CHAPTER III

REVIEW OF MODELING OF CATALYTIC REFORMING PROCESS

3.1 Reforming Reaction [9]

As in any series of complex chemical reaction, reactions occur which produce undesirable products in addition to those desired. Reaction condition have to be chosen that favor the desired reactions and inhibit the undesired ones. Desirable reactions in a catalytic reformer all lead to the formation of aromatics and isoparaffins as follows:

1. Paraffins are isomerized and to some extent converted to naphthenes. The naphthenes are subsequently converted to aromatics.
2. Olefins are saturated to form paraffins which then react as in (1).
3. Naphthenes are converted to aromatics.
4. Aromatics are left essentially unchanged.

Reactions leading to the formation of undesirable products include:

1. Dealkylation of side chains on naphthenes and aromatics to form butane and lighter paraffins.
2. Cracking of paraffins and naphthenes to form butane and lighter paraffins.
3. Polymerization of olefins to form polyolefins.

As the catalyst ages, it is necessary to change the process operating conditions to maintain the reaction severity and to suppress undesired reactions.

There are four major reactions that take place during reforming: (1) dehydrogenation of naphthenes to aromatics, (2) dehydrocyclization of paraffins to aromatics, (3) isomerization, and (4) hydrocracking. The first two of these reactions involve dehydrogenation and will be discussed together.
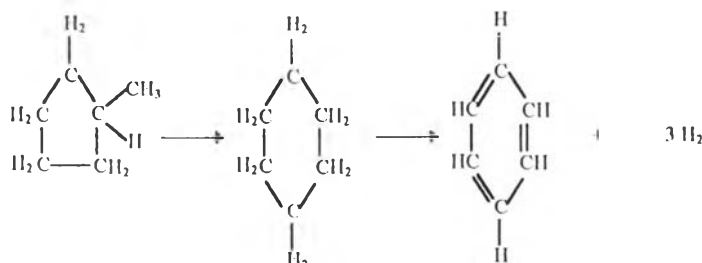
Dehydrogenation Reactions

The dehydrogenation reactions are highly endothermic and cause a decrease in temperature as the reaction progresses. In addition, the dehydrogenation reactions have the highest reaction rates of the reforming reactions which necessitates the use of interheaters between catalyst beds to keep the mixture at sufficiently high temperature for the reaction to proceed at practical rates.

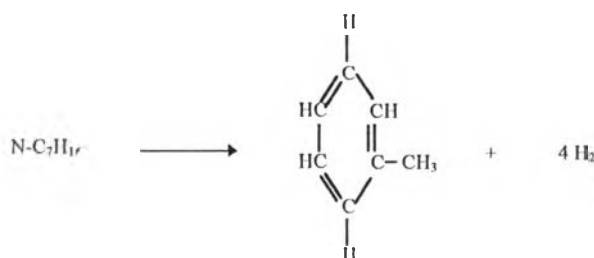The major dehydrogenation reactions are:

(a) Dehydrogenation of alkylcyclohexanes to aromatics.

Methylcyclohexane   Toluene
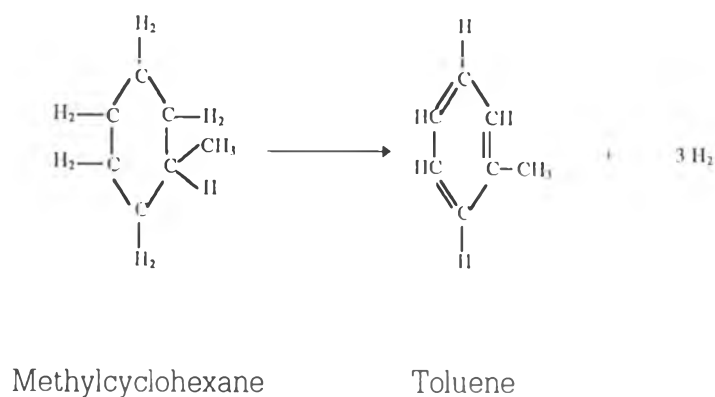
(b) Dehydroisomerization of alkylcyclopentanes to aromatics.

(c) Dehydrocyclization of paraffins to aromatics.

The dehydrogenation of cyclohexane derivatives is a much faster reaction than either the dehydroisomerization of alkylcyclopentanes or dehydrocyclization of paraffins, however all three reactions are necessary to obtain the high aromatic concentration needed in the product to product a high octane.

Aromatics have a higher liquid density than paraffins or naphthenes with the same number of carbon atoms so one volume of paraffins produces only 0.77 volume of aromatics and one volume of naphthenes about 0.87 volume In addition, conversion to aromatics increases the gasoline end point because the boiling points of aromatics are higher than the boiling points of paraffins and naphthenes with the corresponding number of carbons.

The yield of aromatics is increased by:

1. High temperature (increase reaction rate but adversely affects chemical equilibrium).

2. Low pressure (shifts chemical equilibrium "to the right").

3. Low space velocity (promotes approach to equilibrium).

4. Low hydrogen-to-hydrocarbon mole ratios (shift chemical equilibrium "to the right," however, a sufficient hydrogen partial pressure must be maintained to avoid excessive coke formation).
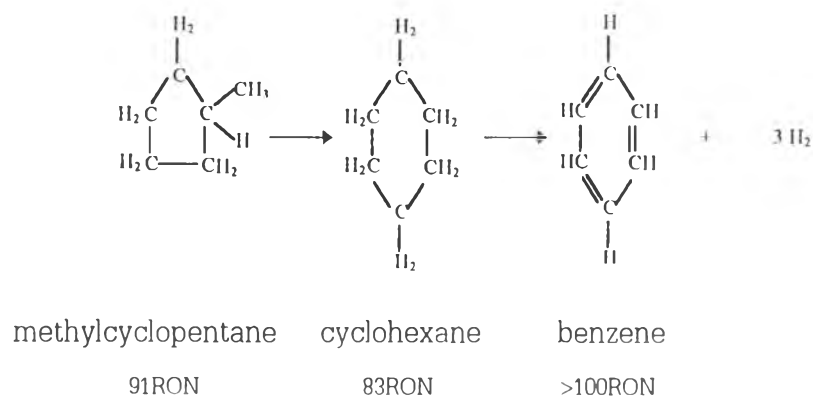
Isomerization Reactions

Isomerization of paraffins and cyclopentanes usually results in a lower octane product than dose conversion to aromatics. However, there is a substantial increase over that of the unisomerized materials. These are fairly rapid reactions with small heat effects.

(a) Isomerization of normal paraffins to isoparaffins.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

(b) Isomerization of alkylcyclopentanes to cyclohexanes, plus subsequent conversion to benzene.

methylcyclopentane   cyclohexane   benzene

91RON   83RON   >100RON

Isomerization yield is increases by:

1. High temperature (which increases reaction rate).

2. Low space velocity

3. Low pressure.

There is no isomerization effect due to the hydrogen/hydrocarbon (H_2/HC) mole ratios but high H_2/HC ratios reduce the hydrocarbon partial pressure and thus favor the formation of isomers

Hydrocracking Reaction

The hydrocracking reaction are exothermic and result in the production of lighter liquid and gas products. They are relatively slow reactions and therefore most of the hydrocracking occurs in the last section of the reactor.

The major hydrocracking reactions involve the cracking and saturation of paraffins.

n-Heptane   Propane   Butane
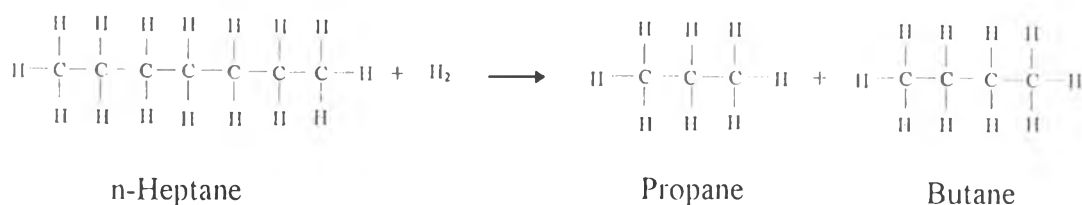
The concentration of paraffins in the charge stock determines the extent of the hydrocracking reaction but the relative of isomers produced in any molecular weight group is independent of the charge stock.

Hydrocracking yields are increased by:

1. High temperature

2. High pressure

3. Low space velocity

In order to obtain high product quality and yields, it is necessary to carefully control the hydrocracking and aromatization reactions. Reactor temperatures are carefully monitored to observe the extent of each of these reactions.

3.2 Reaction Rate [10]

All of above reactions occur in reforming, but all do not proceed at the same rate. For the most part, an engineer assigned to a reforming unit will think more about relative rate of reaction of broad classes of hydrocarbon rather than the reaction rates of individual components. It is well known in reforming that naphthene dehydrogenation is a relatively fast reaction, is endothermic, and is by low hydrogen partial pressure.

A general characterization of relative reaction rates is as below:

Reaction	Reaction rate (Relative rate)	Heat effect
Dehydrocyclization	Slowest (1)	Mildly endothermic
Hydrocracking	Slow (4)	Exothermic
Isomerization	Rapid (12)	Mildly exothermic
Dehydrogenation	Very fast (100)	Quite endothermic

The above relative rates are broad generalizations. For example, the rate of dehydrocyclization of n-octane is much faster than that of n-heptane. In general, the higher the number of carbon atoms per molecule, the more rapid the rates for the above reaction

3.3 Catalyst [4,11,12]

Reforming reactions typically proceed through a number of element steps. For example, a straight paraffins is converted into an isoparaffin by first being converted into an olefin, which isomerized to an isoolefin and then converted into isoparaffin. Correspondingly, the catalyst has two functions, a hydrogenation-dehydrogenation function for the paraffin-olefin conversions and an isomerization function, which is associated with the catalyst acidity. The catalyst used until the early 1950s were chromium oxide or molybdenum oxide supported on alumina, which incorporated both the catalytic function on the surface of the metal oxide. Furthermore developed reforming catalysts have crystallites of a metal such as Pt on an acidic support such as alumina, and the two functions are present in separate phase. The metal (Pt, Pt and Re, or a noble-metal-containing trimetally alloy) provides the hydrogenation-dehydrogenation activity of the supported metal and the isomerization activity of the alumina are much greater than respective activities of the early-generation metal oxides.

3.3.1 Catalyst Poisons

Reforming catalyst are deactivated by various poisons. The most common poisons are sulfur, lead, and other heavy metals, organic or combined nitrogen, and water.

Sulfur is a very common poison which deactivates the metal sites on the catalyst. This deactivation results in higher temperature requirements and decreased liquid yields. Sulfur is a temporary poison and much of the excess sulfur deposited can be removed by continued operation with low sulfur feeds or by special stripping procedures.

Lead and heavy metals are permanent poisons. These often occur when slop naphtha containing lead or others metals is sent to the reformer or naphtha hydrotreater.

Organic nitrogen (not elemental) deactivates the chloride sites on the catalyst by converting to ammonia in the reformer.

Water in large quantities can be a serious problem since it washes chloride from the catalyst.

The best method to prevent poisoning is to carefully monitor the naphtha hydrotreater operation to ensure that poisons are not passed to the reformer.

3.3.2 Catalyst Regeneration and Rejuvenation

During operation coke accumulates on the catalyst and deactivates it by covering metal and acid sites. Usually the cycle is terminated when the catalyst activity has fallen to an unacceptable level, after which the catalyst is regenerated and rejuvenated.

Regeneration

'Regeneration' is the process of removing coke from the catalyst metal and acid sites by burning. Typically the reformer is cooled and purged with nitrogen. The catalyst is then reheated to a specified temperature with circulating nitrogen gas. Air is added to bring the oxygen concentration to a specified level and the

coke burned at a constant level until most of the coke is burned. In later steps of the procedure, higher temperatures and oxygen concentrations are used to burn off the remaining coke deposits in order to complete the regeneration. The catalyst should have less than 0.1% coke after a thorough regeneration.

Rejuvenation

'Rejuvenation' is the process of redispersing the metal crystals produced by agglomeration and replenishing the chlorides lost during regeneration.

The regeneration removes the coke on the catalyst but also leaves the reforming catalyst in poor condition for reforming operation having depleted the chloride and agglomerated the platinum. The catalyst must be rejuvenated before it can be used again. This procedure involves the following steps:

1. High Temperature Air Soak

Recall that it is desired to have very small crystals of metal well distributed over the catalyst pellet. Regeneration agglomerates the platinum into larger crystals which lack the necessary activity. A high temperature "air soak" with high oxygen partial pressure is used to redistribute the platinum.

2. Rechloriding

The water formed in the coke combustion washes a large amount of the chloride from the catalyst. Therefore, a step in the rejuvenation procedures replenishes these chlorides using an organic chloride compound.

3.4 Reaction Schemes for Modeling

Kinetic models of the reforming processes started appearing in late fifties; these are reviewed by Moharir [13] Among these, neither Smith [14] nor Krane et al. [15] considered that five and six members ring naphthenes react according to quite different patterns. The dominant reaction of the six membered naphthenes s by far the direct aromatization. On the other hand, the five membered naphthenes have first to undergo isomerization, which is a slow reaction, before aromatization takes place. Burnett [13] presented a model for the C_7 system alone. Henningsen and Nielson [16] used the following scheme for modeling the reforming reactions:
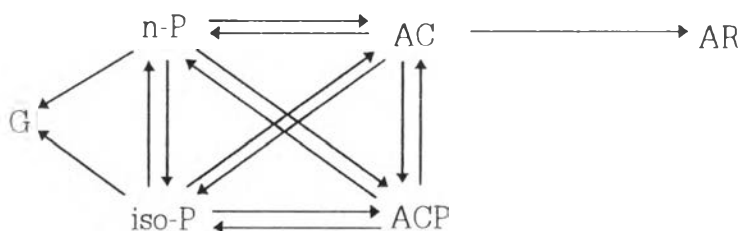

ACH = alkyl cyclohexanes; ACP = alkyl cyclopentanes; G = gas;
iso-P = isoparaffins; n-P = normal paraffins; AR = alkyl benzene

Considering the first order kinetics, a set of differential equations are written to describe the concentration and temperature profiles in the reformer. The effect of deactivation of the acidic function of the catalyst is investigated Based on the economic criteria, it is observed that the optimal temperature policy to be followed depends upon the local conditions.

Moharir et al. [13] broadly classified the reactions into four major groups; dehydrogenation of naphthenes, dehydrocyclization of paraffins, isomerization of

cyclopentanes to cyclohexanes, and isomerization of n-paraffins to iso-paraffins Assuming homogeneous kinetics, rate expressions are developed incorporating catalyst deactivation phenomena. The performance of a three stage reformer with ivestigate heating is simulated. The cumulative temperature drops over the reactors match well, and the product composition reasonably well. A temperature policy is calculated to maximize product quality and minimize catalyst decay, taking aromatization reaction as the most important one.

Wolff and Kramarz [13] considered three progressive reaction schemes for modeling the reforming process. Their final scheme is shown below:
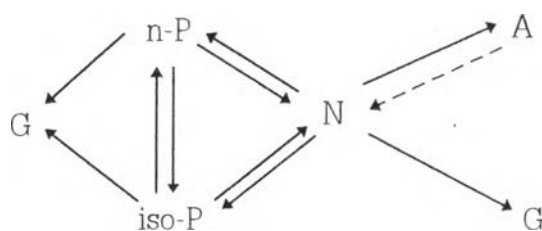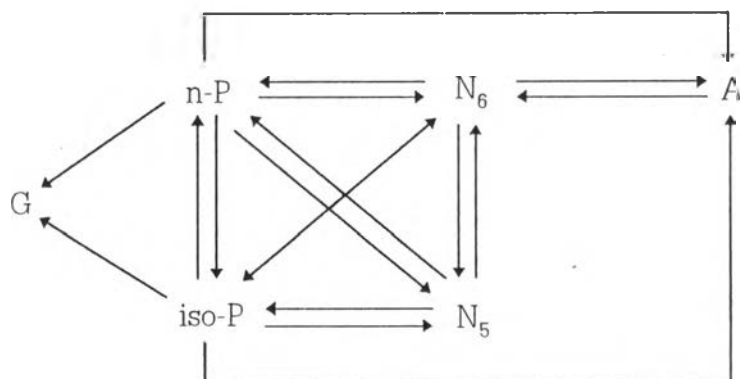

A = aromatics;   N = naphthenes

A similar set of ordinary differential equations are written to describe mass and heat balances. The catalyst deactivation is, however, not considered. The kinetic parameters are evaluated by bringing a close match between the calculated and measured values from two sets of experimental data.

Zhorov et al. [13] considered the important role played by C_5 dehydrocyclization in the aromatization of paraffins. It has also been considered that n-paraffins are reversibly isomerized to iso-paraffins, and five membered naphthenes to six membered. Direct formation of aromatics from paraffins has

also been accounted, these reactions being practically irreversible under platforming conditions.

Jenkins and Stephens [16] considered 70 reactions involving 31 components to model the reforming process. Components with a carbon number of nine or more are handled as the pseudocomponents, that is, aromatics, paraffins and naphthenes.

Equilibrium constants are calculated from thermodynamics. The paraffin and naphthene hydrocracking reactions and the conversion of methyl cyclopentane to benzene are considered non-reversible; all other reactions are reversible. The model results are compared with one of the plant tests in Table 3.1.

Ramage et al. [17] identified thirteen hydrocarbon lumps. On the considerations of selectivity between C_6, C_7 and C_8 species, they used the following network for writing a reaction model:
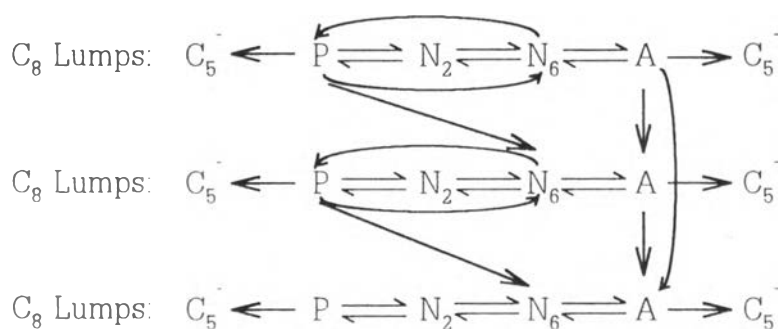
$$C_8 \text{ Lumps: } C_5^- \longleftarrow P \rightleftharpoons N_2 \rightleftharpoons N_6 \rightleftharpoons A \longrightarrow C_5^-$$

$$C_8 \text{ Lumps: } C_5^- \longleftarrow P \rightleftharpoons N_2 \rightleftharpoons N_6 \rightleftharpoons A \longrightarrow C_5^-$$

$$C_8 \text{ Lumps: } C_5^- \longleftarrow P \rightleftharpoons N_2 \rightleftharpoons N_6 \rightleftharpoons A \longrightarrow C_5^-$$

Table 3.1 Plant test compared to model yield in catalytic reforming

Prod., mole% of all feed	Plant Test	Model Result
H_2	120.0	130.7
C_1/C_4	11.5	11.7
C_5	1.6	2.1
$C_6 P$	1.9	2.4
$C_6 N$	0.7	0.2
$C_6 A$	1.2	1.4
$C_7 P$	9.1	8.1
$C_7 N$	1.0	1.6
$C_7 A$	17.7	17.2
$C_8 P$	10.3	10.1
$C_8 N$	0.8	0.9
$C_8 A$	29.1	29.6
$C_9^+ P$	7.1	7.1
$C_9^+ N$	1.0	0.2
$C_9^+ A$	18.0	18.4
$C_6^+ P$	28.4	27.6
$C_6^+ N$	3.4	2.8
$C_6^+ A$	66.1	66.6
Total	97.9	97.0
ΔT per reactor, °F		
1	112	102
2	69	71
3	50	57
4	19	21
Total	250	251
C_5^+, vol%	90.3	89.7
RON.clear	94.7	95.3
RON. + 3 ml TEL/gallon	100.1	100.5
Cat. act.%	-	64.3

Note that for the C_6 components, the reacitons followed a simple consecutive sequence without direct paraffin dehydrocyclization to N_6 steady-

state material balance model is written for a plug flow fixed bed catalytic reformer; a nondissociative Langmuir-Hinshelwood adsorption model is used

Panyavivanond [18] proposed a model for a catalytic reforming process in a system of a fixed-bed reactor with a commercial platinum on alumina catalyst under isothermal and adiabatic mode on operation. The feed was limited to a mixture of C_6 and C_7 hydrocarbons. The new model was based on the assumption that the reaction that the reaction of C_6 and C_7 are independent. The simulated results are in agreement with existing experimental data. The model can be extended to other catalysts by determining the rate constants from experiments using Hogen-Watson rate equations. The model approach may be applicable for catalytic reforming model development of C_8-C_{10} as feedstock. There are the following network for writing a reaction model:

- Reaction network for that reforming of C_6 hydrocarbons
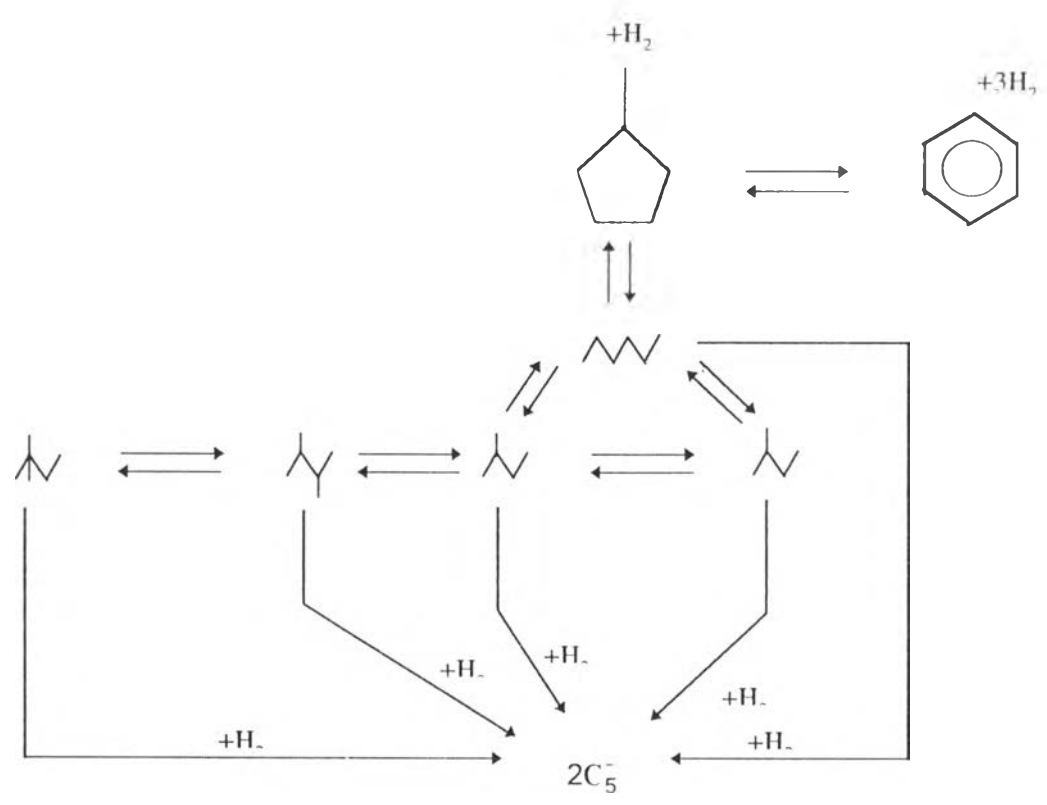
- Lumped reaction network for the reforming of C7 hydrocarbons

$$\text{n-HEPTANE} \rightleftharpoons 5N_7 \xrightarrow{+H_2} \bigcirc \rightleftharpoons \bigcirc +3H_2$$

$$SBP_7 \searrow$$
$$C_6^{-}$$
$$MBP_7 \nearrow$$
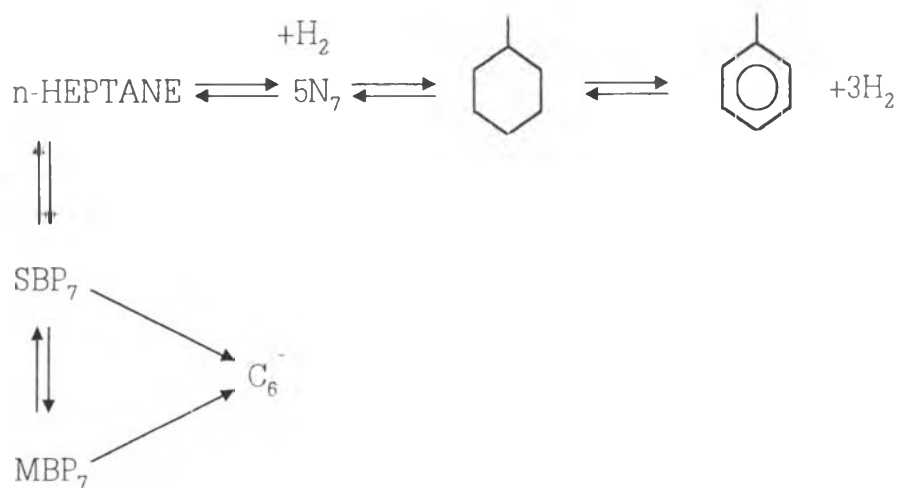
Wapakpetch [19] developed model of catalytic reforming by using platinum-rhenium catalyst and mixture of C_6-C_8 hydrocarbons as feedstock. The assumption and equation of rate of reaction are the same as Panyavivanond's work. The limitation of this model is constant pressure. The simulated results also are in agreement with existing experimental data as same as Panyavivanong's work. There are the following networks for writing a reaction model:

$$C_8+ \text{ Lumps: } \quad C_7 \longleftarrow P \rightleftharpoons N5 \rightleftharpoons N6 \rightleftharpoons A$$

$$C_7 \text{ Lumps: } \quad C_6- \longleftarrow P \rightleftharpoons N5 \rightleftharpoons N6 \rightleftharpoons A$$

$$C_6 \text{ Lumps: } \quad C_5- \longleftarrow P \rightleftharpoons N5 \rightleftharpoons N6 \rightleftharpoons A$$