA}+\theta_{PD}+\theta_{CO}$$

$$\Sigma\theta = (1-\Sigma\theta)( K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{MA}C_{MA}+ K_{PD}C_{PD}+ K_{CO}C_{CO})$$

To comparison with others $K_{MA}C_{MA}$ and $K_{PD}C_{PD}$ is very small, thus can ignore (Schbib et. al., 1996).

$$\Sigma\theta = (1-\Sigma\theta)( K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})$$

$$(1-\Sigma\theta) = 1/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})$$

Replacing $\theta_{Ac}$, $\theta_{Eth}$, $\theta_{H2}$, $\theta_{MA}$, and $\theta_{PD}$ in the rate equations. Obtain :

$$-r_{Ac} = k_{Ac}K_{Ac}C_{Ac}(K_{H2}C_{H2})^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

$$-r_{Ac} = K1C_{Ac}C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

and

$$-r_{Eth} = K2C_{Eth} C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

$$-r_{MA} = K4C_{MA} C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

$$-r_{PD} = K5C_{PD} C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

The catalyst activity equation that used in the simulation model are

$$activity = 1/(1+K_{activity}\Sigma Ac) \qquad (6.27)$$

and

$$activity = K_{activity}EXP(E_{activity}/RT)(a^0)(C_{Ac}) \qquad (6.28)$$

This catalyst activity equation is presented in Hydrogenation of acetylene at transient conditions in the presence of olefins and carbon monoxide over palladium/aluminar that given by Cider and firends(Cider et. al., 1991)

The description of the each twelve models is shown in Table 6.4

**Table 6.4** The type of simulation model and its description

| MODEL TYPE | REACTION RATE EQUATION | W | CATALYST ACTIVITY EQUATION | DESCRIPTION |
|---|---|---|---|---|
| MODEL I | $-R_{Ac} = K1C_{Ac}C_{H2}/W^2$ <br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^2$ <br> $-R_{MA} = K4C_{MA}C_{H2}/W^2$ <br> $-R_{PD} = K5C_{PD}C_{H2}/W^2$ | $W = (1+K_{H2}C_{H2}+K_{Ac}C_{Ac}+$ <br> $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = $1/(1+K_{activity}\Sigma\,Ac\,)$ | $H_2$ dose not break and product dose not be adsorbed |
| MODEL II | $-R_{Ac} = K1C_{Ac}C_{H2}/W^2$ <br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^2$ <br> $-R_{MA} = K4C_{MA}C_{H2}/W^2$ <br> $-R_{PD} = K5C_{PD}C_{H2}/W^2$ | $W = (1+K_{H2}C_{H2}+K_{Ac}C_{Ac}+$ <br> $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = <br> $K_{activity}EXP(E_{activity}/RT)C_{Ac}$ | $H_2$ dose not break and product dose not be adsorbed |
| MODEL III | $-R_{Ac} = K1C_{Ac}C_{H2}/W^3$ <br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^3$ <br> $-R_{MA} = K4C_{MA}C_{H2}/W^3$ <br> $-R_{PD} = K5C_{PD}C_{H2}/W^3$ | $W = (1+K_{H2}C_{H2}+K_{Ac}C_{Ac}+$ <br> $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = $1/(1+K_{activity}\Sigma\,Ac\,)$ | $H_2$ dose not break and product is adsorbed |
| MODEL IV | $-R_{Ac} = K1C_{Ac}C_{H2}/W^3$ <br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^3$ <br> $-R_{MA} = K4C_{MA}C_{H2}/W^3$ <br> $-R_{PD} = K5C_{PD}C_{H2}/W^3$ | $W = (1+K_{H2}C_{H2}+K_{Ac}C_{Ac}+$ <br> $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = <br> $K_{activity}EXP(E_{activity}/RT)C_{Ac}$ | $H_2$ dose not break and product is adsorbed |

**Table 6.4** The type of the simulation model and its description (continue)

| MODEL V | $-R_{Ac} = K1C_{Ac}C_{H2}^{0.5}/W^2$ $-R_{Eth} = K2C_{Eth}C_{H2}^{0.5}/W^2$ $-R_{MA} = K4C_{MA}C_{H2}^{0.5}/W^2$ $-R_{PD} = K5C_{PD}C_{H2}^{0.5}/W^2$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = $1/(1+K_{activity}\Sigma$ Ac ) | $H_2$ break and product dose not be adsorbed and rate $\propto \theta_{H2}$ |
|---|---|---|---|---|
| MODEL VI | $-R_{Ac} = K1C_{Ac}C_{H2}^{0.5}/W^2$ $-R_{Eth} = K2C_{Eth}C_{H2}^{0.5}/W^2$ $-R_{MA} = K4C_{MA}C_{H2}^{0.5}/W^2$ $-R_{PD} = K5C_{PD}C_{H2}^{0.5}/W^2$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = $K_{activity}EXP(E_{activity}/RT)C_{Ac}$ | $H_2$ break and product dose not be adsorbed and rate $\propto \theta_{H2}$ |
| MODEL VII | $-R_{Ac} = K1C_{Ac}C_{H2}^{0.5}/W^3$ $-R_{Eth} = K2C_{Eth}C_{H2}^{0.5}/W^3$ $-R_{MA} = K4C_{MA}C_{H2}^{0.5}/W^3$ $-R_{PD} = K5C_{PD}C_{H2}^{0.5}/W^3$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = $1/(1+K_{activity}\Sigma$ Ac ) | $H_2$ break and product is adsorbed and rate $\propto \theta_{H2}$ |
| MODEL VIII | $-R_{Ac} = K1C_{Ac}C_{H2}^{0.5}/W^3$ $-R_{Eth} = K2C_{Eth}C_{H2}^{0.5}/W^3$ $-R_{MA} = K4C_{MA}C_{H2}^{0.5}/W^3$ $-R_{PD} = K5C_{PD}C_{H2}^{0.5}/W^3$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity = $K_{activity}EXP(E_{activity}/RT)C_{Ac}$ | $H_2$ break and product is adsorbed and rate $\propto \theta_{H2}$ |

**Table 6.4** The type of the simulation model and its description (continue)

| | | | | |
|---|---|---|---|---|
| MODEL IX | $-R_{Ac} = K1C_{Ac}C_{H2}/W^3$ <br><br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^3$ <br><br> $-R_{MA} = K4C_{MA}C_{H2}/W^3$ <br><br> $-R_{PD} = K5C_{PD}C_{H2}/W^3$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ <br><br> $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity $= 1/(1+K_{activity}\Sigma Ac)$ | $H_2$ break and product dose not be adsorbed and rate $\propto \theta_{H2}^2$ |
| MODEL X | $-R_{Ac} = K1C_{Ac}C_{H2}/W^3$ <br><br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^3$ <br><br> $-R_{MA} = K4C_{MA}C_{H2}/W^3$ <br><br> $-R_{PD} = K5C_{PD}C_{H2}/W^3$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ <br><br> $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity $=$ <br><br> $K_{activity}EXP(E_{activity}/RT)C_{Ac}$ | $H_2$ break and product dose not be adsorbed and rate $\propto \theta_{H2}^2$ |
| MODEL XI | $-R_{Ac} = K1C_{Ac}C_{H2}/W^4$ <br><br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^4$ <br><br> $-R_{MA} = K4C_{MA}C_{H2}/W^4$ <br><br> $-R_{PD} = K5C_{PD}C_{H2}/W^4$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ <br><br> $K_{Eth}C_{Eth}+K_{CO}C_{CO})$ | activity $= 1/(1+K_{activity}\Sigma Ac)$ | $H_2$ break and product is adsorbed and rate $\propto \theta_{H2}^2$ |
| MODEL XII | $-R_{Ac} = K1C_{Ac}C_{H2}/W^4$ <br><br> $-R_{Eth} = K2C_{Eth}C_{H2}/W^4$ <br><br> $-R_{MA} = K4C_{MA}C_{H2}/W^4$ <br><br> $-R_{PD} = K5C_{PD}C_{H2}/W^4$ | $W = (1+(K_{H2}C_{H2})^{0.5}+K_{Ac}C_{Ac}+$ <br><br> $K_{Eth}C_{Eth}+K_{CC}C_{CO})$ | activity $=$ <br><br> $K_{activity}EXP(E_{activity}/RT)C_{Ac}$ | $H_2$ break and product is adsorbed and rate $\propto \theta_{H2}^2$ |

The actual data from an industrial plant at date September 9, 1997 to November 12, 1997 is adjusted by the developed dynamic data reconciliation program before used to estimate the values of the rate constant parameters for each model. The parameters are estimated from the sixty plant data points start at the first used of fresh catalyst. All of the rate constant parameters values that estimated are shown in Table 6.5. And then, the different twelve models are simulated by using the input data from the plant design case I (the based reference case of the industrial plant), the simulation results of the all models are compared with the output data from the plant design case I. The comparison results and the percent error of the prediction are shown in the Table 6.6 .

Table 6.6 shows the simulation results of all models compare with the design data and shows the errors for each predicted output variable. The import variables is temperature and acetylene concentration because temperature is more effectively to the rate of reaction, physical and chemical properties of the process and acetylene concentration is the control variable of the process. Thus, to consider the best suitable model, the first variables that should be considered are temperature and acetylene concentration. From Table 6.6, the MODEL V and MODEL XI give the smallest error in the sense of temperature (0.1949%) but the error from MODEL IX (0.2295%) is not far from the smallest value. And in the sense of the outlet acetylene concentration, the MODEL V and MODEL VI give the smaller error than other models.

To find the best model, the plant operating data are obtained and used to check the model performance of each developed models. The models are checked against through the 120 data points since the fresh catalyst life ( 9 Sep 97-10 Jan 98) and the predicted output of each model are then compared with the actual data.

The best suitable model is the MODEL V . Because the MODEL V gives the best fit of the simulation results against the operating data. The simulation results of the MODEL V is shown in this chapter. Figure 6.9 - 6.17 show the comparison of the predicted results and the plant values. Moreover, the other rate laws and the simulation results of the other models are shown in appendix B.

**Table 6.5** The solute parameter values from dynamic parameter estimation

BED I

| Parameter type | MODEL I | MODEL II | MODEL III | MODEL IV | MODEL V | MODEL VI | MODEL VII | MODEL VIII | MODEL IX | MODEL X | MODEL XI | MODEL XII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_1$ | 1.0856E16 | 1.1415E16 | 1.1463E20 | 4.3941E20 | 4.6512E11 | 2.1994E12 | 2.0223E22 | 2.7322E21 | 4.8712E27 | 8.4941E27 | 1.9224E23 | 2.7347E23 |
| $K_2$ | 1.5569E17 | 2.432E17 | 2.4165E22 | 1.3173E23 | 1.8867E13 | 3.5501E13 | 8.1809E23 | 1.6285E23 | 2.2446E26 | 2.3345E26 | 2.6914E22 | 2.7671E22 |
| $K_4$ | 1.0368E16 | 1.7028E16 | 3.5978E20 | 1.4461E20 | 5.1204E11 | 1.2524E11 | 2.1331E23 | 6.2247E22 | 1.3961E27 | 2.1037E27 | 3.6322E23 | 1.1304E24 |
| $K_5$ | 1.1271E18 | 1.3166E18 | 1.7377E25 | 2.5524E25 | 6.448E24 | 1.1512E24 | 3.6403E25 | 1.3852E26 | 2.8263E27 | 1.0194E28 | 2.3675E24 | 2.4253E24 |
| $K_6$ | 7.2715E-4 | 5.1006E-5 | 2.8016E-6 | 1.3049E-6 | 7.2483E-7 | 2.5243E-7 | 4.2993E-5 | 1.3808E-6 | 1.2368E-6 | 2.4165E-5 | 1.0083E-5 | 1.1962E-5 |
| $K_{activity}$ | 2.9916E-5 | 4.9874E-2 | 9.2056E-6 | 3.945E-2 | 2.5863E-5 | 4.4788E-5 | 9.1645E-6 | 1.7613E-3 | 1.4802E-5 | 1.7288E-2 | 9.902E-7 | 2.1719E-3 |
| $E_{activity}$ | - | 2.1527E2 | - | 1.0536E2 | - | 2.5601E3 | - | 4.0254E2 | - | 1.1113E2 | | 2.7139E2 |

## BED II

| Parameter type | MODEL I | MODEL II | MODEL III | MODEL IV | MODEL V | MODEL VI | MODEL VII | MODEL VIII | MODEL IX | MODEL X | MODEL XI | MODEL XII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K1 | 1.0758E17 | 1.276E17 | 3.1131E21 | 1.8464E21 | 6.3512E11 | 4.8682E11 | 7.2224E22 | 2.7065E22 | 1.4127E29 | 2.9039E29 | 3.4321E23 | 1.8801E23 |
| K2 | 2.6445E18 | 2.8405E18 | 2.3708E22 | 1.3315E23 | 2.266E13 | 2.2064E13 | 2.4483E23 | 1.8973E23 | 2.5702E28 | 5.8519E29 | 1.0327E22 | 4.3363E22 |
| K4 | 6.1213E18 | 2.5341E18 | 3.6977E21 | 1.0524E22 | 7.2004E11 | 1.7651E12 | 4.6519E23 | 2.0871E23 | 7.7324E29 | 1.8087E29 | 8.8331F22 | 3.7572E23 |
| K5 | 6.6924E19 | 3.4238E19 | 1.4173E26 | 3.334E26 | 7.75E24 | 4.4128E23 | 5.2716E26 | 1.6074E26 | 3.0279E31 | 1.3449E31 | 1.6842E24 | 2.2804E24 |
| K6 | 8.0632E-4 | 5.1006E-5 | 1.8375E-5 | 2.0128E-5 | 6.6551E-8 | 1.9336E-8 | 3.528E-5 | 1.1821E-5 | 8.4327E-6 | 2.8944E-5 | 1.499E-5 | 2.1443E-6 |
| $K_{activity}$ | 2.1407E-4 | 4.1076E-3 | 3.1486E-4 | 1.2077E-2 | 2.312E-5 | 6.6127E-5 | 5.9845E-4 | 1.9078E-2 | 1.5132E-3 | 7.0267E-3 | 9.0693E-4 | 8.1235E-3 |
| $E_{activity}$ | - | 2.6421E2 | - | 5.3985E2 | - | 4.5717E3 | - | 1.9948E2 | - | 1.1477E2 | - | 2.7677E3 |

## BED III

| Parameter type | MODEL I | MODEL II | MODEL III | MODEL IV | MODEL V | MODEL VI | MODEL VII | MODEL VIII | MODEL IX | MODEL X | MODEL XI | MODEL XII |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K1 | 3.0619E19 | 3.0488E19 | 1.6743E22 | 2.2171E22 | 2.9832E12 | 4.1647E11 | 1.4953E22 | 2.7482E23 | 5.6098E30 | 3.6607E30 | 2.1581E22 | 3.9029E22 |
| K2 | 5.0288E20 | 2.7486E20 | 7.5072E22 | 1.4714E23 | 2.624E13 | 1.1257E13 | 3.4709E21 | 2.6642E21 | 2.5494E29 | 4.9176E29 | 1.0327E23 | 5.4456E24 |
| K4 | 1.7498E19 | 2.3281E19 | 2.3584E23 | 2.3277E23 | 3.8154E12 | 1.3215E12 | 1.299E23 | 8 6339E22 | 2.3685E30 | 1.2887E31 | 2.3335E23 | 1.9783E23 |
| K5 | 1.6703E21 | 3.2802E20 | 5.3573E27 | 4.3203E27 | 9.851E24 | 2.8755E25 | 3.0665E26 | 1.3601E26 | 1.9684E32 | 1.2186E32 | 4.6577E24 | 4.7991E25 |
| K6 | 3.1548E-4 | 2.2892E-5 | 1.8822E-5 | 6.5729E-4 | 4.1909E-8 | 2.1845E-7 | 1.1135E-4 | 1.7141E-5 | 2.2061E-5 | 1.2513E-5 | 1.3407E-5 | 2.1907E-5 |
| $K_{activity}$ | 9.3755E-4 | 1.0779E-3 | 3.9188E-4 | 1.6011E-2 | 9.9879E-5 | 2.236E-6 | 2.1743E-5 | 2.3235E-3 | 8.1801E-5 | 1.0858E-2 | 1.4801E-4 | 2.0202E-2 |
| $E_{activity}$ | - | 5.0446E3 | - | 2.3372E2 | - | 6.0829E2 | - | 2.3405E2 | - | 2.3693E2 | - | 1.7958E3 |

**Table 6.6** The result from simulate by using the plant design-case I input data

| | Temp, K | $H_2$, mol % | CO, mol% | $CH_4$, mol% | $C_2H_2$, mol% | $C_2H_4$, mol% | $C_2H_6$, mol% | MA, mol% | PD, mol% | $C_3H_6$, mol% |
|---|---|---|---|---|---|---|---|---|---|---|
| design case | 318 | 13.758 | 0.0443 | 25.324 | 0 | 38.266 | 8.0087 | 0.0293 | 0.1181 | 13.8199 |
| MODEL I | 319.43 | 13.826 | 0.04412 | 24.36 | 62.85E-6 | 37.267 | 7.486 | 0.0416 | 0.1311 | 13.486 |
| %error | 0.4497 | 0.4925 | 0.4063 | 3.8066 | - | 2.6107 | 6.5266 | 41.98 | 11.007 | 2.402 |
| MODEL II | 319.82 | 13.62 | 0.0512 | 24.51 | 81.05E-6 | 37.79 | 8.7509 | 0.01359 | 0.1241 | 11.7277 |
| %error | 0.5723 | 1.003 | 15.57 | 3.2143 | - | 1.2439 | 9.267 | 53.617 | 5.0804 | 15.139 |
| MODEL III | 316.87 | 13.68 | 0.0482 | 25.683 | 20.32E-6 | 38.32 | 8.0167 | 0.01418 | 0.1201 | 12.6664 |
| %error | 0.3553 | 0.5669 | 8.8036 | 1.4176 | - | 0.1411 | 0.09989 | 51.604 | 1.693 | 8.3466 |
| MODEL IV | 320.34 | 13.51 | 0.0496 | 25.874 | 28.35E-6 | 39.62 | 8.2163 | 0.01511 | 0.1308 | 12.6536 |
| %error | 0.7358 | 1.8025 | 11.9638 | 2.1718 | - | 3.538 | 2.592 | 48.43 | 10.7535 | 8.4392 |
| MODEL V | 318.62 | 13.7868 | 0.0443035 | 25.3163 | 9.9727E-6 | 38.2526 | 8.0072 | 0.02433 | 0.1192 | 13.8185 |
| %error | 0.1949 | 0.209 | 7.9E-3 | 0.0304 | - | 0.035 | 0.0187 | 16.962 | 0.9314 | 0.01013 |
| MODEL VI | 320.92 | 14.3889 | 0.044312 | 25.9922 | 15.696E-6 | 38.2954 | 7.7893 | 0.0421 | 0.1173 | 12.2656 |
| %error | 0.918 | 4.5856 | 0.027 | 2.6386 | - | 0.07683 | 2.7395 | 43.686 | 0.67739 | 11.2468 |
| MODEL VII | 321.13 | 14.3485 | 0.05023 | 25.2017 | 85.5378E-6 | 35.6143 | 9.0501 | 0.0113 | 0.1117 | 13.304 |
| %error | 0.9842 | 4.292 | 13.386 | 0.4825 | - | 6.9296 | 13.0033 | 61.433 | 5.4191 | 3.7333 |
| MODEL VIII | 320.75 | 13.2132 | 0.04624 | 25.584 | 75.986E-6 | 38.016 | 9.1594 | 0.02501 | 0.1103 | 11.5991 |
| %error | 0.8648 | 4.614 | 4.379 | 1.0266 | - | 0.6533 | 14.3668 | 14.641 | 6.6045 | 16.069 |
| MODEL IX | 318.73 | 13.5079 | 0.04426 | 25.3021 | 10.8336E-6 | 38.2558 | 8.0422 | 0.0223 | 0.1195 | 13.8539 |
| %error | 0.2295 | 1.8178 | 0.0903 | 0.0864 | - | 0.02665 | 0.4182 | 23.891 | 1.1854 | 0.246 |

**Table 6.6** The result from simulate by using the plant design-case I input data (continue)

| | Temp, K | $H_2$, mol % | CO, mol% | $CH_4$, mol% | $C_2H_2$, mol% | $C_2H_4$, mol% | $C_2H_6$, mol% | MA, mol% | PD, mol% | $C_3H_6$, mol% |
|---|---|---|---|---|---|---|---|---|---|---|
| MODEL X | 317.22 | 14.0126 | 0.044218 | 26.5968 | 37.581E-6 | 38.8418 | 8.3941 | 0.014503 | 0.1691 | 12.5243 |
| %error | 0.2453 | 1.8505 | 0.1851 | 5.026 | - | 1.5047 | 4.8122 | 50.501 | 43.183 | 9.3749 |
| MODEL XI | 317.38 | 13.8083 | 0.044321 | 25.3102 | 27.317E-6 | 37.0841 | 8.0419 | 0.02462 | 0.1123 | 13.6115 |
| %error | 0.1949 | 0.3656 | 0.0474 | 0.05449 | - | 3.0886 | 0.4145 | 15.9726 | 4.911 | 1.5079 |
| MODEL XII | 316.65 | 13.7888 | 0.044352 | 24.7114 | 48.813E-6 | 36.6313 | 7.9231 | 0.0085 | 0.1206 | 13.2501 |
| %error | 0.4245 | 0.2238 | 0.1173 | 4.5514 | - | 4.2719 | 1.0688 | 70.989 | 2.1168 | 4.123 |
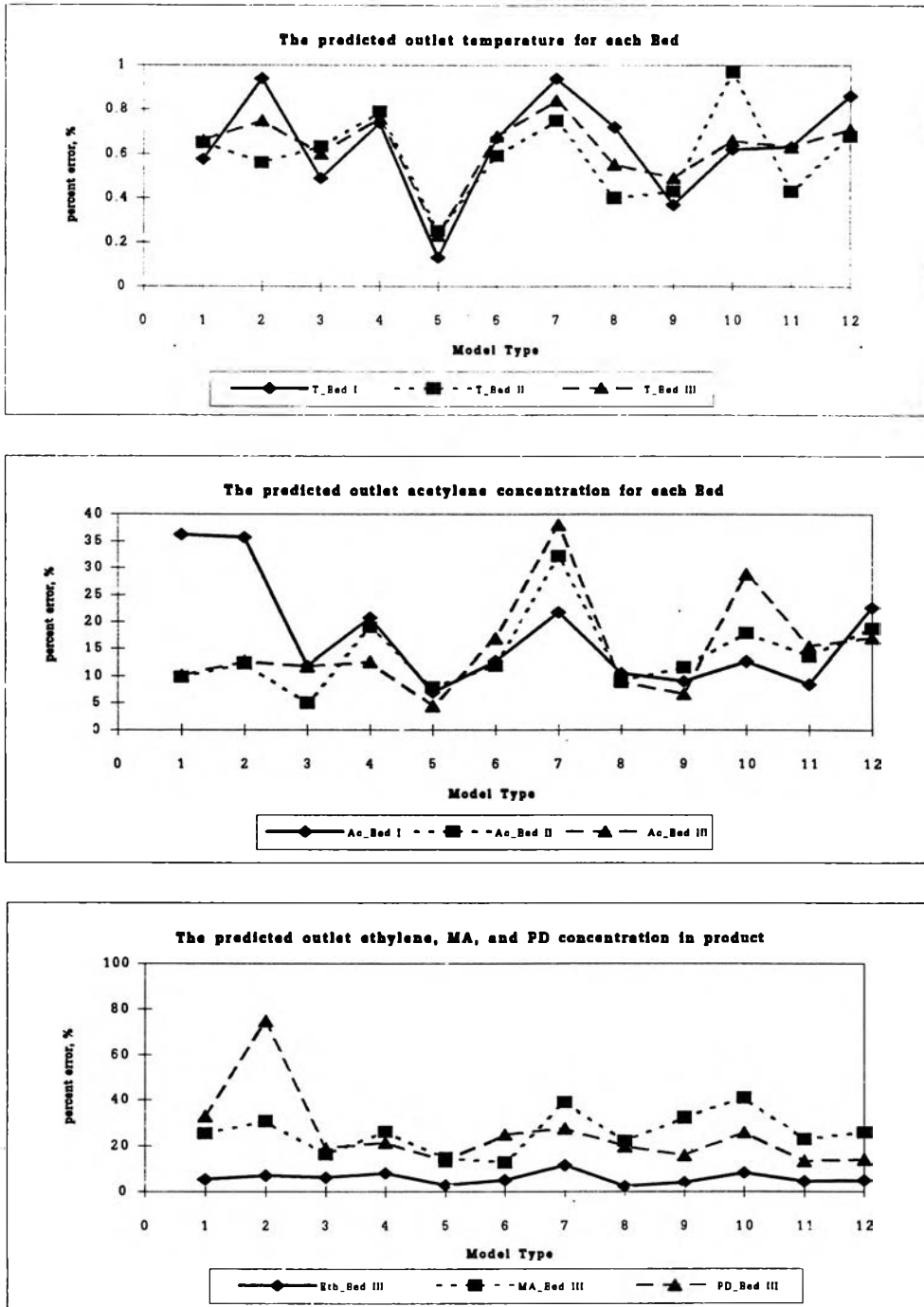
**Figure 6.8** The percent predicted error of each outlet variables of each model types

The graph that shown in the Figure 6.8 is the relationship between the percent predicted error(%error that compared with the actual data) and the model type in the present of each output variables. The X axial is the type of model and the Y axial is the percent error. The model type number 5(MODEL V), the suitable model, gives the smallest of %error in the present of all output variables.

**The simulation result of MODEL V : The best model**
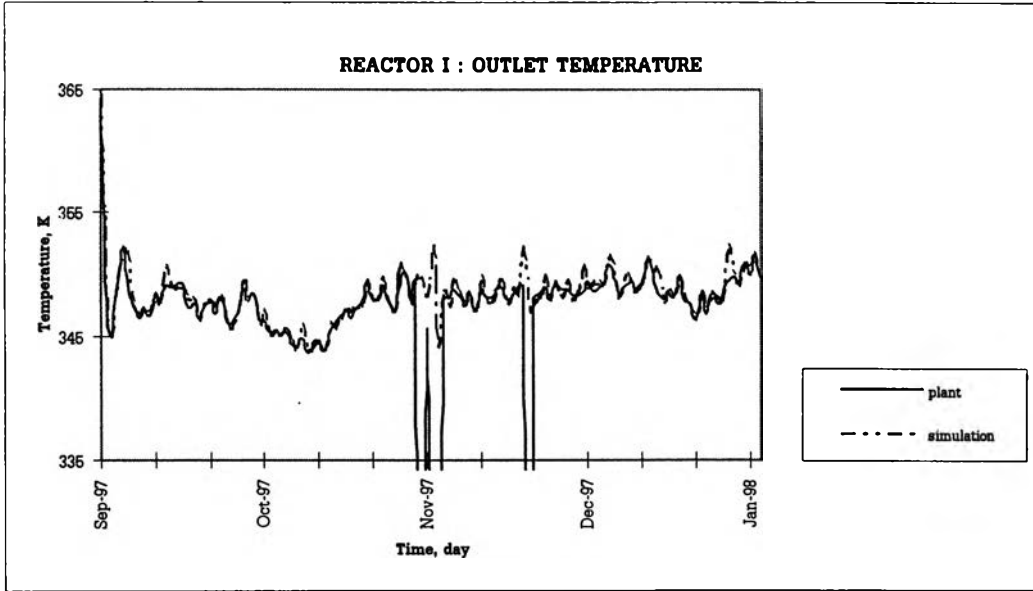


**Figure 6.9**  MODEL V : Outlet temperature of reactor I with error 0.13%
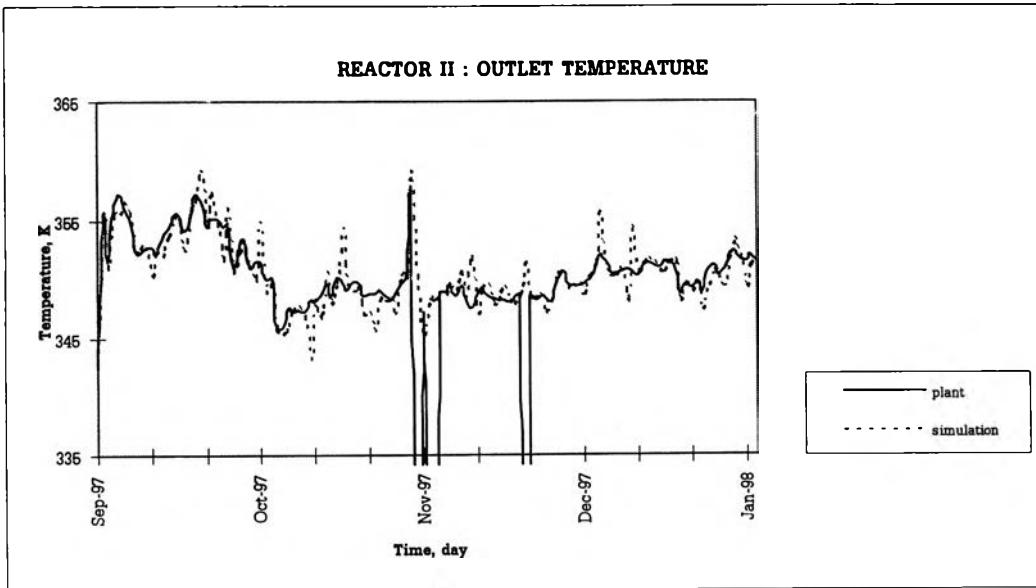


**Figure 6.10**  MODEL V : Outlet temperature of reactor II with error 0.25%
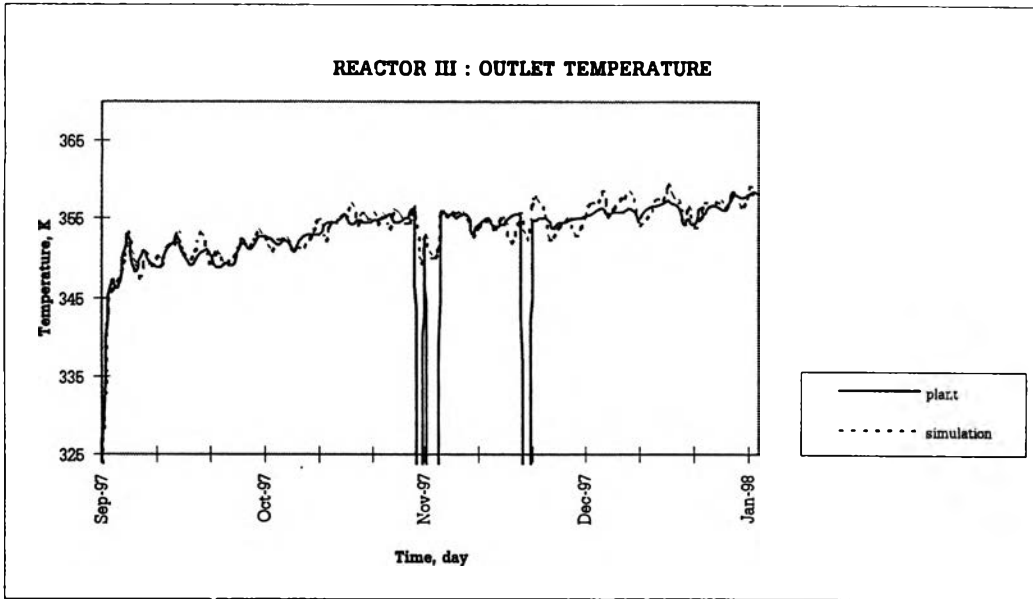
**Figure 6.11** MODEL V : Outlet temperature of reactor III with error 0.23%
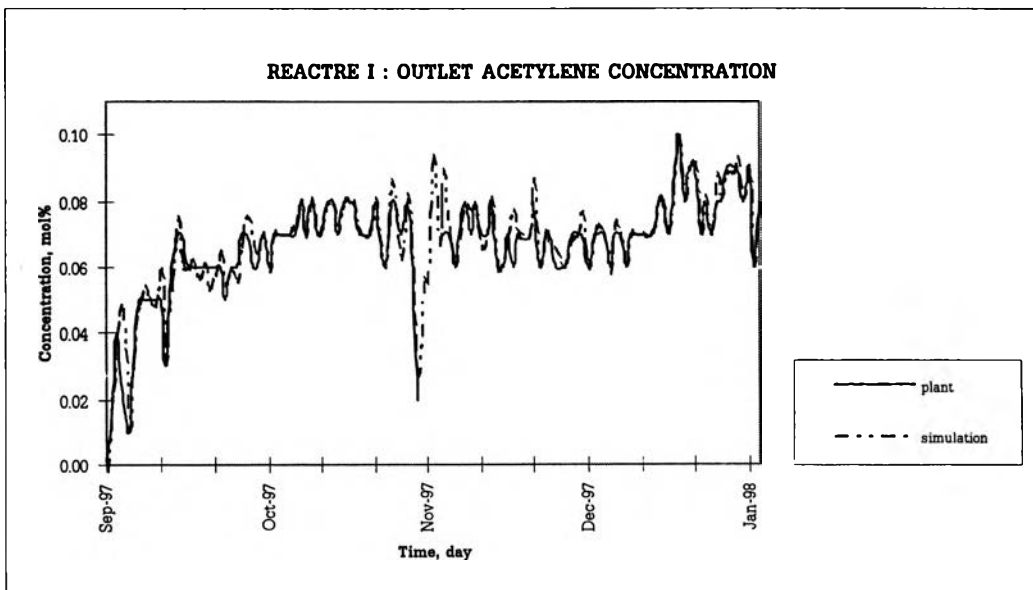


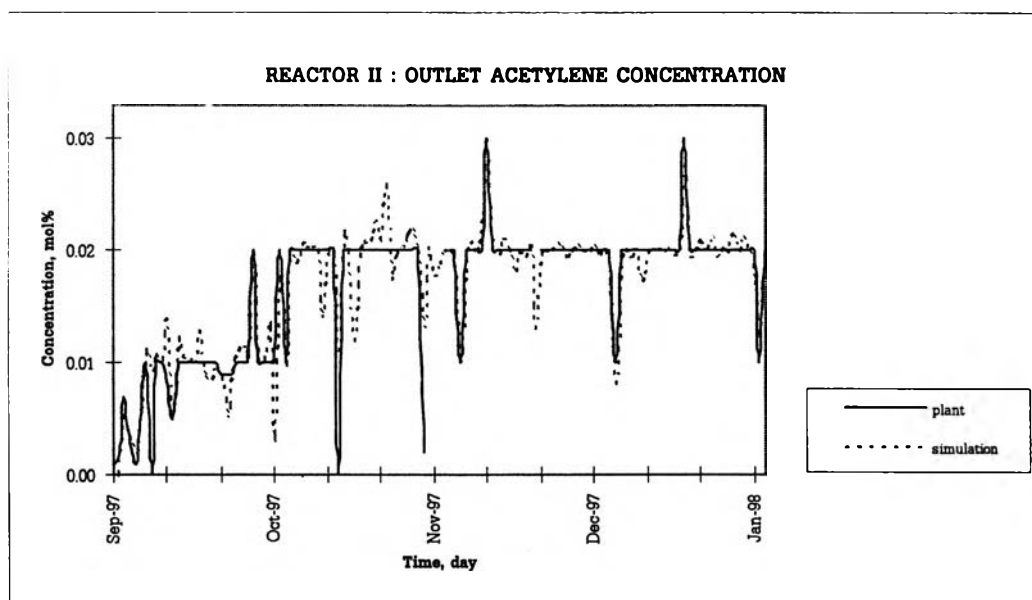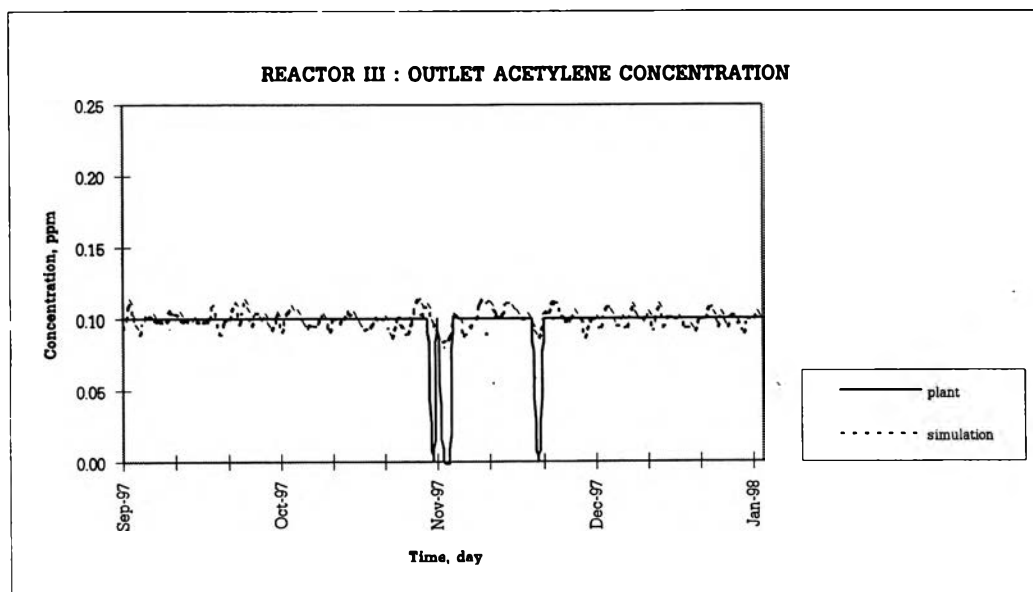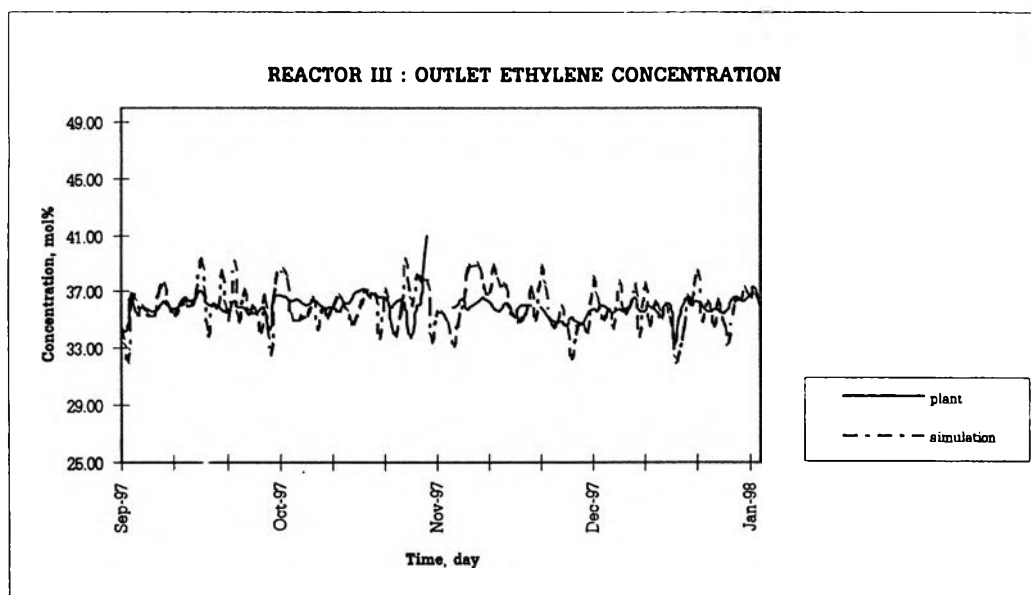**Figure 6.12** MODEL V : Outlet acetylene concentration of reactor I with error 6.9%

**REACTOR II : OUTLET ACETYLENE CONCENTRATION**

**Figure 6.13** MODEL V : Outlet acetylene concentration of reactor II with error 7.79%

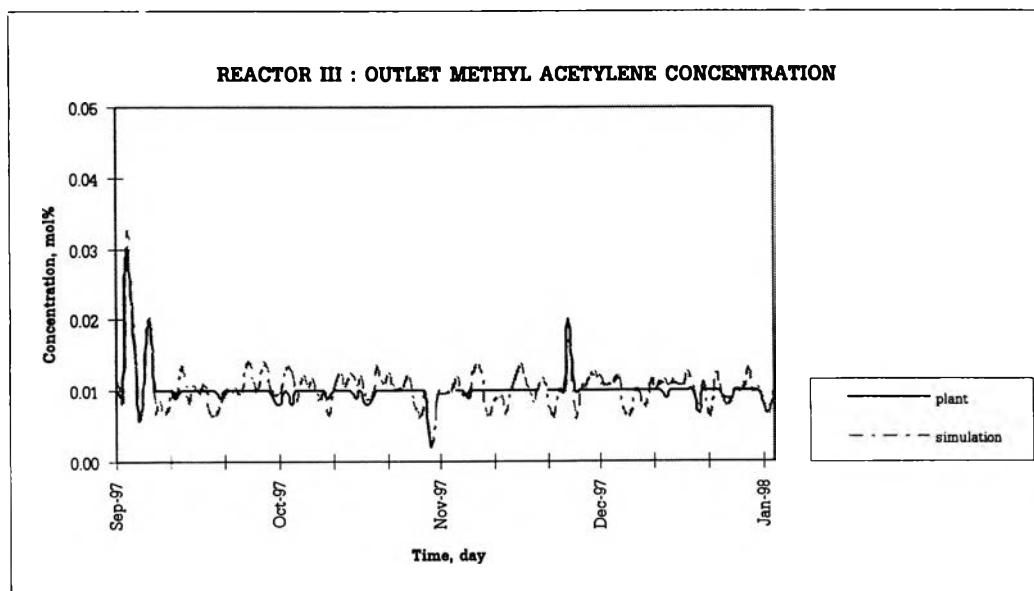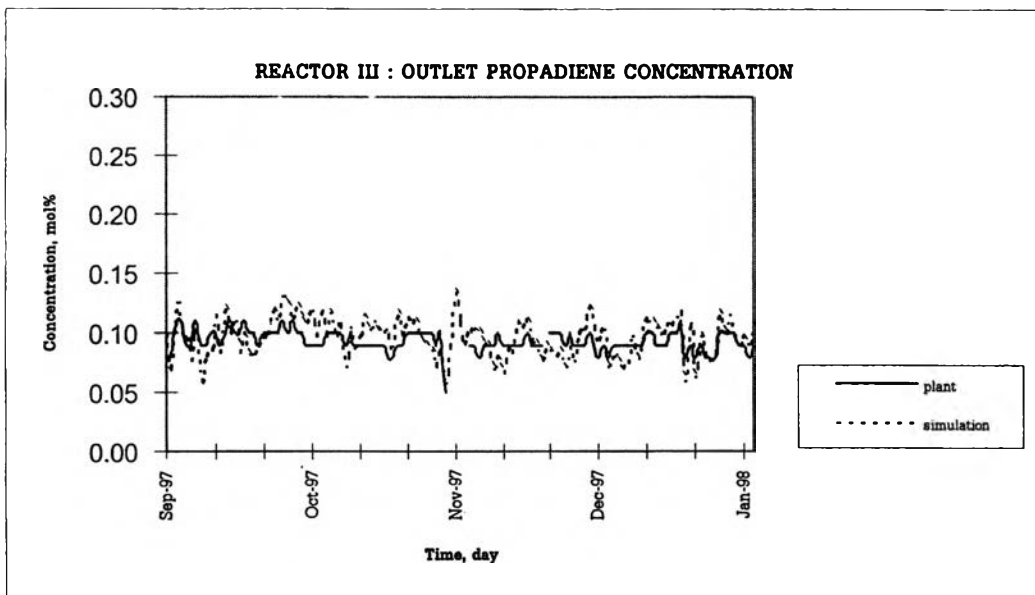**REACTOR III : OUTLET ACETYLENE CONCENTRATION**

**Figure 6.14** MODEL V : Outlet acetylene concentration of reactor III with error 4.41%

**Figure 6.15** MODEL V : Outlet ethylene concentration of reactor III with error 2.87%



**Figure 6.16** MODEL V : Outlet methyl acetylene concentration of reactor III

with error 14.81%

**Figure 6.17** MODEL V : Outlet propadiene concentration of reactor III with error 13.43%

## 6.5 Summary

The catalytic fixed-bed acetylene hydrogenation reactors are approximated by the twenty CSTRs that is connected in series. The four main reaction have the rate laws that are based the following assumption

1. The rate limiting step is a surface rate of reaction.

   The rate of reaction are :

   $$-r_{Ac} = k_{Ac}\theta_{Ac}\theta_{H2}$$

   $$-r_{Eth} = k_{Eth}\theta_{Eth}\theta_{H2}$$

   $$-r_{MA} = k_{MA}\theta_{MA}\theta_{H2}$$

   $$-r_{PD} = k_{PD}\theta_{PD}\theta_{H2}$$

2. The hydrogen breaks into free atom.

3. The product dose not be adsorbed on the catalytic surface.

4. The catalyst activity equation is

   $$activity = 1/(1+K_{activity}\Sigma Ac)$$

And the reaction rate equations are

$$-r_{Ac} = k_{Ac}C_{Ac}C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

$$-r_{Eth} = k_{Eth}C_{Eth}\ C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

$$-r_{MA} = k_{MA}C_{MA}\ C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

$$-r_{PD} = k_{PD}C_{PD}\ C_{H2}^{0.5}/(1+ K_{Ac}C_{Ac}+ K_{Eth}C_{Eth}+ (K_{H2}C_{H2})^{0.5}+ K_{CO}C_{CO})^2$$

$$-r_{CO} = k_{CO}C_{CO}$$

Where the estimated rate constant values are

**Table 6.7** The proper estimated reaction rate constants

| Rate constant | Bed I | Bed II | Bed III |
|---|---|---|---|
| $k_{Ac}$ | 4.651236e11 | 6.351236e11 | 2.983236e12 |
| $k_{eth}$ | 1.886755e13 | 2.266055e13 | 2.624055e13 |
| $k_{MA}$ | 5.120408e11 | 7.200408e11 | 3.815408e12 |
| $k_{PD}$ | 6.448e24 | 7.75e24 | 9.851e24 |
| $k_{CO}$ | 7.248314e-7 | 6.65514e-8 | 4.190915e-8 |
| $k_{activity}$ | 2.586304e-5 | 2.312045e-5 | 9.987904e-6 |

The model can more effectively repeat the process at current operation by adding the real time parameter estimation.

For the next chapter, the developed dynamic data reconciliation program of the process is presented and the benefit of the dynamic data reconciliation will be shown.