CHAPTER IV

MODELING

4.1 Model and Modeling [20]

Model is one of the most fundamental processes of the human mind. Modeling underlies our ability to think and imagine, to use signs and language, to communicate, to generalize from experience, to deal with the unexpected, and to make sense out of the raw bombardment of our sensations. It allows us to see patterns, to appreciate, predict, and manipulate processes and things, and to express meaning and purpose. Models can be considered in three different classifications, depending on how they are derived, described as follows:

1. **Theoretical models** developed using the principles of chemistry and physics of the system represent one alternative. However, the development of rigorous theoretical models may be practical for complex processes if the model requires a large number of differential equations with a significant number of unknown parameters such as chemical and physical properties.

2. **Empirical models** obtains from a mathematical (statistical) analysis of process operating data. This model are sometimes referred to as *Black box* models. The processes being modeled is likened to an opaque box where the input and outputs are known but the inner working of the box are unknown.

3. **Semiempirical models** that are compromise between (1) and (2), with one or more parameters to be evaluated from plant data.

In the last classification, certain theoretical model parameters such as reaction rate coefficients, heat transfer coefficients, and similar fundamental relations usually must be evaluated from physical experiments or from process operating data. Such semiempirical models do have several inherent advantages. They often can be extrapolate over a wider range of operating conditions than purely empirical models which are usually accurate over a very limited range Semiempirical models also provide the capability to infer how unmeasured or unmeasurable process variables vary as the process operating conditions change.

4.2 Catalytic Reforming Unit (CRU) in a Refinery Process

Figure 4.1 shows a diagram of CRU in plant No 2 of Bangchak company. Feedstock of this unit came from Naphtha Pretreater Unit (NPU). This diagram can be simplified as shown in Figure 4.2.

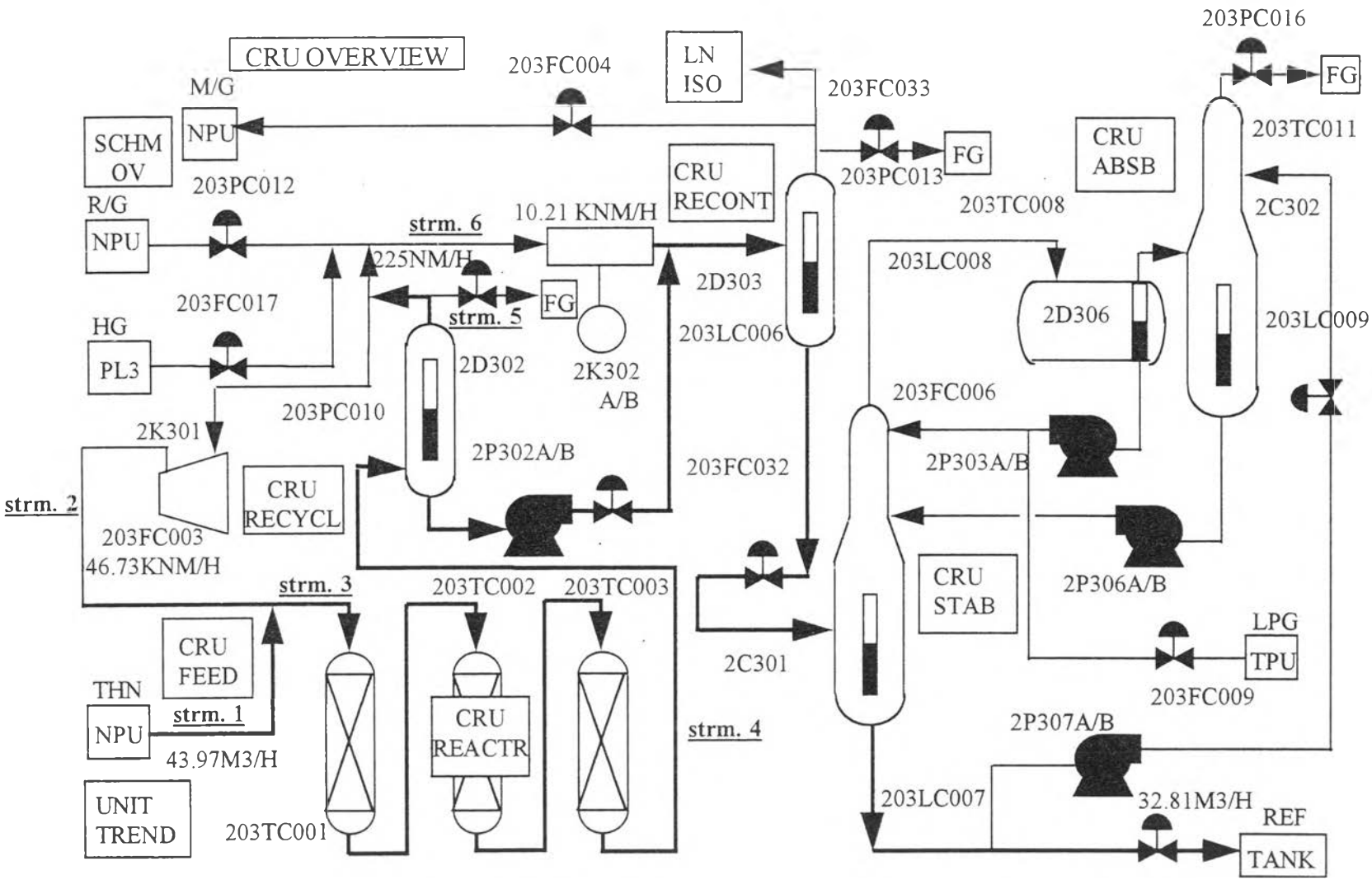

Figure 4.1 Catalytic reforming unit plant No. 2 of Bangchak Refinery

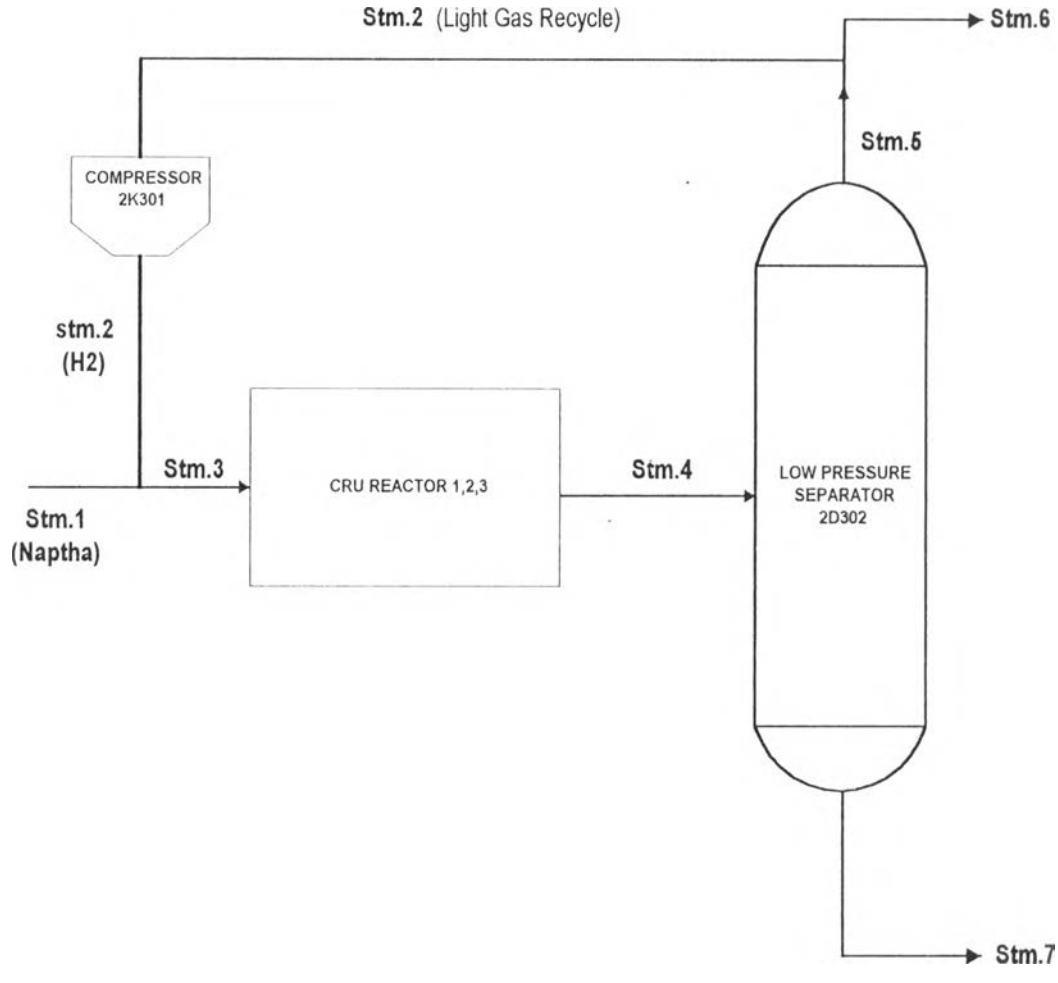

Figure 4.2 Simplifed flow diagram of CRU reactor and CRU recycling.

Figure 4.2 is composed of 3 main units as follow: CRU reactor, compressor and seperator. Data used for modeling the process are collected from feedstock (stm.1), recycle gas (stm.2) and unstabilized (stm.7)

Existing measurement

The relevant data of each stream will be analyzed for composition by gas chromatography and calculated material balance by using PRO II software.

4.3 Development of a Practical Model

The results that from gas chromatography analysis of stream samples taken from the catalytic reforming unit of Bangchak Refinery and material balance from Pro II software are shown in Table 4.1.

Table 4.1 Actual data of catalytic reforming process

	GRP	INPUT (KMole/Hr)	OUTPUT (KMole/Hr)
1	H_2	-	288.92
2	P_1	-	30.5
3	P_2	-	30.81
4	P_3	-	36.95
5	P_4	-	37.97
6	P_5	-	33.94
7	P_6	9.43	12.86
8	P_7	115.9	29.77
9	P_{8+}	118.5	11.67
10	N_6	1.67	0.16
11	N_7	7.17	0.41
12	N_{8+}	13.5	0.96
13	A_6	9.21	13.98
14	A_7	3.17	69.52
15	A_{8+}	8.53	84.94
TOTAL	-	287.08	683.36

Main reactions in this study

- Naphthenes dehydrogenation ($N_n \longrightarrow A_n$)
- Dehydrocyclization Paraffins ($P_n \longrightarrow A_n$)
- Hydrocracking of Paraffins ($P_n \longrightarrow P_1 + P_2 + ... + P_{n-1}$)

and - Isomerization ($nP_n \longrightarrow iP_n$)

Reaction Schemes

Reaction network used in this research is the same as one of Wapakpetch work [19]. The reaction network is shown in Figure 4.3.

C_8+ Lumps: $C_{7-} \leftarrow P \rightleftharpoons$ - N5 $\rightleftharpoons$ N6 $\rightleftharpoons$ A

C_7 Lumps: $C_{6-} \leftarrow P \rightleftharpoons$ N5 $\rightleftharpoons$ N6 $\rightleftharpoons$ A

C_6 Lumps: $C_{5-} \leftarrow P \rightleftharpoons$ N5 $\rightleftharpoons$ N6 $\rightleftharpoons$ A

Figure 4.3 The reaction network [19].

4.3.1 Assumptions

1. The reaction takes place in CSTR reactor.
2. The reaction is operated at steady state condition.
3. Naphthene quantity in output stream is very small, therefore the dehydrogenation reactions of naphthenes to be aromatics an assumed 100% complete. So that napthene dehydrogenation reactions can be treated stoichiometrically.

4. Dehydrocyclization of paraffins is first-order reaction: $A_i=K_i[P_i]$.
5. Aromatic components do not react with other substances.
6. Substances that have similar properties, for example: nP_n and iP_n, are lumped to be a single pseudocomponent,P_n. So isomerization reaction is neglected simple.
7. Hydrocracking reactions are represented by a selectivity relationship.

From the above assumptions, the reaction network can be written as follows:

C_{8+} Lumps: $C_{7-} \leftarrow P_{8+} \rightarrow A_{8+}$

C_7 Lumps: $C_{6-} \leftarrow P_7 \rightarrow A_7$

C_6 Lumps: $C_{5-} \leftarrow P_6 \rightarrow A_6$

And the results from the above assumptions are shown in Table 4.2.

Table 4.2 Adapted data from assumptions of catalytic reforming process

No.	GRP	INPUT (KMole/Hr)	OUTPUT (KMole/Hr)
1	H_2	-	288.92
2	P_1	-	30.5
3	P_2	-	30.81
4	P_3	-	36.95
5	P_4	-	37.97

Table 4.2 (continued)

6	P_5	-	33.94
7	P_6	9.43	12.86
8	P_7	115.9	29.77
9	P_{8+}	118.5	11.67
10	N_6	*	*
11	N_7	*	*
12	N_{8+}	*	*
13	A_6'	9.21	12.31
14	A_7'	3.17	62.35
15	A_{8+}'	8.53	76.44
TOTAL	-	265.09	659.49

* Treated independently as stoichiometric balance

Note : A_i' refers to molar rate of aromatic products(A_i) minus molar rate of aromatic from Dehydrogenation of naphthenes in feedstock(N_i) (i = 6, 7, 8+)

4.3.2 Component balance of the model

4.3.2.1 The related reactions with the model are as follows :

1. Hydrocracking reactions

The three reactions of hydrocracking can be represented schematically as follows:

1) $P_6 + H_2 \xrightarrow{S_{65}} P_{5-}$

2) $P_7 + H_2 \xrightarrow{S_{76}, S_{75}} P_6 + P_{5-}$

3) $P_{8+} + H_2 \xrightarrow{S_{87}, S_{86}, S_{85}} P_7 + P_6 + P_{5-}$

S_{ij} refers to selectivity of i component which change to j component.

Note: $S_{65} \equiv S_{65-}$, $S_{75} \equiv S_{75-}$

$S_{85} \equiv S_{8+5-}$, $S_{86} \equiv S_{8+6}$ and $S_{87} \equiv S_{8+7}$

P_{5-} refers to lumped component of cracked products which the number of carbon atoms are less than or equal to 5 atoms

P_{8+} , A_{8+} refer to paraffins and aromatics which the number of carbon atoms are greater than or equal to 8 atoms.

2. Dehydrocyclization reactions

Similarly, the reactions are as follows:

1) $P_6 \longrightarrow A_6 + 4H_2$

2) $P_7 \longrightarrow A_7 + 4H_2$

3) $P_{8+} \longrightarrow A_{8+} + 4H_2$

4.3.2.2 General form of component balance

$$\begin{bmatrix}\text{Molar}\\ \text{rate in}\\ (C_{Ai})\end{bmatrix} - \begin{bmatrix}\text{Molar}\\ \text{rate out}\\ (C_{Ao})\end{bmatrix} + \begin{bmatrix}\text{Molar rate of}\\ \text{generation}\\ (G)\end{bmatrix} = \begin{bmatrix}\text{Molar rate of}\\ \text{accumulation}\\ dc/dt\end{bmatrix}$$

General form of component balance for steady state condition.

$$\begin{bmatrix}\text{Molar}\\ \text{rate in}\\ (C_{Ai})\end{bmatrix} - \begin{bmatrix}\text{Molar}\\ \text{rate out}\\ (C_{Ao})\end{bmatrix} + \begin{bmatrix}\text{Molar rate of}\\ \text{generation}\\ (G)\end{bmatrix} = 0$$

Component balance for this study

$$\begin{bmatrix}\text{Molar}\\ \text{rate in}\end{bmatrix} - \begin{bmatrix}\text{Molar}\\ \text{rate out}\end{bmatrix} \pm \begin{bmatrix}\text{Molar rate of}\\ \text{cracking}\end{bmatrix} - \begin{bmatrix}\text{Molar rate of}\\ \text{dehydrocyclization}\end{bmatrix} = 0$$

Component balance of each component are as follows

P_6 balance

$$P_{6,in} - P_{6,out} - S_{65} P_{6,in} + S_{76} P_{7,in} + S_{86} P_{8+,in} - \frac{K_6 P_{6,out}}{\tau} = 0 \qquad (1)$$

P_7 balance

$$P_{7,in} - P_{7,out} - (S_{76}+S_{75}) P_{7,in} - \frac{K_7 P_{7,out}}{\tau} + S_{87} P_{8+,in} = 0 \qquad (2)$$

P_{8+} balance

$$P_{8+,in} - P_{8+,out} - (S_{87}+S_{86}+S_{85}) P_{8+,in} - \frac{K_8 P_{8+,out}}{\tau} = 0 \qquad (3)$$

P_{5-} balance

$$P_{5-,in} - P_{5-,out} + S_{65} P_{6,in} + S_{75} P_{7,in} + S_{85} P_{8,in} = 0 \qquad (4)$$

A_6 balance

$$A_{6,in} - A'_{6,out} + \frac{K_6 P_{6,out}}{\tau} = 0 \qquad (5)$$

A_7 balance

$$A_{7,in} - A'_{7,out} + \frac{K_7 P_{7,out}}{\tau} = 0 \qquad (6)$$

A_{8+} balance

$$A_{8+,in} - A'_{8+,out} + \frac{K_8 P_{8+,out}}{\tau} = 0 \qquad (7)$$

Rearranging these equations gives

$$P_{5-,out} - P_{5-,in} = S_{65} P_{6,in} + S_{75} P_{7,in} + S_{85} P_{8+,in} \qquad (8)$$

$$P_{6,out} - P_{6,in} = -\frac{K_6 P_{6,out}}{\tau} - S_{65} P_{6,in} + S_{76} P_{7,in} + S_{86} P_{8+,in} \qquad (9)$$

$$P_{7,out} - P_{7,in} = -\frac{K_7 P_{7,out}}{\tau} - S_{76} P_{7,in} - S_{75} P_{7,in} + S_{87} P_{8+,in} \qquad (10)$$

$$P_{8+,out} - P_{8+,in} = -\frac{K_8 P_{8+,out}}{\tau} - S_{87} P_{8+,in} - S_{86} P_{8+,in} - S_{85} P_{8+,in} \qquad (11)$$

$$A_{6,out} - A'_{6,in} = \frac{K_6 P_{6,out}}{\tau} \qquad (12)$$

$$A_{7,out} - A'_{7,in} = \frac{K_7 P_{7,out}}{\tau} \qquad (13)$$

$$A_{8+,out} - A'_{8+,in} = \frac{K_8 P_{8+,out}}{\tau} \qquad (14)$$

From the above material balance, there are seven equations and nine parameters. Assuming that S_{76} and S_{87} are neglected because hydrocracking of paraffin favour to crack at the middle position of molecule[21].

These equations can be transformed to matrix form as equation(15). The equation(15) is used to find the parameter values of the model.

$$\begin{bmatrix} P_{5,out} - P_{5,in} \\ P_{6,out} - P_{6,in} \\ P_{7,out} - P_{7,in} \\ P_{8+,out} - P_{8+,in} \\ A'_{6,out} - A_{6,in} \\ A'_{7,out} - A_{7,in} \\ A'_{8+,out} - A_{8+,in} \end{bmatrix} = \begin{bmatrix} P_{6,in} & P_{7,in} & P_{8+,in} & 0 & 0 & 0 & 0 \\ -P_{6,in} & 0 & 0 & P_{8+,in} & \frac{-P_{6,out}}{\tau} & 0 & 0 \\ 0 & -P_{7,in} & 0 & 0 & 0 & \frac{-P_{7,out}}{\tau} & 0 \\ 0 & 0 & -P_{8+,in} & -P_{8+,in} & 0 & 0 & \frac{-P_{8+,out}}{\tau} \\ 0 & 0 & 0 & 0 & \frac{P_{6,out}}{\tau} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{P_{7,out}}{\tau} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{P_{8+,out}}{\tau} \end{bmatrix} \begin{bmatrix} S_{65} \\ S_{75} \\ S_{85} \\ S_{86} \\ K_6 \\ K_7 \\ K_8 \end{bmatrix} \quad (15)$$

$$[\quad B \quad] = [\qquad\qquad A \qquad\qquad] [\, X \,]$$

Briefly defined as

$$B = A \,.\, X$$

where

A, B refer to the raw data from the catalytic reforming process including of feedstock and product.

X refers to the calculated parameter values of the model

τ refers to the residence time, τ = V/F

(where V = volume of reactor F = volumetric flow rate)

The procedure of prediction the value of products is as the following steps:

1. Parameters estimation

Application Gauss-Jordan method for solving those equations (Eq.8 - Eq.14)

For a given problem,

$$A.X = B \tag{16}$$

where X refers to the metrix of parameters (S_{65},S_{75},S_{76},S_{85},S_{86},S_{87}, K_6,K_7, and K_{8+} where S_{87} and S_{76})

Multiply the equation (16) by A^{-1}, and obtain

$$A^{-1}(A.X) = A^{-1}B \tag{17}$$

Hence, we have

$$X = A^{-1}B \tag{18}$$

From equation (18), the parameter values can be found by using matrix method.

2. Prediction of the values of products

After the parameter values were found, the further step is to construct the model for predicting the value of products. From the equation(8) to equation(14), they could be rearranged and written in matrix form.

$$P_{5-,out} = P_{5-,in} + S_{65}\,P_{6,in} + S_{75}\,P_{7,in} + S_{85}\,P_{8+,in} \quad (19)$$

$$P_{6,out} = \frac{(1-S_{65})\,P_{6,in}}{1+K_6/\tau} + \frac{S_{76}P_{7,in}}{1+K_6/\tau} + \frac{S_{86}P_{8+,in}}{1+K_6/\tau} \quad (20)$$

$$P_{7,out} = \frac{(1-S_{76}-S_{75})\,P_{7,in}}{1+K_7/\tau} + \frac{S_{87}P_{8+,in}}{1+K_7/\tau} \quad (21)$$

$$P_{8+,out} = \frac{(1-S_{87}-S_{86}-S_{85})\,P_{8+,in}}{1+K_8/\tau} \quad (22)$$

$$A'_{6,out} = A_{6,in} + \frac{K_6(1-S_{65})\,P_{6,in}}{\tau+K_6} + \frac{K_6S_{76}P_{7,in}}{\tau+K_6} + \frac{K_6S_{86}P_{8+,in}}{\tau+K_6} \quad (23)$$

$$A'_{7,out} = A_{7,in} + \frac{K_7(1-S_{76}-S_{75})\,P_{7,in}}{\tau+K_7} + \frac{K_7S_{87}P_{8+,in}}{\tau+K_7} \quad (24)$$

$$A'_{8+,out} = A_{8,in} + \frac{K_7(1-S_{76}-S_{75})\,P_{7,in}}{\tau+K_7} + \frac{K_7S_{87}P_{8+,in}}{\tau+K_7} \quad (25)$$

From the equation(19) to equation(25); which the value of S_{76} and S_{87} = 0, they can be witten in the matrix form as follows:

$$\begin{bmatrix} P_{5-,out} \\ P_{6,out} \\ P_{7,out} \\ P_{8+,out} \\ A'_{6,out} \\ A'_{7,out} \\ A'_{8+,out} \end{bmatrix} = \begin{bmatrix} 1 & S_{66} & S_{75} & S_{86} & 0 & 0 & 0 \\ 0 & \frac{1-S_{66}}{1+K_6/\tau} & 0 & \frac{S_{86}}{1+K_6/\tau} & 0 & 0 & 0 \\ 0 & 0 & \frac{1-S_{75}}{1+K_7/\tau} & & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1-S_{86}-S_{86}}{1+K_8/\tau} & 0 & 0 & 0 \\ 0 & \frac{K_6(1-S_{66})}{\tau+K_6} & 0 & \frac{K_6S_{86}}{\tau+K_6} & 1 & 0 & 0 \\ 0 & 0 & \frac{K_7(1-S_{75})}{\tau+K_7} & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \frac{K_8(1-S_{86}-S_{86})}{\tau+K_8} & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} P_{5-,in} \\ P_{6,in} \\ P_{7,in} \\ P_{8+,in} \\ A_{6,in} \\ A_{7,in} \\ A_{8+,in} \end{bmatrix} \quad (26)$$

When the parameter values are found from solving the equation(15) and the values of feedstock are known, the value of the products can be calculated from the equation (26).

Therefore, the model of catalytic reforming process is the equation(26) which can be used to predict the value of products. Finally, for the total quantity of each aromatic components in product stream are equal to molar rate of $A'_{i,out}$ plus molar rate of N_i and can be written in metrix form as follow :

$$\begin{bmatrix} A_{6,out} \\ A_{7,out} \\ A_{8+,out} \end{bmatrix} = \begin{bmatrix} A'_{6,out} \\ A'_{7,out} \\ A'_{8+,out} \end{bmatrix} + \begin{bmatrix} N_{6,in} \\ N_{7,in} \\ N_{8+,in} \end{bmatrix} \quad (27)$$