CHAPTER 4

REVIEW OF MODELING OF REFORMING PROCESSES

4.1 Introduction

Kinetic models of reforming processes were first developed by Smith (1959) and Krane et al. (1959). Smith considered the modeling of the four reactor reforming system and included temperature effects. The feed is lumped into three groups, paraffins, naphthenes, and aromatics, and the reactions to be considered include conversion of naphthenes into aromatics, conversion of naphthenes into paraffins, hydrocracking of paraffins, and hydrocracking of naphthenes.

Krane et al considered that the naphtha be broken down into its separate components and that these component be lumped into classes of components with similar properties and kinetic behavior. The temperature dependence was not determined.

Henningsen et al. (1970) considered alkylcyclohexanes and alkylcyclopentanes because the dominant reaction of the alkylcyclohexanes is by far the direct dehydrogenation and the alkylcyclopentanes have first to undergo isomerization, which is a slow reaction , before dehydrogenation take places. Followings are reviews of the main models of reforming processes as published in literature.

(1) Smith reforming model,

(2) Krane et al. reforming model, and

(3) Henningsen et al. reforming model

4.2 Smith reforming Model

Kinetic model of the reforming processes with platinum catalyst was studied by Smith (1959). He presented a model by considering four major reactions. The naphtha feed is lumped into paraffins, naphthenes, and aromatics. The four major reactions are

(1) naphthenes $\rightleftharpoons$ aromatics + 3 H_2 (4-1)

(2) paraffins $\rightleftharpoons$ naphthenes + H_2 (4-2)

(3) hydrocracking of paraffins (4-3)

(4) hydrocracking of naphthenes (4-4)

4.2.1 Assumption

The naphtha feed is idealized so that each of hydrocarbon classes- paraffins, naphthenes, and aromatics- is represented by a single compound having the average properties of that class. This reaction system is peculiary amenable of the type of analysis because the major products have the same number of carbon atoms as the original feed constituents, e.g.,

Heptane $\rightleftharpoons$ methylcyclohexane $\rightleftharpoons$ Toluene (4-5)

The nature of close boiling naphtha feed also suggests that each of the hydrocarbon classes in the original feed has the same number of carbon atoms. Thus,

$$M_F = n_P M_P + n_N M_N + n_A M_A \qquad (4\text{-}6)$$

where M_F is the molecular weight of feed.

M_P is the molecular weight of paraffin (C_nH_{2n+2}).

M_N is the molecular weight of naphthene (C_nH_{2n}).

M_A is the molecular weight of aromatic (C_nH_{2n-6}).

n_P, n_N, and n_A are the mole of paraffin, naphthene, and aromatic per mole of feed, respectively. Then,

$$M_F = n_P (C_n H_{2n+2}) + n_N (C_n H_{2n}) + n_A (C_n H_{2n-6}) \qquad (4\text{-}7)$$

Atomic weight of C and H are 12 and 1, respectively. Thus

$$M_F = n_P(12n + 2n + 2) + n_N(12n + 2n) + n_A(12n + 2n - 6) \qquad (4\text{-}8)$$

or

$$14n(n_P+n_N+n_A) = M_F - 2n_P + 6n_A \qquad (4\text{-}9)$$

or

$$n = \frac{1}{14} (M_F - 2n_P + 6n_A) \qquad (4\text{-}10)$$

Since $n_P+n_N+n_A$ = 1 mole of feed. The average value of n characteristic of a given naphtha feed is determined from equation (4-10)

4.2.2 Reactor Model

The system is treated as homogeneous, i.e. only one phase is involved. Reaction rate is derived from the homogeneous reaction.

For the reaction :

$$\text{naphthene (1 mole)} \rightleftharpoons \text{aromatic (1 mole)} + 3\ H_2 \qquad (4\text{-}11)$$

The reaction can be considered by the above rate equation. The forward reaction is $k_f\ p_N$, and the reverse reaction rate is $k_r p_A\ p_{H2}^3$. The net forward reaction rate is

$$\frac{d\ X_N}{d\ (W/F_{HCo})} = k_f\ p_N - k_r\ p_A\ p_{H2}^3 \qquad (4.12)$$

where P_i is the partial pressure of component i.

X_i is the fraction conversion.

W is the weight of catalyst.

F_{HC} is molar feed rate of hydrocarbon at initial condition.

At equilibrium, then

$$k_f p_N = k_r\ p_A\ p_{H2}^3$$

and the equilibrium constant is

$$K_p = k_f/k_r = \frac{p_A\ p_{H2}^3}{p_N} \qquad (4\text{-}13)$$

Substituting and rearranging, the net forward reaction rate is

$$\frac{-d\ X_N}{d\ (W/F_{HCo})} = \frac{k_f\ p_N}{K_p}\left(K_p - \frac{p_A\ p_{H2}^3}{p_N}\right) \qquad (4\text{-}14)$$

Equilibrium and rate constants determined from data obtained from reforming run over extreme ranges of space velocity with Sinclair baker platinum catalyst of virgin activity

are:

$$K_p = \exp\left(46.15 - \frac{46{,}045}{T}\right), \quad atm^3 \tag{4-15}$$

$$k_f = \exp\left(23.21 - \frac{34{,}750}{T}\right), \quad \frac{\text{moles}}{(\text{hr})(\text{lb cat.})(\text{atm})} \tag{4-16}$$

and heat of reaction = 30,500 Btu/mole of H_2 liberated

Similarly, for the reaction

$$\text{naphthene (1 mole)} + H_2 \rightleftharpoons \text{paraffin (1 mole)} \tag{4-17}$$

the equilibrium constant is

$$K_p = k_f/k_r = \frac{p_P}{p_N\, p_{H2}}$$

Substituting and rearranging, the net forward reaction rate is

$$\frac{-d\, X_N}{d\,(W/F_{Hco})} = \frac{k_f}{K_p}\, p_N\, p_{H2} \left(K_p - \frac{p_P}{p_N\, p_{H2}} \right) \tag{4-18}$$

Equilibrium and rate constants are:

$$K_p = \exp\left(8{,}000 - \frac{7.12}{T}\right), \quad atm^{-1} \tag{4-19}$$

$$k_f = \exp\left(35.98 - \frac{59{,}600}{T}\right), \quad \frac{\text{moles}}{(\text{hr})(\text{lb cat.})(\text{atm})^2} \tag{4-20}$$

and heat of reaction = -19,000 Btu/mole of H_2 consumed

The C1 through C5 fractions produced by hydrocracking were observed to occur in approximately equal molar portions. Thus for paraffin cracking the stoichiometric equation would be, for $C_{15}H_{32}$ as an example

$$C_{15}H_{32} + 4H_2 \longrightarrow C_1 + C_2 + C_3 + C_4 + C_5$$

for the general case

$$C_n H_{2n+2} + \frac{(5n-15)}{15} H_2 \longrightarrow n/15\ C_1 + n/15\ C_2 + n/15\ C_3 + n/15\ C_4 + n/15\ C_5$$

or

$$C_n H_{2n+2} + \frac{(n-3)}{3} H_2 \longrightarrow n/15\ C_1 + n/15\ C_2 + n/15\ C_3 + n/15\ C_4 + n/15\ C_5 \qquad (4\text{-}21)$$

The reaction rate is

$$\frac{-d\,X_p}{d\,(W/F_{HCo})} = \frac{kc'}{\pi}\, p_p \qquad (4\text{-}22)$$

Where π is total pressure, and kc is rate constant for hydrocracking of paraffins,

$$kc = \exp\left(42.97 - \frac{62,300}{T}\right), \quad \frac{\text{moles}}{(\text{hr})(\text{lb cat.})} \qquad (4\text{-}23)$$

and heat of reaction = -22,300 Btu/mole of H_2 consumed

Similarly, the stoichiometric balance of hydrocracking of naphthenes is

$$C_n H_{2n} + \frac{n}{3} H_2 \longrightarrow n/15\ C_1 + n/15\ C_2 + n/15\ C_3 + n/15\ C_4 + n/15\ C_5 \qquad (4\text{-}24)$$

The reaction rate is

$$\frac{-dX_N}{d\ (W/F_{HC_0})} = \frac{kc''}{K}\ p_N \qquad (4\text{-}25)$$

where kc'' is rate constant for hydrocracking of naphthenes,

$$kc'' = \exp\left(42.97 - \frac{62,300}{T}\right), \quad \frac{\text{moles}}{(\text{hr})(\text{lb cat.})} \qquad (4\text{-}26)$$

and heat of reaction = -24,300 Btu/mole of H_2 consumed

4.2.3 Material Balance Equation

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

Amount of A introduced per unit time	-	Amount of A leaving per unit time	-	Amount of A converted per unit time	=	Amount of A accumulated per unit time
1		2		3		4	

(4-27)

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

$$\frac{\partial C_j}{\partial t} + \nabla . (C_j u) + \nabla . J_j = R_j \qquad (4\text{-}28)$$

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 (kmol/m^3 fluid)

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

u is the three-dimen ional mass average velocity vector, defined by:

$$u = \sum_j^N \frac{M_j C_j u_j}{\rho_f}$$

where ρ_f is the density of the mixture and u_j represents the velocity of molecules of species j.

∇ is the "nabla" or "del" operator.

For rectangular coordinate system, term ∇ is defined as

$$\nabla = \sum_i \frac{\partial}{\partial x_i} \qquad (4.29)$$

For example, the divergence of a vector function u is

$$\nabla \cdot \mathbf{u} = \frac{\partial u_x}{\partial X} + \frac{\partial u_y}{\partial Y} + \frac{\partial u_z}{\partial Z} \qquad (4\text{-}30)$$

Term $\nabla.(C_j U)$ thus accounts for the transport of mass by convective flow. J_j is the molar flow vector for species j with respect to the mass average velocity.

Reactor in this model is tubular chemical reactor (or fixed-bed reactor) shown in Figure 4-1.

The assumptions of this system are

(1) plug flow reactor,

(2) bulk flow takes place only in the axial direction,

(3) steady state turbulent flow

(4) adiabatic operation.

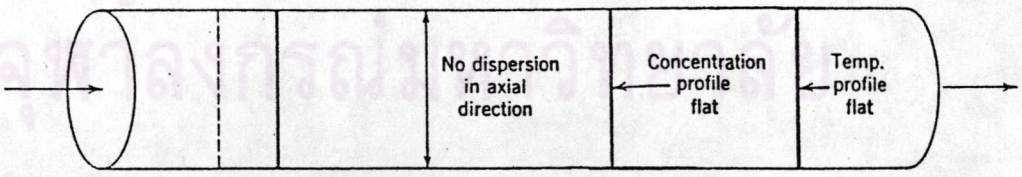


Figure 4-1 Tubular reactor

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

$$-u_s \frac{dC_j}{dZ} = R_j \qquad (4\text{-}31)$$

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,

$$R_j = \Sigma \alpha_{ij} r_i \qquad (4\text{-}32)$$

is the stoichiometric coefficient of component j in the i^{th} reaction and r_i is the reaction rate of i^{th} reaction.

If the reaction is homogeneous the unit could be kmol/m^3 s but for a reaction catalyzed by a solid preference would be given to kmol/kg cat. s and multiplied by the catalyst bulk density, ρ_B, in the reaction, thus Eq.(4.31) can be rewritten as:

$$-u_s \frac{dC_j}{dZ} = \rho_B R_j \qquad (4\text{-}33)$$

Equation (4-33) 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:

$$R_j \rho_B A \, dZ = F_{HC}^{\circ} \, d X_j \qquad (4\text{-}34)$$

where F_{HC}° is the molar feed rate of hydrocarbon at initial condition.

$$\frac{d X_j}{d (W/F_{HC}^{\circ})} = R_j \qquad (4\text{-}35)$$

where A is the cross section area, and X_j is the fraction conversion which defined as the following

$$X_j = \frac{F_j - F_{j\circ}}{F_{HC}^{\circ}} \qquad (4\text{-}36)$$

4.2.4 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

(4-37)

The mathematical expression for Eq.(4-37) is generally called the energy equation. Again reference is made to Bird et al. (1960) for rigorous derivation, in various 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:

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

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

(4-38)

where

Cp_j = the heat of species j

= kcal/kg C or kJ/kg K

λ = thermal conductivity of the mixture

= kcal/m.hr C or kJ/m.s.K

H_j = partial molar enthalpies

= kcal/kmol or kJ/kmol

M_j = molecular weight of species j

u = vector velocity of fluid flow

The meaning for the each term in Eq.(4-38) is :

Term	Meaning
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:

$$\sum_j M_j C_j Cp_j \left(\frac{\partial T}{\partial t} + u\cdot\nabla T\right) = \sum_i (-\Delta H_i)\, r_i + \frac{\partial}{\partial x}\left(\lambda_{e,x}\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial Y}\left(\lambda_{e,Y}\frac{\partial T}{\partial Y}\right) + \frac{\partial}{\partial z}\left(\lambda_{e,z}\frac{\partial T}{\partial z}\right) \qquad (4\text{-}39)$$

where λe = 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, thus result equation is

$$\sum_j M_j C_j Cp_j \left(\frac{\partial T}{\partial t} + u\cdot\nabla T\right) = \sum_i (-\Delta H_i)\, r_i \qquad (4\text{-}40)$$

For the steady state condition, the first term of left hand side of equation (4-40) would be zero. Equation (4-40) becomes

$$\sum_j M_j C_j Cp_j \, (u \cdot \nabla T) = \sum_i (-\Delta H_i) \, r_i \qquad (4\text{-}41)$$

As in the material balance equation, Eq.(4-41) is commonly written as

$$\left(\sum_j \frac{F_j \, Cp_j}{F_{HC}O}\right) \frac{dT}{d(W/F_{HC}O)} = \sum_i (-\Delta H_i) \, r_i \qquad (4\text{-}42)$$

4.2.5 Mathematic Model

Based on an adiabatic fixed-bed reactor, the following equations apply.

Material Balance

For reaction (4-1)

$$\frac{d X_1}{d (W/F_{HC}O)} = r_1$$

and similar equations for reaction (4-2), (4-3), and (4-4). X_1 is the conversion in reaction (4-1), mole naphthenes converted per mole of total feed.

Energy Balance

$$\left(\sum_j \frac{F_j\ Cp_j}{F_{HC}O}\right) \frac{dT}{d(W/F_{HC}O)} = \sum_i (-\Delta H_i)\ r_i$$

The modeling of the four-reactor reforming system is shown in Figure 4-2. The feed stock analysis and operating condition shown in Table 4-1. The system can be solved by Fourth-order Range-Kutta method. The results of calculation is shown in Figure 4-3.

4.2.6 Limitation

The model does not predict product composition in sufficient detail to allow adequate prediction of the product because feedstocks are lumped into three groups -paraffins, naphthenes, and aromatics- and the reaction to be considered include conversion of naphthenes into aromatics, conversion of naphthenes into paraffins, hydrocracking of paraffins, and hydrocracking of naphthenes.

4.3 Krane et al. (1959) reforming model

4.3.1 Assumption

This model assumes that the naphtha be broken down into its separate components and that these components be lumped into classes of components with similar properties and kinetic behavior.

Table 4-1 Feedstock analysis and system operating parameters (Smith, 1959)

Feedstock analysis

Specific gravity = 54.3°API
ASTM distillation, °C

Initial boiling point	83
10%	114
50%	129
90%	155
Endpoint	180
Average molecular weight	114.8

Feedstock components (basis = 100 bbl)

Component	mol %	Average molecular weight	lb	mol	mol/bbl	bbl
Paraffins	31.0	$C_{8.2}H_{18.4}$ = 116.8	8,410	72.0	2.19	32.9
Naphthenes	58.3	$C_{8.2}H_{16.4}$ = 114.8	15,544	135.4	2.33	58.4
Aromatics	10.7	$C_{8.2}H_{10.4}$ = 108.8	2,709	24.9	2.86	8.7
Total	100.0	114.8[a]	26,663	232.3	2.32[a]	100.0

Operating parameters

	Reactor			
	1	2	3	4
Catalyst distribution	1	1	2.75	3.5
WHSV (overall WHSV = 2.75)	22.69	22.69	8.25	6.48
Molar hourly space velocity	0.198	0.198	0.072	0.056
Reactor inlet temperature, °C	506	506	506	506
Reactor pressure, atm	39.9	39.5	39.1	38.1
Recycle ratio, mol/mol fresh feed	6.9			
H_2 in recycle, mol %		85.3		
Recycle molecular weight		6.0		
Flash-drum pressure, atm		35.0		
Flash-drum temperature, °C		38		

[a] Average values

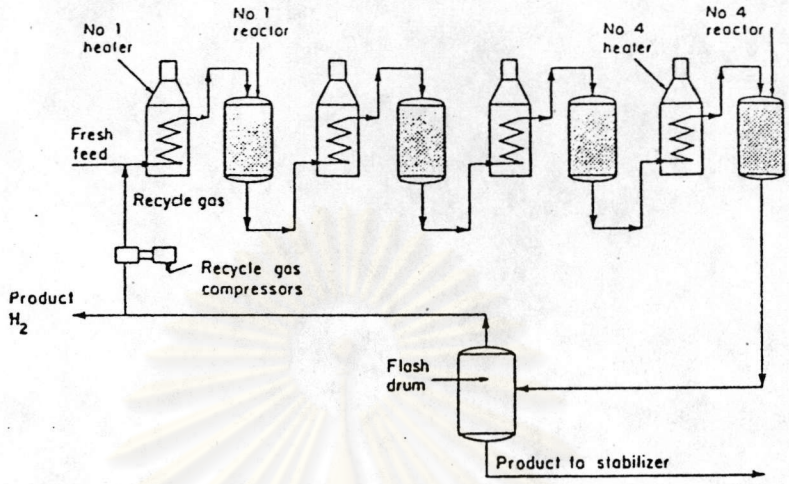


Figure 4-2 Schematic of four-reactor reforming (Smith, 1959)

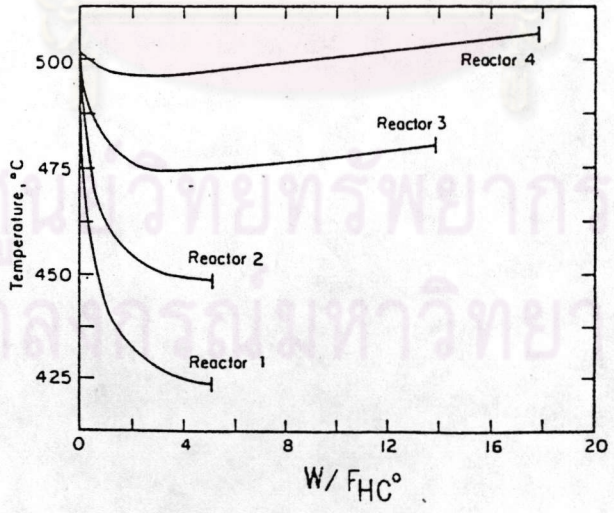


Figure 4-3 Calculated temperature profiles in the four reactors (Smith, 1959)

The process is an isothermal system, and hence the rate constant does not vary at a given operating condition.

4.3.2 Reactor Model and Mathematical model

Krane et al. have reported first-order rate constants for 53 individual reactions characteristic of naphtha reforming (Table 4-2). The rate constant for each reaction is fixed and defined by

$$\frac{dC_i}{d(W/F_{HC}o)} = - k_i C_i \qquad (4\text{-}45)$$

Term k_i is not dependent on temperature because this is an isothermal system. The data obtained from Table 4-2 can be combined into a set of 20 coupled, linear, first-order, ordinary differential equation which account for the rates of formation and of disappearance of hydrocarbons which are:

Hydrocarbon	Carbon atom
paraffins	C_1-C_{10}
naphthenes	C_6-C_{10}
aromatics	C_6-C_{11}

The typical reactions that occur in the reforming reactions, are very complex. Krane have reported the following reactions

- o Dehydrogenation of naphthenes
- o Dehydrocyclization of paraffins
- o Hydroisomerization of aromatics
- o Hydrogenation
- o Hydroisomerization of naphthenes.

- o Hydrocracking of paraffins
- o Hydrocracking of naphthenes
- o Hydrocracking of aromatics

4.3.2 Mathematical Model

Thus, all isomeric species are lumped into one pseudo-compound of a given carbon number and type. For example, the rate equation for the C_6 paraffins, is

$$\frac{dC_{P6}}{d(W/F_{HC}o)} = \underset{\langle 1\rangle}{0.0089 \cdot C_{P10}} + \underset{\langle 2\rangle}{0.0068 \cdot C_{P9}} + \underset{\langle 3\rangle}{0.0025 \cdot C_{P8}} + \underset{\langle 4\rangle}{0.0014 \cdot C_{P7}}$$

$$+ \underset{\langle 5\rangle}{0.01\ C_{N6}} - \underset{\langle 6\rangle}{0.0059\ C_{P6}} \qquad (4\text{-}46)$$

where P is the paraffins
N is the naphthenes
A is the aromatics
C is the concentration, mol/100 of feed.

The equation (4-46) accounts for the formation of hexane from hydrocracking of paraffins (terms ⟨1⟩, ⟨2⟩, ⟨3⟩, and ⟨4⟩), hydroisomerization of naphthenes (term ⟨5⟩), and includes the disappearance of hexane by hydrocracking to lighter paraffins (term ⟨6⟩)

4.3.3 Limitation

The limitation in this model is that the process is an isothermal mode of operation. Thus, the rate constant does not vary at a given operating condition.

Table 4-2 **First-order rate constants for naphtha-reforming reactions**[†]

Typical reaction conditions: 496°C, hydrogen-to-naphtha molar ratio = 5 : 1, 6.8 to 30 atm total pressure, and 0.30 wt % Pt on alumina catalyst

	$k \times 10^2$, h^{-1}		$k \times 10^2$, h^{-1}
Dehydrocyclization k_1:		Hydroisomerization of aromatics k_4:	
$P_{10} \longrightarrow N_{10}$	2.54	$A_{10} \longrightarrow P_{10}$	0.16
$P_9 \longrightarrow N_9$	1.81	$A_9 \longrightarrow P_9$	0.16
$P_8 \longrightarrow N_8$	1.33	$A_8 \longrightarrow P_8$	0.16
$P_7 \longrightarrow N_7$	0.58	$A_7 \longrightarrow P_7$	0.16
$P_6 \longrightarrow N_6$	0		
Dehydrogenation k_2:		Hydrocracking of naphthenes k_5:	
$N_{10} \longrightarrow A_{10}$	24.50	$N_{10} \longrightarrow N_9$	1.34
$N_9 \longrightarrow A_9$	24.50	$N_{10} \longrightarrow N_8$	1.34
$N_8 \longrightarrow A_8$	21.50	$N_{10} \longrightarrow N_7$	0.80
$N_7 \longrightarrow A_7$	9.03	$N_9 \longrightarrow N_8$	1.27
$N_6 \longrightarrow A_6$	4.02	$N_9 \longrightarrow N_7$	1.27
Hydrocracking of paraffins k_3:		$N_8 \longrightarrow N_7$	0.09
$P_{10} \longrightarrow P_9 + P_1$	0.49		
$P_{10} \longrightarrow P_8 + P_2$	0.63	Hydrogenation k_6:	
$P_{10} \longrightarrow P_7 + P_3$	1.09	$A_6 \longrightarrow N_6$	0.45
$P_{10} \longrightarrow P_6 + P_4$	0.89		
$P_{10} \longrightarrow 2P_5$	1.24	Hydrocracking of aromatics k_7:	
$P_9 \longrightarrow P_8 + P_1$	0.30	$A_{10} \longrightarrow A_9$	0.06
$P_9 \longrightarrow P_7 + P_2$	0.39	$A_{10} \longrightarrow A_8$	0.06
$P_9 \longrightarrow P_6 + P_3$	0.68	$A_{10} \longrightarrow A_7$	0.00
$P_9 \longrightarrow P_5 + P_4$	0.55	$A_9 \longrightarrow A_8$	0.05
$P_8 \longrightarrow P_7 + P_1$	0.19	$A_9 \longrightarrow A_7$	0.05
$P_8 \longrightarrow P_6 + P_2$	0.25	$A_8 \longrightarrow A_7$	0.01
$P_8 \longrightarrow P_5 + P_3$	0.43		
$P_8 \longrightarrow 2P_4$	0.35	Hydroisomerization of naphthenes k_8:	
$P_7 \longrightarrow P_6 + P_1$	0.14	$N_{10} \longrightarrow P_{10}$	0.54
$P_7 \longrightarrow P_5 + P_2$	0.18	$N_9 \longrightarrow P_9$	0.54
$P_7 \longrightarrow P_4 + P_3$	0.32	$N_8 \longrightarrow P_8$	0.47
$P_6 \longrightarrow P_5 + P_1$	0.14	$N_7 \longrightarrow P_7$	0.20
$P_6 \longrightarrow P_4 + P_2$	0.18	$N_6 \longrightarrow P_6$	1.48
$P_6 \longrightarrow 2P_3$	0.27		

P, N, and A denote paraffin, naphthene, and aromatic, respectively, and the subscript is the carbon number.

† (Krane et al., (1959))

4.4 Henningsen et al. Reforming Model

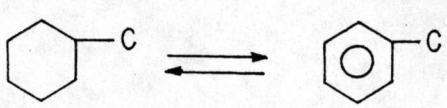
4.4.1 Assumption

The system is a plug flow reactor. The reaction rates are presented by simple first order kinetics. The system assumes the ratio between hydrogen and hydrocarbon is constant through out the reactors, approximately 7. Furthermore, the pressure drop through the reactor is neglected. The system is adiabatic and rate constants follow Arrhenius dependency. The system uses a dual function catalyst which consists of a dehydrogenation-hydrogenation component and an acidic component, $Pt-Al_2O_3$.

4.4.2 Reactor Model and Mathematical Model

Neither Smith (1959) nor Krane et al. (1959) considered different pattern of five and six membered ring naphthenes reactions. The dominant reaction of the six membered naphthenes, alkylcyclohexane, is very rapid direct dehydrogenation. On the other hand, the five membered naphthenes, alkylcyclopentanes, have first to undergo isomerization which is a slow reaction, before dehydrogenation can take place. Henningsen et al. (1970) used the following scheme for modeling the reforming reactions as shown in Figure 4-4. The major types of reactions are :

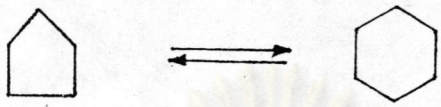
(a) dehydrogenation of C_6 ring naphthenes



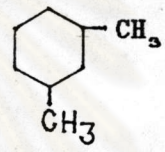
$$+ \quad 3\ H_2 \qquad (4\text{-}50)$$

(b) Isomerization of paraffins and naphthenes

n-Octane ⇌ 3-Methylheptane (4-51)

 (4-52)

(c) Cyclisation (and ring opening)

3-Methylheptane ⇌  + H_2 (4-53)

(d) Hydrocracking

2-Methylheptane + H_2 ⟶ Isopentane + propane + ... (4-54)

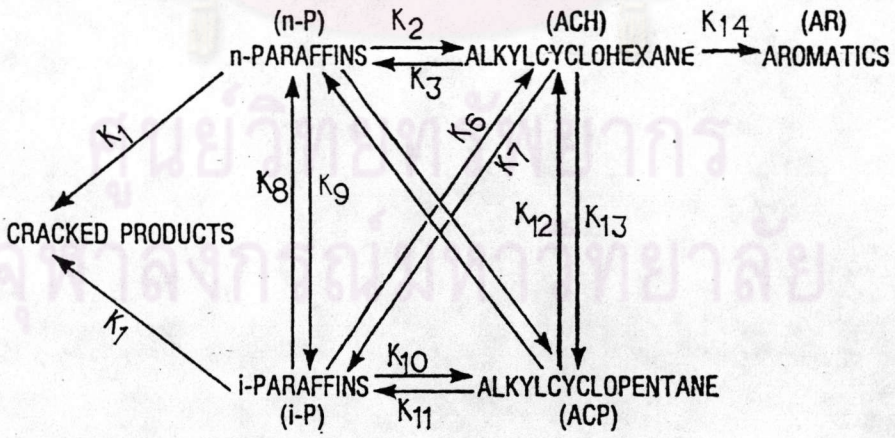


Figure 4-4 Scheme of general reaction of reforming processes

(Henningsen et al., (1970))

Considering the first order kinetics, a set of differential equations can be written to describe the concentration and temperature profiles in the reformer. The effect of deactivation of the acidic function of the catalyst is investigated. Henningsen et al. have reported the rate constants for the components in a C_6 naphtha assuming Arrhenius depenency as shown in Table 4-3 of a hydrogen pressure of approximately 30 atm and a hydrogen-hydrocarbon ratio of approximately 7. Also shown in Table 4-3 are the heats of reaction needed to calculate the temperature effects.

4.4.3 Limitation

The rate constants are estimated at temperature of 500 °C and hydrogen partial pressure of 30 atm. Because the total hydrocarbon pressure may have some effect on the rate constant due to adsorption on the active sites of the catalyst, the rate constants in this model only apply at specified hydrocarbon partial pressures.

Table 4-3 Reaction rate constant, $K = Ao\ e^{-E/RT}$

Reaction	K_i	Frequency Factor ln A_o	Activation Energy, E kcal/mole	Heat of reaction, ΔH kcal/mole
NP ⟶ C	K_1	30.5	55.0	−12.0
NP ⟶ ACH	K_3	23.1	45.0	+10.0
NP ⟶ IP	K_9	21.9	40.0	0.0
NP ⟶ ACP	K_5	23.1	45.0	+10.0
IP ⟶ C	K_1	30.5	55.0	-12.0
IP ⟶ NP	K_6	19.6	40.0	0.0
IP ⟶ ACH	K_8	23.1	45.0	+10.0
IP ⟶ ACP	K_{10}	23.1	45.0	+10.0
ACH ⟶ NP	K_2	24.2	45.0	-10.0
ACH ⟶ IP	K_7	26.5	45.0	-10.0
ACH ⟶ ACP	K_{12}	23.5	40.0	0.0
ACH ⟶ AR	K_{14}	20.4	30.0	+50.0
ACP ⟶ NP	K_4	21.6	45.0	-10.0
ACP ⟶ IP	K_{11}	24.2	45.0	-10.0
ACP ⟶ ACH	K_{13}	21.2	40.0	0.0

(Henningsen et al., (1970))