

CHAPTER III

PROCEDURE SECTION

3.1 Process Selection

In this work, catalytic reforming plant was chosen as basis process. It is because reformate is an important component contained in gasoline pool, the second highest component used in oil blending. However, this process also produces the hazard substances, benzene (carcinogenic compound) and carbon dioxide (global warming substance). Thereby, a proper process design and a good financial and environmental management are necessary.

3.2 Design Variables

Actually, the new designed process flow sheet of this work almost looked like that commercial process flow sheet but the new different heat integration networks would be created.

This work concentrated in studying to find:

- 1) what capacity of plant
- 2) what operating temperature at reactor
- 3) what type of heat exchanger network

are suitable by means of both financial and environmental risk management. Three capacities of plant, two types of operating temperatures, and two types of heat exchanger networks ($3 \times 2 \times 2 = 12$ design), were set to examine which design will be an optimum one.

Table 3.1 Effects of design parameters on finance and environment

Design variable Parameters	Consequent Results
Plant Capacity	Different plant capacities make many particular profits relying on the future Thai economic condition. Moreover, the harmful emitted chemicals are varied depending on rate of production.
Reactor Temperature	Various temperatures may not only lead to specific benzene and carbon dioxide amounts produced but also cause each unique utility cost and different revenues from dissimilar yields of products.
Heat Exchanger Network	On account of many definite designed networks, a variety of heat exchanger costs, utility cost and global warming impacts certainly appear.

3.3 Variable Setting

3.3.1 Capacity

They were set by considering past reformat demand and supply in Thailand and making trend lines to find opportunity of setting up a new plant. Then, the possible three plant capacities were chosen, regarding the existed plant capacity in Thailand. This process is built for serving its product for only blending in gasoline to improve octane number. So, the gasoline demand and supply data can be used to calculate both of reformat; usually gasoline pool consists 35% reformat.

Table 3.2 Gasoline demand and supply of Thailand. (Petroleum Institute of Thailand, 2004)

Year	supplies	demands	d -s
1996	137	119	-18
1997	160	127	-33
1998	149	124	-25
1999	149	121	-28
2000	138	117	-21
2001	143	118	-25
2002	142	126	-16
2003	168	133	-35
2004	168	140	-28
2005	168	147	-21
2006	168	156	-12
2007	168	165	-3
2008	168	174	6

Table 3.3 Existing reforming unit capacities in Thailand. (Petroleum Institute of Thailand, 2004)

Refinery	Capacities (kbd)	Licensor	Start up year
Thai oil	50.0	UOP	1992/1993
Rayong Refinery	28.0	SIPM	1995
Esso Refinery	30.0	UOP	1997/1993
BangChak Refinery	14.5	Engelhard	1989/1993
Star petroleum	17.5	UOP	1996

In this work, processes, having 14,20,26 kbd plant capacity, were chosen in studying.

3.3.2 Reactor Operating Temperature

Generally, temperature is regarded as the one of important factors for any reforming unit. Typically, four reactors have to be used to complete all reactions and each one has different particular temperature values. So, WAIT (Weighted Average Inlet Temperature) was introduced to represent overall temperatures. Customarily, WAIT is around 440-520 °C. For this work, temperatures of reactors were set at 495 °C and 501°C.

3.3.3 Type of Heat Exchanger Network

First heat exchanger network was constructed from “Pinch Analysis Theory” and the other was established by “Reducing loop of network”. In this work, $\Delta T_{\min} = 10$ °C was used in designing network.

3.4 **Process Simulation and Design**

For finding the design, the plant, having 20 kbd of capacity, was used as a basis in calculation. In addition, two operating temperatures, 495 °C and 501 °C, were also set as additional basis to see the advantage of each one.

3.4.1 Reaction Part

In this part, Polymath was used as a tool to solve the kinetic reactions. However before reaching that step, all reforming reactions had to be created. After that, those basis temperatures were introduced in to a model to calculate reactor output of 20 kbd plant, basis for calculation. Consequently, the benzene, product and by-product amounts of each temperature would appear.

The kinetic models for catalytic reforming were first proposed by Krane *et al.* (1959). Then the important improvement of model was carried out by Jenkins and Stephen (1980) and Ancheyta-Juarez & Anguilar-Rodriguez (1994). They added an correlation for Krane’s models. Thus, the general form of equations is:

$$\frac{dN_i}{d\left(\frac{A_c}{w}\right)} = -k_i N_i \quad (3.1)$$

$$k_i = k_i^0 \left(\frac{p}{21}\right)^\alpha \exp\left[\frac{E_i}{R} \left(\frac{1}{T^0} - \frac{1}{T}\right)\right] \quad (3.2)$$

where A_c is the activity of the catalyst for particular reaction and w is the space velocity. The k_i is the corrected rate constant, k_i^0 is the original rate constant given by Krane at the pressure of 21 bar, p is the system pressure in the bar, and α is the correction coefficient. If the pressure is expressed in psigs, the ratio within the bracket becomes $(p/300)$. T_0 is the reference temperature and T is the temperature corresponding to the constant k_i .

The recommend values of the original rate constants (k^0) were given in Table 3.4. Besides, the values for the exponent α suggested by Jenkins for different reaction types were shown in Table 3.5. The value for the activation energies E_i of the various reactions were taken from Henningen (1970) (see Table 3.6).

Table 3.4 Reaction original rate constants (k^0) for the calculation of catalytic reforming kinetic by the method of Krane *et al.*

Reaction	$k \cdot 10^2$	Reaction	$k \cdot 10^2$
$P_{10} \rightarrow N_{10}$	2.54	$A_{10} \rightarrow A_7$	0.00
$P_{10} \rightarrow P_9 + P_1$	0.49	$P_9 \rightarrow N_9$	1.81
$P_{10} \rightarrow P_8 + P_2$	0.63	$P_9 \rightarrow P_8 + P_1$	0.30
$P_{10} \rightarrow P_7 + P_3$	0.89	$P_9 \rightarrow P_7 + P_2$	0.39
$P_{10} \rightarrow P_6 + P_4$	1.09	$P_9 \rightarrow P_6 + P_3$	0.68
$P_{10} \rightarrow 2P_5$	1.24	$P_9 \rightarrow P_5 + P_4$	0.55
$N_{10} \rightarrow N_9$	0.54	$N_9 \rightarrow P_9$	0.54
$N_{10} \rightarrow P_{10}$	1.34	$N_9 \rightarrow N_8$	1.27
$N_{10} \rightarrow N_8$	1.34	$N_9 \rightarrow N_7$	1.27
$N_{10} \rightarrow N_7$	0.80	$N_9 \rightarrow A_9$	24.50

Table 3.4 (Continue)

Reaction	$k \cdot 10^2$	Reaction	$k \cdot 10^2$
$A_{10} \rightarrow P_{10}$	0.16	$A_9 \rightarrow A_8$	0.05
$A_{10} \rightarrow A_9$	0.06	$A_9 \rightarrow A_7$	0.05
$A_{10} \rightarrow A_8$	0.06	$P_8 \rightarrow N_8$	1.33
$P_8 \rightarrow P_7 + P_1$	0.19	$N_7 \rightarrow P_7$	0.20
$P_8 \rightarrow P_6 + P_2$	0.25	$N_7 \rightarrow A_7$	9.03
$P_8 \rightarrow P_5 + P_3$	0.43	$A_7 \rightarrow P_7$	0.16
$P_7 \rightarrow 2P_4$	0.35	$P_6 \rightarrow N_6$	0.00
$N_8 \rightarrow P_8$	0.47	$P_6 \rightarrow P_5 + P_1$	0.14
$N_8 \rightarrow N_7$	0.09	$P_6 \rightarrow P_4 + P_2$	0.18
$N_8 \rightarrow A_8$	21.50	$P_6 \rightarrow 2P_3$	0.27
$A_8 \rightarrow P_8$	0.16	$N_6 \rightarrow P_6$	1.48
$A_8 \rightarrow A_7$	0.01	$N_6 \rightarrow A_6$	4.02
$P_7 \rightarrow N_7$	0.58	$A_6 \rightarrow N_6$	0.45
$P_7 \rightarrow P_6 + P_1$	0.14	$P_5 \rightarrow P_4 + P_1$	0.12
$P_7 \rightarrow P_5 + P_2$	0.18	$P_5 \rightarrow P_3 + P_2$	0.15
$P_7 \rightarrow P_4 + P_3$	0.39		

where A – aromatics, N – cycloalkanes, P – alkanes; the subscripts represent the number of carbon atoms in molecule.

Table 3.5 The correction exponent coefficient (α)

Reaction Type	α
Dehydrocyclization	-0.700
Hydrocracking	0.433
Hydrodealkylation	0.050
Dehydrogenation	0.000

Table 3.6 Value for the parameters: rate constants, pre-exponential factors, activation energies, heat of reaction

Reaction	Activation energy, E, kcal/mol	Heat of reaction, ΔH , kcal/mol
NP \rightarrow C	55.0	-12.0
NP \rightarrow ACH	45.0	+10.0
NP \rightarrow IP	40.0	0.00
NP \rightarrow ACP	45.0	+10.0
IP \rightarrow C	55.0	-12.0
IP \rightarrow NP	40.0	0.00
IP \rightarrow ACH	45.0	+10.0
IP \rightarrow ACP	45.0	+10.0
ACH \rightarrow NP	45.0	-10.0
ACH \rightarrow IP	45.0	-10.0
ACH \rightarrow ACP	40.0	0.00
ACH \rightarrow AR	30.0	+50.0
ACH \rightarrow NP	45.0	-10.0
ACH \rightarrow IP	45.0	-10.0
ACH \rightarrow ACP	40.0	0.00

where:

NP = normal paraffin (n-alkanes)

C = hydrocracking products

IP = iso-paraffins (i-alkanes)

ACH = alkyl-cyclohexanes

ACP = alkyl-cyclopentanes

AR = aromatic

3.4.2 Separation Part

In this part, the separation process was founded in PROII. The reactor output stream was the separation part input. Then it could be found the benzene, product and by-product amounts of each basis temperature.

However, those amounts are nearly similar to quantity coming from reaction part. So, the benzene, product and by-product amounts could be obtained from output of reaction equations in the previous phase.

3.4.3 Heat Exchanger Design

From the previous step, the required energy of each stream was known too. Therefore, PROII could handle heat exchanger networks, both pinch network and practical network, of each basis temperature.

3.5 Data

3.5.1 Financial Data

3.5.1.1 *Equipment Cost*

Once obtaining each design structure, the equipment costs were gained, based on prices from Seider *et al.* (1998).

Since the basis process was set at capacity of 20 kbd, equipment costs of other different capacity plants could be carried out by relying on the ground of economy of scale. The algorithm was depicted in Equation 3.3.

$$\frac{C_1}{C_2} = \left(\frac{PC_1}{PC_2} \right)^{0.6} \quad (3.3)$$

where C = equipment cost, PC = plant capacity.

3.5.1.2 *Raw material, Fuel oil Usage and By-product Production*

From simulating plant at 20 kbd, it obtained one particular raw material, product, and by-product rate. In addition, fuel oil and water demands were known for individual heat integration type. On that ground, it was used to calculate so that information of other production rates by Equation 3.4 was obtained. Besides, in Table 3.7, it also shows the all chemical substances incorporated in the process.

$$\left(\frac{PR_1}{PR_2} \right) = \left(\frac{RM_1}{RM_2} \right) = \left(\frac{FO_1}{FO_2} \right) = \left(\frac{W_1}{W_2} \right) = \left(\frac{BP_1}{BP_2} \right) \quad (3.4)$$

where PR = production rate, RM = raw material, BP = by-product, FO = fuel oil, W = water.

Table 3.7 Related chemical substances in process

Chemical Type	Chemical Substances
Raw material	Naphtha
Product	Reformate
By-products	Hydrogen, LPG
External Utilities	Fuel oil, Water

3.5.1.3 Prices of Material

Prices of used and produced commodities, such as raw material, product, by-products and external utilities, in plant operating year were calculated by creating the trend line from data in the past of Thailand.

3.5.2 Environmental Data

In this study, overall amount of hazardous substance, produced from each design, is regarded as environmental impact for each design.

3.5.2.1 Benzene Amount

According to the exiting kinetic model, the occurred benzene quantity of each basis design was known.

Since temperature is the key factor that makes different amount of produced benzene. Thereby, the benzene amount from both 495 °C and 501 °C process were used in calculating other production rates, further than only 20 kbd. That algorithm was shown in below equation.

$$\left(\begin{array}{c} BZ_1 \\ BZ_2 \end{array} \right) = \left(\begin{array}{c} PR_1 \\ PR_2 \end{array} \right) \quad (3.5)$$

where BZ = benzene amount, PR = production rate.

3.5.2.2 Carbon dioxide Amount

Normally, the generated carbon dioxide of this plant comes from two sources, the coke burning in regeneration cycle and the fuel usage to supply the required energy of plant.

As for the coke burning source, it produces just only little carbon dioxide amount when comparing with the other source. Its carbon dioxide production rate also depends on the reacting temperature (Appendix E). In the case of energy using source, by two-heat exchanger network type accomplishments, amounts of produced carbon dioxide- occurring from burning fuel oil to serve a hot utility - were revealed for individual one. That was done by converting required external hot energy to formed carbon dioxide relying on property of heating fuel, fuel oil, in Table 3.8.

Table 3.8 Fuel oil properties

Fuel oil properties	Value
Heating value (kj/gal)	160,000
Carbon dioxide emission (kg/kl)	3,025

As the same idea of previous topics, carbon dioxide occurrence could be set as a ratio to a production rate as showing in below equation.

$$\left(\frac{CD_1}{CD_2} \right) = \left(\frac{PR_1}{PR_2} \right) \quad (3.6)$$

where CD = carbon dioxide amount, PR = production rate.

3.5.2.3 Environmental Impact

To find overall environmental impact, amount of carbon dioxide and benzene are combined to be representative impact for each design. In

this work, benzene was valued to have 3.5 times impact greater than carbon dioxide, due to higher concern in the carcinogenic hazardous effect. Hence, the formula of environmental impact evaluation could be derived as in Equation 3.7.

$$\text{Environmental impact} = 3.5 * \text{benzene amount} + \text{carbon dioxide amount} \quad (3.7)$$

3.5.3 Uncertainty

In this work, the standard deviation was used to represent uncertainty of information. Generally, there are three main sources of uncertainties: from the economic data in the past, calculation method and from the values calculated in data section.

In case of the economic data, the standard deviations, for normal distribution, were directly figured from its own past data. As for calculation method, the uniform random distribution was used to represent the uncertainties of the calculated values. The deviations of calculated financial values were set to be $\pm 25\%$ according to Peters and Timmerhaus (1991). Besides for the environmental prospect, the environmental impact was also set to have $\pm 20\%$ uncertainty. Finally, in this study, values in data section were assumed to have no uncertainties, due to lack of evaluating approach and simplification.

3.6 Financial and Environmental Impact Evaluations under Uncertainties

In order to apply the uncertainties into the evaluation step, GAMS program was used as an assistant tool in this phase. The risk curves of both finance and environment were able to be created. Moreover, expected values of profit and environmental impacts were also acquired through the life cycle of the plants.

Financial evaluation could be done by finding the net present expected profit, average profit, of each design. To evaluate the net present (NPV) of each design, its cash flow was computed in each year of the projected life of the plant. Then, by the interest rate (typically 15% for most company management), each cash flow was discounted to its present worth. The sum of all discounted cash flow was the net present values.

Environmental impact can be considered from the amount of hazardous substances occurrence over through the plant operating years.

3.7 Multi-objective Optimization

One of the popular methods for multi-objective optimization is the summation of weighted objective functions method. The idea of this method is to maximize a convex combination of objectives and therefore to convert the multi-objective problem to a single objective function; for that ground, it was chosen to be a tool in selecting the compromise design between two conflict objectives, profit (P) and environmental impact (EI) in this work. Applying the compromise programming approach, the two-objective optimization problem was expressed by Equation 3.8.

$$Max \omega_i = \alpha \left(\frac{P - P^L}{P^U - P^L} \right)^i + (1 - \alpha) \left(\frac{EI - EI^L}{EI^U - EI^L} \right)^i \quad (3.8)$$

where P is profit value of each design, EI is the environmental impact value of each design, $P^U = \max P$, $P^L = \min P$, $EI^U = \max EI$, $EI^L = \min EI$, i is a design type, $0 \leq \alpha \leq 1$ and α is the parametric weighting function of profit.