



## CHAPTER 5

### MATHEMATICAL MODEL AND SIMULATION

As discussed in Chapter 4, neither Smith nor Krane et al. considered the reactions of five and six membered ring naphthene, alkylcyclopentane and alkylcyclohexane. Results from experimental study by Emmett (1951) showed that the dominant reaction of the six membered naphthenes, alkylcyclohexanes, into aromatics is the fastest reaction. On the other hand, the five membered naphthenes, alkylcyclopentane, have first to undergo isomerization, which is a slow reaction, before dehydrogenation takes place. Henningsen et al. (1970) used the following scheme for modeling the reforming reactions by using platinum on alumina catalyst. Feedstock is lumped into normal paraffins, isoparaffins, alkylcyclopentanes, alkylcyclohexanes, and aromatics. The limitation of this model is the prediction of aromatics composition. The rate constants were estimated at specified hydrogen and total hydrocarbon partial pressures which may have some effect on the rate constants due to adsorption on the active sites of the catalyst. After 1970, other works have used the modeling approach of Henningsen et al. in different pattern. But product compositions for catalytic reforming, particularly benzene, toluene is not included in the models.

With limitation of the previous models, a new model for catalytic reforming is thus developed taking into consideration the limits of all previous models. The reactor used in new the model is an adiabatically catalytic fixed-bed reactor. The

catalyst used in the new model is based on the experiment of Marin et al., (1982) and Van Trimpont et al., (1986, (1988)). The catalyst used in their experiment was the commercial reforming catalyst CK 306 of Cyanamide-Ketjen (Akzo Chemie), having a surface area of  $179 \text{ m}^2/\text{g}$  and containing 0.59 wt% Pt and 0.67 wt% Cl. The catalyst was crushed and sieved to 0.4-1.0 mm. size.

### 5.1 Assumptions

In the development, the following assumptions are made

(1) A one-dimensional plug flow model is used to represent the catalytic fixed-bed reactor in which concentration and temperature gradients occur only in the axial direction.

(2) The catalytic fixed-bed reactor is operated at a steady state flow condition.

(3) The heat flux by molecular diffusion, heat conduction and heat radiation are negligible.

(4) Pressure drop through the reactor is negligible.

(5) Since in the plant, the hydrogen partial pressure is always kept at a high value, the catalyst deactivation is therefore assumed to be neglected.

In the new model, the development of a mathematical model of the catalytic reforming we adopt on approach in which:

(1) The feed is classified into  $C_6$  and  $C_7$  hydrocarbons. The reaction models of  $C_6$  and  $C_7$  hydrocarbons for the new model are shown in Figure 5-1 and 5-2, respectively.

(2) The equilibrium reactions of  $C_6$  and  $C_7$  hydrocarbons such as benzene and toluene are negligible.

(3) The mathematical model consists of material and energy balances as reviewed in Chapter 4.

(4) The rate equations for  $C_6$  hydrocarbons (as shown in Figure 5-1) are obtained from Marin et al. (1982) which used platinum on alumina catalyst. The main reforming reactions are isomerization, ring closure, ring expansion followed by dehydrogenation and hydrocracking in which the isomerization on a single-site surface reaction (acid alumina function) is rate determining step. The rate equations used Hougen-Watson rate equations in which the influence of temperature on the adsorption on a site of surface reaction is considered. The  $C_6$  hydrocarbons in the new model are n-hexane, 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (22DMB), 2,3-dimethylbutane (23DMB), methylcyclopentane (MCP), and benzene (BZ).

(5) The rate equations of  $C_7$  hydrocarbons (as shown in Figure 5-2) are obtained from Van Trimont et al., (1988) for isomerization, ring closure, ring expansion, hydrocracking reactions, and from Van Trimont et al., (1986) for dehydrogenation of methylcyclohexane. The  $C_7$  hydrocarbons are n-heptane, single-branched isoheptane (SBP7), multibranched isoheptane (MBP7), five ring naphthenes with seven carbon atoms (5N7), methylcyclohexane (MCH), and toluene (TOL).

The first simulation with  $C_6$  hydrocarbons is to be compared with experimental data from Marin et al. (1988) and Christoffel (1979). The second simulation with  $C_7$  hydrocarbons is to be compared with experimental data from Heinemann (1951), Hettlinger et al. (1955), Van trimont et al. (1986), and Van Trimont et al. (1988). An attempt to simulate an catalytic fixed-bed reactor for benzene and toluene from a narrow boiling  $C_6$  to  $C_7$  (140 to 228 °F) East-West Texas (EWT) is to be made and the simulated results are compared with pilot plant data by using the Platforming processes developed by the Universal Oil

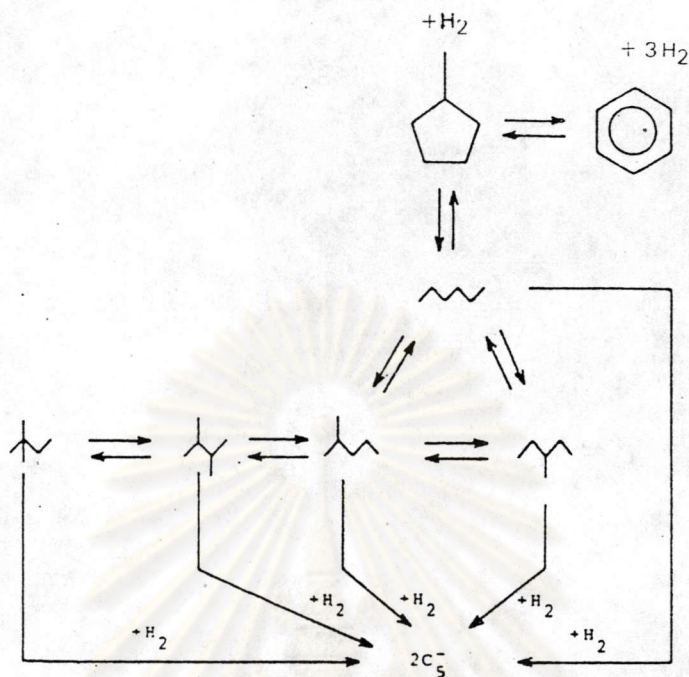


Figure 5-1 Reaction network for the reforming of C6 hydrocarbons (Marin et al., (1982))

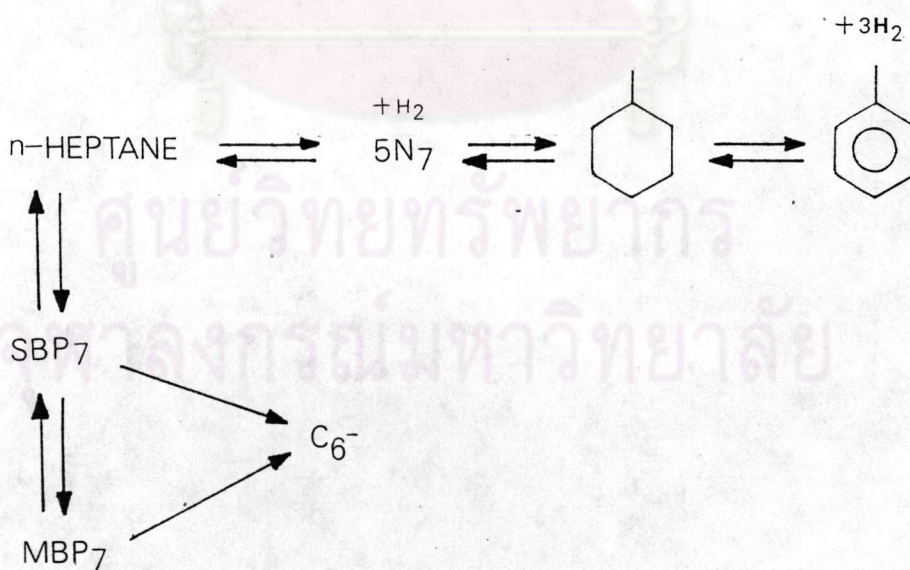


Figure 5-2 Lumped reaction network for the reforming of C7 hydrocarbons (Van Trimont et al., (1988))

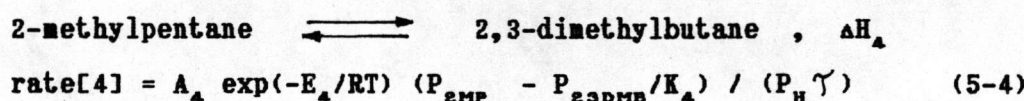
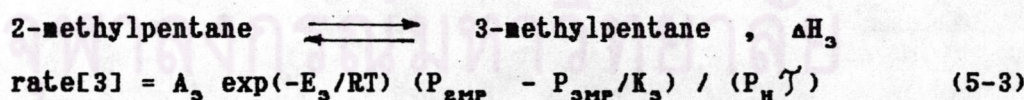
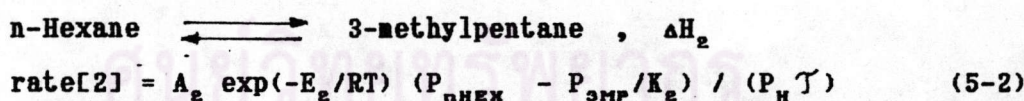
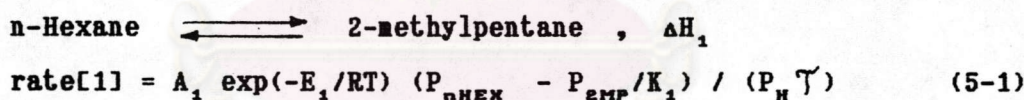
Products Co (Meerbott et al., (1954)).

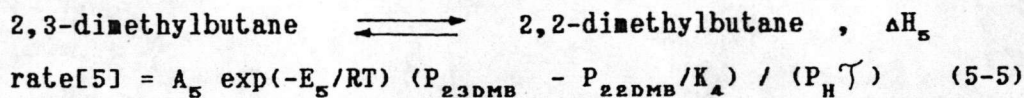
## 5.2 Reactor Model

Reaction rates: Marin et al. (1982) have reported rate equations of the  $C_6$  hydrocarbon of naphtha over a commercial reforming  $Pt-Al_2O_3$  catalyst. The main reforming reactions are isomerization, ring closure, ring expansion followed by dehydrogenation and hydrocracking. The rate equations of the Hougen-Watson type are used in this model. The feedstocks are n-hexane, 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane, 2,3-dimethylbutane, methylcyclopentane (MCP), and benzene (BZ).

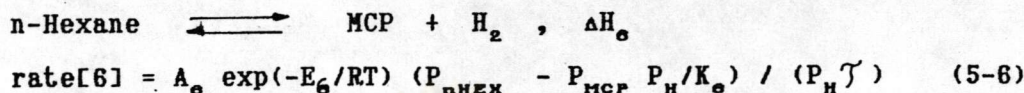
The rate equations for isomerization, ring closure, ring expansion, hydrocracking of  $C_6$  hydrocarbon can be written as

### isomerization

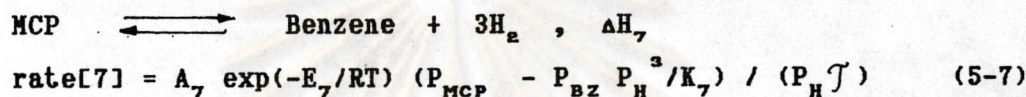




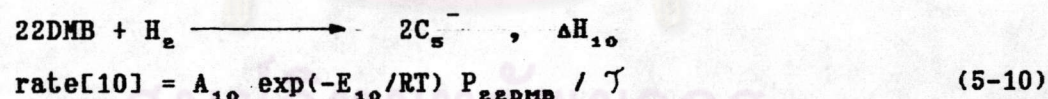
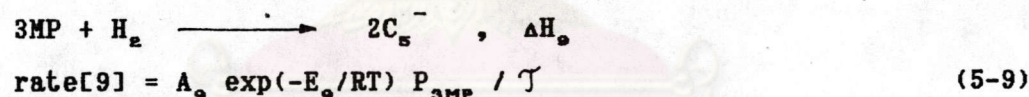
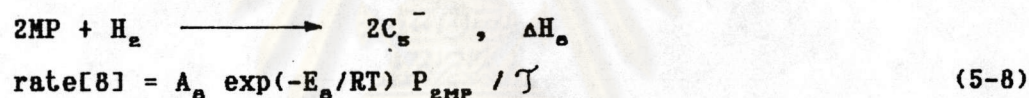
ring closure



ring expansion



hydrocracking

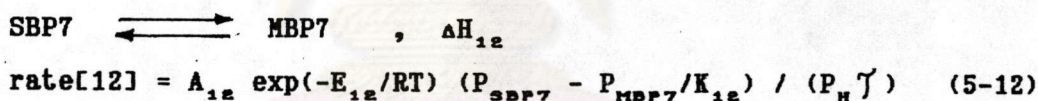
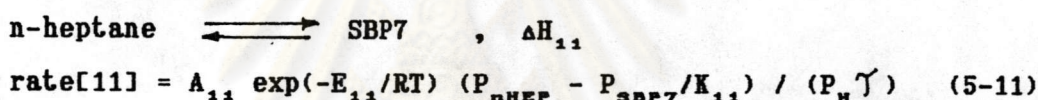


$A_1$  to  $A_{10}$  and  $E_1$  to  $E_{10}$  are Arrhenius constants and activation energies of Eq.(5-1) to (5-10), respectively, as shown in Table 5-1.  $P_{\text{nHEX}}$ ,  $P_{2\text{MP}}$ ,  $P_{3\text{MP}}$ ,  $P_{22\text{DMB}}$ ,  $P_{23\text{DMB}}$ ,  $P_{\text{BZ}}$ ,  $P_{\text{MCP}}$ ,  $P_H$  and  $K_1$  are the partial pressures of n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, benzene, methylcyclopentane, hydrogen and

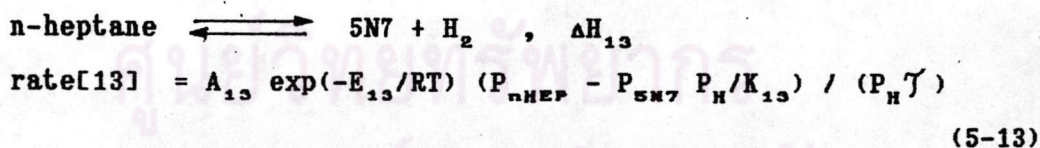
equilibrium constant of  $i^{\text{th}}$  reaction, respectively.  $\gamma$  is adsorption constant as shown in Table 5-1.

The rate equation of  $C_7$  hydrocarbon are obtained for isomerization, ring closure, ring expansion from Van Trimpont et al. (1988), and dehydrogenation of methylcyclohexane into toluene from Van Trimpont et al. (1986). The feedstock are single-branched iso-heptane (SBP7), multibranched isoheptane (MBP7), and five-ring naphthenes with seven carbon atom (5N7), n-heptane, methylcyclohexane, and toluene. The rate expressions for isomerization, ring closure, ring expansion, dehydrogenation of methylcyclohexane and hydrocracking are written as

isomerization



ring closure



ring expansion

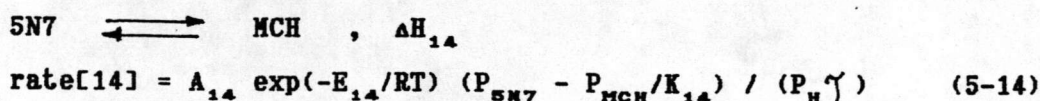
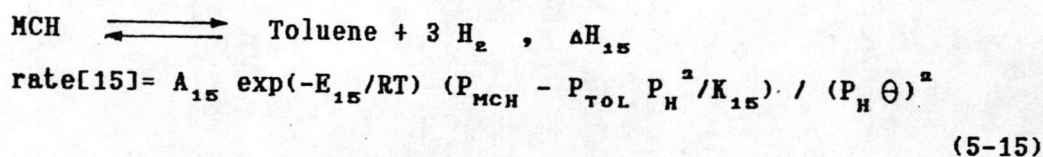


Table 5-1 Arrhenius constants, activation energies and adsorption constant for C<sub>6</sub> hydrocarbons obtained from Marin et al., (1982)

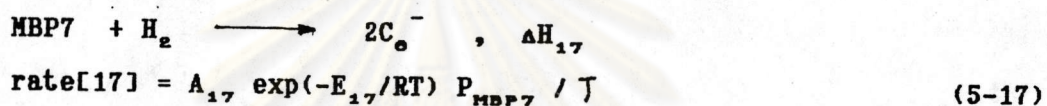
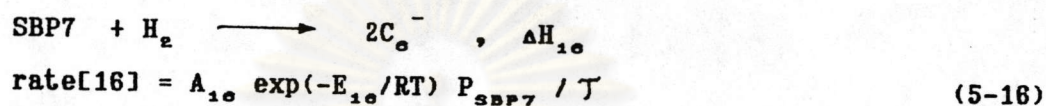
| Reaction  | A <sub>i</sub><br>kmol/kg cat. h          | E <sub>i</sub><br>kJ/mol |
|---|---|--------------------------|
| Isomerization   | A <sub>1</sub> = 1.715 x 10 <sup>10</sup> | 147.3                    |
|   | A <sub>2</sub> = 1.510 x 10 <sup>10</sup> | 147.3                    |
|   | A <sub>3</sub> = 8.766 x 10 <sup>8</sup>  | 125.2                    |
|   | A <sub>4</sub> = 8.587 x 10 <sup>9</sup>  | 147.3                    |
|   | A <sub>5</sub> = 1.029 x 10 <sup>9</sup>  | 125.2                    |
| Ring closure  | A <sub>6</sub> = 4.004 x 10 <sup>17</sup> | 264.6                    |
| Ring expansion  | A <sub>7</sub> = 8.496 x 10 <sup>10</sup> | 147.3                    |
| Hydrocracking   | A <sub>8</sub> = 6.759 x 10 <sup>8</sup>  | 147.3                    |
|   | A <sub>9</sub> = 9.494 x 10 <sup>8</sup>  | 147.3                    |
|   | A <sub>10</sub> = 9.494 x 10 <sup>8</sup> | 147.3                    |
| common adsorption term:   |   |                          |
| $\gamma = (1 + K_{HEX} (P_{nHEX} + P_{2MP} + P_{3MP} + P_{22DMB} + P_{23DMB}) / P_H + K_{MCP} P_{MCP} / P_H)^2$ |   |                          |
| $K_{HEX} = 7.601, K_{MCP} = 2.016 \times 10^2$  |   |                          |



dehydrogenation of methylcyclohexane



hydrocracking



$P_{\text{nHEP}}, P_{\text{SBP7}}, P_{\text{MBP7}}, P_{\text{SM7}}, P_{\text{MCH}}$  and  $P_{\text{TOL}}$  are the partial pressures of n-heptane, single-branched isoheptanes, multibranched isoheptanes, five-ring naphthenes with seven carbon atoms, methylcyclohexane and toluene, respectively.  $\mathcal{T}$  and  $\Theta$  are the adsorption constant for the acid and metal adsorption terms,  $A_1$  to  $A_{10}$  and  $E_1$  to  $E_{10}$  are shown in Table 5-2.

### 5.3 Model Development

Under the stated assumptions for the new model of the catalytic reforming, the system equations take the following form

#### Material Balance

$$\frac{dX_j}{d(W/F_{\text{H}_2\text{O}})} = R_j \quad (5-18)$$

Table 5-2 Arrhenius constants, activation energies and adsorption constant for C<sub>7</sub> hydrocarbons obtained from (Van Trimpont et al., (1986) and (1988))

| Reaction   | A <sub>i</sub><br>kmol/kg cat. h           | E <sub>i</sub><br>kJ/mol |
|--|--|--------------------------|
| Isomerization  | A <sub>11</sub> = 1.83 x 10 <sup>6</sup>   | 87.75                    |
|  | A <sub>12</sub> = 1.83 x 10 <sup>6</sup>   | 87.75                    |
| Ring closure   | A <sub>13</sub> = 2.48 x 10 <sup>17</sup>  | 256.4                    |
| Ring expansion   | A <sub>14</sub> = 9.08 x 10 <sup>17</sup>  | 256.4                    |
| Dehydrogenation of<br>methylcyclohexane  | A <sub>15</sub> = 3.45 x 10 <sup>11a</sup> | 121.7                    |
| Hydrocracking  | A <sub>16</sub> = 1.43 x 10 <sup>17b</sup> | 256.4                    |
|  | A <sub>17</sub> = 1.43 x 10 <sup>17b</sup> | 256.4                    |
| <p>Adsorption term for the acid function</p> $\tau = (P_H + K_{CO-}P_{CO-} + K_{P7}P_{P7} + K_{M7}P_{M7} + K_{TOL}P_{TOL}P_H)/P_H$ $K_{CO-} = 107, K_{P7} = 21.9, K_{M7} = 659, K_{TOL} = 70.3 \text{ bar}^{-1}$                         |  |                          |
| <p>Adsorption term for the metal function</p> $\theta = (1 + K_{MCH}P_{MCH} + A \exp(-\Delta H^\circ/RT) (P_{MCH}/P_H)^2)$ $K_{MCH} = 0.27 \text{ bar}^{-1}, A = 1.47 \times 10^{10} \text{ bar}, \Delta H^\circ = 99.77 \text{ kJ/mol}$ |  |                          |

<sup>a</sup> Units in (kmol bar)/kg of catalyst h).

<sup>b</sup> Units in kmol/(kg of catalyst h bar).

Energy Balance .

$$\frac{(\sum_j F_j C_{p,j}) dT}{F_{H_2O} d(W/F_{H_2O})} = \sum_i (-\Delta H_i) r_i \quad (5-19)$$

where  $R_j$  is net rate of multi-reaction of component j.  
 $r_i$  is reaction rate of reaction i.  
 $F_j$  is molar flow rate of component j.  
 $F_{j0}$  is molar flow rate of component j at initial condition.

W is weight of catalyst.

T is temperature.

$X_j$  is fraction conversion of component j which defined as

$$X_j = \frac{F_j - F_{j0}}{F_{H_2O}}$$

$C_{p,j}$  is heat capacity of species j

$\Delta H_i$  is heat of reaction of reaction i.

The thermodynamic properties, heat capacity, heat formation, Gibbs free energy of formation and equilibrium constants are calculated for different reactions in Appendix A and C. The transport properties and viscosities of gas mixture are in Appendix D.

The global rates of reactions for different components are given as follows:

For C<sub>6</sub> hydrocarbon

$$F[1] = \frac{dX_{\text{rHEX}}}{d(W/F_{\text{HC}O})} = -\text{rate}[1]-\text{rate}[2]-\text{rate}[6] \quad (5-20)$$

$$F[2] = \frac{dX_{\text{EMP}}}{d(W/F_{\text{HC}O})} = \text{rate}[1]-\text{rate}[3]-\text{rate}[4]-\text{rate}[8] \quad (5-21)$$

$$F[3] = \frac{dX_{\text{OMP}}}{d(W/F_{\text{HC}O})} = \text{rate}[2]+\text{rate}[3]-\text{rate}[9] \quad (5-22)$$

$$F[4] = \frac{dX_{\text{EEDMB}}}{d(W/F_{\text{HC}O})} = \text{rate}[5]-\text{rate}[10] \quad (5-23)$$

$$F[5] = \frac{dX_{\text{EODMB}}}{d(W/F_{\text{HC}O})} = \text{rate}[4]-\text{rate}[5] \quad (5-24)$$

$$F[6] = \frac{dX_{\text{MOP}}}{d(W/F_{\text{HC}O})} = \text{rate}[6]-\text{rate}[7] \quad (5-25)$$

$$F[7] = \frac{dX_{\text{BZ}}}{d(W/F_{\text{HC}O})} = \text{rate}[7] \quad (5-26)$$

$$F[8] = \frac{dX_{\text{H}}}{d(W/F_{\text{HC}O})} = \text{rate}[6]+3*\text{rate}[7]-\text{rate}[8]-\text{rate}[9]-\text{rate}[10] \quad (5-27)$$

$$F[9] = \frac{dX_{\text{C}_1}}{d(W/F_{\text{HC}O})} = (\text{rate}[8]+\text{rate}[9]+\text{rate}[10])*2*0.07 \quad (5-28)$$

$$F[10] = \frac{dX_{C_2}}{d(W/F_{HC O})} = (\text{rate}[8] + \text{rate}[9] + \text{rate}[10]) * 2 * 0.31 \quad (5-29)$$

$$F[11] = \frac{dX_{C_3}}{d(W/F_{HC O})} = (\text{rate}[8] + \text{rate}[9] + \text{rate}[10]) * 2 * 0.38 \quad (5-30)$$

$$F[12] = \frac{dX_{C_4}}{d(W/F_{HC O})} = (\text{rate}[8] + \text{rate}[9] + \text{rate}[10]) * 2 * 0.21 \quad (5-31)$$

$$F[13] = \frac{dX_{C_5}}{d(W/F_{HC O})} = (\text{rate}[8] + \text{rate}[9] + \text{rate}[10]) * 2 * 0.03 \quad (5-32)$$

For C<sub>7</sub> hydrocarbon

$$F[14] = \frac{dX_{nHEP}}{d(W/F_{HC O})} = -\text{rate}[11] - \text{rate}[13] \quad (5-33)$$

$$F[15] = \frac{dX_{TOL}}{d(W/F_{HC O})} = \text{rate}[15] \quad (5-34)$$

$$F[16] = \frac{dX_{MCH}}{d(W/F_{HC O})} = \text{rate}[14] - \text{rate}[15] \quad (5-35)$$

$$F[17] = \frac{dX_{SM7}}{d(W/F_{HC O})} = \text{rate}[13] - \text{rate}[14] \quad (5-36)$$

$$F[18] = \frac{dX_{SDP7}}{d(W/F_{HC O})} = \text{rate}[11] - \text{rate}[12] - \text{rate}[16] \quad (5-37)$$

$$F[19] = \frac{dX_{MBP7}}{d(W/F_{H_2O})} = \text{rate}[12] - \text{rate}[17] \quad (5-38)$$

$$F[20] = \frac{dX_H}{d(W/F_{H_2O})} = \text{rate}[13] + 3 * \text{rate}[15] - \text{rate}[16] - \text{rate}[17] \quad (5-39)$$

$$F[21] = \frac{dX_{C1}}{d(W/F_{H_2O})} = (\text{rate}[16] + \text{rate}[17]) * 2 * 0 \quad (5-40)$$

$$F[22] = \frac{dX_{C2}}{d(W/F_{H_2O})} = (\text{rate}[16] + \text{rate}[17]) * 2 * 0.187 \quad (5-41)$$

$$F[23] = \frac{dX_{C3}}{d(W/F_{H_2O})} = (\text{rate}[16] + \text{rate}[17]) * 2 * 0.375 \quad (5-42)$$

$$F[24] = \frac{dX_{C4}}{d(W/F_{H_2O})} = (\text{rate}[16] + \text{rate}[17]) * 2 * 0.313 \quad (5-43)$$

$$F[25] = \frac{dX_{C5}}{d(W/F_{H_2O})} = (\text{rate}[16] + \text{rate}[17]) * 2 * 0.125 \quad (5-44)$$

$$F[26] = \frac{dX_{C6}}{d(W/F_{H_2O})} = (\text{rate}[16] + \text{rate}[17]) * 2 * 0 \quad (5-45)$$

The selectivity of cracked products for the reforming of  $C_6$  hydrocarbons are 0.07, 0.31, 0.38, 0.21 and 0.03 for methane, ethane, propane, butane and pentane, respectively (Marin et al., (1982)).

The selectivity of cracked products for the reforming of  $C_7$  hydrocarbons are 0, 0.187, 0.375, 0.313, 0.125 and 0 for

methane, ethane, propane, butane, pentane and n-hexane, respectively (Van Trimpont et al. (1988)).

The material balance and energy balance equations for various components are obtained after the mole fraction of all reacting systems and the total pressure are substituted by  $p_i = x_i P$  in the equation  $i$  which  $x_i$  is mole fraction of component  $i$ . The energy balance equations can be written for each hydrocarbon as

For  $C_6$  hydrocarbon

$$\left( \frac{dT}{d(W/F_{HC0})} \right)_1 = \frac{1}{C_{PMIX}} \left[ \begin{aligned} &(-\Delta H_1) \text{ rate}[1] + ((-\Delta H_2) \text{ rate}[2] \\ &+ (-\Delta H_3) \text{ rate}[3] + (-\Delta H_4) \text{ rate}[4] + (-\Delta H_5) \text{ rate}[5] \\ &+ (-\Delta H_6) \text{ rate}[6] + (-\Delta H_7) \text{ rate}[7] + (-\Delta H_8) \text{ rate}[8] \\ &+ (-\Delta H_9) \text{ rate}[9] + (-\Delta H_{10}) \text{ rate}[10] \end{aligned} \right]$$

For  $C_7$  hydrocarbon

$$\left( \frac{dT}{d(W/F_{HC0})} \right)_2 = \frac{1}{C_{PMIX}} \left[ \begin{aligned} &(-\Delta H_{11}) \text{ rate}[11] + ((-\Delta H_{12}) \text{ rate}[12] \\ &+ (-\Delta H_{13}) \text{ rate}[13] + (-\Delta H_{14}) \text{ rate}[14] + (-\Delta H_{15}) \text{ rate}[15] \\ &+ (-\Delta H_{16}) \text{ rate}[16] + (-\Delta H_{17}) \text{ rate}[17] \end{aligned} \right] \quad (5-47)$$

where  $C_{p_{MIX}}$  is the heat capacity of gas mixture.

$F_{HC0}$  is total molar flow rate of hydrocarbons at initial condition.

The overall rate of temperature change along the reactor is obtained by adding the contribution of individual reactions:

$$F(27) = \left( \frac{dT}{d(W/F_{HC0})} \right)_{OVERALL} = \left( \frac{dT}{d(W/F_{HC0})} \right)_1 + \left( \frac{dT}{d(W/F_{HC0})} \right)_2 \quad (5-48)$$

Thus, the mathematical model can be written in a set of system equations as

for C<sub>6</sub> hydrocarbon

$$F(N) = f(X_{nHEX}, X_{2MP}, X_{3MP}, X_{22DMB}, X_{23DMB}, X_{MCP}, X_{BZ}, X_H, X_{CS-}, T, P) \quad (5-50)$$

where  $N=1, \dots, 13$ .

The boundary conditions at  $W/F_{HC0} = 0$ ,  $X_{nHEX}$ ,  $X_{2MP}$ ,  $X_{3MP}$ ,  $X_{22DMB}$ ,  $X_{23DMB}$ ,  $X_{MCP}$ ,  $X_{BZ}$ ,  $X_H$ ,  $X_{CS-} = 0$ ,  $T = T_{IN}$ , where  $T_{IN}$  is the temperature at the reactor inlet.

for C<sub>7</sub> hydrocarbon

$$F(N) = f(X_{nHEP}, X_{TOL}, X_{MCH}, X_{5M7}, X_{5BP7}, X_{MDF7}, X_H, X_{CS-}, T, P) \quad (5-51)$$

where  $N=14, \dots, 26$ .



The boundary conditions at  $W/F_{HC0} = 0, X_{OHEP}, X_{TOL}, X_{MCH}, X_{BN7}, X_{SBP7}, X_{MBP7}, X_H, X_{CO-} = 0, T = T_{IM}$ .

### 5.3 Development of Computer Code

The mathematical model of equation (5-50), and (5-51) are solved by the fourth-order Runge-Kutta method (Constantinides, 1987) to get concentration and temperature at different values of the independent variable ( $W/F_{HC0}$ ). C programming language is used and subroutines are shown in Figure 5-3. The subroutines perform various operation such as reading of physical properties from data bank, etc. The simulation, solving of the system of differ-ential equations, is carried out on a microcomputer.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

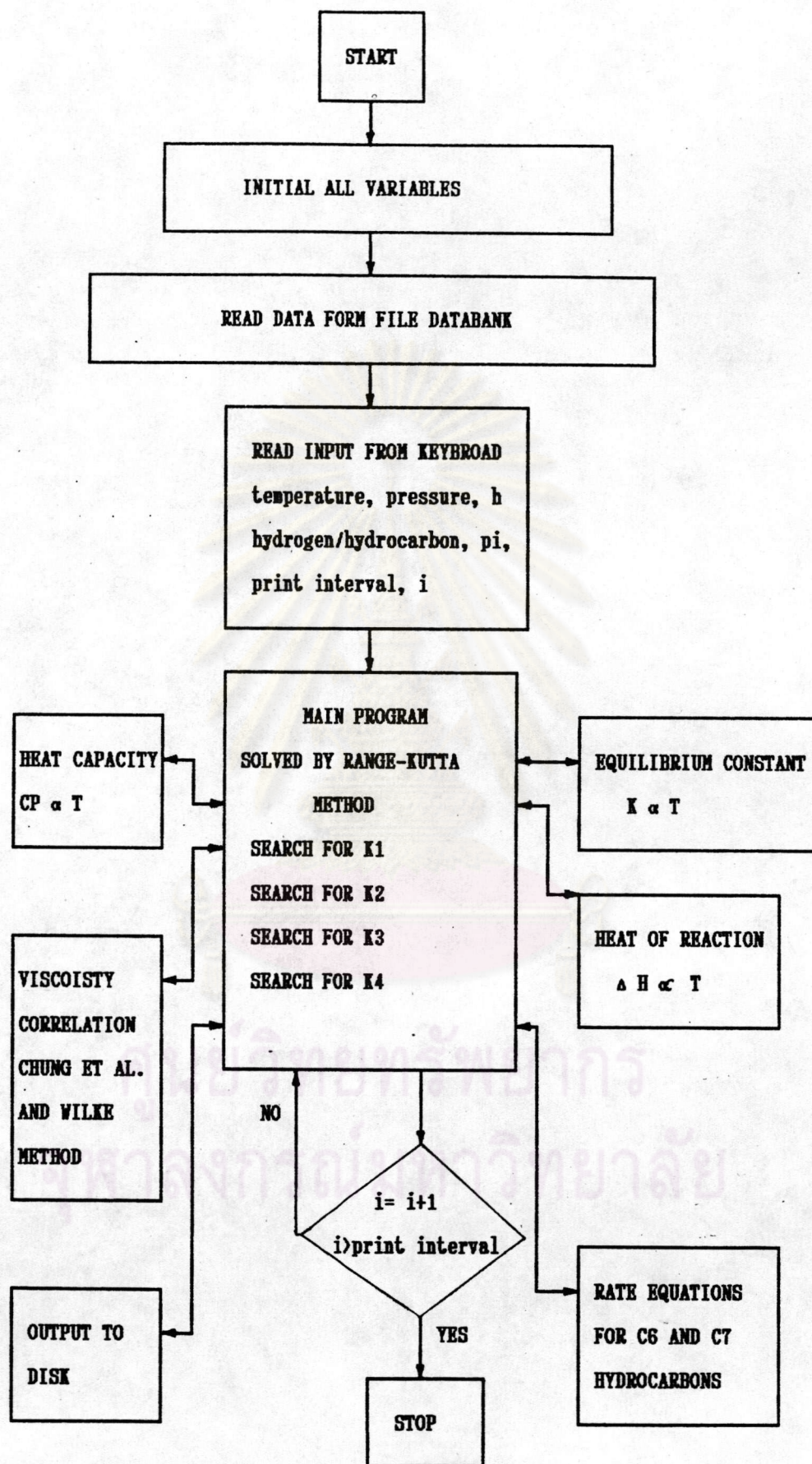


Figure 5-3 Flow chart of the programming