MODELLING OF REACTIVE DISTILLATION FOR THE PRODUCTION OF METHYL TERT-BUTYL ETHER (MTBE): PARAMETRIC SENSITIVITY STUDY ON KINETIC MODEL

By

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UNIVERSITI SAINS MALAYSIA

2021

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Project report submitted in partial fulfilment of the requirement for the degree of Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

Symbol	Description	Unit
a	Activity	-
B	Bottom product flowrate	mol/s
c	Total number of components	-
C	Concentration	mol/dm3
D	Distillate flowrate	mol/s
F	Total feed flowrate	mol/s
Fj	Feed flowrate of stage j	mol/s
Hj	Liquid holdup of stage j	mol
hL	Partial molar enthalpy of liquid	J/mol
hV	Partial molar enthalpy of vapour	J/mol
ΔHR	Heat of reaction	J/mol
Keq	Thermodynamic reaction equilibrium constant	-
kf	Forward rate constant	s-1
Lj	Liquid flowrate from stage j	mol/s
N	Total number of stages	-
P	Pressure	Pa
R	Total number of reactions	-
Rj	Total rate of generation of moles on stage j	mol
r	Reflux ratio	-
s	Reboil ratio	-
T	Temperature	K

t	Time	s
v	Stoichiometric coefficient	-
Vj	Vapour flowrate from stage j	mol/s
W	Weight of catalyst	kg
x	Liquid composition	-
y	Vapour composition	-
z	Feed composition	-

t	Time	s
Vj	Vapour flowrate from stage j	mol/s

Greek letter

δj Parameter for reaction occurrence on stage j

$\emptyset$ Fugacity coefficient

γ Activity coefficient

Subscripts

i Component number   -

j Stage number   -

r Reaction number   -

T Total   -

Superscripts

f Feed   -

L Liquid   -

R Reaction (s)   -

V Vapour   -

LIST OF ABBREVIATION

Symbol	Description
EQ	Equilibrium
IB	Isobutylene
MeOH	Methanol
TBA	Tert-Butyl Ether
DME	Dimethyl Ether
DIB	Diisobutenes
VLE	Vapour-Liquid Equilibrium
MTBE	Methyl Tertiary Butyl Ether
UNIQUAC	Universal Quasi-Chemical
CSTR	Continuous Stirred Tank Reactor
x	Mole Fraction

PEMODELAN PENYULINGAN REAKTIF UNTUK PENGHASILAN METHYL TERT-BUTYL ETHER (MTBE):
KAJIAN SENSITIVITI PARAMETRIK TERHADAP MODEL KINETIK

ABSTRAK

Pemodelan penyulingan reaktif untuk pengeluaran MTBE telah dikemukakan dalam tesis ini. Kolum penyulingan reaktif dimodelkan dengan menggunakan modul RADFRAC dalam perisian ASPEN Plus V10 untuk pengeluaran MTBE. Simulasi dilakukan berdasarkan keseimbangan. Sebelum menjalankan simulasi, semua data yang diperlukan dikumpulkan. Data kinetik yang merupakan pekali persamaan keseimbangan dikumpulkan dari persamaan keseimbangan. Nilai yang diperoleh adalah 357.094, -1492.77, -77.4002 dan 0.507563. Nilai ini dimasukkan kedalam ekspresi K_{eq} terbina dalam Aspen Plus V10. Model simulasi disahkan dengan membandingkan dengan data yang diterbitkan. Setelah disahkan, simulasi kemudian digunakan untuk menjalankan kajian kepekaan parametrik pada model kinetik. Kesan perubahan pada data kinetik dan empat keadaan operasi pilihan yang berbeza seperti kadar aliran suapan metanol, kadar aliran suapan butena campuran, nisbah refluks dan komposisi isobutilena pada hasil simulasi dari segi ketulenan MTBE dan penukaran isobutilena dikaji secara terperinci. Nilai individu terbaik untuk setiap keadaan operasi ditentukan. Kemudian pengoptimuman dilakukan. Nilai yang dioptimumkan adalah, 209.3 mol/s bagi aliran suapan metanol, 583.2 mol/s bagi aliran suapan butena campuran, 7 bagi nisbah refluks dan 0.357 bagi pecahan mol isobutilena. Dari sekumpulan nilai ini, ketulenan MTBE dan penukaran isobutilena sebanyak 100.00 % berjaya dicapai. Kajian ini menunjukkan bahawa perubahan parameter mempengaruhi prestasi proses penyulingan reaktif untuk pengeluaran MTBE.

MODELLING OF REACTIVE DISTILLATION FOR THE PRODUCTION OF METHYL TERT-BUTYL ETHER (MTBE): PARAMETRIC SENSITIVITY STUDY ON KINETIC MODEL

ABSTRACT

Modelling of reactive distillation for the production of MTBE has been presented in this thesis. A reactive distillation column modelled by using RADFRAC module in the Aspen Plus V10 software for the production of MTBE. The simulation was done on an equilibrium basis. Prior to running the simulation, all the necessary data were collected. The kinetic data which is the coefficients of the equilibrium equation were collected from the equilibrium equation. The values obtained were 357.094, -1492.77, -77.4002 and 0.507563. These values were entered into the Aspen Plus V10 built-in K_{eq} expression. The simulated model was verified by comparing to the published data. Once it was verified, the simulation was then used to carry out parametric sensitivity study on kinetic model. The effect of changes in the kinetic data and four different operating conditions of choice such as the feed flowrate of methanol, the feed flowrate of mixed butenes, the reflux ratio and the composition of isobutylene on the simulation results in terms of MTBE purity and isobutylene conversion were studied in detail. The individual best values for each operating conditions were determined. Then optimization carried out. The optimized values were 209.3 mol/s for methanol feed flowrate, 583.2 mol/s for mixed butenes feed flowrate, 7 for reflux ratio and 0.357 for isobutylene mole fraction. From these set of values, a MTBE purity and isobutylene conversion of 100.00 % obtained successfully. This study shows that the changes in parameters influences the performance of reactive distillation process for the production of MTBE.

CHAPTER 1

INTRODUCTION

Chapter 1 introduces the overview of this research and some introduction to methyl tert-butyl ether (MTBE) and the reactive distillation technology. In general, this chapter summarises the modelling of reactive distillation column for the production of MTBE using computer simulation which is Aspen Plus V10, problem statement and objective of this final year project.

1.1 Research Background

Methyl tert-butyl ether (MTBE), also known as tert-butyl methyl ether is an organic compound with a chemical formula of $(CH_3)_3COCH_3$. The structural formula of MTBE is:
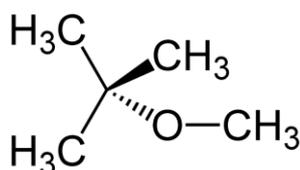
MTBE is a liquid that is sparingly soluble in water, volatile, flammable, and colourless. Over 90.0% application of MTBE is in the octane enhancer industry, almost all MTBE supply is used for reformulated and oxygenated gasoline blending. Octane enhancer works to improve fuel compression in engine before detonation. As a result, the power of the vehicle's engine is enhanced for higher efficiency. Oxygenates are hydrocarbons that contain one or more oxygen atoms, oxygenate blending increases oxygen to the fuel and so reduces the amount of carbon monoxide and unburned fuel in the exhaust gas, thus reducing smog. MTBE has been produced in very large quantities for use as a gasoline additive since about 1979 to meet the goals of Clean Air Act in USA. Catalytic etherification of isobutylene with methanol is a single-step route to synthesis MTBE. MTBE can be produced using reactive distillation column. Reactive Distillation is a combination of both reaction and distillation process in a single unit operation. It

combines both chemical reactions and physical separations into a single equipment. This makes the use of reactive distillation column is much preferable comparing to conventional method where reaction followed by distillation process separately in sequence. With the aid of computer, reactive distillation column for the production of MTBE is modelled and simulated using Aspen Plus V10. This alternative helps reducing the capital investment and complexities on developing a reactive distillation column.

1.2   Problem Statement

Reactive distillation process has become crucial for its potential for process intensification reactions. The most important benefit of reactive distillation is the reduction in cost as two process carried out in the same device at same time. Developing reactive distillation column is challenging because of the complexities in column design, process synthesis and operability of reactive distillation processes. The difficulties in modelling of complex reactive distillation can be overcome by using the aid of computer simulation such as Aspen Plus V10. Generally, the kinetic model implementation in reactive distillation process model is based on batch process. In this case, the kinetic model should be developed in a batch process manner and then implemented into the continuous process of reactive distillation. The reaction parameters in continuous mode are initially assumed the same as batch mode. In reality, the actual parametric values are unknown due to different mode of process. Through parametric sensitivity study, the optimized values of parameter in kinetic model could be obtained specifically for continuous process of reactive distillation.

1.3 Objectives

The objectives of this study are:

i. To develop reactive distillation model for MTBE synthesis using Aspen Plus V10.

ii. To verify the reactive distillation model and perform simulation studies.

iii. To perform parametric sensitivity study on kinetic model of the reactive distillation for MTBE synthesis.

CHAPTER 2

LITERATURE REVIEW

In this chapter, the previous discoveries and reviews available from credible scientific records and references that are related to this final year project topic presented. This chapter covers about the methyl tert-butyl ether (MTBE), reactive distillation, modelling of the reactive distillation column for the production of MTBE, process description on MTBE production, sustainability issues and market of MTBE.

2.1 Methyl Tert-Butyl Ether (MTBE)

Methyl tertiary butyl ether (MTBE) is an oxygenated chemical which is used as additive for gasoline to improve the octane number (Seddigi et al., 2014). This increases the combustion efficiency of gasoline by supplying extra oxygen during the combustion process (Sudibyo et al., 2011). Thus carbon monoxide from internal combustion engines reduced with air pollution as well (Siddiqui and Gondal, 2014). MTBE is a liquid that is sparingly soluble in water that is volatile, flammable, and colourless (Dhanke and Prashant, 2019). MTBE is commonly found in drinking water and capable of contaminating large water volumes due to its physicochemical properties. MTBE can be produced using reactive distillation column (Sudibyo et al., 2011).

2.2 Reactive Distillation

The reactive distillation have been given special attention for its ability on process intensification for certain types of chemical reactions (Popken et al., 2001). In reactive distillation, two processes can be carried out in one equipment which saves the costs to run the process (Taylor and Krishna, 2000). Modelling reactive distillation column is complicated because of the complexities due to the interaction between reaction and distillation (Chen et al., 2000).

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2.3   Modelling of Reactive Distillation

There is no general design for reactive distillation column due to the complexities in reactive distillation processes and the uncertainty in the model parameters (Pilavachi et al., 1997). Understanding the thermodynamic and kinetic theories, these difficult problems can be handled. Mostly, mathematical models for reactive distillation derived from conventional distillation calculations based on equilibrium stage model (Chen et al., 2000). The development of the model is done by undertaking the mass and energy balance (Steffen et al., 2012). However, by using computer simulation, modelling of complex reaction distillation column can be simplified (Pilavachi et al., 1997). Reactive distillation column for the production of MTBE consists of three sections which are rectification, reaction and stripping section (Sudibyo, 2012). Simulations done in Aspen Plus by using RADFRAC model which is an equilibrium model (Sudibyo et al., 2011). **Figure 2.1** shows the RADFRAC model from Aspen Plus for reactive distillation column simulation (Gautam et al., 2013).
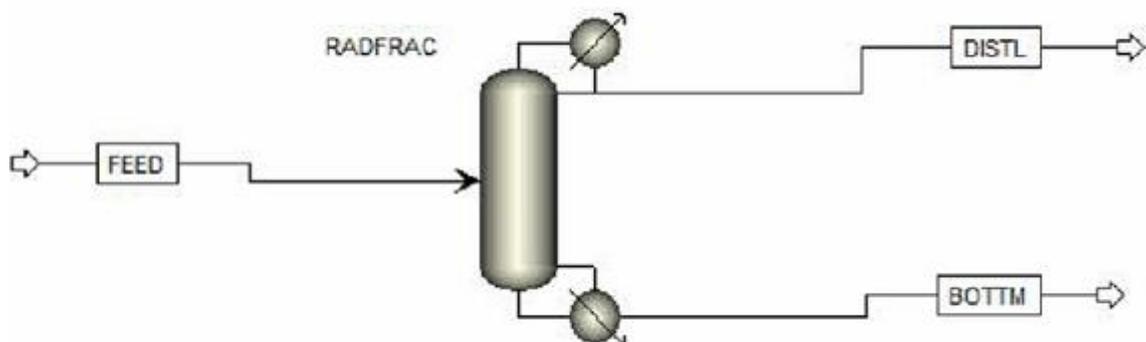
Figure 2.1 RADFRAC Model from Aspen Plus (Gautam et al., 2013)

2.4 Mathematical Modelling

The reaction assumed to be adiabatic and take place in the liquid phase. Each reactive stage is considered as continuously stirred tank reactor (CSTR) with perfect mixing. The liquid and vapour leaving any stage are assumed to be in phase equilibrium by neglecting the heat of mixing of liquid and vapour mixtures. The vapour hold-up and the hydrodynamic effect are neglected as well. (Murat et al., 2003).

2.4.1 The Overall Material Balance for Equilibrium stage j

$$F_j + L_{j-1} + V_{j+1} + \delta_j R_j = L_j + V_j$$

(mol/s) (Murat et al., 2003) (2.1)

2.4.2 Unsteady State Component i Material Balance

$$H_j \frac{dx_{j,i}}{dt} = \left(z_{j,i}F_j + x_{j-1,i}L_{j-1} + y_{j+1,i}V_{j+1}\right) - \left(x_{j,i}L_j + y_{j,i}V_j\right) + \delta_j \sum_{r=1}^{R} \left(v_{r,i}r_{j,r}\right)$$

(mol/s) (Murat et al., 2003) (2.2)

Where,

j is the stage number, j=1,2…, N-1

i is the component number, i=1,2…, c

r is the specific reaction number, r=1,2,…, R

$z_{j,}$, $x_{j,i}$, $y_{j,i}$ are component i mole fractions

F_j is feed flow

L_j is the liquid flow

V_j is the liquid flow

v_r is the stoichiometric coefficient of component.
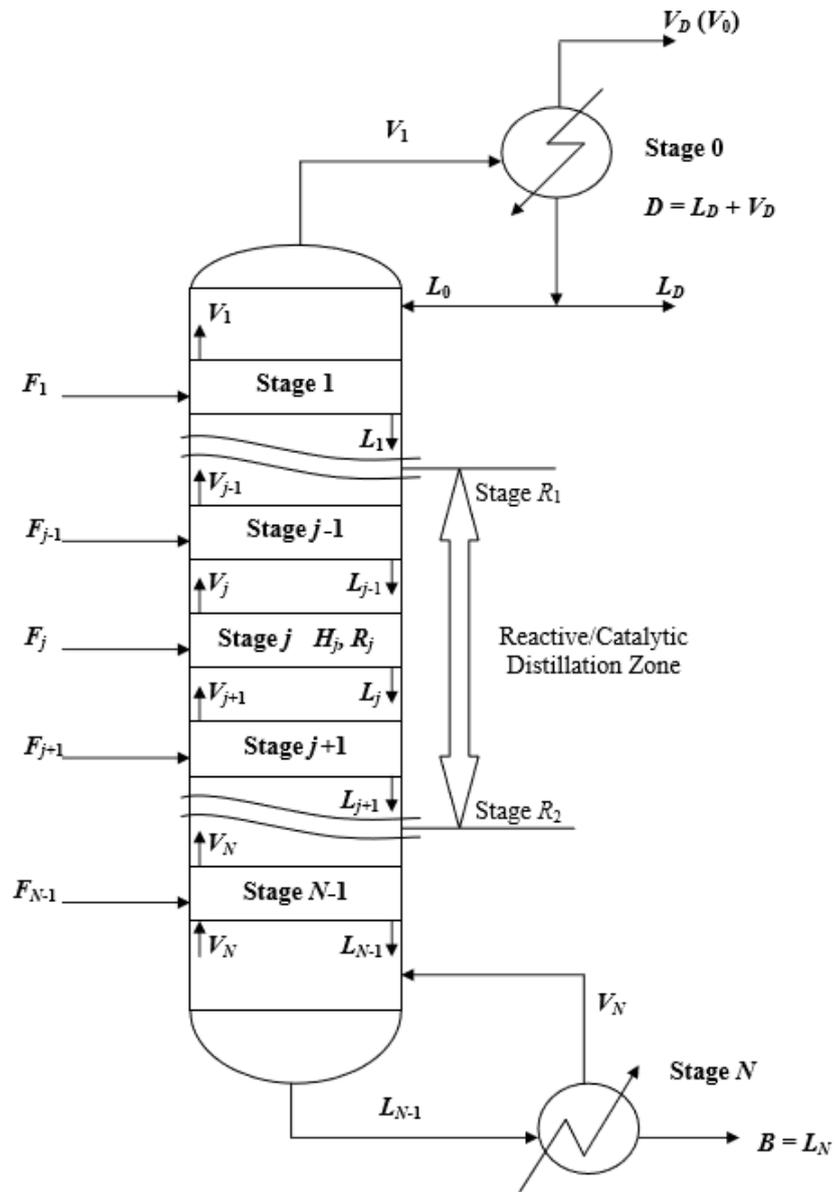
Figure 2.2 *Schematic Representation of a Reactive Distillation Column (Murat et al.,*

2003)

2.4.3 Energy Balance

$$F_j \sum_{i=1}^{c} z_{j,i}\left(h_{j,i}^{f} - h_{j,i}^{L}\right) + L_{j-1} \sum_{i=1}^{c} x_{j-1,i}\left(h_{j-1,i}^{L} - h_{j,i}^{L}\right) + V_{j+1} \sum_{i=1}^{c} y_{j+1,i}\left(h_{j+1,i}^{V} - h_{j,i}^{L}\right)$$

$$-\delta_j W_j \sum_{r=1}^{R} \left(\Delta H_{j,r}^{R}\right)_{j,r} = V_j \sum_{i=1}^{c} x_{j,i}\left(h_{j,i}^{V} - h_{j,i}^{L}\right)$$

(mol/s) (Murat et al., 2003) (2.3)

Where,

h^L is the partial molar enthalpy of liquid (J/mol),

h^V is the partial molar enthalpy of vapour (J/mol),

ΔH^R is the heat of reaction (J/mol),

W is the weight of catalyst (kg).

2.4.4 Phase Equilibrium

$$y = \frac{\gamma P^0}{\phi P} x$$

(Murat et al., 2003) (2.4)

The vapour phase assumed to be ideal so that the entire fugacity coefficients $\emptyset$ for the system are equated to unity. The activity coefficients γ calculated from the UNIQUAC method. The saturated vapour pressure P_0 calculated from the Antoine equation and P is the total pressure (Murat et al., 2003).

2.4.5 Summation (Constraint) Equations

The compositon of liquid and vapour component on each stage of reactive distillation column should sum up to unity. The summation equations are shown below.

$$\sum_{i=1}^{c} x_{j,i} = 1.0$$

(Liquid phase) (Murat et al., 2003)   (2.5)

$$\sum_{i=1}^{c} y_{j,i} = 1.0$$

(Vapour phase) (Murat et al., 2003)   (2.6)

2.4.6 Kinetic Model

The principal reaction between methanol (MeOH) and isobutylene (IB) for MTBE synthesis is:

$$CH3OH\ (MEOH) + (CH3)2C = CH2\ (IB) \Leftrightarrow (CH3)3COCH3\ (MTBE)$$

(Murat et al., 2003)   (2.7)

The activity based rate model is:

$$\text{rate} = Wqk_f \left(\frac{a_{IB}}{a_{MEOH}} - \frac{a_{MTBE}}{K_{eq} a_{MEOH}} \right)$$

(mol/s) (Murat et al., 2003)   (2.8)

Where,

W is the weight of catalyst (kg),

q is the amount of acid groups on the resin per unit mass (4.9 equiv/kg).

The forward rate constant, k_f is:

$$k_f = 3.67 \times 10^{12} \exp\left(-\frac{11110}{T}\right)$$

(mol/s equiv) (Murat et al., 2003)   (2.9)

The rate constant units are based on equiv of hydrogen ions present in the catalyst.

The equilibrium constant K_{eq} is given by:

$$K_{eq} = 284 \exp[f(T)]$$

and

$$f(T) = A_1 \left(\frac{1}{T} - \frac{1}{T_0}\right) + A_2 \ln\left(\frac{T}{T_0}\right) + A_3(T - T_0) + A_4(T^2 - T_0^2) + A_5(T^3 - T_0^3) +$$

$$A_6(T^4 - T_0^4)$$

(Murat et al., 2003)   (2.10)

Where,

$T_0 = 298.15$ K,

$A_1 = -1.49277 \times 10^3$ K,

$A_2 = -77.4002$,

$A_3 = 0.507563$ K^{-1},

$A_4 = 9.12739 \times 10^{-4}$ K^{-2},

$A_5 = 1.10649 \times 10^{-6}$ K^{-3},

$A_6 = -6.27996 \times 10^{-10}$ K^{-4}.

2.5   Process Description

2.5.1 Main Reaction

Direct etherification of isobutylene with methanol produces MTBE. This exothermic, liquid phase reaction is catalysed by strong acidic macroreticular ion-exchange resins in a temperature range from 40 to 100°C and pressure range from 7 to 20 atm. Since the MTBE reaction is exothermic, a lower temperature slightly favours isobutylene conversion (Caetano et al., 1994). The main reaction equation is shown below:

$$(CH_3)_2C = CH_2 + CH_3OH \rightleftharpoons (CH_3)_3COCH_3$$
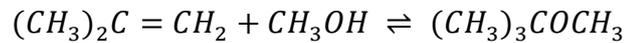
$$\text{isobutylene} + \text{methanol} \rightleftharpoons \text{MTBE}$$

(2.11)

MTBE will exit as bottom product, the excess methanol will form azeotrope with MTBE and exit together with the composition of approximately 97% and 3% respectively. The reactor effluent enters the separation step. The unconverted methanol collected as top product forming azeotrope with the C4 hydrocarbons (Miracca et al., 1996).

2.5.2 Methanol/Isobutylene Ratio

Excess of methanol at the reaction stage will increase the conversion of isobutylene. An isobutylene conversion rate of more than 98% can be obtained by using a methanol to isobutylene molar ratio greater than 1.06 in the MTBE reaction process (Koga, 1955).

2.5.3   Choice of Catalyst

The green catalyst, Amberlyst-15 used as the catalyst for this reaction. Amberlyst-15 is a macro reticular polystyrene based ion exchange resin with strongly acidic sulfonic group. It is nontoxic and it exhibits good catalytic performance, is easy to obtain, cheap in price, and can also be reused three times as recovered catalyst with almost identical catalytic activity during the reaction (Nawaz, 2017).

2.5.4   Side Reactions

There are 3 side reactions that might occur during the reaction, forming undesired by products. The first reaction is dimerization of isobutylene, forming diisobutenes (DIB). DIB can cause deactivation of the catalyst by filling the macropores and thus preventing the reactants from reaching the active sites on the catalyst. The second reaction is methanol condensation, which will form dimethyl ether (DME) and water. The water formed by methanol condensation can react with isobutylene, forming another by products, tert-butyl alcohol (TBA) (Caetano et al., 1994). The equations of the side reactions are shown below:

Dimerization of isobutylene to diisobutenes (DIB):

$$2(CH_3)_2C = CH_2 \rightarrow (CH_3)_3CCH_2(CH_3)C = CH_2$$

$$2 \text{ isobutylene} \rightarrow 2,4,4 - \text{trimethyl} - 1 - \text{pentene}$$
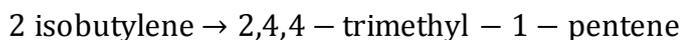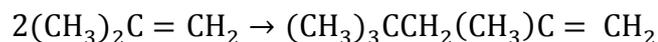
(2.12)

The formation of dimethyl ether (DME):

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$\text{methanol} \rightarrow \text{DME} + \text{water}$$
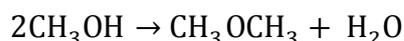
(2.13)

The formation of tert-butyl alcohol (TBA):

$$(CH_3)_2C = CH_2 + H_2O \rightarrow (CH_3)_3COH$$
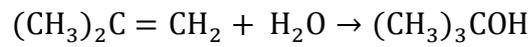
$$\text{methanol} + \text{water} \rightarrow \text{TBA}$$

(2.14)

However the side products formed from this reaction are very small in quantity. Thus it can be considered as negligible (Murat et al., 2003).

2.5.5 Isobutylene Conversion and Selectivity

Isobutylene conversion higher than 90% can be reached for each reaction stage in the temperature range of (40 - 80 °C). The selectivity can be very high (> 99%) (Miracca et al., 1996).

2.6   Sustainability Issues

2.6.1   Environmental Factors

MTBE has high resistance against biodegradation since it is miscible in water. The leakage or spill of MTBE will contaminate groundwater and leads to offensive odour and taste (Nesbitt et al., 1999). In this process, water, pure butenes, dimethyl ether (DME), diisobutane (DIB) and tert-butyl ether (TBA) produced as wastes. The composition of dimethyl ether (DME), diisobutane (DIB) and tert-butyl ether (TBA) are in a small composition compared to water and pure butenes thus it is negligible (Murat et al., 2003).

2.6.2   Safety Factors

This issue is analyzed from the aspect of temperature and pressure. Desired temperature should be maintained throughout the process to prevent any possible accidents from occuring. The production of MTBE is under low temperatue which minimize the chance of flammability eventhough MTBE and methanol are extremely flammable (Nesbitt et al., 1999).

2.6.3   Health Factors

MTBE is of concern to the drinking water supply because of its strong taste and odor, tendency to migrate rapidly in groundwater and resistance to conventional water treatment processes which eventually leads to potential risk to human health (Gullick and LeChevallier, 2000). Isobutylene is a colourless gas and liquid under pressure with a sweet gasoline odour. Isobutylene gives negative impacts to those who breathe it in. It will cause dizziness, drowsiness and unconsciousness. Exposure to isobutylene can cause irritation on eyes, nose and throat. Inhalation of moderate concentration of isobutylene will cause dizziness, drowsiness and unconsciousness (Latif et al., 2018).

2.7   MTBE Market

Based on (Transparency Market Research), the global MTBE market is divided into gasoline, isobutylene, solvent and extraction. The gasoline portion is expected to lead the MTBE market. Asia Pacific is the largest consumer of MTBE for gasoline blending due to the expanding vehicle fleets and growing urbanization. The widespread availability of MTBE as a cheap feedstock and being an attractive substitute to aromatics in gasoline is driving the Asia-Pacific market. On the other hand, Europe and North America will also prevail as major markets for MTBE as there has been a steady expansion of the use of MTBE in the refinery sector in these regions due to the anti-knocking properties that suits well to reduce wear and tear of the heavy-duty machinery in the refinery sector.

CHAPTER 3

METHODOLOGY

This chapter discloses the information on the methods applied in this final year project. It includes the overview of research methodology, collection of data from literature, Aspen Plus simulation, model verification with published data, parametric sensitivity study, data analysis and report writing.

3.1   Overview of Research Methodology

In order to achieve those research objectives mentioned in Chapter One, an equilibrium model of reactive distillation for the production of MTBE developed. Aspen Plus V10 software was used for modelling and simulation purpose. Firstly, it is started with the study of equilibrium model of reactive distillation. A simulation was done based on the the data collected from the literature. The model then validated with the simulation data obtained from the literature. After the model verified, parametric sensitivity study carried out. The parameter is the kinetic data of the equilibrium model which is the coefficients of the equilibrium equation. Then some operating conditions were chosen for the sensitivity study. The operating conditions chosen were the feed flowrate of methanol, the feed flowrate of mixed butenes, the reflux ratio and the composition of isobutylene in the feed flowrate of the mixed butenes. **Figure 3.1** shows the methodology flowchart for this work.
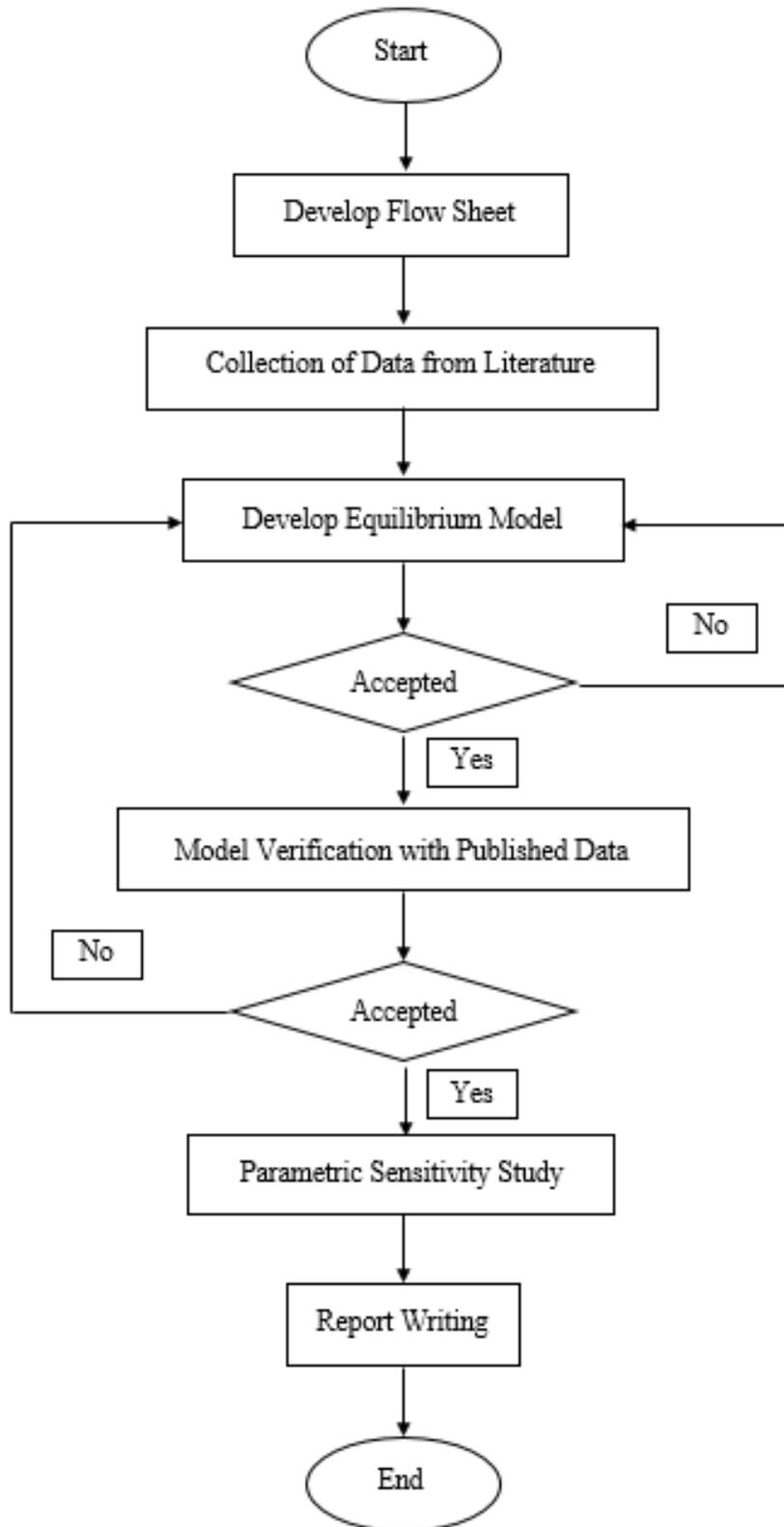
Figure 3.1 *Overall Methodology Flowchart*

3.2   Collection of Data from Literature

The simulation of this paper is working on the etherification reaction between methanol and isobutylene to form MTBE in a reactive distillation column. In order to start the simulation, some simulation basis is required such as feed specification, column configuration, operating condition and kinetic data. Those information is collected from literature by Sudibyo et al. (2011).

At the beginning, all important information required in modelling and simulation of reactive distillation column were collected. The information included kinetic model of MTBE synthesis, equilibrium stage model and vapor-liquid equilibrium model. All the common specifications for a reactive column and some special variables which relate to the types of models such as feed specifications and physical properties were specified.

As the basis for this simulation work, it is assumed that 197 mol/s MTBE is produced. The reactive distillation column has a total number of 17 stages. There are two feed stages in the column which is a methanol feed on stage 4 and a Mixed Butenes feed on stage 11. The column pressure is set at 11atm whereas the reflux ratio is 7. **Table 3.1** shows the summary of the simulation basis.

Table 3.1 *Feed Specification and Column Configuration (Sudibyo et al., 2011)*

Quantity	Units	Methanol	Butenes
Feed	mol/s	215.5	549
Temperature	K	320	350
Pressure	atm	12	12
Feed stage	-	4	11
MeOH	-	1.0	0.000
IB	-	0.0	0.3558
MTBE	-	0.0	0.000
1-Butene	-	0.0	0.6442

Column Configuration

Quantity	Units	Value
Number of stages, N	-	17
Column Pressure, P	atm	11
Reaction stages	-	11
Reflux Ratio, r	-	7
Bottom Flow, B	mol/s	197

Some assumptions were taken into account for this simulation. The MTBE system assumed to consist of 4 components, which are methanol, isobutylene, MTBE and 1-Butene. The inert (C4 components) in MTBE system are quite similar to each other in physical and chemical properties, thus it is represented by 1-Butene. The by products are very small in quantity and can be considered negligible (Murat et al., 2003).

Since the simulation is to be done on an equilibrium basis, the kinetic data which is the coefficients of the equilibrium equation obtained from the equilibrium equation given in the literature by Sudibyo et al. (2011). Some simple calculations were made on the equilibrium equation in order to get the form as in the Aspen Plus V10 built-in K_{eq} expression. The calculations for the coefficients of the equilibrium equation are shown below.

$$\ln K_{eq} = \ln K_{eq0} + A_1\left(\frac{1}{T} - \frac{1}{T_0}\right) + A_2\ln\left(\frac{T}{T_0}\right) + A_3(T - T_0) + A_4(T^2 - T_0^2) +$$

$$A_5(T^3 - T_0^3) + A_6(T^4 - T_0^4)$$

(Sudibyo et al., 2011) (3.1)

Where,

$T_0 = 298.15$ K,

$K_{eq0} = 284$,

$A_1 = -1.49277 \times 10^3$ K,

$A_2 = -77.4002$,

$A_3 = 0.507563$ K^{-1},

$A_4 = 9.12739 \times 10^{-4}$ K^{-2},

$A_5 = 1.10649 \times 10^{-6}$ K^{-3},

$A_6 = -6.27996 \times 10^{-10}$ K^{-4}.

The equation (3.1) above was collected from literature by Sudibyo et al. (2011). This equation then solved by substituting the values given for the unknowns. Once the equation solved, the values for the coefficients of the equilibrium equation can be obtained as shown below.

$$\ln K_{eq} = (357.0939701) + \left(\frac{-1492.77}{T}\right) + (-77.4002)\ln(T) + (0.507563)(T) +$$

$$(-9.12739 \times 10^{-4})(T^2) + (1.10649 \times 10^{-6})(T^3) + (-6.27996 \times 10^{-10})(T^4)$$

(3.2)

Where,

357.0939701 = A,

-77.4002 = B,

0.507563 = C,

-9.12739×10⁻⁴ = D,

1.10649×10⁻⁶ = E,

-6.27996×10⁻¹⁰ = F.

This coefficients of the equilibrium equation will be entered directly into Aspen Plus V10 built-in K_{eq} expression prior to running the simulation. However, only the values of A, B, C and D can be entered into Aspen Plus V10 built-in K_{eq} expression since Aspen Plus V10 only allows first four values of coefficients to be filled in as shown in **Figure 3.10** later.

3.3 Aspen Plus Simulation

Aspen Plus V10 simulator is used to carry out the simulation for both equilibrium and non-equilibrium model. The simulation model is run step by step from component key-in until the setup of reactive distillation column.

3.3.1 Component Selection

Four components such as methanol, isobutylene, MTBE and 1-butene were entered in the Component ID as shown in the **Figure 3.2** below.
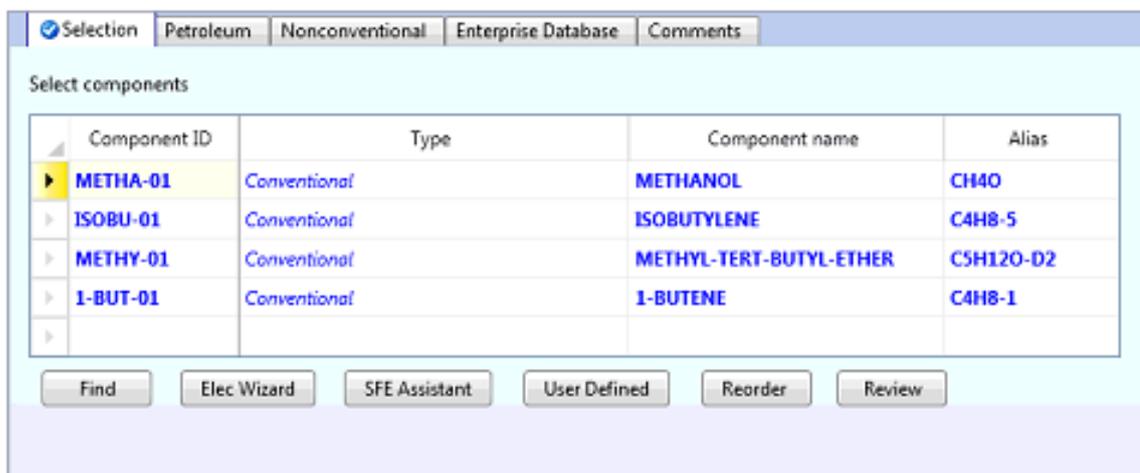
Figure 3.2 Components Selection in Aspen Plus V10

3.3.2   Method for Simulation

Next, UNIQUAC thermodynamics model is selected as the method for the

simulation as shown in the **Figure 3.3** below.
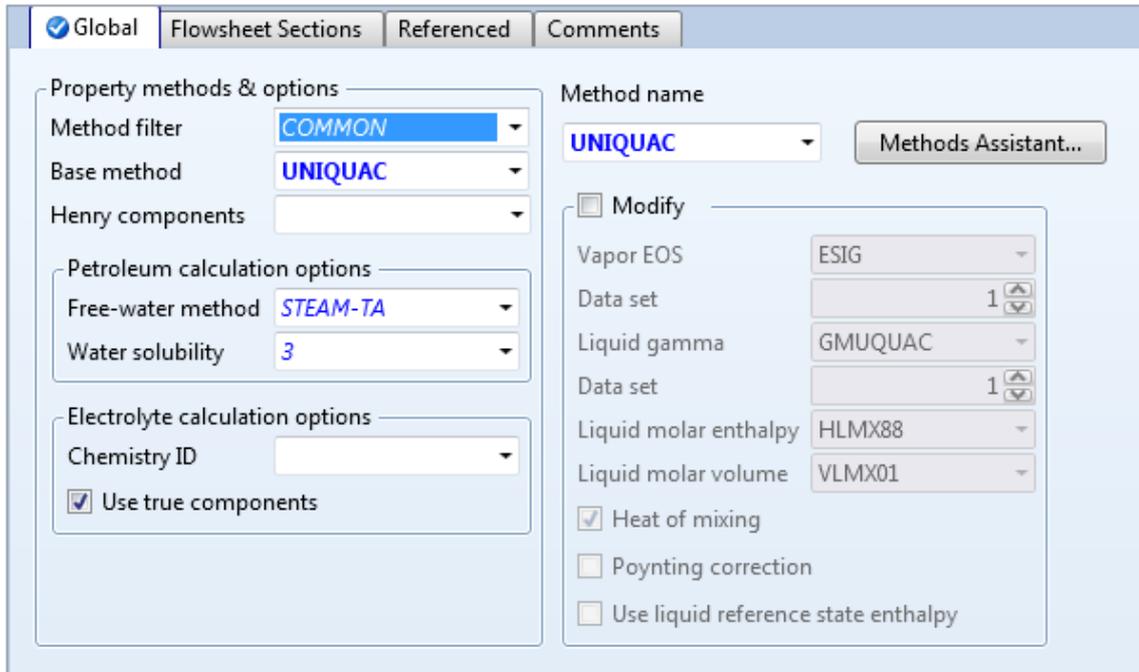
Figure 3.3 *Model Selection in Aspen Plus V10*

Before moving to process flowsheet, properties analysis is run in order to check the

properties of those components selected.

3.3.3 Main Flowsheet

RADFRAC model is selected for the simulation. Two feed streams which consist of methanol, isobutylene and 1-butene were linked with the RADFRAC. Two product streams which is the top and bottom product were the output from the RADFRAC. The main flowsheet is shown in the **Figure 3.4** below.
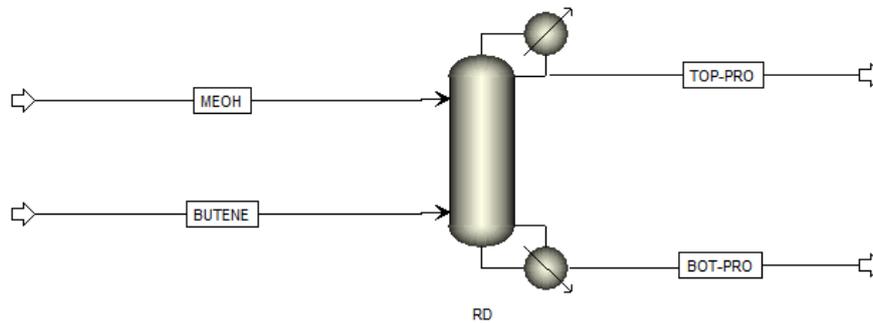
Figure 3.4 RADFRAC in Aspen Plus V10