

**STEADY STATE MULTIPLICITY IN THE  
REACTIVE DISTILLATION OF METHYL TERT-  
BUTYL ETHER (MTBE) SYNTHESIS: STABILITY  
ANALYSIS**

**FIETRIEY ATIERA SHAHIDA BINTI ADNAN**

**UNIVERSITI SAINS MALAYSIA**

**2021**

**STEADY STATE MULTIPLICITY IN THE  
REACTIVE DISTILLATION OF METHYL TERT-  
BUTYL ETHER (MTBE) SYNTHESIS: STABILITY  
ANALYSIS**

by

**FIETRIEY ATIERA SHAHIDA BINTI ADNAN**

**Project report submitted in fulfilment of the requirements  
for the degree of  
Bachelor of Chemical Engineering**

**2021**

## ACKNOWLEDGEMENT

First and foremost, I would like to convey my greatest gratitude to Almighty God, who blesses me with knowledge, strength and determination in order to complete the Final Year Project research successfully. Without His, completing the thesis will be very challenging, and it may never be completed.

Next, I would like to take this opportunity to dedicate my sincere appreciation to my supervisor, Dr. Muhamad Nazri Murat for his amazing encouragement, guidance and research advices throughout the research period. Despite the fact that this is my first time conducting a modelling simulation for a reactive distillation column, Dr. Nazri is always sincerely teach me and assist me whenever I encounter any difficulties during conduction this research. Without his advices and guidance, this research project will have a lot of mistakes and errors.

In addition, I would like to express my deepest thanks to my family who always gives full support and motivated me whenever I faced hardship during this difficult time due to pandemic COVID-19. I owe them a debt of gratitude for their unwavering encouragement and moral support throughout my research. Their unwavering encouragement and faith in me led me to complete my research successfully. Apart from that, I also want to express my gratitude to all my friends for their kindness cooperation and helping hands in guidance my carrying out the simulation. In the middle of carried out their final year project, they are willing to sacrifice their time in guiding and helping me out through the progress. They also would not mind sharing their valuable knowledge. Furthermore, I want to thank all the staff in School of Chemical Engineering for any kind of supports.

Finally, I would like to sincerely thanks to all the people who involves in this research directly or indirectly since due to their contributions, I able to complete this research successfully. Thank you.

Fietriey Atiera Shahida Binti Adnan

June 2021

## TABLE OF CONTENTS

<b>ACKNOWLEDGEMENT</b>	<b>ii</b>
<b>TABLE OF CONTENTS</b>	<b>iv</b>
<b>LIST OF TABLES</b>	<b>vi</b>
<b>LIST OF FIGURES</b>	<b>vii</b>
<b>LIST OF SYMBOLS</b>	<b>ix</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xi</b>
<b>LIST OF APPENDICES</b>	<b>xii</b>
<b>ABSTRAK</b>	<b>xiii</b>
<b>ABSTRACT</b>	<b>xiv</b>
<b>CHAPTER 1 INTRODUCTION</b>	<b>1</b>
1.1 Research Background	1
1.2 Problem Statement	5
1.3 Research Objectives	6
1.4 Scope of Study	6
<b>CHAPTER 2 LITERATURE REVIEW</b>	<b>7</b>
2.1 Methyl tert-butyl ether (MTBE)	7
2.2 Synthesis of MTBE	7
2.3 Modelling of Reactive Distillation	8
2.3.1 Vapour-Liquid Equilibrium Model	8
2.3.2 Equilibrium Stage Model	10
2.3.3 Mathematical Modeling	12
2.3.3(a) Material and energy balance	13
2.3.3(b) Phase equilibrium	15
2.3.3(c) Summation equations	15
2.4 Multiple Steady State	16

2.5	Stability Analysis	17
2.6	Sustainability	18
	<b>CHAPTER 3 METHODOLOGY</b>	<b>20</b>
3.1	Overview of Research Methodology	20
3.2	Research Methods	21
3.2.1	Data Collection from Literature	22
3.2.1(a)	Reaction Kinetics	22
3.2.1(b)	MTBE Reactive Distillation Column	23
3.2.1(c)	Simulation Basis	24
3.2.2	Procedure in Aspen Plus for MTBE Synthesis	25
3.2.3	Verification of Model	31
3.2.4	Multiplicity Steady State Analysis	31
3.2.5	Stability Analysis	32
	<b>CHAPTER 4 RESULT AND DISCUSSION</b>	<b>33</b>
4.1	Validation and Comparison of Simulation Results with Literature	33
4.1.1	Temperature and Liquid Composition Profile	34
4.2	Multiple Steady State Analysis	35
4.3	Stability Analysis	37
	<b>CHAPTER 5 CONCLUSION AND FUTURE RECOMMENDATIONS</b>	<b>38</b>
5.1	Conclusion	38
5.2	Recommendations for Future Research	38
	<b>REFERENCES</b>	<b>40</b>
	APPENDICES	44

## LIST OF TABLES

	<b>Page</b>
Table 3.1 Feed specification and operating condition for MTBE synthesis (Nijhuis et al., 1993).....	24
Table 4.1 Data comparison between literature and simulated model. ....	33
Table 5.1 Stream summary of the proposed model validation.....	44

## LIST OF FIGURES

	<b>Page</b>
Figure 1.1 Configuration of reactive distillation (Taylor & Krishna, 2000).....	2
Figure 2.1 Schematic representation of a reactive distillation column (Murat et al., 2003). .....	13
Figure 3.1 Flowchart of overall methods of the study. ....	21
Figure 3.2 Configuration of reactive distillation column for MTBE synthesis (Wang et al., 2003).....	23
Figure 3.3 Component selected for MTBE synthesis. ....	25
Figure 3.4 UNIQUAC/RK property method is used.....	26
Figure 3.5 Main flowsheet of RD column for MTBE synthesis. ....	26
Figure 3.6 Specification data of methanol feed. ....	27
Figure 3.7 Specification data of mixed butenes feed. ....	27
Figure 3.8 Column configuration for MTBE synthesis. ....	27
Figure 3.9 Feed Location of methanol and mixed butenes. ....	28
Figure 3.10 Specification data of RD column at condenser pressure. ....	28
Figure 3.11 Liquid holdup at reactive zone starting from stage 4 to stage 11. ....	28
Figure 3.12 Liquid holdup of 6400 kg in reactive zone. ....	29
Figure 3.13 Stoichiometry equation involved for MTBE synthesis. ....	29
Figure 3.14 Kinetic data involved in forward reaction. ....	29
Figure 3.15 Kinetic data involved in backward reaction. ....	30
Figure 3.16 Flowchart of Aspen Plus procedures. ....	30
Figure 4.1 Temperature profile at MeOH feed at stage 10. ....	35
Figure 4.2 Liquid composition profile at MeOH feed at stage 10. ....	35



Figure 4.3 Isobutene conversion as a function of reflux ratio.....37

## LIST OF SYMBOLS

<b>Symbol</b>	<b>Description</b>	<b>Unit</b>
$a$	Activity	-
$c$	Total number of components	-
$F_j$	Feed flowrate of stage $j$	mol/s
$h^L$	Partial molar enthalpy of liquid	J/mol
$h^V$	Partial molar enthalpy of vapour	J/mol
$\Delta H^R$	Heat of reaction	J/mol
$K_{eq}$	Thermodynamic reaction equilibrium constant	-
$k_r$	Reaction rate constant	mol/(s equiv)
$L_j$	Liquid flowrate from stage $j$	mol/s
$M_r$	Relative molecular weight	g/mol
$N$	Total number of stages	-
$P$	Pressure	Pa
$P^o$	Saturated vapour pressure	Pa
$q$	Ion exchange capacity	equiv/kg
$R_j$	Total rate of generation of moles on stage $j$	mol
$r_j$	Rate of reaction on stage $j$	mol/s
$T$	Temperature	K
$t$	Time	S
$v$	Stoichiometric coefficient	-
$V_j$	Vapour flowrate from stage $j$	mol/s
$W$	Weight of catalyst	kg
$x$	Liquid composition	-
$y$	Vapour composition	-

$z$  Feed composition -

***Greek letters***

$\delta_j$  Parameters for reaction occurrence on stage  $j$  (0 or 1)

$\emptyset$  Fugacity coefficient

$\gamma$  Activity coefficient

***Subscript***

$i$  Component number

$j$  Stage number

$r$  Reaction number

***Superscript***

$f$  Feed

$L$  Liquid

$R$  Reaction (s)

$V$  Vapour

## LIST OF ABBREVIATIONS

RD	Reactive Distillation
MTBE	Methyl Tert-Butyl Ether
TAME	Tertiary Amyl Methyl Ether
MEOH	Methanol
IB	Isobutene
VLE	Vapour Liquid Equilibrium
LLE	Liquid-Liquid Equilibrium
EQ	Equilibrium Stage Model
MSS	Multiple Steady State
CSTR	Continuous Stirred Tank Reactor
NRTL	Non-Random Two Liquid Equation
UNIQUAC	Universal Quasi-Chemical Model
UNIFAC	UNIQUAC Functional-Group Activity Coefficient Model
RK	Redlich-Kwong Equation

## **LIST OF APPENDICES**

Appendix A      Stream Summary Resulted from Aspen Plus

**KEADAAN MANTAP BERGANDA DALAM TURUS PENYULINGAN  
BERTINDAK BALAS UNTUK PENGHASILAN METIL TERT-BUTIL ETER  
(MTBE): ANALISIS KESTABILAN**

**ABSTRAK**

Turus penyulingan bertindak balas telah mendapat banyak perhatian kerana potensi besarnya di dalam proses intensifikasi. Oleh kerana itu, kajian sintesis metil tert-butil eter (MTBE) dalam turus penyulingan bertindak balas dikaji dan model keseimbangan dikembangkan dengan menggunakan Aspen Plus V10. Model yang dicadangkan itu dibuktikan dengan membandingkan hasil simulasi dengan data simulasi yang diterbitkan daripada literatur. Model ini mampu memperoleh penukaran isobutena dan ketulenan MTBE yang tinggi untuk sistem pemangkin heterogen yang sangat diinginkan dalam proses pembuatan MTBE di dalam industri. Perbandingan profil suhu dan profil komposisi yang diperolehi daripada simulasi juga memberikan hasil yang memuaskan. Model yang dicadangkan dapat digunakan sebagai alat untuk analisis keadaan mantap berganda dalam turus penyulingan bertindak balas MTBE. Disimpulkan bahawa hanya satu keadaan mantap sintesis MTBE yang dapat ditemui apabila menggunakan konfigurasi lajur yang sama dalam Aspen Plus V10. Analisis kepekaan dilakukan untuk mengkaji pengaruh nisbah refluks pada penukaran isobutena. Dari analisis ini, ditunjukkan bahawa ketulenan MTBE dan penukaran isobutena adalah maksimum pada nisbah refluks 7. Penyulingan bertindak balas MTBE yang stabil dapat dicapai kerana pemodel keseimbangan telah menghasilkan keadaan stabil yang tinggi.

**STEADY STATE MULTIPLICITY IN THE REACTIVE  
DISTILLATION OF METHYL TERT-BUTYL ETHER (MTBE) SYNTHESIS:  
STABILITY ANALYSIS**

**ABSTRACT**

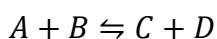
Reactive distillation (RD) has garnered a lot of attention due to its tremendous potential for process intensification. Due to that, the methyl tert-butyl ether (MTBE) synthesis in reactive distillation (RD) column was studied and an equilibrium model was developed by using Aspen Plus V10. The proposed model was validated by comparing the simulation results with the published simulation results from the literature. The model obtained high isobutene conversion and MTBE purity for heterogenous catalyzed system, which is desirable in the industrial MTBE production process. The comparisons on temperature profiles and liquid composition profile of RD column also yielded promising results. The proposed model can be used as a tool for the analysis of multiple steady state in RD column of MTBE. It is concluded that only single steady state of MTBE synthesis that can be found when using the same column configuration in Aspen Plus V10. Sensitivity analysis is conducted to study the influence of reflux ratio on the isobutene conversion. From this analysis, it was shown that MTBE purity and isobutene conversion were maximum at reflux ratio of 7. Stable reactive distillation of MTBE can be achieved since the equilibrium modelling has developed higher steady state solution.

# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

Currently, people are showing great interest in multifunctional reactors that incorporate in-situ separation of products from reactants. Usually, reactive distillation (RD) is the most suitable technique for in-situ separation. This is because it is widely utilized and has attracted a lot of attention in recent years, particularly in-situ product removal. The reversible reaction scheme can be used to illustrate the reactive distillation process:



where the boiling points of the components will be in sequence A, C, D and B (Taylor & Krishna, 2000). The RD column is divided into three zones which are reactive zone in the middle, with non-reactive rectifying and stripping zones located at the top and bottom part of the column. The rectifying zone functions to recover reactant B from the product stream C. Meanwhile, the reactant A is removed from the product stream D in the stripping section. The products are separated in-situ in the reactive zone, shifting the equilibrium to the right and preventing any unwanted side reactions between the reactants A (or B) and the product C (or D). Figure 1.1 depicts the RD configuration.



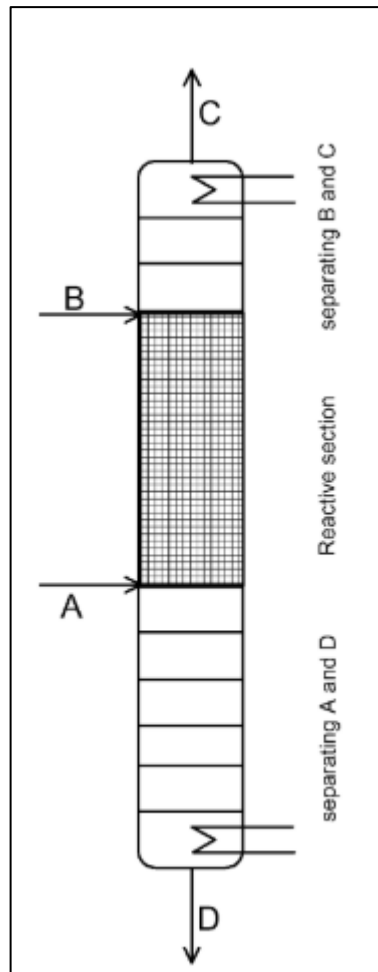


Figure 1.1 Configuration of reactive distillation (Taylor & Krishna, 2000).

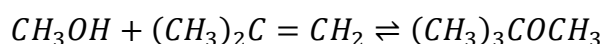
RD has arisen as a very successful approach because it can integrate the chemical reaction and separation process in a single equipment. Its ability in process intensification for certain types of chemical reactions gives many advantages as it lowers the capital and operational cost, improves energy integration, increases the conversion of reactants in equilibrium limited reactions, reduce the production of waste, and improved product quality (Al-Harathi et al., 2009; Jana, 2011; Kanse et al., 2014; López-Arenas et al., 2006; Purohit et al., 2013; Sneesby et al., 1998). Reactive distillation will also be beneficial if the mixture of species from the reactor product capable to form multiple azeotropes with each other as the conditions of reactive

distillation can allow the azeotropes to “reacted away” through reaction (Kanse et al., 2014; Murat et al., 2003).

In addition to the aforementioned benefits of RD, there are several limitations and disadvantages in reactive distillation column highlighted by Taylor & Krishna, (2000) that required improvement including volatility constraints. In order to maintain the high concentration of reactants and low concentration of products in the reaction zone, the reagent and products used must have a suitable volatility. Besides, we must identify suitable reactions with ideal residence time requirement. If the residence time for the reactions is long, a large column size and tray holdup are required, necessitating the consideration of a reactor-separator arrangement which will be more cost-effective. Furthermore, scaling up to large flowrates will be difficult due to the problems that we need to face in designing reactive distillation column since there is an issue related to the liquid distribution in packed reactive distillation column.

Before 1980, the reactive distillation process was used for esterification reactions particularly for methyl and ethyl acetate but it also was underutilized in other areas (Kanse et al., 2014; Sneesby et al., 1998). It is difficult to develop reactive distillation column due to complexities in column design, process synthesis and operability of reactive distillation process coming from the interaction of reaction and distillation (Kanse et al., 2014). The advent of an in-situ separation functions within the reaction zone will results in complex interactions between vapour-liquid equilibrium, liquid mass transfer, intra-catalyst diffusion for heterogeneously catalysed processes and chemical kinetics (Taylor & Krishna, 2000). However, it was only recently demonstrated that difficult or unsolvable reaction-separation modelling problems can be solved with the aid of computer simulation.

Over the last two decades, study on heterogeneously catalysed reactive distillation has been applied to various industrial processes, including the well-known process for producing octane booster methyl tert-butyl ether (MTBE), the methyl acetate process and the Nylon 6,6 process. Research on MTBE synthesis using reactive distillation have included simulation, design method, reactive azeotrope and more recently, the phenomena of multiplicity of steady states. The following chemical reaction equation is used to produce MTBE by direct addition of methanol to isobutene using sulphonated ion exchange resin as catalyst:



In the MTBE synthesis using reactive distillation, it is preferable to achieve a bottom product comprising high purity of MTBE and a distillate comprising high purity of n-butene. High isobutene conversion is desired to produce a distillate containing just trace amounts of isobutene. However, various researchers have detected the existence of multiple steady states in a design study of MTBE using reactive distillation.

Several theoretical studies suggested the presence of multiple steady-states in MTBE synthesis. The multiplicity steady states and non-linear behaviours are proven to occur typically in continuous stirred tank reactors (CSTRs) that have been triggered by heat effects or kinetic instability (Chen et al., 2002; Purohit et al., 2013). It is known that the complexity of the reactive distillation process has caused unusual responses to changes in the operating parameters. Chen et al., (2002), in his study mentioned that the key operating parameters that are important to observe the multiplicity steady-state in reactive distillation are the reflux ratio and reboil ratio. This is because the involvement of chemical reactions in reactive distillation has caused a rapid change in

the composition of the product without having major changes in the feed-split or energy balance. Thus, to understand how the columns respond to changes in the operating parameters, it is, necessary to know in which operating system (controlled reaction or controlled fractionation) the reactive distillation will operate.

## **1.2 Problem Statement**

In a reactive distillation column, there is the possibility for a multiplicity steady-state can occur. The interaction between separation and the chemical reaction that exhibits complex behaviour such as high nonlinearity may contribute to the steady-state multiplicity and instability of the system. Multiplicity steady-state exists in a reactive distillation column for the synthesis of methyl tert-butyl ether (MTBE). It was reported in the literature that there is the existence of three steady states where two of them are stable and the third is unstable. The possibility to have two different conversions of the reactants can be obtained if using the same column configuration. From the previous study done by Jacobs & Krishna in 1993, it is stated that for a reactive distillation column that develops a multiplicity steady state, the same column configuration will give two different conversions of reactants if they using different starting point at reaction equilibrium. In their study, high conversion correlates to the residue curves starting near the n-butene-methanol azeotrope and low conversion correlates to the residue curves starting from pure isobutene if use the same column configuration. In this study, the high conversion of the reactants in stable steady-state conditions in a reactive distillation column is study to obtain high product purity.

### **1.3 Research Objectives**

The main objective of this study is to understand the steady-state multiplicity for MTBE production using a reactive distillation column in terms of process stability and profitability. To achieve the main purpose, the following objectives are needed:

- i. To simulate a reactive distillation model for MTBE production using Aspen PLUS.
- ii. To validate the simulation for the production of MTBE through comparison with the reported data.
- iii. To study the multiple steady-state in the MTBE system based on the Aspen PLUS simulation.

### **1.4 Scope of Study**

In this study, the reactive distillation column for MTBE synthesis was analysed through the simulation using Aspen Plus V10. The equilibrium model of reactive distillation column for MTBE synthesis was used. In the production of MTBE, isobutene and methanol were used as reactants. With the aid of simulation tool, the model can be verified by simulation and used for multiple steady state analysis in reactive distillation. Then, the validation of the model was done by comparing the data from literature. The data of isobutene conversion were calculated manually. After the model was verified, the multiple steady state analysis is studied in Aspen Plus V10 and calculated the isobutene conversion obtained using Microsoft Excel Software. Stability and profitability analysis is carried out after the study of multiplicity steady state in MTBE system.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Methyl tert-butyl ether (MTBE)**

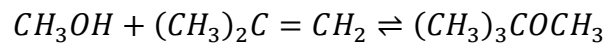
Methyl tertiary butyl ether (MTBE) is a chemical compound that is used mainly in gasoline blending as an octane booster to enhance the hydrocarbon combustion efficiency (Al-Harhi et al., 2009). It also has been widely used as a solvent, chemical reagent, and antiknock additive (Sudibyo et al., 2011). MTBE is a volatile, flammable, and colourless liquid that is water-immiscible. It has a low vapour pressure and can be blended with other fuels without the need for phase separation (Al-Harhi et al., 2009).

MTBE acts as an oxygenated fuel to replace lead-based additives to enhance the octane number of fuels (Wang et al., 2003). According to Deeb et al., (2003), the use of reformulated and oxygenated fuels in some urban regions in the United States increased significantly due to the amendments of the Clean Air Act (CAAA) of 1990. Oxygenates that are added to the vehicle fuels can minimize the emissions of carbon monoxide to the environment. In order to fulfill the requirements of the CAAA, the United States Environmental Protection Agency (U.S. EPA) has implemented the Oxyfuel Program in 1992 and the Reformulated Gasoline Program (RFG) in 1995. MTBE is excellent gasoline blending additive followed by EtOH as it is the most commonly used in the United States due to its high octane level, low feedstocks cost (MeOH and isobutene), and low production cost (Deeb et al., 2003).

#### **2.2 Synthesis of MTBE**

A reversible exothermic reaction between methanol and isobutene usually in the presence of other inert C<sub>4</sub> components will form methyl tert-butyl ether (MTBE) (S. Hauan et al., 1997). MTBE can be produced using acidic catalyst consisting of

sulphonated ion exchange resin (Amberlyst 15, CVT resin) through the direct addition of methanol to isobutene in the liquid-phase reaction (Al-Harhi et al., 2009; Rehfinger & Hoffmann, 1990; Sudibyo et al., 2012). The chemical reaction for the MTBE synthesis is shown in the following equation:



Production of MTBE often uses a mixed C4 feed of isobutene and n-butene that is difficult to separate (Wang et al., 2003). Hence, a reactive distillation column for efficient production of MTBE is used as it offers an alternative method to separate isobutene from n-butene with the conversion of isobutene and methanol up to 100% can be achieved (Sudibyo et al., 2011; Taylor & Krishna, 2000; Wang et al., 2003).

## **2.3 Modelling of Reactive Distillation**

The design and operation of a reactive distillation system are far more complex than those of conventional reactor or distillation columns. When an in-situ separation function is introduced into the reaction zone, it causes complex interactions between phase equilibrium, vapour-liquid equilibrium, vapour-liquid mass transfer, and the reaction kinetic model. Since the reaction and separation occurs at the same time in reactive distillation, thus both experimental investigation and modelling processes faced some problems. Thus, thermodynamics plays an important role in understanding and designing the process related to separation operation.

### **2.3.1 Vapour-Liquid Equilibrium Model**

Vapour-liquid equilibrium model (VLE) is important in separation process has it been used to calculate the liquid phase activity coefficient of a liquid mixture. There are several VLE model that has been used for the production of MTBE. The models that

have been studied by researchers are Wilson equation, Non-random two liquid equation (NRTL), Universal Quasi-Chemical model (UNIQUAC) and UNIQUAC Functional-group Activity Coefficient model (UNIFAC).

Lee & Westerberg, (2001) has used the Wilson equation extensively for the simulation of MTBE synthesis in reactive distillation. In order to apply Wilson equation, two adjustable parameters are used to represent binary interactions between molecules (Towler & Sinnott, 2013). It can be extended to multicomponent systems with only binary parameters (Towler & Sinnott, 2013). However, it is difficult to predict the formation of a second liquid phase if utilized this method (Towler & Sinnott, 2013).

NRTL equation needs to have three parameters for each binary pair, where two of the parameters are energies of interaction which is similar with Wilson parameters and the third being a randomness factor that describes the tendency of molecules  $i$  and  $j$  to be randomly distributed in the mixture (Towler & Sinnott, 2013). NRTL equation can predict the liquid-liquid equilibrium (LLE) or VLE (Towler & Sinnott, 2013). NRTL is the model that are suitable for highly non-ideal systems and has been successfully employed in simulation of MTBE synthesis (Bao et al., 2002).

UNIQUAC model may be used to analyse VLE, LLE and vapour-liquid-liquid equilibrium cases. It has another significant advantage in which the component concentrations are a function of volume and area fractions instead of mole fractions (Seader et al., 2011). The UNIQUAC model is commonly used in reactive distillation processes, particularly in MTBE synthesis because it has been reported by many researchers to describe the non-ideality of liquid phase in the synthesis of MTBE (Steinar Hauan et al., 1995; Nijhuis et al., 1993; Taylor & Krishna, 2000). UNIQUAC model is mathematically more complex than NRTL, although it has less adjustable



parameters. In the absence of experimental data, the UNIFAC model can estimate the binary interaction parameters (Towler & Sinnott, 2013).

The UNIFAC method can be used to estimate binary interaction parameters for the UNIQUAC model (Towler & Sinnott, 2013). However, there are several limitations of the UNIFAC method that must be considered which are pressure should not be greater than a few bars, temperature should be less than 150 °C, all components must be condensable at near-ambient conditions, components should not have more than 10 functional groups (Towler & Sinnott, 2013).

All of the models presented above can perform comparably for moderately non-ideal systems. For the non-ideality in liquid phase, UNIQUAC model has been extensively used for the production of MTBE. Despite the fact that UNIFAC model is based on the extension of UNIQUAC model, this model cannot obtain satisfactory performance in MTBE process.

### **2.3.2 Equilibrium Stage Model**

Most of the mathematical models of reactive distillation are extended from the equilibrium stage models (EQ) of conventional distillation column calculations (Murat et al., 2003). The liquid and vapour phases that leave the stage are claimed to be in phase equilibrium and the equilibrium stage is correlated with the MESH equations (Mohamed et al., 2003; Taylor & Krishna, 2000). The MESH equations include the Material balance, Equilibrium relationship, Summation equation, and Heat balance. Taylor & Krishna, (2000) described several classes of computer-based methods that have been developed to solve the equations of the EQ stage model. The developed computer-based methods included the tearing methods, relaxation methods, homotopy continuation methods, minimisation method, and inside-out algorithm.

Tearing methods include the dividing of the model equations into groups that need to be solved separately (Taylor & Krishna, 2000). Relaxation methods can be used as a reactive distillation model solution with MESH equations written in the unsteady-state form and then, the numerical integration is used to find the steady-state solution (Mohamed et al., 2003; Taylor & Krishna, 2000). This approach is closely similar to the dynamic model; but it is not commonly used because it was formerly considered to be time-consuming for computers (Taylor & Krishna, 2000). However, this reason is not applicable anymore since the high-performance personal computer (PC) available in the market are affordable, and there is no critical issue related to the processing time associated with the PC when utilized the relaxation method.

Homotopy continuation methods are the most commonly used to solve problems that are found quite difficult to solve using other methods (e.g., Newton's). Singh et al., (2005) illustrated the use of homotopy continuation for the analysis of steady-state in reactive distillation systems. The studies on MTBE and methyl acetate columns indicate that continuation with respect to catalytic weight (or reactive tray holdup) is an effective method to obtain a converged solution to the highly non-linear MEH equations (Mole, Equilibrium, and Heat balance equations). The minimisation method is utilized to solve the MESH equations but this approach is rather slow to converge (Taylor & Krishna, 2000). Inside-out algorithm approaches known as 'RadFrac' in Aspen Plus requires the addition of new parameters in the model equations to be used as primary iteration variables (Taylor & Krishna, 2000).

The reviews related to the equilibrium stage models above are mostly being used for the steady-state simulation. The non-equilibrium model needs to be considered for

dynamic simulation to obtain a more proper description for the performance of the reactive distillation column.

### **2.3.3 Mathematical Modeling**

Several assumptions are made for the simplicity of the modelling prior to developing the mathematical model equations. Such assumptions are justified in such a way that the developed model is applicable to achieve a steady-state reactive distillation system. This assumption is based on (Murat et al., 2003):

- The column operates adiabatically thus no heat loss to surrounding
- The reaction occurs in the liquid phase
- Each reactive stage is treated as a perfectly mixed continuous stirred tank reactor (CSTR)
- The vapour and liquid leaving any stage are in phase equilibrium
- Negligible heat of mixing between the mixtures of liquid and vapour
- Vapour holdup is assumed to be negligible
- In the current modeling work, the hydrodynamic effects are neglected to simplify the modelling complexities.

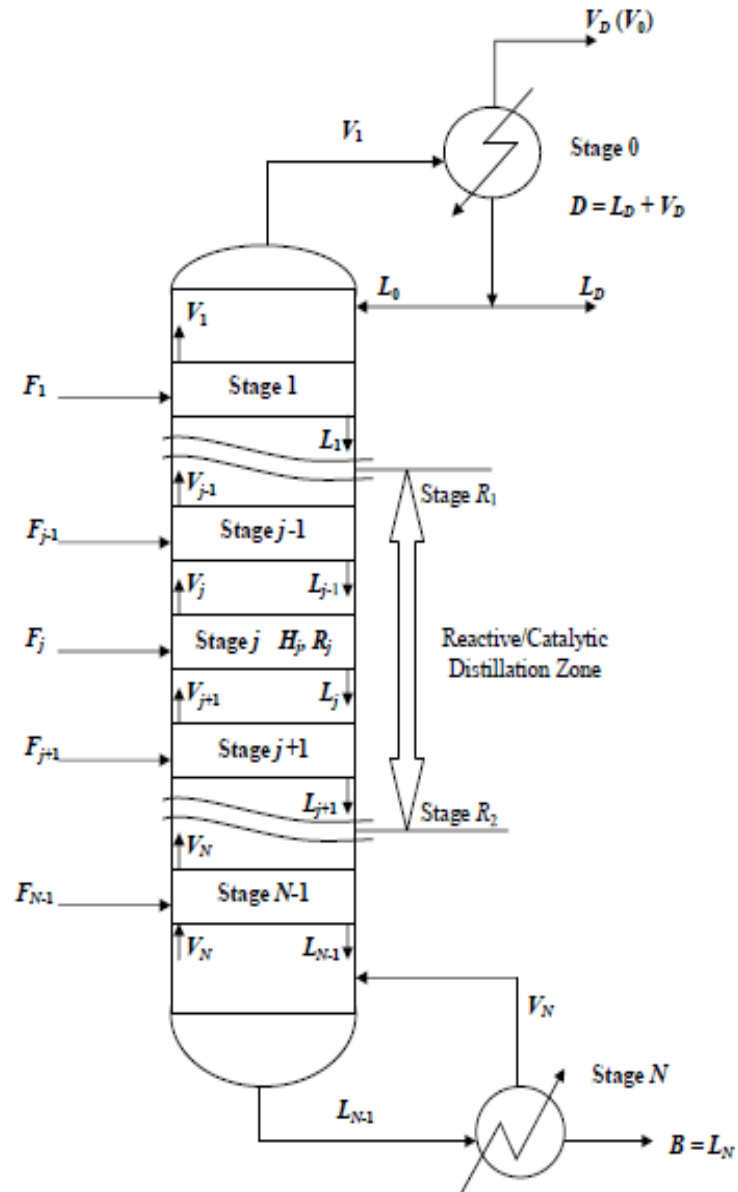


Figure 2.1 Schematic representation of a reactive distillation column (Murat et al., 2003).

The model equations which are the mass and energy balance, vapour-liquid equilibrium (VLE) model, summation equations, and kinetic model are presented with the reference to the column configuration given in Figure 2.1 (Murat et al., 2003).

### 2.3.3(a) Material and energy balance

The material and energy balance are important in calculating the liquid and vapour flow rates of the distillation column.

**Overall material balance for equilibrium stage  $j$**

$$F_j + L_{j-1} + V_{j+1} + \delta_j R_j = L_j + V_j \quad 2.1$$

**Unsteady state component I material balance**

$$H_j \frac{dx_{ji}}{dt} = (z_{j,i}F_j + x_{j-1,i}L_{j-1} + y_{j+1,i}V_{j+1}) - (x_{j,i}L_j + y_{j,i}V_j) + \delta_j \sum_{r=1}^R (v_{r,i}r_{j,r}) \quad 2.2$$

where  $j = 1, 2 \dots N - 1$ ;  $i = 1, 2 \dots c$ ;  $r = 1, 2, \dots R$

$j$  is the stage number,

$i$  is the component number,

$r$  is the specific reaction number.

The following concepts are very helpful in understanding and clarifying the material balance that has been derived:

- The liquid holdup on stage  $j$ ,  $H_j$  is defined as the molar quantity of liquid mixture that remains or is held at a certain level on stage  $j$ .
- $R_i$  is the total number of moles generated or disappear through reaction on stage  $j$ .
- $r_{i,r}$  is the reaction rate  $r$  on stage  $j$  (mol/s). Parameter  $\delta_j$  (0 or 1) refers to reaction occurrence on stage  $j$ . When a reaction occurs on stage  $j$ ,  $\delta_j$  is set to unity but when there is no reaction;  $\delta_j$  is set to zero value.
- Symbols  $z_{j,i}$ ,  $x_{j,i}$ ,  $y_{j,i}$  are component  $i$  mole fractions of feed flow  $F_j$  (mol), liquid flow  $L_j$  (mol), and vapour flow  $V_j$  (mol) on stage  $j$  respectively.
- The  $v_{r,i}$  term is the stoichiometric coefficient of component  $i$  for reaction  $r$ .

### **Energy balance**

$$F_j \sum_{i=1}^c z_{j,i} (h_{j,i}^f - h_{j,i}^l) + L_{j-1} \sum_{i=1}^c x_{j-1,i} (h_{j-1,i}^l - h_{j,i}^l) + V_{j+1} \sum_{i=1}^c y_{j+1,i} (h_{j+1,i}^v - h_{j,i}^l) - \delta_j W_j \sum_{r=1}^R (\Delta H_{j,r}^R) r_{j,r} = V_j \sum_{i=1}^c x_{j,i} (h_{j,i}^v - h_{j,i}^l) \left( \frac{J}{s} \right) \quad 2.3$$

where

$h^L$  denotes partial molar enthalpy of liquid (J/mol),

$h^V$  denotes partial molar enthalpy of vapour (J/mol),

$\Delta H^R$  is the heat of reaction (J/mol), and

$W$  is the weight of catalyst (kg).

### **2.3.3(b) Phase equilibrium**

The non-ideality in vapour and liquid phases for a non-ideal system of MTBE are taken into consideration by introducing the fugacity coefficient  $\phi$  and activity coefficient  $\gamma$  to Raoult's Law as follow:

$$y = \frac{\gamma P^O}{\phi P} x \quad 2.4$$

The vapour phase is considered to be ideal in order to equate the entire fugacity coefficients  $\phi$  for the system to unity. The activity coefficients  $\gamma$  that describe the non-ideality of the liquid phase are determined from the UNIQUAC method. The saturated vapour pressure  $P^O$  is calculated from the Antoine equation and  $P$  is the total pressure of the system.

### **2.3.3(c) Summation equations**

Summation of the liquid and vapour component composition mole fraction on each stage of reactive distillation column must equal to unity. The summation equations are shown as follow:

$$\text{Summation equation for liquid composition component } i \text{ on stage } j \\ \sum_{i=1}^c x_{j,i} = 1.0 \quad 2.5$$

*Summation equation for vapour phase composition component i on stage j*

$$\sum_{i=1}^c y_{j,i} = 1.0 \quad 2.6$$

## 2.4 Multiple Steady State

In order to design a reactive distillation process, it is necessary to identify all multiple steady states within the practical domain of operating variables, determine whether they are desirable, and comprehend on how the column responds to changes in operation variables. Several theoretical studies suggested that there is an existence of multiple steady-states (MSS) in MTBE synthesis. In the research of Nijhuis et al., (1993) and Jacobs & Krishna, (1993), multiple solutions are found when the methanol feed location varies. Klaus Dieter Mohl et al., (1999) studied the presence of MSS in a reactive distillation column using rigorous bifurcation experimental analysis. It is concluded that MSS exists when input variables of reflux ratio, R and heating rate, Q have been selected. The effect of the intraparticle transport resistance during the catalytic process in a reactive distillation column has been taken into consideration which results in two different types of multiplicities (K. D. Mohl et al., 2001).

Purohit et al., (2013) proposed a new approach based on the thermal stability analysis used for nonisothermal CSTRs, where the intersection between nonlinear generation term and linear removal term will exhibits multiplicity. This enables the MSS to be determined without the need for bifurcation analysis. However, Chen et al., (2002) explained the used of Damkohler number (Da) as a bifurcation parameter for the bifurcation analysis to study the influence of kinetics on MSS behaviour for the syntheses of MTBE and tertiary amyl methyl ether (TAME) by reactive distillation (Chen et al., 2002). As a result, for an MTBE synthesis, MSS are found at high values of Da whereas, in TAME synthesis, the MSS is found at low values of Da. It is expected

that solution multiplicities will disappear below the critical value of  $Da$  but there is a range of  $Da$  at which high conversions of reactants are predicted without solution multiplicities (Chen et al., 2002).

At the simultaneous physical and chemical equilibrium, the same column configuration will give two different conversions of reactants when a different type of starting point is used (Jacobs & Krishna, 1993; Nijhuis et al., 1993). Nijhuis et al., (1993) studied the influence of temperature and reflux ratio on the isobutene conversion. A relatively low temperature in the reactive section will result in high isobutene conversion and vice versa. High conversion of isobutene will be obtained and it does not depend on the reflux ratio,  $R$  given that the  $R$  reaches the minimum value 4. However, low conversion of isobutene is observed at the  $R < 4$ . Furthermore, the methanol to isobutylene feed ratio of 1 will result in 99.2% conversion of isobutylene and 99.7% MTBE purity. However, lower ratios ( $< 1$ ) can result in excess isobutylene hence will lower the conversion value (Al-Harhi et al., 2009).

## **2.5 Stability Analysis**

The stability of the column plays an important part to verify the existence of multiple steady-state in the production of fuel ether MTBE. Heat generation and heat removal term will display non-linear behaviour if there is an increase in temperature where this term will intersect at three points suggesting that there is a presence of three steady states (Purohit et al., 2013). Normally, the middle steady state is unstable while the upper and lower steady states are stable (Klaus Dieter Mohl et al., 1999; Purohit et al., 2013). K. D. Mohl et al., (2001) discussed the influence of  $Da$  and feed rate in determining the stability of the different steady states. In his study, it is reported that increasing the feed rate from 15 kg/hr to 90 kg/hr and  $Da$  from 0.075 to 0.45 will give



stable steady-state solutions. It is confirmed that the stable and unstable steady state branches are alternate with each other when the feed rate is reduced and  $Da$  is increasing.

## **2.6 Sustainability**

Sustainability describes the management of resources without exhausting them for future generation, in which environmental, social and economic considerations are brought into harmony in the search for a better quality of life. On the other hand, sustainable development refers to the process that aim to improve the long-term economic well-being and quality of life while not jeopardizing future generations' ability to meet their own demands. The Sustainable Development Goals (SDGs) are a set of measures that aimed to end the poverty, protect the environment, and ensuring human well-being on a worldwide scale to achieve a better and more sustainable future for all.

Reactive distillation (RD) has emerged as an innovative approach for process intensification with significant economic advantages over conventional reactor followed by separator process. Process intensification is closely related to Sustainable Development Goal 9 which is about industry, innovation and infrastructure as its aims to develop or improve processes that are more flexible, have a lower environmental effect, improved safety and use less energy consumption (Zondervan et al., 2015). RD which combines separation and chemical reaction in a single operation can reduced energy requirements, lower solvent use, reduced equipment investment and have greater selectivity.

In this study of RD column on MTBE synthesis, it is considered as a sustainable way of study. This is due to the fact that the research was conducted using Aspen Plus

V10 simulation. Using the software, the research can be completed more quickly than a traditional experiment. Computer-aided simulation tool are often cheaper, easier to conduct and to some extent, much faster than normal experiments. With the increase of environmental problems, the use of computer-aided simulation is way better than the traditional experiment. However, the traditional experiment was also important since all the data provided in the literature was taken from the experiment and use to perform the simulation. In the traditional experiment research, the chemicals often were used in a large quantity for the process of MTBE synthesis. Thus, the simulation study could be seen as a beneficial study which could save time, cost and reduce chemical usage.

## **CHAPTER 3**

### **METHODOLOGY**

Methods and materials are necessary components required for the simulation to be carried out in this chapter. At beginning, the overview of the methodology was shown and followed by the research procedure of the simulation approach. Multiple steady state and stability analysis as well as profitability analysis of the research will end of this chapter.

#### **3.1 Overview of Research Methodology**

The research objective mentioned in the first chapter can be achieved by developing a process model for reactive distillation to produce methyl tert-butyl ether (MTBE) through esterification process by using Aspen Plus V10 simulator. After the verification of proposed model, then it was used to study the relationship of the reflux ratio and feed stage of methanol towards the conversion of isobutene and purity of MTBE obtained at the end of the process.

Firstly, a suitable reactive distillation block 'RadFrac' in Aspen Plus V10 is used to simulate the data collected from the literature. For the reactive distillation or 'RadFrac' block, suitable information and assumption have been considered. Then, the proposed equilibrium model was validated by comparing the simulation results to the data from the literature. After the verification process was succeeded, multiple steady state analysis was carried out by manipulating the value of the reflux ratio and methanol feed location using Aspen Plus V10. The data were manipulated manually in Aspen Plus V10 and used in Microsoft Excel to do the calculation of conversion. At the end of the simulation, all the results were tabulated, plotted and discussed further.

### 3.2 Research Methods

Figure 3.1 depicts the overall methodology flowchart of this study.

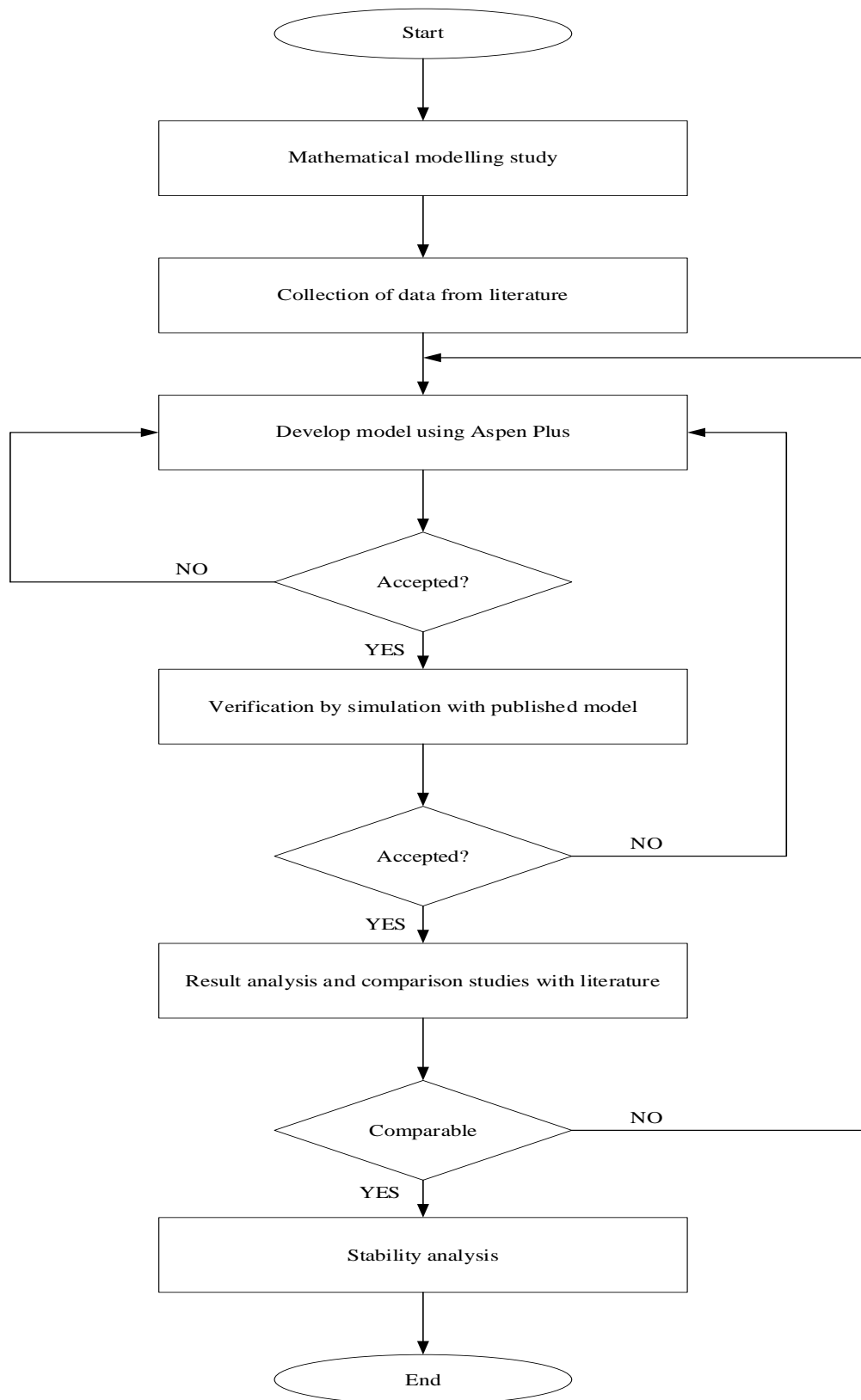


Figure 3.1 Flowchart of overall methods of the study.

### 3.2.1 Data Collection from Literature

From the published journals, all the important parameters needed for modelling and simulation of the reactive distillation column for the synthesis of MTBE were extracted from (Nijhuis et al., 1993; Panda et al., 2014; Rehfinger et al., 1990). The important information includes the kinetic model involved in the production of MTBE, the equilibrium stage model, and vapour-liquid equilibrium model.

#### 3.2.1(a) Reaction Kinetics

Synthesis of MTBE occurs due to the exothermic reaction between methanol (MeOH) and isobutene (IB). The liquid-phase reaction is catalysed by an acid catalyst like Amberlyst 15 (Jacobs & Krishna, 1993). A typical mixed butenes feed for MTBE synthesis has around 40% of isobutene and 60% of n-butene, which is inert and does not react. A slight stoichiometric excess of methanol is usually fed to increase the isobutene conversion into MTBE (Nijhuis et al., 1993; Sudibyo et al., 2011). Isobutene has been chosen to be the limiting reactant to enhance maximum conversion of isobutene. The reaction is shown in Equation 3.1 below:



The activity based rate model has been taken from (Nijhuis et al., 1993; Panda et al., 2014) and is given below:

$$rate = qk_r \left( \frac{a_{IB}}{a_{MeOH}} - \frac{a_{MTBE}}{K_{eq} a_{MeOH}^2} \right) \quad 3.2$$

$$r_{forward} = 3.67 \times 10^{12} \exp \left[ \left( \frac{-92440}{RT} \right) \frac{x_{IB}}{x_{MeOH}} \right] \quad 3.3$$

$$r_{backward} = 2.67 \times 10^{17} \exp \left[ \left( \frac{-134454}{RT} \right) \frac{x_{MTBE}}{x_{MeOH}^2} \right] \quad 3.4$$

### 3.2.1(b) MTBE Reactive Distillation Column

For the production of MTBE, the reactive distillation column has a total number of 17 stages including a total condenser and a partial reboiler (Nijhuis et al., 1993). MTBE RD column consists of three section which are rectification, reaction and stripping section. Reactive stages are located in the middle of the column, stage 4 down to and including stage 11. The column has two feed streams which are methanol feed and mixed butenes feed which are fed in on stage 10 and 11, respectively. The isobutene feed (as mixed butenes) is preferred to be located at the bottom of the reactive zone, since isobutene is highly volatile component. Methanol is preferred to be located near the top of the reactive zone because methanol is the least volatile component in MTBE system.

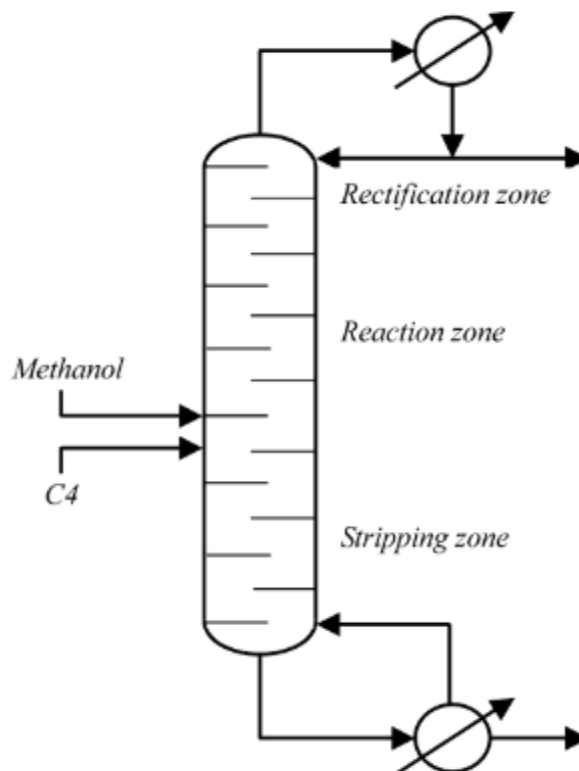


Figure 3.2 Configuration of reactive distillation column for MTBE synthesis (Wang et al., 2003).

### 3.2.1(c) Simulation Basis

The simulation of the MTBE column is conducted using the rigorous distillation model 'RadFrac' from the Aspen Plus V10. In the simulation of MTBE synthesis, the liquid phase activities have been calculated using UNIQUAC and Redlich-Kwong equation is used for equation of state calculation (Nijhuis et al., 1993). As the basis for the simulation, it is assumed that 197 mol/s of MTBE is produced (Nijhuis et al., 1993). The column pressure is 11 bar and the reflux ratio is equal to 7. In reactive zone, 6400 kg of catalyst is introduced. Every reactive stage is assumed to be in chemical equilibrium. The feed specification and operation conditions are summarized in Table 3.1.

Table 3.1 Feed specification and operating condition for MTBE synthesis (Nijhuis et al., 1993).

<b>Feed Specifications and Operating Conditions</b>			
<b>Parameters</b>	<b>Unit</b>	<b>Methanol feed</b>	<b>Mixed butenes feed</b>
<b>Feed rate</b>	mol/s	206.0	549.0
<b>Temperature, T</b>	K	320.0	350.0
<b>Pressure, P</b>	bar	11	11
<b>Feed stage</b>	-	10	11
$x_{MeOH}$	-	1.0000	0.0
$x_{IB}$	-	0.0	0.355
$x_{n-butene}$	-	0.0	0.644
<b>Column specification</b>			
<b>Number of stages, N</b>	-		17
<b>Reaction stages</b>	-		4-11
<b>Pressure, P</b>	bar		11
<b>Reflux ratio</b>	-		7