

## CHAPTER 3

### REVIEW OF MODELLING OF REFORMING PROCESSES

The modelling of reforming processes have been studied for many years. The studies in the early stage used Platinum on alumina catalyst, and the development of model was done continuously. Lately, bimetallic catalyst such as Platinum-Rhenium (Pt-Re) and Platinum-Iridium (Pt-Ir) were introduced in the development. The second metal in the catalyst acts as a stabilizer and at the same time suppresses catalyst deactivation better than the catalyst that uses Platinum only. Up to the present, there are many studies that use Platinum-Rhenium on alumina catalyst. This chapter will review those studies in fixed-bed reactor.

#### MOBIL's Study

A kinetic model of the catalytic reforming processes was developed by Mobil Research and Development in 1980. The study used Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst in fixed-bed reactor and experimental conditions were 454, 482, 521 °C reaction temperature; 8, 12, 20 bar hydrogen pressure; 1, 4 bar hydrocarbon pressure. This study determines the

chemical interactions of a system which contains over 300 chemical species. A complete modelling of this complex system will be very difficult to solve. Therefore, kinetic lumpings are used for this complex reaction system as shown in Table 3-1.

### 1. Assumptions

1. The nonlinear rate expressions were in the pseudo-monomolecular form, thus the nonlinear parameter estimation problems can be transformed into two simpler linear problems.

2. The kinetic model is based on Langmuir-Hinshelwood adsorption.

3. The heats of reaction and free energy data are determined a priori from thermodynamic data.

4. The reaction steps were consistent with known pure component behavior. For example, a benzene cracking reaction was not allowed.

Table 3-1 Reforming Model-Kinetic Lumps

Carbon Number	Six-Carbon Ring <u>Naphthenes (N6)</u>	Five-Carbon Ring <u>Naphthenes (N5)</u>	<u>Paraffins (P)</u>	<u>Aromatics (A)</u>
C8+	C8+Cyclohexanes	C8+Cyclopentanes	C8+Paraffins	C8+Aromatics
C7	Methylcyclohexanes	C7 Cyclopentanes	Heptane	Toluene
C6	Cyclohexanes	Methylcyclopentanes	Hexanes	Benzene
C5-			C5-hydrocarbons	

From the experiments for the relation between aromatic selectivity (aromatic weight yield/weight hydrocarbon charged; for paraffins, cyclopentanes and cyclohexanes) with carbon number it was found that the selectivity of paraffins and cyclopentanes changes considerably from six-carbon to seven-carbon and eight+-carbon. For hydrocarbons containing 8 or more carbon atoms, the selectivity within a molecular class does not vary significantly due to the similarity of their aromatization equilibrium. Therefore, the carbon number distribution required within molecular classes are C5-, C6, C7 and C8+.

The reaction network which defines the chemical interconversions between the 13 kinetic lumps is shown in Figure 3-1. This reaction network results from kinetic studies on pure components and narrow boiling naphthas. The reforming reactions compose of cracking, ring closure, ring isomerization and dehydrogenation. Those reactions between lumps of same carbon number are reversible while those reactions of different carbon number classes are irreversible.

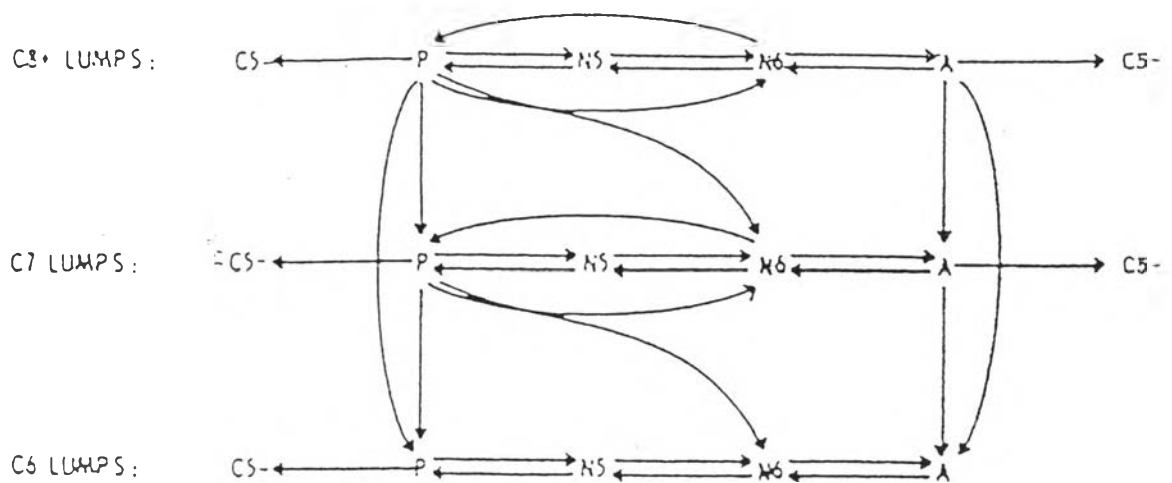


Figure 3-1 Reforming lump reaction network (N, cyclopentane and cyclohexane naphthenes ; P, paraffins; A, aromatics; C5-, pentane and lighter hydrocarbon)

## 2. Reactor Model

Reaction rates for the reforming system are described by pseudo-monomolecular rates of change of the 13 kinetic lumps. The rates of change of the lumps are represented by first-order expressions. Steady state material balances for the hydrocarbon lumps written over a differential catalyst volume,  $dv$ , are

$$\frac{d\bar{w}}{dv} = \phi \bar{K} \bar{w} \quad (3-1)$$

where

$$\phi = \frac{\frac{pV_c}{FRT} k_\phi}{1 + K_h P_h + \frac{pG}{F} \bar{K}_a \bar{w}} \quad (3-2)$$

$p, P_h$	=	total and hydrocarbon pressure
$V_c$	=	total catalyst volume
$T$	=	temperature
$F$	=	total molar flow
$G$	=	mass flow rate hydrocarbon charge
$\bar{K}_a, K_h$	=	adsorption equilibria coefficients
$\bar{w}$	=	vector of hydrocarbon weight fractions
$\bar{K}$	=	pseudo-monomolecular selectivity rate constant matrix
$k_\phi$	=	real time rate constant

Equation (3-1) is derived for a plug-flow, fixed-bed reactor. The Langmuir-Hinshelwood adsorption model is employed. Hydrocarbon weight fraction,  $w_j$ , is defined on a  $H_2$ -free basis where

$$w_j = p_j F M_j / p G (1-h) \quad (3-3)$$

$h$  is the weight fraction yield of  $H_2$ , typically 0.01 to 0.02 and therefore  $(1-h) \cong 1$ . The hydrogen yield ( $h$ ) can be calculated from a hydrogen atom balance on the 13 hydrocarbon lumps.

$M_j$  and  $p_j$  are the molecular weight and partial pressure of lump  $j$ , respectively.

$\phi$  is the catalyst activity function incorporating the adsorption equilibria effects.

$\bar{K}$  is the pseudo-monomolecular selectivity rate constant matrix whose elements are  $k_{ji}/k_\phi$ .

The form of the rate constants employed for  $k_{ji}$  and  $k_{\phi}$  is

$$k = k^{\circ} \exp \left[ -\frac{E}{R} \left[ \frac{1}{T} - \frac{1}{756} \right] \right] (p_h/1220)^n \quad (3-4)$$

where  $k$  is either  $k_{ji}$  or  $k_{\phi}$  and  $k^{\circ}$  is the rate constant at the reference conditions,  $E$  is the activation energy, and  $n$  is the reaction order in  $H_2$ .  $p_h$  in this experiment is maintained essentially constant with single pass hydrogen.

The pseudo-monomolecular form of Eq. (3-1) can be used to simplify the parameter estimation into a selectivity problem (determine  $\bar{K}$ ) and an activity problem (determine  $\phi$ ). This reduces the original highly nonlinear problem into two simpler linear problems. The separation is accomplished by defining the selectivity time,  $\tau$ , such that

$$\frac{d\bar{w}}{d\tau} = \bar{K}\bar{w} \quad (3-5)$$

where

$$d\tau = \phi dv \quad (3-6)$$



Equation (3-5) can be integrated directly to give

$$\bar{w}(\tau) = \bar{X} \exp(\Lambda\tau) \bar{X}^{-1} \bar{w}(0) \quad (3-7)$$

where  $\bar{X}$  is the matrix of eigenvectors and  $\Lambda$  is the eigenvalues of the selectivity matrix  $\bar{K}$ . Since one of the

selectivity rate constant in  $\bar{K}$  is 1.0, that is  $k_{\phi}/k_{\phi} = 1$ . This property allows the elements of  $\bar{K}$  to be determined from data alone. The selectivity time,  $\tau$ , does not need to be known.

Once  $\bar{K}$  is known, only the activity function  $\phi$  containing the realtime rate constant,  $k_{\phi}$  and adsorption equilibrium constants remain to be determined. Then, solution to the activity kinetic problem requires integration of the selectivity transformation Eq.(3-6).

$$\int_0^{\tau_f} \frac{1}{\phi} d\tau = \int_0^1 dv = 1 \quad (3-8)$$

where  $\tau_f$  is the selectivity time at the end of reactor

The integration is taken over the total catalyst bed whereas the selectivity Eq.(3-7) is integrated over total extent of reaction (as defined by yield of cracked products,  $C_{5-}$ ).

### 3. Experiment and Parameter Estimation

An isothermal fixed-bed reactor with single pass hydrogen was used to generate the data. Feedstocks consisted of three  $C_6$  component blends,  $C_6+C_7$  component naphthas, a  $C_6$  to  $C_8$  component naphtha, and  $C_6$  to  $C_{11}$  component naphthas.

Parameters (rate coefficients, activity energies, the hydrogen pressure dependencies, and adsorption equili-

brium constants) can be determined by dividing into step and using appropriated data to estimate each parameter (Ramage et al.(1980)).

The fitting sequence is based on the following partitioning of the 13x13 selectivity rate constant matrix( $\bar{K}$ ) which are shown below

$$\bar{K} = \begin{bmatrix} \begin{bmatrix} \text{C8+} \\ \text{Reversible} \\ \text{Subset} \end{bmatrix} & \begin{bmatrix} 0 \end{bmatrix} & \begin{bmatrix} 0 \end{bmatrix} & \begin{bmatrix} \end{bmatrix} \\ \begin{bmatrix} \text{C8+} \\ \text{Cracking} \\ \text{to C7} \end{bmatrix} & \begin{bmatrix} \text{C7} \\ \text{Reversible} \\ \text{Subset} \end{bmatrix} & \begin{bmatrix} 0 \end{bmatrix} & \begin{bmatrix} 0 \end{bmatrix} \\ \begin{bmatrix} \text{C8+} \\ \text{Cracking} \\ \text{to C6} \end{bmatrix} & \begin{bmatrix} \text{C7} \\ \text{Cracking} \\ \text{to C6} \end{bmatrix} & \begin{bmatrix} \text{C6} \\ \text{Reversible} \\ \text{Subset} \end{bmatrix} & \begin{bmatrix} \end{bmatrix} \\ \begin{bmatrix} \end{bmatrix} & \begin{bmatrix} \text{C5-formation} \end{bmatrix} & \begin{bmatrix} \end{bmatrix} & \begin{bmatrix} \end{bmatrix} \end{bmatrix}$$

for  $w = (8+N6, 8+N5, 8+P, 8+A, 7N6, 7N5, 7P, 7A, 6N6, 6N5, 6P, 6A, C5-)$

This model accurately predicts the selectivity for reforming naphthas. Figure 3-2 and 3-3 show that the model predicts reformate composition as a function of feedstock and process condition.



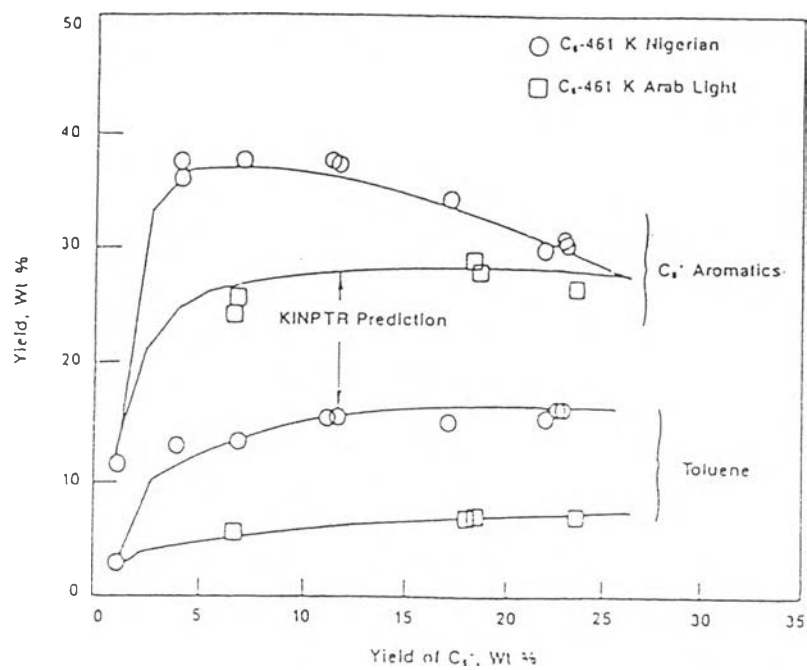


Figure 3-2 Effect of feedstock type on aromatic selectivity

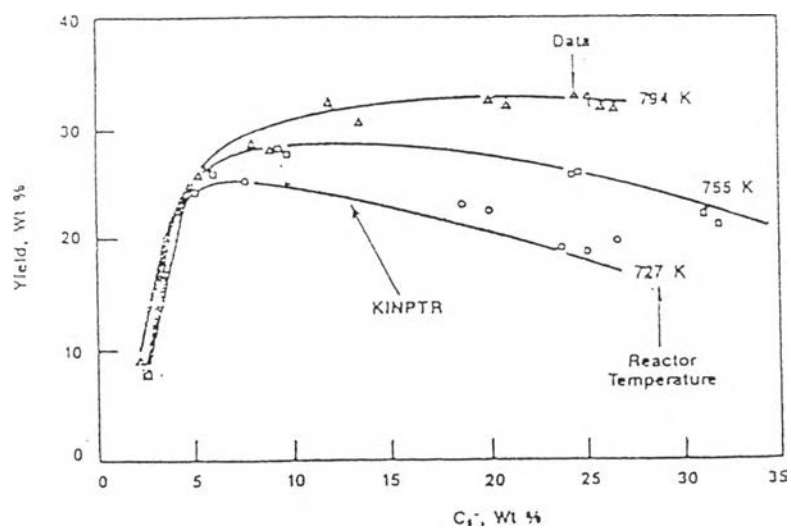


Figure 3-3 Effect of temperature on C<sub>8</sub>+ aromatic selectivity at 20 bar

## Marin and Froment's Study

Kinetic model for C<sub>6</sub> hydrocarbons on Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst in a fixed-bed reactor was studied by Marin and Froment in 1982. The temperature was varied from 420 to 500 °C, and pressure from 1.6 to 16 bar. They presented the model by considering the reaction network shown in Figure 3-4.

### 1. Assumptions

1. The model was represented by Hougen-Watson rate equation.

2. Deactivation was neglected because of high hydrogen partial pressure.

3. Pressure drop in the reactor was neglected due to an assumption that molar hydrogen/hydrocarbon ratio was constant.

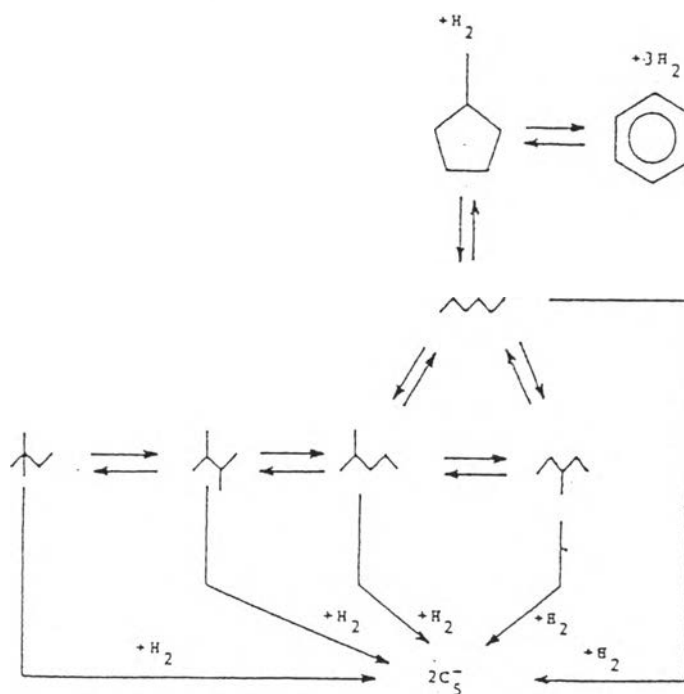


Figure 3-4 Reaction network of C<sub>6</sub> hydrocarbon

## 2. Experiment

This study used C<sub>6</sub> hydrocarbon feedstock and  $W/F_{HC}^0$  curves were determined in the fixed-bed reactor at total pressures ranging from 10 to 16 bar, molar hydrogen/hydrocarbon inlet ratios from 10 to 20 and temperatures from 420 to 500 °C.

## 3. Reactor Model

### 3.1. Material Balance Equation

From the law of conservation of mass on a volume element for the reactor :

$$\begin{array}{ccccccc}
 \left| \begin{array}{l} \text{Amount of A} \\ \text{introduced} \\ \text{per unit time} \end{array} \right| & - & \left| \begin{array}{l} \text{Amount of A} \\ \text{leaving} \\ \text{per unit time} \end{array} \right| & - & \left| \begin{array}{l} \text{Amount of A} \\ \text{converted} \\ \text{per unit time} \end{array} \right| & = & \left| \begin{array}{l} \text{Amount of A} \\ \text{accumulated} \\ \text{per unit time} \end{array} \right| \\
 1 & & 2 & & 3 & & 4 \\
 \end{array} \tag{3-9}$$

The general form of the continuity equation for a chemical species  $j$  reacting in a flowing fluid with varying density, temperature, and composition is :

$$\frac{\partial C_j}{\partial t} + \nabla \cdot (C_j u) + \nabla \cdot J_j = R_j \tag{3-10}$$

Note: The derivation for continuity equation for the component of fluid flowing in a reactor is considered in detail in texts on transport process (e.g. Bird et al. (1960)).

The term and symbols used in this equation have the following meaning :

$C_j$  is the molar concentration of species  $j$  (kmole/m<sup>3</sup> of fluid)

$\frac{\partial C_j}{\partial t}$  is the non-steady state term expressing accumulation or depletion

$u$  is the three dimensional mass average velocity vector, defined by :

$$u = \sum_i^N M_i C_i u_i$$

where  $\rho_f$  is the density of mixture and  $u_j$  represents the velocity of molecules of species  $j$

$\nabla$  is the "nabla" or "del" operator

For rectangular coordinate system, term  $\nabla$  is defined as

$$\nabla = \sum_i \frac{\partial}{\partial x_i} \quad (3-11)$$

For example, the divergence of a vector function  $u$  is

$$\nabla \cdot u = \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \quad (3-12)$$

Reactor in this model is tubular chemical reactor (or fixed-bed reactor) shown in Figure 3-5.

The assumptions of this system are

- (1) plug flow reactor
- (2) bulk flow takes place only in axial direction
- (3) steady state turbulent flow
- (4) adiabatic operation

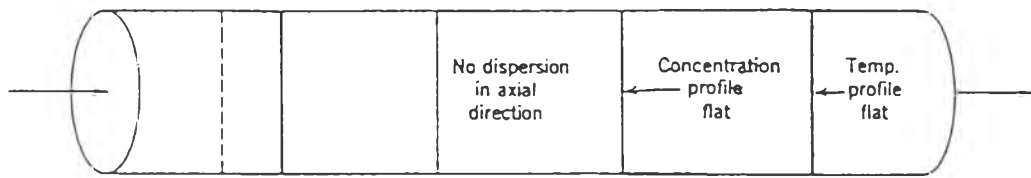


Figure 3-5 Tubular reactor

From the above assumptions, the component mole balance equation reduces to

$$-u_s \frac{dC_j}{dz} = R_j \quad (3-13)$$

where  $u_s$  is the superficial velocity, volume rate of flow through a unit cross-section area of the solid plus fluid.

$R_j$  is the total rate of change of the amount of  $j$  because of reaction which defined as the following, for multireaction,

$$R_j = \sum \alpha_{ij} r_i$$

$\alpha_{ij}$  is the stoichiometric coefficient of component  $i$  in the  $i^{\text{th}}$  reaction and  $r_i$  is the reaction rate of  $i^{\text{th}}$  reaction

If the reaction is homogeneous the unit could be  $\text{kmol/m}^3 \cdot \text{s}$  but for a reaction catalyzed by a solid preference would be given to  $\text{kmol/kg cat} \cdot \text{s}$  and multiplied by the catalyst bulk density,  $\rho_B$ , in the reaction, thus Eq. (3-13) can be rewritten as :



$$-u_s \frac{dC_j}{dz} = \rho_B R_j \quad (3-15)$$

Equation (3-15) is obtained from a material balance on a reference component  $j$ , over an elementary cross section of the tubular reactor, containing an amount of catalyst ( $dW$ ). Indeed, as previously mentioned, rate equations for heterogeneously catalyzed reactions are generally referred to unit catalyst weight, rather than reactor volume, in order to eliminate the bed density. Obviously, different packing densities between the laboratory reactor in which kinetic data were determined and the industrial reactor, calculated on the basis of these data would lead to different results.

When use is made of conversion, the material balance for over an elementary weight of catalyst may be written as :

$$R_j \rho_B A dz = F_{HC} dx_j \quad (3-16)$$

where  $F_{HC}^\circ$  is the molar feed rate of hydrocarbon at initial condition

$A$  is the cross section area

$x_j$  is the fraction conversion which defined as the following

$$x_j = \frac{F_j - F_{j0}}{F_{HC}} \quad (3-17)$$

Then, material balance is

$$\frac{dx_j}{d(W / F_{HC})} = R_j \quad (3-18)$$

### 3.2. Energy Balance Equation

In an energy balance over a volume element of a chemical reactor, kinetic, potential, and work terms may usually be neglected relative to the heat of reaction and other heat transfer terms so that the balance reduces to

Amount of heat added per unit time	-	Amount of heat out per unit time	-	Heat effect of the reaction per unit time	=	Variation of heat content per unit time
1		2		3		4

(3-19)

In mathematical expression for equation (3-19) is generally called the energy equation. Again reference is made to Bird et al. (1960) for rigorous derivation, invarious coordinate system, of the fundamental energy equation. The following form, with respect to a rectangular coordinate system, contains the phenomena that are of importance in reactor :

$$\sum_j M_j C_j C_{p_j} \left( \frac{\partial T}{\partial t} + u \cdot \nabla T \right) = \sum_i (-\Delta H_i) r_i + \nabla \cdot (\lambda \nabla T) - \sum_j J_j \nabla H_j + Q_{RAD}$$

(1)      (2)                      (3)                      (4)                      (5)                      (6)

(3-20)



where  $C_{p_j}$  is the heat of species  $j$  (kcal/kg. C or kJ/kg.K)

$\lambda$  is the thermal conductivity of the mixture  
(kcal/m.hr.°C or kJ/m.s.K)

$H_j$  is the partial molar enthalpies (kcal/kmol or  
kJ/kmol)

$M_j$  is the molecular weight of species  $j$

$u$  is the vector velocity of fluid flow

The meaning for the each term in equation(3-20) is:

<u>Term</u>	<u>Meaning</u>
1	Change of heat with time
2	Convective flow
3	Heat effect of the chemical reactions
4	Heat transport by conduction
5	Energy flux by molecular diffusion
6	Radiation heat flux

Furthermore, by neglecting the heat radiation and diffusion term, and lumping the heat conduction, the result becomes :

$$\sum_j M_j C_j C_{p_j} \left( \frac{\partial T}{\partial t} + u \cdot \nabla T \right) = \sum_i (-\Delta H_i) r_i + \frac{\partial}{\partial x} \left( \lambda_{e,x} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda_{e,y} \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \lambda_{e,z} \frac{\partial T}{\partial z} \right) \quad (3-21)$$

where  $\lambda_e$  is an effective thermal conductivity

For the tubular reactor, and the adiabatic reactor, the heat conductivity in the z-direction is usually much smaller than the heat transport by convection (from assumption, flow only in z-direction), thus the resulting equation is

$$\sum_j M_j C_j C_{p_j} \left( \frac{\partial T}{\partial t} + u \cdot \nabla T \right) = \sum_i (-\Delta H_i) r_i \quad (3-22)$$

For the steady state condition, the first term of left hand side of equation (3-22) would be zero. Equation (3-22) becomes

$$\sum_j M_j C_j C_{p_j} (u \cdot \nabla T) = \sum_i (-\Delta H_i) r_i \quad (3-23)$$

As in the energy balance equation, equation (3-23) is commonly written as

$$\left( \sum_j \frac{F_j C_{p_j}}{F_{HC}} \right) \frac{dT}{d(W / F_{HC})} = \sum_i (-\Delta H_i) r_i \quad (3-24)$$

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

From the experimental data, they obtained the parameter estimation by minimization of objective function

$S(\theta)$ :

$$S(\theta) = \sum_{j=1}^v \sum_{l=1}^v w_{jl} \sum_{i=1}^n (Y_{ij} - Y_{ij})(Y_{ii} - Y_{ii}) \quad (3-25)$$

where  $v$  is the number of responses,  $n$  the number of performed experiments and  $w_{jl}$  the  $(j,l)$  elements of the inverse of the covariance matrix of the experimental errors on the responses  $Y$ .  $S(\theta)$  was minimized by means of a generalized Marquardt technique. Rate equations and parameters are shown in Table 3-2. Experimental conversions are compared with those obtained by integration of Eq.(3-25) in Figure 3-6.

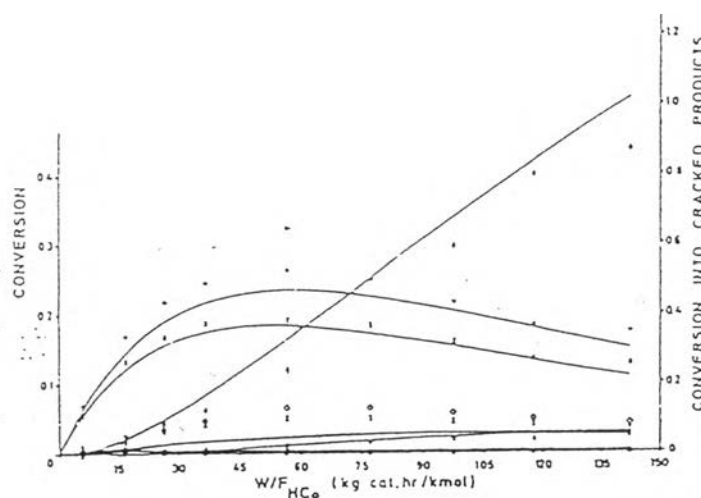


Figure 3-6 Conversion at 460 °C, 16 bar and n-hexane feed

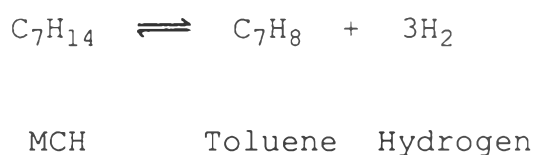
**Table 3-2** Reaction rate equations, parameter estimates.

<b>Isomerization :</b>	rate = $A_0 \exp(-E/RT)(p_A - p_B/K_{A-B})/(p_H \Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
nH $\rightleftharpoons$ 2MP	1.715E+10	147.3
nH $\rightleftharpoons$ 3MP	1.510E+10	147.3
2MP $\rightleftharpoons$ 3MP	8.766E+08	125.2
2MP $\rightleftharpoons$ 2,3DMB	8.587E+09	147.3
2,3DMB $\rightleftharpoons$ 2,2DMB	1.029E+09	125.2.3
<b>Hydrocracking :</b>	rate = $A_0 \exp(-E/RT) p_A / (\Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
2MP + H <sub>2</sub> $\rightarrow$ 2C <sub>5</sub> <sup>-</sup>	6.759E+08	147.3
3MP + H <sub>2</sub> $\rightarrow$ 2C <sub>5</sub> <sup>-</sup>	9.494E+08	147.3
2,2DMB + H <sub>2</sub> $\rightarrow$ 2C <sub>5</sub> <sup>-</sup>	1.076E+09	147.3
<b>Ring closure :</b>	rate = $A_0 \exp(-E/RT)(p_A - p_B p_H / K_{A-B}) / (p_H \Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
nH $\rightleftharpoons$ MCP + H <sub>2</sub>	4.004E+17	264.6
<b>Ring expansion:</b>	rate = $A_0 \exp(-E/RT)(p_A - p_B p_H^3 / K_{A-B}) / (p_H \Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
MCP $\rightleftharpoons$ Bz + 3H <sub>2</sub>	8.496E+10	147.3
<u>Common Adsorption Term :</u>		
$\Gamma = (1 + K_{Hex}(p_{nH} + p_{MP} + p_{DMB}) / p_H + K_{MCP} p_{MCP} / p_H)^2$		
$K_{Hex} = 7.601 ; K_{MCP} = 2.016E+02$		

### Jothimurugesan et al.'s Study

In 1985, Jothimurugesan, Bhatia and Srivastava investigated the kinetics of dehydrogenation of methylcyclohexane (MCH) in a fixed-bed reactor at atmospheric pressure and over a temperature range from 325-425 °C.

The reaction is represented as:



#### 1. Assumptions

1. The kinetic model is analyzed on the basis of Langmuir-Hinshelwood kinetics and rate constants follow Arrhenius temperature dependency.

2. The system is a fixed-bed reactor which assumed the ratio between hydrogen and hydrocarbon to be constant throughout the reactor, approximately 5.

3. Pressure drop through the reactor is neglected.

#### 2. Experiment

Reactions were carried out in a fixed-bed reactor in the presence of added hydrogen and the results of different feedstocks between pure MCH and MCH+Tol (in

different concentrations) was investigated at temperature 325, 350, 375, and 425 °C, pressure 1 bar, and hydrogen/hydrocarbon is 5.

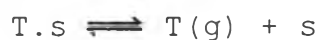
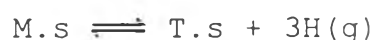
### 3. Reactor Model

From the study and experiment on the reaction of dehydrogenation of MCH, they found that the mechanism of this reaction can be written as follows:

1. MCH was adsorbed on the surface of catalyst, represented by



2. The dehydrogenation step can be shown in the series of steps as:



From the above mechanism, the isothermal rate equations are given in Table 3-3 and the results will be used to compare with the experimental data.

**Table 3-3** Possible Isothermal Rate Equations for the Reaction



model	rate-controlling step	rate equation
SA	single-site adsorption of methylcyclohexane	$r = k(p_M - p_T p_H^3 / K) / (1 + K_M p_T p_M^3 / K + K_T p_T + K_H p_H + K_N p_N)$
SS	single-site surface reaction	$r = k K_M (p_M - p_T p_H^3 / K) / (1 + K_M p_M + K_T p_T + K_H p_H + K_N p_N)$
DS	dual-site surface reaction	$r = k N_M (p_M - p_T p_H^3 / K) / (1 + K_M p_M + K_T p_T + K_H p_H + K_N p_N)^2$

N represents inert nitrogen

Rate equations were eliminated when any of the derived adsorption equilibrium constants were negative. Table 3-4 gives the rate models with all positive constants which were retained on statistical grounds after the isothermal regressions. From the data, SA-2 (adsorption of both methylcyclohexane and toluene) was considered to be the best model.

**Table 3-4** Models Remaining after Isothermal Regression for the Reaction



model	rate-controlling step	rate equation
SA-2	adsorption of methylcyclohexane <sup>a</sup>	$r = k(p_M - p_T p_H^3 / K) / (1 + K_T p_T)$
SS-2	single-site surface reaction <sup>a</sup>	$r = k K_M (p_M - p_T p_H^3 / K) / (1 + K_M p_M + K_T p_T)$
DS-2	dual-site surface reaction <sup>a</sup>	$r = k K_M (p_M - p_T p_H^3 / K) / (1 + K_M p_M + K_T p_T)^2$

<sup>a</sup>Only T is being adsorbed

The effect of temperature on rate constants was as determined the Arrhenius equation. From the data which experimented by Jothimurugesan et al., shown the following relations

$$k = 1366 \exp(-6200/T_{\text{abs}}) \quad (3-26)$$

$$K_T = 0.0633 \exp(1600/T_{\text{abs}}) \quad (3-27)$$





Van Trimfont et al.'s Study

In 1986, Van Trimfont, Marin and Froment studied and experimented the reforming process of  $C_7$  hydrocarbon in a tubular reactor. The temperature varied between  $420\text{ }^\circ\text{C}$  and  $500\text{ }^\circ\text{C}$ , total pressure between 4 and 16 bar. The kinetic analysis of the experimental data was based on the reaction network in Figure 3-7.

1. Assumptions

1. This study used Pt-Re/ $\text{Al}_2\text{O}_3$  catalyst under non-deactivating conditions.

2. The kinetic analysis of reforming reaction can be explained by Langmuir-Hinshelwood kinetic.

3. Internal diffusion was neglected.

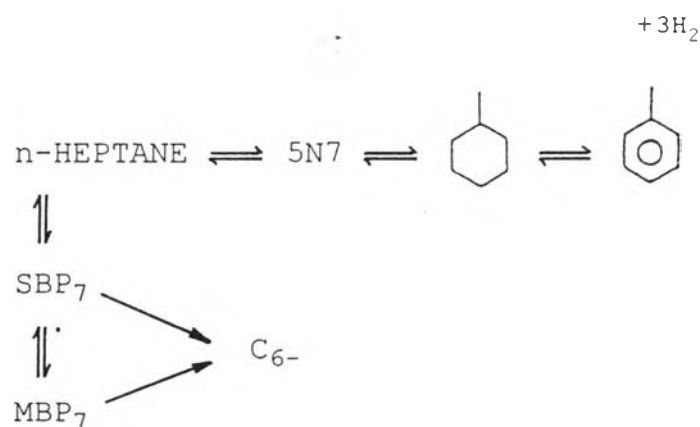


Figure 3-7 Lumped reaction network for the  $C_7$  hydrocarbon

## 2. Experiment

This study used C<sub>7</sub> hydrocarbon feedstock and  $W/F_{HC}^0$  curves were determined in the fixed-bed reactor at total pressures ranging from 4 to 16 bar, molar hydrogen/hydrocarbon ratios from 1 to 30 and temperatures from 420 to 500 °C.

## 3. Reactor Model

The model discrimination for this system was based on the regression of 1548 experimental conversions divided over six responses : the conversions into the single- and multi-branched isoheptanes, the hydrocracked products, the cyclopentanes, methylcyclohexane and toluene.

Van Trimfont et al. selected the Hougen-Watson rate equation for this study. The obtained rate equations and parameters are shown in Table 3-5. Comparison of the experimental and calculated conversions are shown in Figure 3-8.

**Table 3-5** Reaction rate equations, parameter estimates  
for the reforming of C<sub>7</sub> hydrocarbon on PtRe/Al<sub>2</sub>O<sub>3</sub>

<b>Isomerization :</b>	rate = $A_0 \exp(-E/RT)(p_A - p_B / K_{A-B}) / (p_H \Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
$nP_7 \rightleftharpoons SBP_7$	3.85E+14	201.1
$nP_7 \rightleftharpoons MBP_7$	1.51E+14	201.1
<b>Hydrocracking :</b>	rate = $A_0 \exp(-E/RT) p_A / (p_H \Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
$iP_7 + H_2 \rightarrow 2C_6^-$	1.46E+17	241.0
<b>Ring closure :</b>	rate = $A_0 \exp(-E/RT)(p_A - p_B p_H / K_{A-B}) / (p_H \Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
$nC_7 \rightleftharpoons 5N_7 + H_2$	1.77E+31	454.1
<b>Ring expansion:</b>	rate = $A_0 \exp(-E/RT) (p_A - p_B / K_{A-B}) / (p_H \Gamma)$	
	$A_0$ (kmole/kg cat.h)	E(kJ/mole)
$5N_7 \rightleftharpoons MCH$	1.05E+24	332.6
<b>Dehydrogena- tion of methyl- cyclohexane :</b>	rate = $A_0 \exp(-E/RT)(p_{MCH} - p_{Tol} p_H^3 / K_{A-B}) / \theta$	
	$A_0$ (kmole/kg cat.h.bar)	E(kJ/mole)
$MCH \rightleftharpoons Tol + 3H_2$	2.69E+11	154.6
<u>Adsorption term for the acid function :</u>		
$\Gamma = (p_H + K_{C6-} p_{C6-} + K_{P7} p_{P7} + K_{Tol} p_{Tol} p_H) / (p_H)$		
$K_{C6-} = 90.1 ; K_{P7} = 9.0 ; K_{Tol} = 7.5 \text{ bar}^{-1}$		
<u>Adsorption term for the metal function :</u>		
$\theta = 1 + K_{nP7} p_{nP7} + K_{MCH} p_{MCH} + K_{Tol} p_{Tol}$		
$K_{nP7} = 1.84 \text{ bar}^{-1} ; K_{MCH} = 2.23 \text{ bar}^{-1} ; K_{Tol} = 12.7 \text{ bar}^{-1}$		

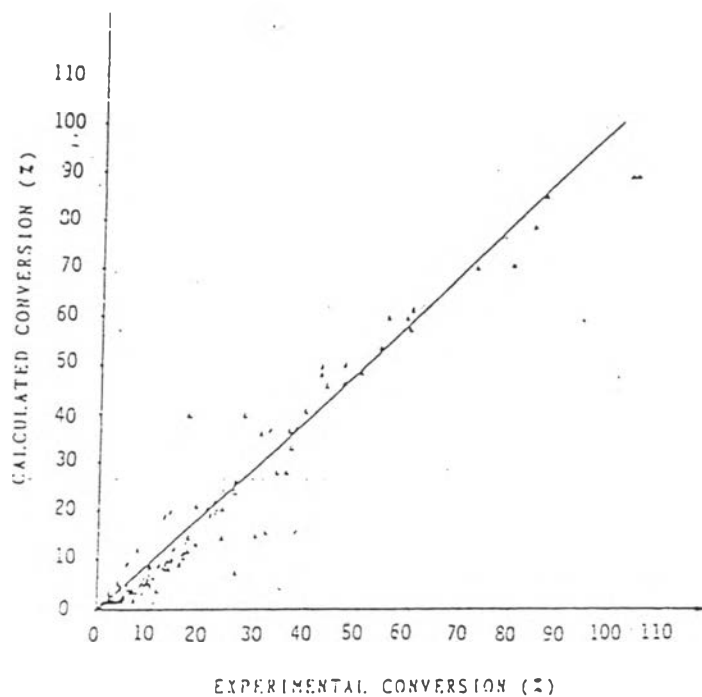


Figure 3-8 Experimental versus calculated conversions over the range of experimental conditions.

### Summary of Existing Modelling

The kinetic models studied above can be summarized as follows

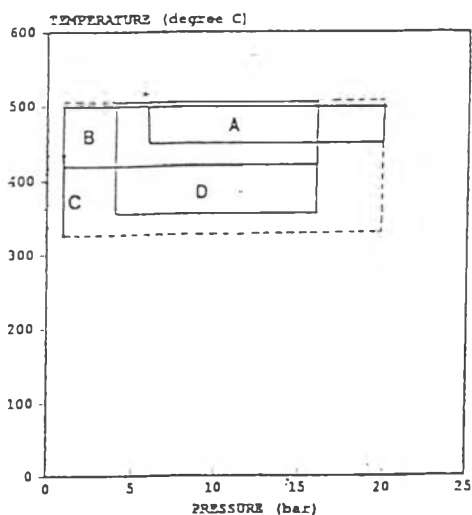


Figure 3-9 Comparison of each model in its operating condition (A, MOBIL'S; B, Marin's; C, Jothimurugesan's; D, Van Trimfont's)

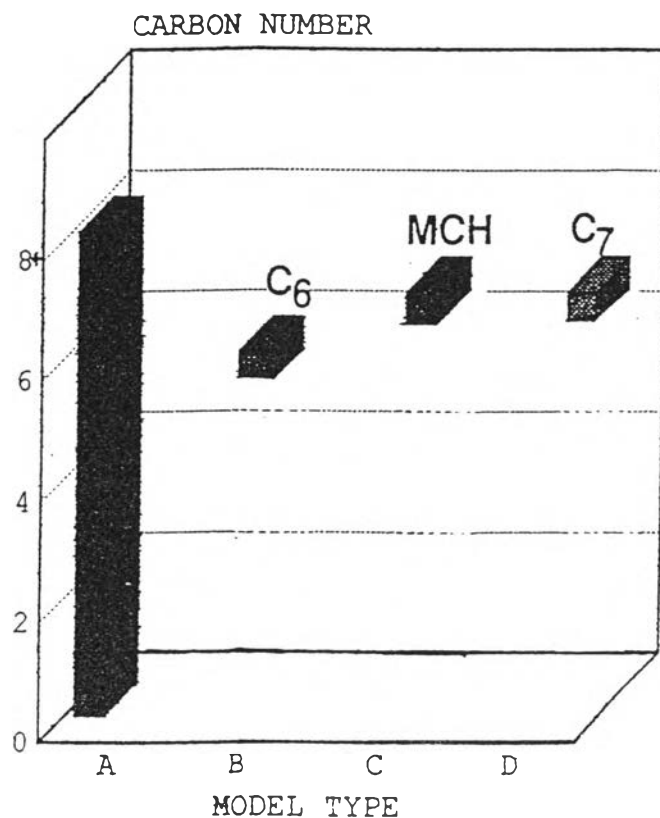


Figure 3-10 Comparison of each model which using the different feedstock.

From the above figure, we obtain the new models which can predict the behavior of reforming process in the range of temperature and pressure which cover all the past experimentals. The new models are then developed by using the advantage of each model and assuming the reaction between  $C_6$  and  $C_7$  hydrocarbons are independent. The new models are as follows:

1. The model that uses Marin and Froment's mechanism (for C<sub>6</sub> hydrocarbons) and Van Trimfornt's mechanism (for C<sub>7</sub> hydrocarbons).

2. The model that uses Marin and Froment's mechanism (for C<sub>6</sub> hydrocarbons), Jothimurugesan's mechanism (for dehydrogenation of MCH) and Van Trimfornt's mechanism (for C<sub>7</sub> hydrocarbons except dehydrogenation of MCH).

3. The model that uses MOBIL's mechanism (without interaction between C<sub>6</sub> and C<sub>7</sub> hydrocarbons)

The new models will be explained in detail in the Chapter 4.