MODELING AND SIMULATION OF REACTIVE DISTILLATION COLUMN FOR THE PRODUCTION OF METHYLTERTIARY BUTYL ETHER (MTBE) INCORPORATING STRUCTURED OR RANDOM PACKING

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by

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NOMENCLATURE

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
F_j	Feed flowrate of stage j	mol/s
H_j	Liquid holdup of stage j	mol
HTR	Total reactive holdup	mol
HT	Total liquid holdup throughout column	mol
h_L	Partial molar enthalpy of liquid	J/mol
h_V	Partial molar enthalpy of vapour	J/mol
ΔHR	Heat of reaction	J/mol
K_{eq}	Thermodynamic reaction equilibrium constant	-
k_f	Forward rate constant	s-1
L_j	Liquid flowrate from stage j	mol/s
N	Total number of stages	-
P	Pressure	Pa
q	Ion exchange capacity	Equiv/kg
R	Total number of reactions	-
R_j	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	-
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

ε	Rate of reaction per mole of mixture	s^{-1}
δj	Parameter for reaction occurrence on stage j	-
$\emptyset$	Fugacity coefficient	-
γ	Activity coefficient	-

Subcript

c	Critical
i	Component number
j	Stage number
r	Reaction number
T	Total

Superscript

f	Feed
L	Liquid
R	Reaction (s)
V	Vapour

LIST OF ABBREVIATIONS

CSTR	Continuous Stirrer Tank Reactor
EQ	Equilibrium
IB	Isobutene
MeOH	Methanol
MESH	Aterial, Equilibrium, Summation, Heat
MTBE	Methyl Tertiary Butyl Ether
NEQ	Non-Equilibrium
NRTL	Non-Random Two Liquid
NTS	Number of Theoretical Stage
R-K	Redlich-Kwong
R-K-S	Redlich-Kwong-Soave
TAEE	Tertiary Amyl Ethyl Ether
TAME	Tertiary Amyl Methyl Ether
TBA	Tertiary Butyl Alcohol
UNIFAC	UNIQUAC Functional-group Activity Coefficient
UNIQUAC	Universal Quasi-Chemical
VLE	Vapour-Liquid Equilibrium

PEMODELAN DAN SIMULASI PENYULINGAN BERTINDAK BALAS UNTUK PENGHASILAN METIL TERTIER BUTIL ETER (MTBE) BERGABUNG DENGAN PEMBUNGKUSAN BERSTRUKTUR ATAU RAWAK

ABSTRAK

Satu simulasi penyulingan kolum bertindak balas berperingkat telah dibangunkan untuk penghasilan metil tertier butil eter (MTBE). Model yang dianjur telah disahkan dengan membandingkan data simulasi yang diperolehi daripada Aspen Plus dengan data simulasi daripada literatur. Profil suhu dan profil komposisi yang diperolehi daripada simulasi menunjukkan kesetujuan rapat dengan data yang diperolehi daripada data literatur yang dilaporkan. Asas simulasi penyulingan kolum bertindak balas berperingkat telah ditetapkan. Asas simulasi tersebut telah menganggap penyulingan tindak balas berperingkat tersebut mempunyai jumlah 17 peringkat. Penyulingan bertindak balas berperingkat tersebut mempunyai dua aliran suapan, metanol masuk ke peringkat tiga dan butena masuk ke peringkat sebelas. Tekanan kolum yang digunakan adalah 11 atm. Nisbah refluks adalah 7. Dengan konfigurasi kolum dan keadaan operasi yang optima, penghasilan isobutena sehingga 99.9% telah diperolehi daripada simulasi.

Terdapat 26 pembungkusan struktur dan rawak yang berbeza terdapat di Aspen Pus V8.8 telah dipilih untuk kajian ini. 13 pembungkusan struktur dan 13 pembungkusan rawak yang berbeza telah disimulasi dengan menggunakan simulasi asas yang dicadangkan. Bahagian pembungkusan untuk penghasilan MTBE telah ditetapkan dari peringkat 4 sebagai peringkat permulaan ke peringkat 11 sebagai peringkat akhir. Setara dengan ketinggian teori plat (HETP), penurunan tekanan dan ketahanan cecair telah ditentukan untuk pembungkusan struktur dan pembungkusan rawak yang berbeza. Keputusan dari simulasi untuk penghasilan MTBE telah berbanding dengan keputusan optima yang berkaitan dengan penghasilan isobutena dan penulenan MTBE.

MODELING AND SIMULATION OF REACTIVE DISTILLATION COLUMN FOR THE PRODUCTION OF METHYLTERTIARY BUTYL ETHER (MTBE) INCORPORATING STRUCTURED OR RANDOM PACKING

ABSTRACT

A simulation of reactive distillation column has been developed for the production of methyl tertiary butyl ether (MTBE). The proposed model was validated by comparing the simulated results obtained from Aspen Plus with the simulation data from the literature. The temperature and composition profiles obtained from simulations showed close agreement with the literature reported data. The simulation basis of reactive distillation column was set. It is assumed that the reactive distillation column has a total number of 17 stages. The reactive distillation column has two feed streams, which is a methanol feed on stage 3 and a mixed butenes feed on stage 11. The column pressure used is 11atm. The reflux ratio is 7. With the optimised column configuration and operating conditions, an isobutene conversion up to 99.9 was obtained through simulation.

There are 26 different structured and random packings available in Aspen Plus V8.8 are selected in this research. 13 different structured packings and 13 different random packings are simulated by using simulation basis proposed. The packing section of MTBE synthesis set from stage 4 as starting stage and stage 11 as ending stage. The height equivalent of a theoretical plate (HETP), pressure drop and liquid holdup has been determined for different catalytic packing. Simulation results for MTBE synthesis are compared with optimised results that cover the isobutene conversion and MTBE purity.

CHAPTER ONE

INTRODUTION

1.1 Reactive Distillation Column

Reactive distillation is an excellent example of process innovation. In a conventional chemical plant, there are reaction sections and separation sections as show in Figure 1.1 (a). These have their own vessels and equipment, but they are often linked together by material and energy recycles. In reactive distillation, separation and reaction occur in the single vessel as shown in Figure 1.1 (b). This can result in significant reductions in both energy and equipment in system that have appropriate chemistry and appropriate vapor-liquid phase equilibrium.
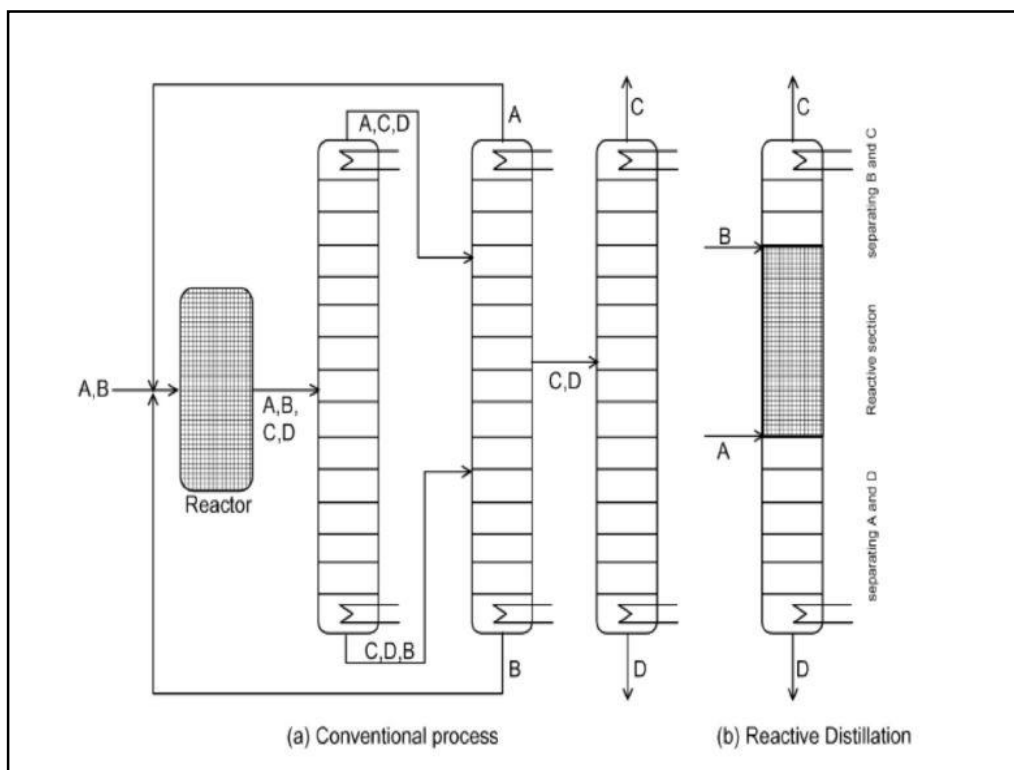
Figure 1.1: Process schemes for a reactive sequence where C and D are both desired products. (a) Conventional process of a reactor followed by a distillation column. (b) Reactive distillation process (Frey and Stichlmair, 1999, Taylor and Krishna, 2000).

The recovery of ammonia in the classic Solvay process for soda ash of the 1860s may be cited as probably the first commercial application of reactive distillation. At 1980s, enormous demand for methyl tertiary butyl ether (MTBE) gained separate status as a promising multifunctional reactor and separator.

Reactive distillation is attractive in those systems where certain chemical and phase equilibrium conditions exist. Consider the system in which the chemical reaction involves two reactants (A and B) producing two products (C and D). The reaction takes place in the liquid phase and is reversible.

$$A + B \leftrightarrow C + D \qquad (1.1)$$

For reactive distillation to work, we should be able to remove the products from the reactants by distillation. This implies that the products should be lighter and / or heavier than the reactants. In terms of the relative volatilities of the four components, an ideal case is when one product is the lightest and the other product is the heaviest, with the reactants being the intermediate boiling components.

1.1.1 Advantages of reactive distillation

Reactive distillation offers several advantages over conventional reactor-separator configurations, there are (Taylor and Krishna, 2000):

i. Conversion improvement

    The removal of the products from the reaction zone drove the reversible reaction toward the product side leading to improved conversion of reactant.

ii. Azeotropes overcome

    For chemical systems that tend to form azeotropes, reactive distillation prevents azeotropic mixtures by reacting away participating components.

iii. Reduce side product formation

Consecutive reactions are reduced by removing products from the liquid reaction phase, thereby maintaining low product concentrations in the reaction zone.

iv. Direct heat integration and avoid hot-spots

The heat of the reaction can be directly used to evaporate components for exothermic reactions. The amount of total of heat required can be reduced and avoid the occurrence of hot-spots.

v. Capital savings

Downstream processing of reactants and products are simplified due to the removal of components in reaction zone

The business drivers are

- Economical (prosperity)

  Variable cost, capital expenditure and energy requirement reduction. In all cases these are reduced by 20% or more, when compared to the classic set-up of a reactor followed by distillation.

- Environmental (planet)

  Lower emissions to the environment. In all cases carbon dioxide and diffusive emissions are reduced.

- Social (people)

  Improvements on safely, health and society impact are obtained by lower reactive content, lower run away sensitivity and lower space occupation.

1.1.2 Limitations of reactive distillation implementation

However, although reactive distillation sounds like a great idea, its area of application is fairly restricted. Both the chemistry and the vapor-liquid equilibrium phase must be suitable. The limitations of reactive distillation involved:

i. Temperature mismatch

In the conventional multiunit flow sheet, the reactors can be operated at their optimum pressures and temperatures that are selected to be the most favourable for their given chemical kinetics. The distillation columns can be operated at their optimum pressures and temperatures that are selected to be the most favourable for their vapor-liquid equilibrium properties. Hence, there must be no mismatch in the temperatures that are favourable for reaction and the temperatures that are favourable for separation. The temperatures throughout the column are fixed by tray compositions because reaction and separation both occur in a single vessel at essentially a single pressure.

ii. Unfavourable volatilities

Relative volatilities is the major limitation for the application of reactive distillation. The components must be such that the reactants can be contained in the column and the products can be easily removed from the top and / or from the bottom.

iii. Slow reaction rates

Another limitation for reactive distillation is the need for reasonably large specific reaction rates. If the reactions are very slow, the required tray holdups and number of reactive trays would be too large to be economically provided in distillation column.

iv.   Other restrictions

Reactive distillation is limited to liquid-phase reactions because there is very little holdup in the vapor phase. The heats of reaction must be modest to prevent large changes in vapor and liquid rates through the reactive zone. A highly exothermic reaction could completely dry up the trays.

1.2 MTBE synthesis

The MTBE synthesis by using reactive distillation column is essentially a ternary system with inert. The liquid-phase reversible reaction is

$$Methanol + Isobutene \leftrightarrow MTBE \tag{1.2}$$
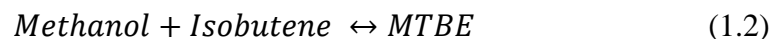
The heavy component is MTBE, which leaves the reactive distillation column in the bottoms. The isobutene feed is contained in a mixed C4 stream from an upstream refinery unit. This stream contains a number of other C4 hydrocarbons because of the difficulty of separating the various components with very similar relative volatilities. In the numerical example, we assume that n-butene is the chemically inert component. Most of this inert component leaves in the distillate stream.

1.3 Packing material

Packing material may be divided into the following three classes:

- Random or dumped packing: This packing consists of discrete pieces of packing of a specific geometrical shape which are randomly packed in a column shell.

- Structured packing: This packing consists of crimped layers of wire-mesh or corrugated sheets which form a distinctive pattern. These sheets consist of triangular corrugated channels arranged in parallel planes. Each parallel plane is

placed side-by-side with opposing 45º inclination angles and the gas and liquid is forced into these "closed" flow channels. Additionally, the elements are stacked at alternating 90º angles and inducing sharp directional changes in the two-phase flow.

- Grids: This type of packing is similar to structured packing except, instead of wire-mesh or corrugated sheets an open-lattice structure is used.

Random packing was developed first, followed by structured packing and grids. The two most widely used types are random and structured packing. Grids are limited to primarily heat transfer and wash services (Kister, 1992).

1.4 Problem statement

Different type of catalytic packings can be chosen to carry out production of MTBE in reactive distillation column. However, the performance of different catalytic packings that has been investigated are still limited, especially the choice of suitable catalytic packings is a major problem when reactive distillation for MTBE synthesis implemented on a commercial scale.

Due to the limited investigation of different catalytic packings especially for MTBE synthesis, simulation have to be performed to further justify the performance of packings for the MTBE synthesis towards long term service. Since reactive distillation process is complicated, mathematical models are necessary to describe the operational behaviour of the reactive distillation column.

Currently, there are reported studies on structured and random packings using simulation method for different process but there has been no study of structured and random packings carried out specific for MTBE synthesis by using reactive distillation column. Thus, it is necessary to perform simulation of different structured and random packings to analyse the performance in the MTBE synthesis process.

1.5 Research objectives

There are some objectives which expected to be achieved at the end of this project:

i.   To develop a steady state model of reactive distillation system by using Aspen Plus;

ii. To verify the model by simulating the developed model and compare result of simulation with the published data;

iii. To analyse the performance of different structured and random catalytic packings by determine the HETP, liquid holdup and pressure drop of packings ;

iv. To determine suitable catalytic packings by analysing the performance of MTBE synthesis with different structured and random catalytic packings in reactive distillation column.

1.6 Scope of study

In this study, the performance of different type of structured and random packings in reactive distillation for MTBE synthesis was modelled and simulated by using Aspen Plus V8.8. From the basic principles of reaction and separation processes, the model equations describing reactive distillation process can be developed. With the aid of simulation tool, the model can be verified by simulation and used for determining the

optimal performance of structured and random packing in reactive distillation. Then, comparison study was performed to compare the performance of different type of structured packing and random packings suitable for MTBE synthesis that can obtained high conversion of isobutene and high purity of MTBE.

1.7 Thesis overview

This thesis consists of five chapters covering introduction, literature review, materials and methodology, results and discussions and conclusions.

Chapter One consists of the introduction of the research, problem statement, research objectives and the scope of study. The research background included general information, advantages and limitations of reactive distillation, synthesis of MTBE and type of packing material in reactive distillation. Problem statement described the problems associated and further defined the research objectives.

Chapter Two included the literature review to provide descriptions of similar or related studies in order to have better understandings on the present study. This chapter provides literature review on MTBE synthesis, development of reactive distillation processes, modeling of reactive distillation, simulation of reactive distillation, and development of structured and random packing.

Chapter Three described the materials and methodology used in this study. Details of reactive distillation model development, as well as the simulation and comparison study were outlined in this chapter.

Chapter Four showed the results and discussion of the research, including models performance analysis and simulation data obtained from Aspen Plus V8.8, and the comparison between the performance of different type of structured and random packing on MTBE process in reactive distillation column.

Lastly, Chapter Five concluded and summarized the results and discussions obtained in this research.

CHAPTER TWO

LITERATURE REVIEW

2.1 MTBE synthesis

MTBE reactive distillation process was patented several decades ago, and the process was widely used in the petroleum industry. Many reactive distillation columns were installed around the world to produce MTBE, which was blended into gasoline. This process was probably the largest application of reactive distillation in terms of the number of columns and total production capacity.

In 1980, the first patent registered to MTBE synthesis for Chemical Research and Licensing Company (Sneesby et al., 1998). It was commercialised for MTBE synthesis in 1982 (Sneesby et al., 1997) and MTBE production is now its most important area of application. Of the many new MTBE plants that are currently in either the planning or construction phases, most will use processes based around reaction distillation.

MTBE is produced by reaction of isobutene and methanol; the liquid-phase reaction is catalysed by an acidic catalyst, for example Amberlyst 15 (Al‑Jarallah et al., 1988, Zhang and Datta, 1995). MTBE synthesis utilizing the reactive distillation technology can achieved conversion of isobutene up to 99.99% (DeGarmo et al., 1992, Zhang and Datta, 1995).

2.2 Reactive distillation processes in commercial operation

Technology providers CDTECH and Sulzer Chemtech have used scale-up methods of reactive distillation successfully. The major commercial process technology provider, CDTECH licensed up to now over 200 commercial scale processes. The catalytic distillation in commercial operation licensed from CDTECH are as shown in Table 2.1.

Table 2.1: The number of catalytic distillation in commercial operation licensed from CDTECH (G. Jan, 2007).

Process	Number
Ethers: MTBE, TAME, ETBE	69
Hydrogenation of aromatics and light sulphur	50
Hydrodesulfurisation	21
Isobutylene production from C4 stream	3
Ethyl benzene production	3
Total	**146**

For Sulzer, their company reports the industrial commercial scale applications without disclose numbers as shown in Table 2.2.

Table 2.2: The industrial commercial scale applications reported from Sulzer Company (G. Jan, 2007).

Process	Industrial column location
Acetate	
Synthesis of ethyl, butyl and methyl acetate	Europe
Hydrolysis of methyl acetate	Europe and Asia
Acetalisation	
Synthesis of methylal	Europe and Asia
Removal of methanol from formaldehyde	Europe
Fatty acid esters	Asia

Eastman's first methyl acetate reactive distillation tower started up in 1980. It is more that 80 m tall with a diameter of about 4 m. The process (including condenser and reboiler) is made of five different materials of construction. The second plant, built seven years later with the benefit of operating experience, is virtually identical (geometry, staging, dimensions, capacity) except for some sieve tray detail in the upper non-reactive zones.

2.3 Modeling of reactive distillation processes

The design and operation issues for reactive distillation systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in situ separation function within the reaction zone leads to complex interactions between phase equilibrium, vapor-liquid equilibrium, vapor-liquid mass transfer and reaction kinetic model. Through the understanding with

the thermodynamics and kinetic theories of reactive distillation processes, the complex problem about reactive distillation can be handled.

2.3.1 Thermodynamics of reactive distillation

First introductory review of thermodynamics on reactive distillation was provided by Frey and Stichlmair at 1999. The knowledge of phase equilibrium, vapour-liquid equilibrium and chemical reaction equilibrium are essential for the design of reactive distillation processes.

2.3.1.1 Phase equilibrium

The general expression of phase equilibrium relationship is:

$$y = Kx \tag{2.1}$$

where y is the vapour composition, K is constant for phase equilibrium expression and x is the liquid composition. K-value is in simplest from by using Raoult's Law for ideal mixture. For non-ideal mixture, the K-value is more complex than the K-value of ideal mixture. It is recommended to include liquid phase activity coefficient to determine the degree of departure from the ideal behaviour (Frey and Stichlmair, 1999).

2.3.1.2 Vapour liquid equilibrium model

For vapour liquid equilibrium model, the model used to calculate the liquid phase activity coefficient of a liquid mixture is called activity coefficient model. The models that reported by researchers are Wilson equation, Non-random two liquid equation (NRTL), Universal Quasi-Chemical model (UNIQUAC) and UNIQUAC Functional-group Activity Coefficient model (UNIFAC).

Wilson equation is the model widely applied in reactive distillation process for simulation of MTBE synthesis (Lee and Westerberg, 2001). NRTL is the model that applicable to immiscible systems and successful applied in MTBE synthesis simulation (Bao et al., 2002). UNIQUAC model is widely used in reactive distillation processes especially MTBE synthesis because this method is reported by a lot researchers to describe the non-ideality of liquid phase in the synthesis of MTBE (Hauan et al., 1995, Taylor and Krishna, 2000). UNIFAC model is the extension of UNIQUAC model (Sneesby et al., 1998). It is widely applied in reactive distillation simulation and usually preferred for use in design but there are specific limitations of the method that need to consider:

- Temperature below 150 ℃

- Pressure should not be greater than a few bar

- No non-condensible components or electrolytes

- Components must not contain more than 10 functional groups

All the models discussed above are able to perform comparably for moderately non-ideal system. UNIQUAC and NRTL models are frequently useful for species that are dissimilar, partially soluble and form two liquid phases but Wilson model is inapplicable (Sandler, 1999). For the non-ideality in liquid phase, UNIQUAC model able to this case that similar as the case of MTBE synthesis. However, the UNIFAC model cannot obtain satisfactory performance in MTBE process even though this model is based on the extension of UNIQUAC model (Rehfinger and Hoffmann, 1990). The summary of vapour liquid equilibrium model utilized in different condition are as shown in Table 2.3.

Table 2.3 Vapour liquid models that suitable for different conditions.

System	Wilson	NRTL	UNIQUAC	UNIFAC
Moderately non-ideal system	√	√	√	√
Dissimilar species, partially soluble and form two liquid phases		√	√	
Non-ideality in liquid phase			√	

For highly no-ideal system, the vapour phase non-ideality should also be taken into account. Fugacity coefficient model is the vapour liquid equilibrium model used to calculate the vapour phase fugacity coefficient of a vapour mixture. The fugacity coefficient model included Redlich-Kwong (R-K) equation, Redlich-Kwong-Soave (R-K-S) equation and Peng-Robinson equation.

Redlich-Kwong (R-K) equation can be applied to calculate the vapour phase non-ideality in the simulation of MTBE synthesis (Jacobs and Krishna, 1993, Nijhuis et al., 1993, Hauan et al., 1995). Redlich-Kwong_Soave (R-K-S) equation is an extended version of R-K equation that can be applied near the critical properties of component mixture. This model can be applied in reactive distillation system, especially MTBE synthesis (Higler et al., 1999, Bao et al., 2002, Sneesby et al., 1998). Peng-Robinson equation is an equation related to R-K-S equation and able to overcome the instability of R-K-S method and near the critical point. However, due to the unavailability of binary interaction parameter, this equation has been not used in modeling of reactive distillation (Sinnott, 1998).

From the equations introduced above, the most popular equation that can being applied in reactive distillation systems are Redlich-Kwong equation.

2.3.1.3 Reaction kinetics

The chemical reaction kinetics are required in reactive distillation modeling to describe the reaction mechanism. The reaction kinetics can be obtained from batch reaction experiment. There are several experimental studies has been carried out for MTBE synthesis. One of the most popular synthesis of MTBE is from methanol and isobutene catalysed by ion exchange resin Amberlyst 15.

The principal reaction of MTBE synthesis is:

$$Methanol\ (MeOH) + Isobutene\ (IB) \leftrightarrow MTBE \qquad (2.2)$$
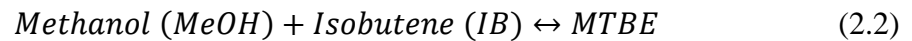
The most popular model used in reactive distillation modeling and simulation of MTBE synthesis is proposed by Rehfinger and Hoffmann (1990), which is based on activity coefficient and equilibrium constant:

$$r = qk_f\left(\frac{a_{IB}}{a_{MeOH}} - \frac{a_{MTBE}}{K_{eq}a_{MeOH}^2}\right) \qquad (2.3)$$

where k_f is the forward rate constant and K_{eq} is the equilibrium constant, q is the ion exchange capacity and a is the activity coefficient.

There are different chemical kinetics form proposed by Bao et al. (2002) for heterogeneous kinetic of MTBE:

$$-r_{IB} = k_f C_{IB} - k_r C_{MTBE} \qquad (2.4)$$

where k_f is the forward rate constant and k_r is the reverse rate constant, C is concentration and r_{IB} is the reaction rate respect to isobutene.

Another kinetic model for homogeneously catalysed MTBE synthesis that proposed from Venimadhavan et al. (1994):

$$\varepsilon = k_f(a_{MeOH} - \frac{a_{MTBE}}{K_{eq}}) \hspace{3cm} (2.5)$$

where ε is the reaction rate per mol of mixture.

2.3.2 Equilibrium (EQ) stage models

The equilibrium stage models of conventional distillation calculations can be extended for reactive distillation process modeling. The liquid and vapour phase are assumed to be in equilibrium in equilibrium stage model and associated with the MESH equations. The Mesh equations included Material balance, Equilibrium relationship, Summation equation and Heat balance. Computer-based methods developed for solving the equilibrium stage model equations included tearing methods, relaxation methods, homotopy-continuation methods, minimisation method and inside-out algorithm.

Tearing methods is dividing the model equations into groups to be solved separately. Relaxation methods is writing the MESH equations in unsteady-state form and it utilized numerical integration to find the solution of steady-state. The relaxation methods performance are closely to dynamic models but it consuming a lot computer time. Homotopy-continuation methods was first method that applied to reactive distillation problem. This methods normally applied to the problems that very difficult to solve with other methods. Minimisation method is used to minimized the sum of squares of non-linear functions without calculate derivatives but this method is rather slow to converge. Inside-out algorithm is combined with Newton's method for multicomponent separation process calculations. RADFRAC introduced in Aspen Plus is utilized the combination

methods between Newton's and inside-out algorithm for solving reactive distillation problems (Taylor and Krishna, 2000)**.**

The Newton method is most common computer-based method applied for numerical solution. One of the significant advantage of Newton method over other methods is the quadratic convergence near the solution but Newton's method is difficult to converge especially for highly non-ideal system. Hence, after combine with inside-out algorithm, which is Newton inside-out algorithm, the poor convergence problem can be overcome when the non-idealities are strong.

The reviews related to equilibrium stage models above are mostly applied for steady state simulation. For dynamic simulation, it needs to consider non-equilibrium stage model to obtained more essential and proper description of the reactive distillation column performance.

2.3.3 Reactive distillation modeling for MTBE synthesis

The development of MTBE synthesis by using reactive distillation system cause the number of publications on modeling and simulation for the MTBE processes increased. Table 2.4 shows both of the equilibrium (EQ) stage and non-equilibrium (NEQ) stage models were utilised in steady state and dynamic simulation of MTBE.

Table 2.4: Reactive Distillation Modeling and Simulation for MTBE Synthesis

Reference	Modeling Classification		Vapour-Liquid Model		Kinetic Model	
	Equilibrium Stage	Non-Equilibrium Stage	Liquid	Vapour	Homogeneous	Heterogeneous
Jacobs and Krishna (1993)	Steady State	-	UNIQUAC	R-K	-	Equation 2.3
Nijhuis et al. (1993)	Steady State	-	UNIQUAC	R-K	-	Equation 2.3
Venimadhavan et al. (1994)	Steady State	-	Wilson	-	Equation 2.5	-
Zhang and Datta (1995)	Steady State	-	UNIFAC	Ideal	-	Equation 2.3
Guttinger and Morari (1997)	Steady State	-	Wilson	Ideal	-	Equation 2.3
Hauan et al. (1997)	Steady State / Dynamic	-	UNIQUAC	R-K	-	Equation 2.3
Sneesby et al. (1998)	Steady State / Dynamic	Steady State / Dynamic	UNIFAC	R-K-S	-	Equation 2.3
Higler et al. (1999)	-	Steady State / Dynamic	UNIQUAC	R-K-S	-	Equation 2.3
Lee and Westerberg (2001)	Steady State	-	Wilson	Ideal	Equation 2.5	Equation 2.3
Bao et al. (2002)	Steady State	-	NRTL	R-K-S	-	Equation 2.4

2.4 Reactive distillation design

Most conceptual design models are based on the equilibrium stage model. However, the possibility of using non-equilibrium models for reactive distillation design was developed recently and there are number of papers suggest that non-equilibrium models have place in commercial reactive distillation design practice (Taylor and Krishna, 2000).

2.4.1 Conceptual design

Barbosa and Doherty (1988) developed the fixed point method for the design of single-feed reactive distillation columns. The method is based on the following assumptions:

- The column is adiabatic

- The molar heat of vaporisation is constant

- The heat of mixing is negligible

- Sensible heat effects can be ignored

- The heat of reaction is negligible compared to the enthalpy of the vapor

- The feed is a saturated liquid

- Phase equilibrium is achieved on each stage

- The column operates with a partial condenser

These assumptions ensure that the vapor and liquid flows inside the column are constant, thereby permitting the energy balances to be solved essentially independent of the remaining stage equations.

2.4.2 Graphical design methods

A graphical (Ponchon-Savarit type) design procedure for reactive distillation columns based on the transformed composition variables of Barbosa & Doherty (1988) is described by Espinosa, Scenna and Perez (1993). The MTBE process is used to illustrate their method.

Lee, Hauan, Lien and Westerberg (2000a,b) and Lee et al. (2000d) have recently presented an in-depth analysis of the classical Ponchon-Savarit and McCabe-Thiele graphical methods for reactive distillation.

2.4.3 Design via optimisation methods

Reactive distillation design via optimisation methods has been the subject of a few studies. Ciric and Gu (1994) formulated a mixed integer nonlinear programming model, solution of which yields the optimal number of equilibrium stages, feed rates and reflux ratios at a minimal annual cost.

Gumus and Ciric (1997) used a bilevel optimisation procedure to explore the design of reactive distillation columns that could have more than one liquid-phase. The number of phases and the phase equilibria were determined by minimising the Gibbs free energy.

Eldarsi and Douglas (1998b) used the optimisation capability in Aspen Plus to optimise an MTBE column. Their study indicated that the market price of the MTBE product, the cost of the butylenes, the isobutylene composition and utility costs all influence the MTBE.

2.4.4 From conceptual design to column design

Subawalla and Fair (1999) discuss the several importance key design parameters in an actual column design, that included pressure, reactive zone location, reactant feed ratio, feed location, catalyst mass, number of equilibrium stages, reactive zone height, column diameter, reflux ratio, and HETP. The paper reported detailed step-by-step procedure for designing a reactive distillation column. However, the procedure is not applicable to all reactive distillation processes.

2.4.5 Reactive distillation design in industrial practice

Pinjala, DeGarmo, Ulowetz, Marker and Luebke (1992) used the non-equilibrium model RATEFRAC to model MTBE processes in columns filled with Koch KataMax packing. Frey, Ozmen, Hamm, Injala and DeGarmo (1993) have reported that RATEFRAC has been used to accurately predict the performance of commercial reactive distillation processes in Germany and Texas. That the model has been validated for the design of tertiary amyl methyl ether (TAME), ethyl tertiary butyl ether (ETBE), and tertiary amyl ethyl ether (TAEE) units with data from semi-commercial operations.

2.5 Design guidelines for reactive distillation column

In order to achieve a stable and desirably optimum operating condition for reactive distillation operation, some guidelines for choosing appropriate column specifications are discussed with respect to the production of MTBE.

2.5.1 Selection of Operating Pressure

The maximum and minimum operating pressure depends on condenser coolant and reboiler heating medium temperature (DeGarmo et al., 1992; Subawalla and Fair, 1999).

For MTBE synthesis, quite high operating pressure is preferable in order to reduce the relative volatility of isobutene (most volatile component in MTBE system) to maintain minimum amount of isobutene in liquid phase for reaction. Accordingly, many researchers reported optimum operating pressure of 11 bar or 11 atm. for MTBE synthesis. Some researchers reported operating pressure of less than 11 bar but no one has reported less than 6 bar (as known to author). Usually smaller operating pressure accompanied with specification of smaller number of theoretical stages used.

2.5.2 Reactive Zone Location

The reactive zone location depends on activity of catalyst at distillation conditions and the relative volatility of reactants and products (DeGarmo et al., 1992; Subawalla and Fair, 1999). The reactive section should be located where the concentration of at least one reactant (preferably the limiting reactant) is the maximum. For MTBE synthesis, the reactive zone located slightly towards the top of the column to enhance the reaction because the most volatile component is isobutene (the limiting reactant). Additionally, almost pure MTBE can be obtained at bottom of column when the reactive zone is slightly to the top of column to enhance the stripping of MTBE downwards. Although methanol is the least volatile component (heaviest), thermodynamic non-ideality forces methanol to behave like low-boiling component. This is because methanol forms minimum boiling azeotropes with C_4 components (isobutene and 1-Butene) (Subawalla and Fair, 1999).

2.5.3 Reactant Ratio and Feed Location

A slight stoichiometric excess of methanol for the MTBE synthesis has been reported in literature by many researchers. Isobutene has been chosen to be the limiting reactant to enhance maximum conversion of isobutene. It is not desirable to have to much

excess of methanol because it might cause the methanol to accumulate in the column and going down the column, thus reducing the amount of MTBE formed as well as purity of MTBE at the bottom of the column. 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. Not only that, in the case of MTBE synthesis, methanol feed location can be varied in the reactive zone since methanol behaves like low-boiling point component if the amount of excess of methanol is small in the column after reaction.

2.5.4 Catalyst Mass

Selecting an appropriate amount of catalyst is another important aspect in heterogeneously catalysed reactive distillation column. Inadequate catalyst volume reduces the residence time and gives poor conversion whereas excess of catalyst may result in product decomposition particularly when it is inappropriately located (Subawalla and Fair, 1999). For MTBE synthesis, increases the catalyst mass will increase the reaction conversion up to a certain point. Further increase in catalyst mass will have negligible amount of reaction conversion.

2.5.5 Number of Theoretical Stages

The number of theoretical stages in reactive distillation column may be estimated once the reactive zone and the catalyst mass are specified. Short-cut method such as Fenske and Underwood method give reasonable estimates for the non-reactive stripping and rectification section (Subawalla and Fair, 1999). Many researchers have reported a