

CHAPTER 2 LITERATURE REVIEW AND THEORIES

This chapter presents some important literatures and theories which relates to this thesis.

2.1 Literature review

Salimi, Depeyre [1] developed a dynamic model mathematical model for a packed distillation column. Their objective was to compare dynamic behavior of a plate with a packed column. This model was applied for a batch system to fractionate the BTX (Benzene, Toluene, Xylenes) mixture. Simulation of these models was done by SPEEDUP, which had an equation-oriented approach to solve differential algebraic equations (DAE) sets. The result showed that the fractionation time for the packed column was shorter than for the plate column. Moreover, when the number of stage was increased, the separation time for the packed column was decreased linearly too.

Wesselingh [2] proposed non-equilibrium models for distillation column. Three models which are a depropanizer column, a packed absorber and extractive distillation were studied. The feed for the first case contained four components which are pentane, butane, propane and ethane. This column was to split the feed between butane and propane. It used the "Flash" unit in Chemsep program and Peng Robinson equation of state to describe the phase equilibrium and enthalpies. The second case was a packed absorber which used to absorb a small amount of acetone from a large stream of nitrogen. This column was filled with Raschig rings by adding the water as a solvent. This model was used NRTL equations for the phase equilibrium of the ternary mixture (acetone-nitrogen-water) and also Chemsep program. He found that an HETP may be a useful way of summarizing experience. However in multicomponent mixtures, HETP was hardly predictable. The last one was the extractive distillation column of methylcyclohexane (MCH) and toluene. These two components have close boiling points so they could not be separated by conventional distillation. This model used UNIFAC model to describe the strongly non-ideal vapor equilibrium and Chemsep program to generate the bubble cap columns.

Orlando et al. [3] studied the separation of C_8 - C_{14} hydrocarbon in a laboratory packing distillation column. The internal column consisted of Sulzer DX gauze stainless steel structured packing. The main objective was to evaluate the performance of pilot distillation column which was used for separating 98 % weight of C_{10} minus (C_{10}^-) as top product of the column. The PRO/II software simulator was used to compare the experimental results with the calculated ones. Prior to the experimental tests, simulation studies using commercial software PRO/II were performed in order to establish the optimum operating conditions (smallest reflux ratio) for the distillation column, especially concerning operating pressure, feed temperature and feed location. Height equivalent to a theoretical plate (HETP) from the simulation model could be calculated by the double Film Theory as shown in equation 2.1.

$$HETP = \frac{\ln \lambda}{\lambda - 1} \left(\frac{u_{Gs}}{k_G a_e} + \lambda \frac{u_{Ls}}{k_L a_e} \right) \quad (2.1)$$

The simulation showed the optimal operating conditions were 20 theoretical stages (20 in the enriching section and 10 in the stripping section), middle feed location and 800 mbar of pressure and feed temperature was 25°C. Moreover, the results from the simulation showed that the simulation results fitted very well with the experimental tests with 3.2 % maximum deviation in the temperature profile. HETP from the experimental data was 0.11 m for each section. The results showed that the error for HETP evaluation occurred in the top section of the column. Therefore, more reliable HETP values were found in the bottom section which liquid flow rates were much greater.

Scenna et al. [4] studied the start-up procedure of the reactive distillation column which produces the ethyl acetate production. They used the READYS program to generate the start-up operation of this process. They found that the operation with infinite reflux ratio responses avoiding the steady state. Moreover, they found that the column which filled initially with feed reach a steady state substantially before than the other initial options.

Yang et al. [5] proposed the method to improve the safety operation of a new MTBE process which produced from the reaction of methanol and isobutene. They used Dynamic Operator Training Simulator (DOTS) to generate the safety operation. The results showed that inlet temperature of reactor (R201) at 40°C was suitable for the process operation because it just take 35 minute to reach a steady state. Moreover, they studied the steam supply for Catalytic Distillation Column (C201). They found that the process which was operated with maximum steam supply for C201 was taken a time to reach a steady state when compared with the constrained steam supply.

2.2 Theories

The theoretical parts are divided into two main sections which are the basic of packed column and the operation of pilot distillation column in R&D department.

2.2.1 Distillation in packed column

Packed column is often used for distillation when the separation is relatively easy and the required column diameter is not very large. They are generally less expensive than the plate column and have a lower pressure drop. The main disadvantage of packed column is the difficulty in getting good liquid distribution particularly for large diameter column or very tall column. Although, liquid is spread evenly over the packing at the top of the column, liquid tends to move toward the wall and to flow through the packing in preferred channels. Regions of high liquid flow tend to have low vapor flow, and the local variations in L/V decrease the separation that can be achieved. To minimize this effect, tall columns are often split into sections with redistributors every 3 to 4 m.

The column height is usually based on the number of theoretical plates and the height equivalent to a theoretical plate (HETP). For structured sheet-metal packings gives slightly better separation than dumped packings. Therefore, the HETP values are nearly constant over a three- to fourfold range of flow rates. Even more efficient are the gauze-type packings with HETP values that increase from about 3 to 6 in. (0.1 to 0.2m) over a fourfold range of velocities. The gauze is completely wetted even at low flow rates and HETP can be predicted from fundamental equations for mass transfer in wetted channels. There is no corresponding theory for other structured packing or for dumped packing because it is difficult to predict the wetted area. Low surface tension tends to increase the wetted area but too low may lead to foaming, which increases HETP.

2.2.2 Section of distillation column [6]

The two sections in distillation column are rectifying section and stripping section. The definition and the function of each section is shown below.

Rectifying section is defined as the space from the upper end of the flash section to the top of the tower. It includes all plates above the feed plate. When the feed is fed into the flash section, the vapor phase and the liquid phase of the feed can be separated. Vapor phase will flow upwards to the upper part of the tower. The liquid reflux will flow downwards and contact with the rising vapor phase when passing through the trays in the upper part of the tower. At the top of the tower the light fractions are highly concentrated and purified. Therefore the function of the upper part of a rectification tower is to concentrate the light fractions in the vapor phase from the feed.

Stripping section is the space from the lower limit of the flash section to the bottom of the tower. It includes all plates below the feed plate and itself. The liquid phase from the feed will flow to the stripping section together with the liquid from the rectification section where the liquid phase contacts countercurrently with the rising vapor phase for heat transfer and mass transfer. A portion of the bottom stream is heated into vapor in the bottom reboiler and the vapor is returned to the tower as vapor reflux. The function of the section is to concentrate the heavy fractions in the liquid phase from the feed to guarantee product quality and to increase the yields of the overhead products.

2.2.3 Efficiency of packed column

2.2.3.1 Overall column efficiency

$$\text{Overallefficiency } (\eta_o) = \frac{\text{Number of actual stages}}{\text{Number of theoretical stages}} \quad (2.2)$$

2.2.3.2 Murphree efficiency

The Murphree tray efficiency (η_o) is based on a semi-theoretical model that assumes that the vapor between trays is well mixed as same as the liquid in the downcomer. It is

defined for each tray according to the separation achieved on each tray. The Murphree efficiency is therefore the change in vapor composition from one plate to the next divided by the change that would have occurred if the vapor leaving were in equilibrium with the liquid leaving as shown in equation 2.3.

$$\eta_M = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} \quad (2.3)$$

Where:

η_M	=	Murphree efficiency
y_n	=	Actual concentration of vapor leaving plate n
y_{n+1}	=	Actual concentration of vapor leaving plate n
y_n^*	=	Concentration of vapor in equilibrium with liquid downpipe from plate n

2.2.3.3 Height equivalent to a theoretical plate

Distillation and absorption separation processes using packed beds for vapor and liquid contacting have an equivalent concept referred to as the plate height or the height equivalent to a theoretical plate (HETP). HETP is the ratio of the total height and the number of theoretical plates as shown in equation 2.4.

$$HETP = \frac{H}{N_t} \quad (2.4)$$

Where:

$HETP$	=	The height equivalent to theoretical plate
H	=	The total packed height
N_t	=	The number of theoretical plates

In industrial practice, the HETP concept is used to convert empirically the number of theoretical trays to packing height. Most data have been derived from small-scale operations and they do not provide a good guide to the values which will be obtained on full-scale plant. However, the tray efficiency can be estimated more accurately than packed height equivalent to a theoretical stage (HETP).

2.2.3.4 The overall height of a transfer unit

New concept in the analysis of packed column on the method of transfer units is proposed in this section. This method is more appropriate because the changes in compositions of the liquid and vapor phases occur differentially in a packed column rather than in stepwise fashion as in tray column. In this method, height of packing required can be evaluated either based on the gas-phase or the liquid-phase. The packed height (Z) is calculated using the following formula:

$$Z = N \times H \quad (2.5)$$

For gas phase: $Z = N_{oy} \times H_{oy}$ (2.6)

For liquid phase: $Z = N_{ox} \times H_{ox}$ (2.7)

Where:

Z	=	The total packed height
N	=	Number of transfer units (NTU)
H	=	Height of transfer units (HTU)

The number of transfer units (NTU) required is a measure of the difficulty of the separation. A single transfer unit gives the change of composition of one of the phases equal to the average driving force producing the change. The NTU is similar to the number of theoretical trays required for tray column. Hence, a larger number of transfer units will be required for a very high purity product.

The height of a transfer unit (HTU) is a measure of the separation effectiveness of the particular packing for a particular separation process. The values of HTU can be estimated from empirical correlations or pilot plant tests but the applications are rather restricted.

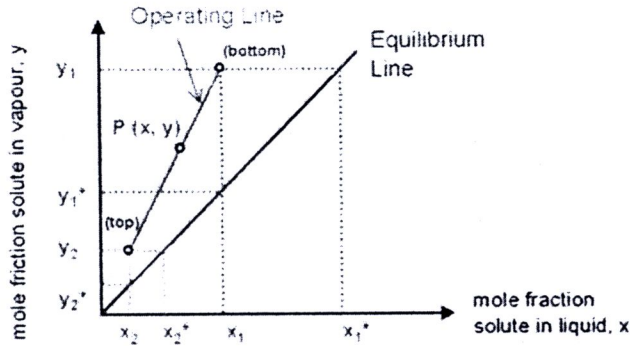


Figure 2.1 Relationship between mole fractions in vapor phase and liquid phase

For gas phase: $N_{oy} = \frac{y_1 - y_2}{\Delta y_L}$ (2.8)

$$H_{oy} = \frac{G_y}{K_y a} \quad (2.9)$$

$$\overline{\Delta y_L} = \frac{(y_1 - y_1^*) - (y_2 - y_2^*)}{\ln \left[\frac{(y_1 - y_1^*)}{(y_2 - y_2^*)} \right]} \quad (2.10)$$

$$\frac{1}{K_y a} = \frac{1}{k_y a} + \frac{m}{k_x a} \quad (2.11)$$

For liquid phase:

$$N_{ox} = \frac{x_1 - x_2}{\Delta x_L} \quad (2.12)$$

$$H_{ox} = \frac{G_x}{K_x a} \quad (2.13)$$

$$\Delta x_L = \frac{(x_1^* - x_1) - (x_2^* - x_2)}{\ln \left[\frac{(x_1^* - x_1)}{(x_2^* - x_2)} \right]} \quad (2.14)$$

$$\frac{1}{K_x a} = \frac{1}{k_x a} + \frac{1}{m k_y a} \quad (2.15)$$

Where:

G_y	=	Mass velocity of vapor phase
G_x	=	Mass velocity of liquid phase
$K_y a$	=	Overall volumetric mass-transfer coefficient for vapor phase
$K_x a$	=	Overall volumetric mass-transfer coefficient for liquid phase
$k_y a$	=	Individual mass-transfer coefficient for vapor phase
$k_x a$	=	Individual mass-transfer coefficient for liquid phase
m	=	Slope of equilibrium curve

2.2.4 Dynamic simulation

Dynamic plant simulation is a powerful tool that helps managers and engineers link the business operations to the process operations by increasing productivity and profitability. First, dynamic simulation empowers chemical producers to ensure safety. It helps predict the consequences of equipment failures and other operational problems and ensure that a plant is designed to safely handle such events. Second, it also helps improve operability i.e. a plant has sufficient flexibility to move from one operating points to another in a minimum of time without off-spec products. Next, it helps solve product quality and environmental emission problems by ensuring that control scheme can deal with disturbances. Moreover, it also used for testing the start-up and shut-down procedure and troubleshooting the operational problems.

At present, there are many dynamics simulator available. Chemical engineers can choose the most suitable one for their works. Aspen Dynamics is one of the most reliable tools used for studying the process performance such as start-up operation, operability, flexibility and safety.

2.2.5 Pilot distillation column of R&D building

Pilot distillation is located on site#3 in R&D building. The pilot distillation is designed to test the separation compare with the real plant distillation column. The others application of the pilot distillation is to prepare sample for other projects such as n-hexane and isopar projects. Its schematic and list of unit is shown in the Figure 2.2 and Table 2.1, respectively.

There are two feed tanks (100 liters) for this distillation unit in order to use as a spare feed tank. The feed is introduced to the column using nitrogen or pump. There are five feed locations as shown in Figure 2.2. The feed is introduced above the gas-liquid distributors (chimney tray). There are some literature said that poor distribution along the column occurred in pilot column (small size column). Therefore, the gas-liquid distributors are installed in order to redistribute the gas and liquid in the column. The contactor in this distillation column used packing from Sulzer named “Laboratory Packing” Figure 2.3. The specification of this packing is shown in Appendix A. The packing diameter and height is around 70.5 mm and 50 mm, respectively.

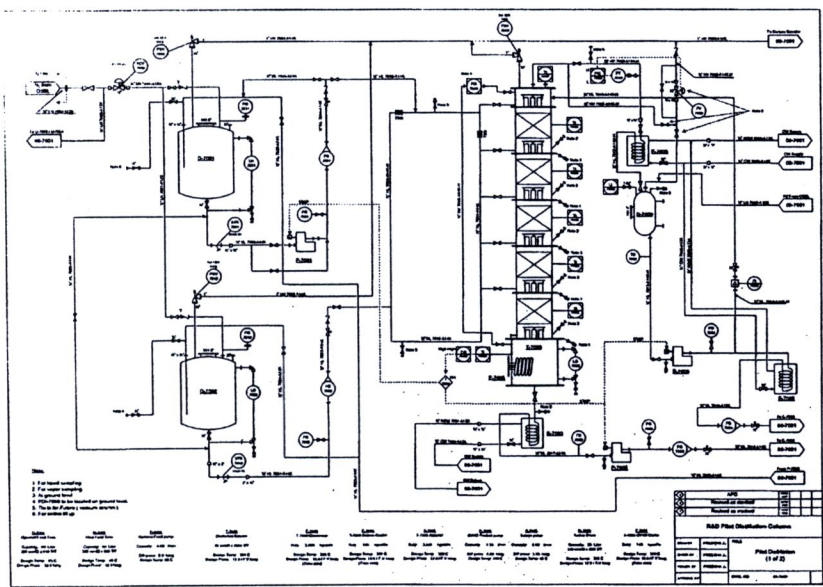


Figure 2.2 Pilot distillation schematic

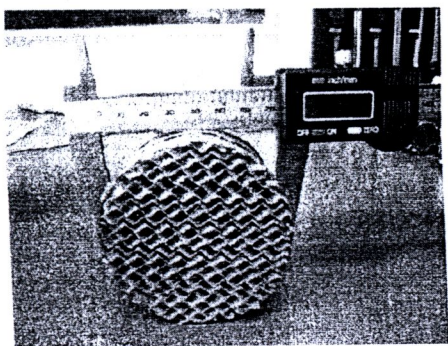


Figure 2.3 Sulzer packing using in distillation column

Table 2.1 ROC’s pilot distillation column equipment

CODE	Type	Name
D-7000	Drum	Reflux Drum
D-7001	Drum	Feed Tank I
D-7002	Drum	Feed Tank II
D-7004	Drum	Distillate Product Drum
D-7005	Drum	Bottom Product Drum
E-7000	Heat Exchanger	Condenser
E-7002	Heat Exchanger	Distillate Cooler
E-7003	Heat Exchanger	Bottom Cooler
P-7000	Pump	Reflux Pump
P-7001	Pump	Feed Pump
P-7005	Pump	Bottom Pump
T-7000	Column	Distillation Column

There are five layers of packing which the total height is 450 mm (9 packing packs) of each layer. When the feed is introduced to the column at designed tray, it is flowed down to the bottom of the column which has submerge heater as shown in Figure 2.4. The temperature range of this heater is around 40-300°C. The bottom level can be control at 2-5 liters from side glass. Then the sample at the bottom of the column is heated until it becomes vapor which flow up to the top of the column. At the middle of each packing layer, the temperature sensor is installed in order to measure the temperature of the fluid at that packing layer. The sensor is sent the signal to the control room.

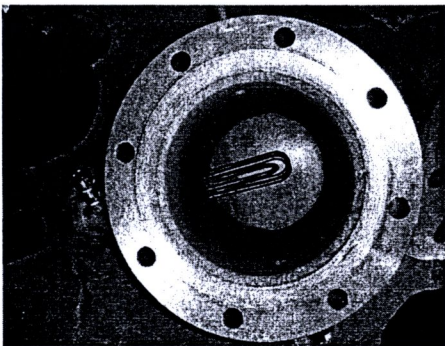


Figure 2.4 Heater at bottom of the column

The vapor is flowed through the packing along the column then, the vapor is passed to the condenser which is E-7000. Condenser aimed to condense the vapor to be liquid product. The cooling water is generated from the chiller which can operate at 5-30°C. Type of this cooler is counter current heat exchanger. The condensed product is drawn to and kept at the reflux drum in order to use as a reflux flow and to be distillate product. In order to avoid low level in the reflux drum, the level in the reflux drum should be over 30% then the reflux pump can be turn on. Percentage of level in the reflux drum is measured by the censer and sent the signal to the same DCS as mentioned above. In this pilot, the reflux flow can be set by adjusting the stroke of reflux pump (P-7000) while distillate flow can be controlled by adjusting the distillate flow meter.

Because of high temperature at the bottom, the bottom product must pass bottom cooler before introducing to the bottom product pump (no more than 65°C). The flow of bottom product is controlled by adjusting the bottom flow meter. All of the products have sampling point including product along the column. The side drawn product can be taken at the sampling point. The higher tube is for taking vapor sample while the lower one is for taking liquid phase product. Finally, all products are sent to separation lab in order to analyze the composition using Gas Chromatography Mass Spectrometer (GCMS).

2.2.6 Start-up procedure of ROC's pilot distillation column

Before the column is started-up, the control valve of Distillate, Bottom and Reflux must be closed. In the start-up operation of ROC's pilot distillation column, the start-up procedure of ROC's pilot distillation column is dived into 5 steps below.

1. Feed stream from Optional Feed Tank (D-7001) is introduced to the pilot distillation column (T-7000) by adjusting Rotameter (FG-7001) until the sump level is full while the Reflux drum level maintains around 25% of the total volume.
2. The temperature of the heater is adjusted to boil up the liquid in the column until the sump level remains 60-70% and then turn of the feed.
3. The feed rate is introduced to the lower packing of the column again and then waits until the Reflux drum level is increased to 30% of the total volume.
4. The total reflux flow is fed to the column by also controlling the Reflux drum and Sump level.
5. Adjust three parameters which are Distillate rate, Reflux rate and Bottom rate to the target value and wait until the column is reached to a steady state.,