

**MODELING AND SIMULATION OF REACTIVE
DISTILLATION COLUMN FOR THE PRODUCTION OF
DIMETHYL CARBONATE (DMC)**

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DIMETHYL CARBONATE (DMC)**

by

LOW PUI SAN

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for the degree of Bachelor of Chemical Engineering**

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LIST OF SYMBOLS

Symbol	Description	Unit
B	Bottom Flow	kg/hr
C_i	Concentration of the i component	mol/L
$\Delta h^{\circ}_{v,i}$	Standard heat of vaporisation	kJ/mol
$h^{\circ}_{fL,i}$	Standard heat of formation of component	kJ/mol
i	Component index	-
N	Number of stages	-
P_c	Critical pressure	kPa
Q_i	surface area parameter of the i component	-
r_i	Reaction rate of the i component	L/mol.min
r	Reflux ratio	-
R_i	volume parameter of the i component	-
T	Temperature	K
T_b	Normal boiling point temperature	K
T_c	Critical temperature	K
W	Weight of catalyst	kg/hr

LIST OF ABBREVIATIONS

DMC	Dimethyl Carbonate
EQ	Equilibrium
MeOH	Methanol
MESH	Material, Equilibrium, Summation, Heat
NRTL	Non-Random Two-Liquid
PC	Propylene Carbonate
PG	Propylene Glycol
RD	Reactive Distillation
RK	Redlich-Kwong
UNIQUAC	Universal Quasi-Chemical
VLE	Vapor-liquid equilibrium

**PEMODELAN DAN SIMULASI TURUS PENYULINGAN BERTINDAK
BALAS UNTUK PENGHASILAN DIMETIL KARBONAT (DMC)**

ABSTRAK

Tujuan utama penyelidikan ini adalah untuk membangunkan model simulasi bagi turus penyulingan bertindak balas untuk penghasilan dimetil karbonat (DMC) dengan menggunakan Aspen Plus sebagai platform pemodelan. Penyelidikan ini juga meliputi kajian terhadap kesan yang mempengaruhi reka bentuk dan keadaan operasi bagi sesuatu turus. Kajian ini bermula dengan pengesahan model matematik yang sesuai untuk pengisian simulasi iaitu Aspen Plus. Model yang dicadangkan telah disahkan kebolehan aplikasinya setelah hasil simulasi dibandingkan dengan data simulasi yang diterbitkan dari literatur dan hasil data dari Aspen Plus. Analisis and perbandingan telah dilakukan setelah simulasi lengkap and beroperasi.

Prestasi turus penyulingan bertindak balas telah diperolehi setelah mengenalpasti konfigurasi turus dan keadaan operasi yang optima. Penghasilan propilena karbonat sehingga 94% telah diperolehi daripada simulasi dengan parameter turus yang optima.

**MODELING AND SIMULATION OF REACTIVE DISTILLATION
COLUMN FOR THE PRODUCTION OF DIMETHYL CARBONATE (DMC)**

ABSTRACT

The main objective of this research is to develop a simulation model of reactive distillation column for the production of dimethyl carbonate using Aspen Plus as a modeling platform. In this research, the effects that influenced the design and operating condition of the column were also studied. It started with verify the mathematical models that suitable for the simulation software which is Aspen Plus. The proposed model was validated by comparing the simulated results obtained from the published data from literature and with results from Aspen Plus. Analysis and comparison has been performed after the simulation complete and converges.

The performance of reactive distillation column was obtained by determining the optimum column configuration and operating conditions at 333K, 1 atm. A propylene carbonate conversion up to 94% was obtained through simulation with the optimized column parameter.

CHAPTER ONE

INTRODUCTION

1.1 RESEARCH BACKGROUND

Reactive Distillation (RD) is a combination of separation and reaction in a single vessel. RD comprises with the combination of chemical reaction with separation such as distillation, stripping, absorption extraction, adsorption, crystallization and membrane separation (Kai and Kienle, 2003). The advantages offered by RD able to perform difficult separations, surpass equilibrium limitation and able to achieve high selectivity. The research of RD on various aspects such as modeling and simulation, process synthesis, column hardware, non-linear dynamics and control etc. is in progress from past till now (Rameshwar et al., 2004).

A model is a simplified representation of a system to compare with the real system. The main function of a model is to predict the behaviour of a real system when there is a change occurs on the system. The prediction of the model should be close to the reality. Simulation is the manipulation and operation of a model in a specified system. Through simulation, the operation of the model can be studied. The steady state simulation of the synthesis process of DMC in an RD column will be conducted by Aspen Plus (Huang et al., 2014).

Dimethyl carbonate (DMC) has its demand since year 1990 due to its fuel properties which are important to the oil industry (Michael et al., 1997). There are many alternatives process in producing DMC. However, the potentially important

reactions as candidates for RD is transesterification of production of DMC through the reaction of methanol and ethylene (propylene) carbonate (Kai and Achim, 2003).

There are several ways to produce DMC such as methanolysis of urea and direct synthesis of DMC from propylene carbonate (PC) and methanol (MeOH). But, urea methanolysis to DMC having some problems which are having low production of selectivity and high molar ratio of methanol to urea. For the transesterification reaction of PC and MeOH, the products form a homogeneous azeotrope with reactant MeOH in distillate of RD column. No side-product formations were observed from any of the experiments performed. In this reaction, the yield of DMC is higher than other routes. Hence, the use of an RD process to operate the transesterification of PC and MeOH was suitable (Johannes et al., 2013a).

In the process analysis, the effects of operating parameters, simulated composition and temperature profiles are important. Furthermore, the influence of the operating parameters on the PC conversion and the product purities was investigated to identify a suitable operating range to produce a high-purity DMC and PG on an industrial-scale. The influence of the reflux ratio, the molar feed ratio between MeOH and PC and the catalyst mass fraction in the feed was studied (Johannes et al., 2013a).

The idea of RD came out when some chemical reactions and physical separations have some overlapping operating parameters. The combinations of the two processes into a single process unit surely giving significant benefits. The benefits involve of avoidance of reaction equilibrium, higher conversion, selectivity and yield, removal of side reactions, reduction of investment cost and so forth (Harmsen, 2007).

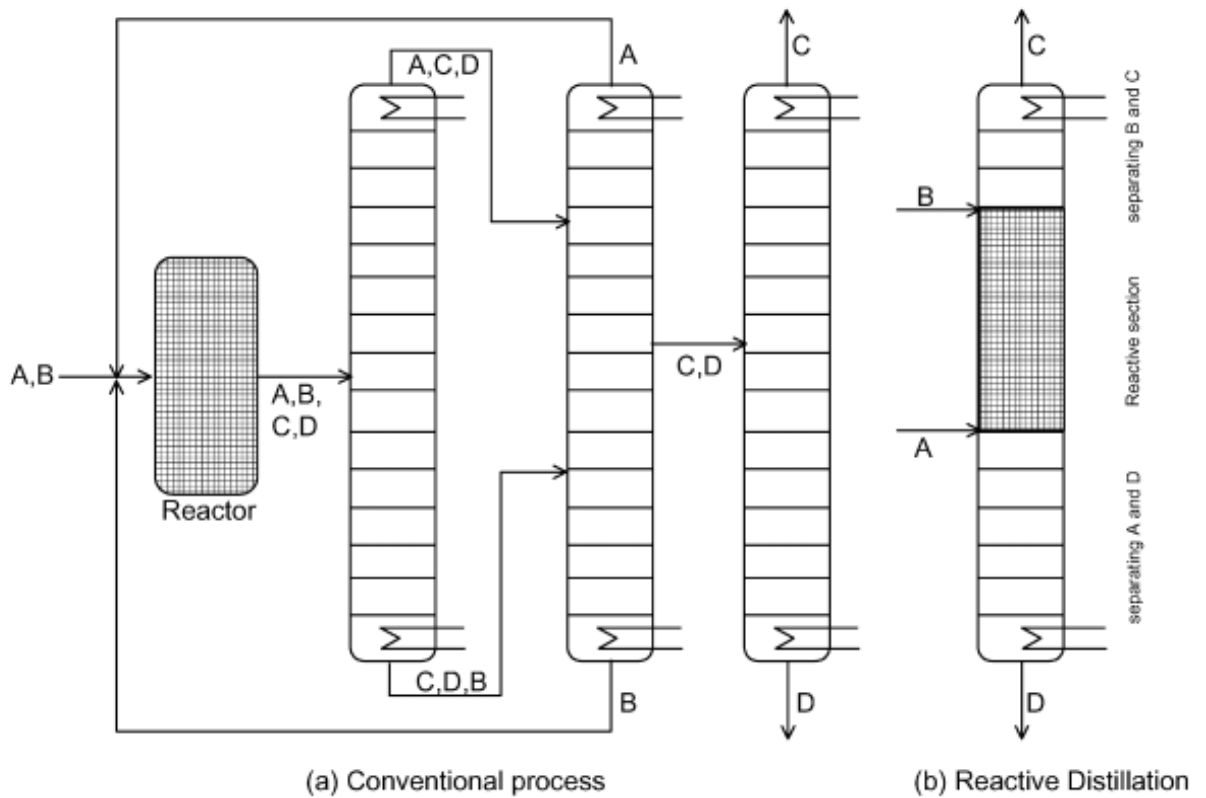


Figure 1 (a) Typical configuration of a conventional process

(b) The reactive distillation configuration. Adapted from Stichlmair Frey (1999).

Reactive Distillation become the most widely applied process intensification technique today as the focus of the chemical and process industry has shifted towards the development and application of the integrated process. Apart from the advantages mentioned, improvement of process efficiency and safety tends to bring the trend of development of reactive distillation.

Due to the potential of reactive distillation technology, there are many characteristics of RD which are still in the stages of conceptual understanding. To enhance the knowledge of RD, proper understandings of the basic principles and

fundamental of reaction and separation are needed in order to solve the problems of RD no matter in research area or industry field.

1.2 PROBLEM STATEMENT

Current research mostly focuses on the research for the synthesis of DMC with homogeneous catalyst. An experimental on screening heterogeneous and homogeneous catalysts for the transesterification of propylene carbonate (PC) with MeOH has been discussed in an earlier publication by Johannes et al. (2013b). However, none of the screened heterogeneous catalysts was sufficiently active to allow for the integration of this reaction into an RD column. Researchers have previously published literature on synthesis of DMC and PG by transesterification of PC and methanol with heterogeneously catalysed in a batch reactor (Song et al., 2017). In addition, no study is reported on the simulation of reactive distillation column on the transesterification of PC and methanol with heterogeneously catalysed. Hence, simulation on heterogeneously catalysed DMC synthesis is described here that makes uses for further investment on industrial scale plant.

1.3 RESEARCH OBJECTIVES

The objectives of this research are: -

- i. To develop a reactive distillation model for the production of dimethyl carbonate (DMC) using Aspen Plus.
- ii. To verify the proposed model by comparing the simulated results obtained from the model with the reported experimental data.

- iii. To study the effect of operating parameters such as methanol feed location, reflux ratio, total number of theoretical stages and reactive zone location towards achieving higher conversion of product.
- iv. To compare the performance of RD by using homogeneous and heterogeneous catalyst through simulation.

1.4 SCOPE OF STUDY

Several scopes have been determined to achieve the target of research which are develop a reactive distillation model using Aspen Plus. In addition, verify the model with experimental data. Lastly, perform simulation by changing the parameters of operating condition.

CHAPTER TWO

LITERATURE REVIEW

2.1 DMC SYNTHESIS

DMC was first manufactured from methanol and phosgene in 1910s (Li et al., 2006). Back and then, new route to produce DMC free of phosgene which is oxidative carbonylation (oxy-carbonylation) of methanol has developed. The oxy-carbonylation and carbonylation of methyl nitrite have replacing the traditional phosgenation of methanol process which involves very toxic compounds (Bruno et al., 2014). After that, the transesterification of ethylene carbonate with methanol was claimed for DMC production which has been used until now.

To reduce the environmental impacts and to minimize the risks to human health, the development of new alternative routes to produce DMC are introduced. The new alternative processes are transesterification of cyclic carbonate, transesterification of urea, carbonylation of methanol and oxidation of dimethoxy methane (Bruno et al., 2014).

The transesterification process is more considerable in manufacturing DMC (Fang and Liu, 2007). DMC production from carbon dioxide also has been studied before. However, it must be operated at critical temperature and pressure with high energy consumption (Chayanit et al., 2016).

The most studied alternative for DMC synthesis is the transesterification of ethylene carbonate, due to its high productivity, selectivity of DMC and the co-

generation of glycol carbonate (Bruno et al., 2014). However, the high value of propylene glycol produced in the transesterification of propylene become an interesting alternative for DMC synthesis too.

Since the transesterification reaction is limited by thermodynamic equilibrium with a low conversion, reactive distillation became a good choice to enhance the conversion by continually remove the product from the reaction (Huang et al., 2014). In the transesterification reaction, the most abundant products formed are dimethyl carbonate and unreacted methanol at the distillate of column. The mixture forms a minimum-boiling homogeneous azeotrope. The azeotropic mixtures require further separation to obtain a high purity DMC product. A few methods are suggested for the azeotropic separation such as installation of extractive distillation, membrane pervaporation and pressure-swing distillation. It was also known that reactive distillation technology can be applied to overcome the limitation of conventional distillation azeotropic separation.

2.2 AZEOTROPIC COMPOSITION

An azeotrope is the mixture where the liquid has the same composition as the vapor somewhere in the composition range between the pure component endpoints. (Kevin and Donald, 2014). Distillation only be able to separate the components up to the azeotropic composition, therefore knowledge of the presence of azeotropes is important for further separations.

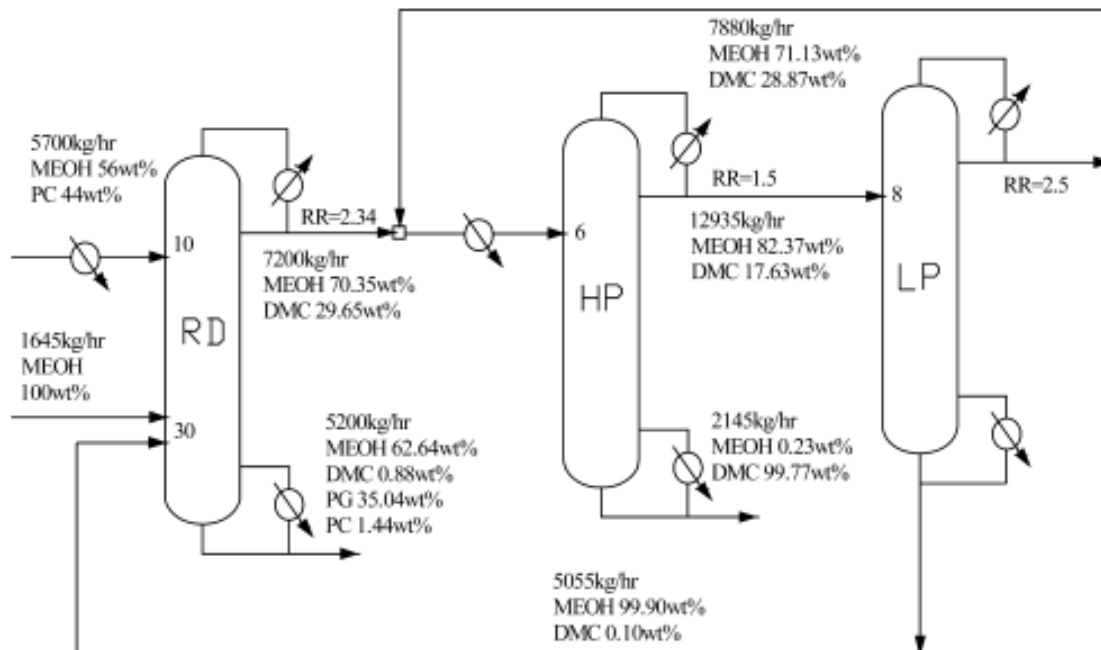


Figure 2.1 Flowsheet of the traditional process of the DMC synthesis system with pressure columns (Huang et. al., 2014).

An azeotrope composition is formed at the top of the RD column and the DMC and methanol mixture become a challenge for the purification of DMC. Hence, further separation at the top of RD column is needed. Several studies had been proposed to break the azeotrope (Li et al., 2017). From Figure 2.1, the installation of high pressure (HP) column is to separate the DMC from methanol and hence produce higher purity of DMC in the bottom of HP column. The composition of DMC and methanol azeotrope varies with the change of pressure.

2.3 INDUSTRIAL REACTIVE DISTILLATION PROCESSES

Catalytic Distillation Technologies, Inc. (CDTECH) engages in the research, development, and commercialization of catalytic distillation based processes for the chemical, petrochemical and refining industries. The company was founded in 1988 and is based in Pasadena, Texas. Its catalytic distillation concept is used for various

process applications. It includes of etherification for ethers production; selective hydrogenation for olefins saturation and isomerization, benzene saturation and gasoline hydrodesulfurization, alkylation for ethylbenzene and cumene production.

CDTECH, who had licensed up to over 200 commercial scale processes and 146 of these are in commercial operation at 2006 (Harmsen, 2007). The process applications are:

- Eastman’s first methyl acetate reactive distillation tower started up in 1980.
- The process is made of five different materials of construction.
- An annual capacity is more than 200,000 metric tonnes per year methyl acetate.
- The second plant, built seven years later is virtually identical with operating experience.

As shown, Table 2.1 indicates the process applications licensed from CDTECH in 2006. Table 2.2 shows the process applications CDTECH offers for licensing.

Table 2.1 Catalytic distillation in commercial operation in 2006

Process	Number
Ethers: MTBE, TAME, ETBE	69
Hydrogenation of aromatics and light sulfur	50
Hydrodesulfurisation	21
Isobutylene production from C ₄ stream	3
Ethyl benzene production	3
Total	146

Table 2.2 CDTECH Reactive distillation

<i>CDHydro</i> [®]	<p>Selective hydrogenation using catalytic distillation:</p> <ul style="list-style-type: none"> • MAPD reduction in mixed C_{3S} • C₄ diolefins reduction in mixed C_{4S} <p>(hydroisomerisation option)</p> <ul style="list-style-type: none"> • C₄ acetylenes reduction in mixed C_{4S} • C₅ diolefins reduction in mixed C_{5S} <p>(hydroisomerisation option)</p> <ul style="list-style-type: none"> • C₆ acetylenes reduction in mixed C_{6S} • Benzene reduction in LSR and reformat streams • Mercaptan reduction in C₄/C₅/C₆ olefinic streams • Hydrogenation of benzene to produce cyclohexane
<i>CDHDS</i> [®] and <i>CDHDS+</i> [®]	<p>Desulfurization using catalytic distillation:</p> <ul style="list-style-type: none"> • FCC gasoline • Jet fuel/kerosene
<i>HDSelect</i> [®]	Selective desulfurization of mid catalytic naphtha
<i>CDSelect</i> SM	Low cost desulfurization of low sulfur catalytic naphtha
<i>CDAlky</i> SM	Sulfuric acid alkylation of olefins
<i>CDMtbe</i> [®]	MTBE production from mixed C _{4S} and methanol
<i>CDEtbe</i> [®]	ETBE production from mixed C _{4S} and ethanol
<i>CDTame</i> [®]	TAME production from mixed C _{5S} and methanol
<i>CDTae</i> [®]	TAEE production from mixed C _{5S} and ethanol
<i>CDEthers</i> [®]	Co-production of ethers from mixed C ₄ -C _{7S} and methanol
<i>CDEtherol</i> [®]	Selective hydrogenation of diolefins within ether processes above
<i>ISOMPLUS</i> [®]	Isomerisation of <i>n</i> -olefins to iso-olefins
<i>Dimer₈</i> SM	Dimerisation of iso-olefins in C ₄ streams
<i>CDCumene</i> [®]	Alkylation of benzene with propylene
<i>CDIB</i> [®]	Decomposition MTBE to high-purity isobutylene
<i>CDTECH</i> <i>EB</i> [®]	Alkylation of benzene with ethylene
<i>BASF SELOP</i>	Selective hydrogenation of C _{4S} and C _{5S} for diolefin reduction
<i>CDAcrylamide</i> SM	Hydration of acrylonitrile to acrylamide
<i>Sulze</i> Butene-1	Superfractionation of mixed C _{4S} to produce high-purity butene-1

The number of chemical process industries applying reactive distillation column technology has been increased from year to year. Hence, the simulation work become important and used as a tool to verify the applicability of chemical synthesis.

2.4 MODELING OF REACTIVE DISTILLATION

The design and operation consideration of reactive distillation system are more complex compared to other reactors or conventional distillation column. By considering the process is in steady state, the equilibrium stage model is described first.

2.4.1. Thermodynamics of Reactive Distillation

Thermodynamics are the key factor to reactive separation design which provide the basic relations used in the process models (Kai and Achim, 2003). If the assumption of phase and chemical equilibrium is used, only a limited amount of data are required to develop a model for RD process.

The phase equilibrium of the DMC synthesis system is complex due to the existence of a binary azeotrope mixture of DMC and MeOH (Huang et al., 2017). Hence, to obtain an accurate phase equilibrium of the system, UNIQUAC model is used. The UNIQUAC equation also used to describe the non-idealities in the liquid-phase.

Vapor-liquid equilibrium (VLE) data are available for all the binary pairs. Reaction kinetics is developed and VLE data available is used to predict the RD column performance and verify the model predictions. For azeotropic separations applications, the recommended property methods are Wilson, NRTL and UNIQUAC (Aspen Plus User Guide February, 2000).

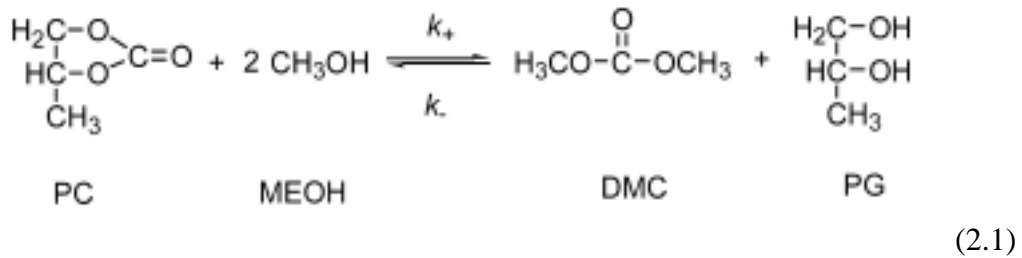
The Wilson model which cannot handle two liquid phases and is not supported for the prediction of liquid-liquid equilibria. Meanwhile, the concept of NRTL equation is

based on the hypothesis of Wilson that local concentration around a molecule is different from the bulk concentration. Therefore, the UNIQUAC model is preferable.

Among the published literature, the UNIQUAC model is frequently used by the researcher due to its suitability to the system. In Huang et al., (2014) and Hsu et al., (2010), VLE is described by a UNIQUAC model for the liquid phase and RK model for the vapor phase. Regression has been performed based on the experimental VLE data by obtaining the UNIQUAC model parameters of the system.

2.4.2. Reaction Kinetics

The reaction kinetics will depend on the type of reaction taking place. For instance, propylene carbonate react with methanol in the presence of a catalyst to form dimethyl carbonate and propylene glycol. The overall liquid-phase reversible transesterification reaction can be expressed as follow:



In the work published by Huang et al. (2014), the transesterification of PC and MeOH has been studied using sodium methoxide as a catalyst as it is a promising candidate in the industrial application. The kinetics equation of the reaction is expressed as follow:

$$r_{PC} = k_F C_{PC} C_{MeOH} - k_R \frac{C_{DMC} C_{PC}}{C_{MeOH}} \quad (2.2)$$

$$k_F = 16551.8 - \exp\left(\frac{41373.5}{RT}\right) \quad (2.3)$$

$$k_R = 19254.75 - \exp\left(\frac{28285.5}{RT}\right) \quad (2.4)$$

Equilibrium (EQ) Stage Models

For equilibrium stage model, the vapor and liquid phase are assumed to be in thermodynamic equilibrium. The fresh or recycled feeds are brought into contact with the vapor from stage below and liquid from the stage above. Hence, the vapor and liquid that leave the stage are assumed to be in an equilibrium with each other. Then, the equations that model equilibrium stages known as the MESH (material balance, phase equilibrium relation, summation equation, heat balance) equations. All the time derivatives of MESH equations are equal to zero if the reaction is considered under steady state conditions (Kai and Achim, 2003). Schematic diagram of an equilibrium stage is shown in Figure 2.2.

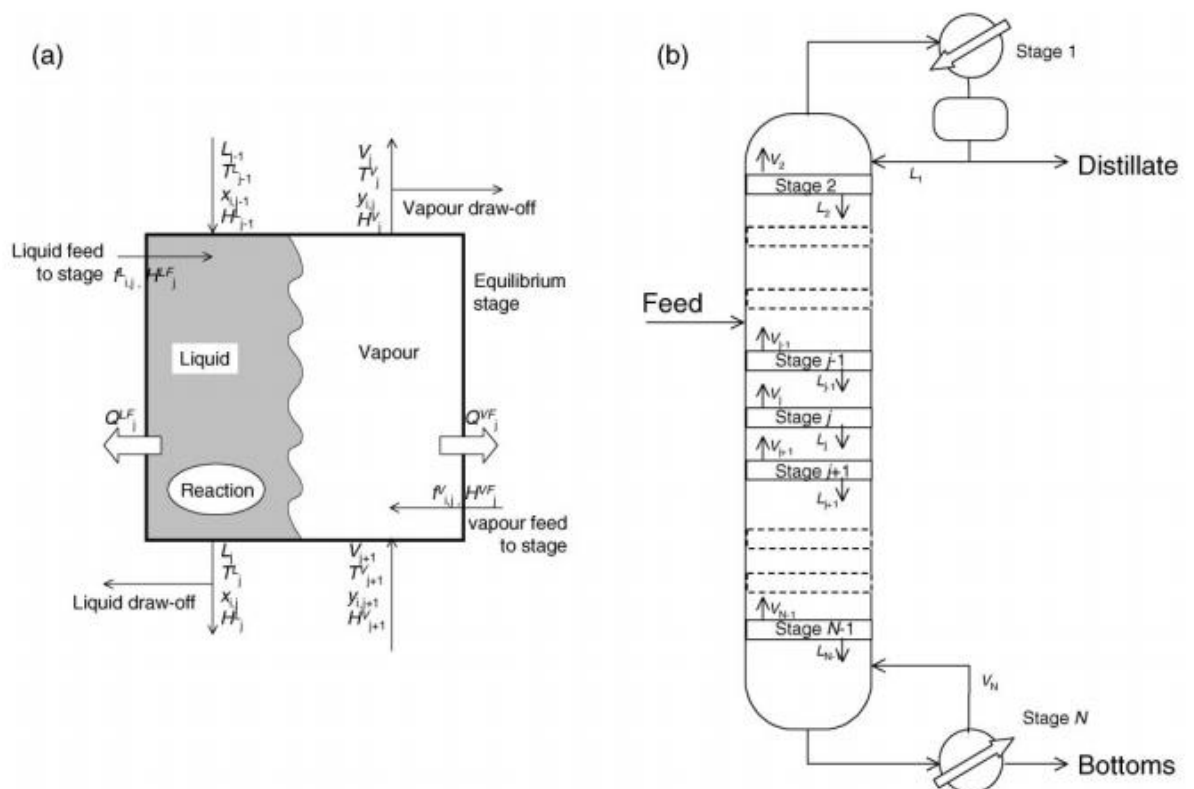


Figure 2.2 (a) The equilibrium stage. (b) Multi-stage distillation column.

From a dynamic equilibrium model as reported by Joel et al. (1987), the following assumptions were made:

- The mixture reaches reaction and phase equilibrium simultaneously on each tray.
- The solutions are dilute (temperature change can be neglected due to small difference).
- The liquid holdup is constant on each tray (the vapor holdup is neglected).

Constant molar overflow is assumed.

2.5 CONCEPTUAL DESIGN OF REACTIVE DISTILLATION

Many research and development activities are on trend to introduce the development of RD into other chemical processes. Hence, the development of reliable tools for the design of RD process become the important fields of current research activities (Kai and Achim, 2003). However, the combination of process reaction and separation in one-unit operation may cause the behaviour of RD become very complex.

Under such circumstances, the RD still offering the benefits of operation (Baur et al., 2000) (Moshood and Muhammad, 2006):

- Higher conversion for equilibrium-limited reactions.
- Azeotropes could be reacted away and simplifying the phase equilibrium behaviour.
- Improved product selectivity due to the removal of products from the reaction zone.
- Heat integration are obtained as the heat generated in the chemical reactions is used for vaporisation.

- Capital savings as two processes can be carried out at the same time,

Since an ideal two-reactant-two-product reactive distillation column are considered, the model assumptions are (Moshood and Muhammad, 2006):

- Ideal vapor-liquid equilibrium.
- Equimolar overflow except in the reaction zone.
- Constant relative volatilities.
- Heat of reaction and vaporization are fixed.
- Feed and reflux are saturated liquid.

The assumptions model used is to capture the essential dynamics and qualitative properties of a typical RD column.

2.5.1. Conceptual Design Methods

This design methods concentrate on the initial stages of the design of a reactive distillation column which obtaining some parameters such as number of stages, feed location and the operating parameters. A fixed-point method for single-feed reactive distillation columns was developed by Barbosa and Doherty (1988).

2.5.2. Optimisation Design Methods

Optimisation methods can cover the synthesis and the design steps. It can provide various column configurations and provide the optimum structure and operating parameters. It is also a time consuming methods and more suitable for analysing a wide variety of flowsheet configuration. This method is able to provide solutions which are close to the global optimum.

2.5.3. Graphical Design Methods

This method is very useful in the synthesis of various design alternatives, however, the information of the column design and operating parameters are limited. Also, the graphical methods can be applied to the mixtures with maximum of four components.

2.6 REACTIVE DISTILLATION DESIGN IN INDUSTRIAL PRACTICE

The reaction conversion has been increased in reactive distillation by removing the product and simplifies the separation by reacting away the azeotropes. The number of researches in this field has increased rapidly for process design, steady-state behaviour description and dynamics and control (Wang et al., 2010). Since transesterification known as a typical equilibrium-limited reaction, thus reactive distillation can be used to improve conversion.

CHAPTER THREE
MODELING AND SIMULATION STRATEGY

3.1 MATHEMATICAL MODELING

Based on Pilavachi et al., (1997), there are still no generally accepted design methods for reactive distillation. It is due to the difficulty associated with the modeling of the processes and the model parameters. The mathematical model equations can be established into mass balance equation, heat balance equation, phase equilibrium equation, summation equation and reaction kinetics equations (Fang, and Xiao, 2004). The schematic configuration of the reactive distillation column is shown in Figure 3.

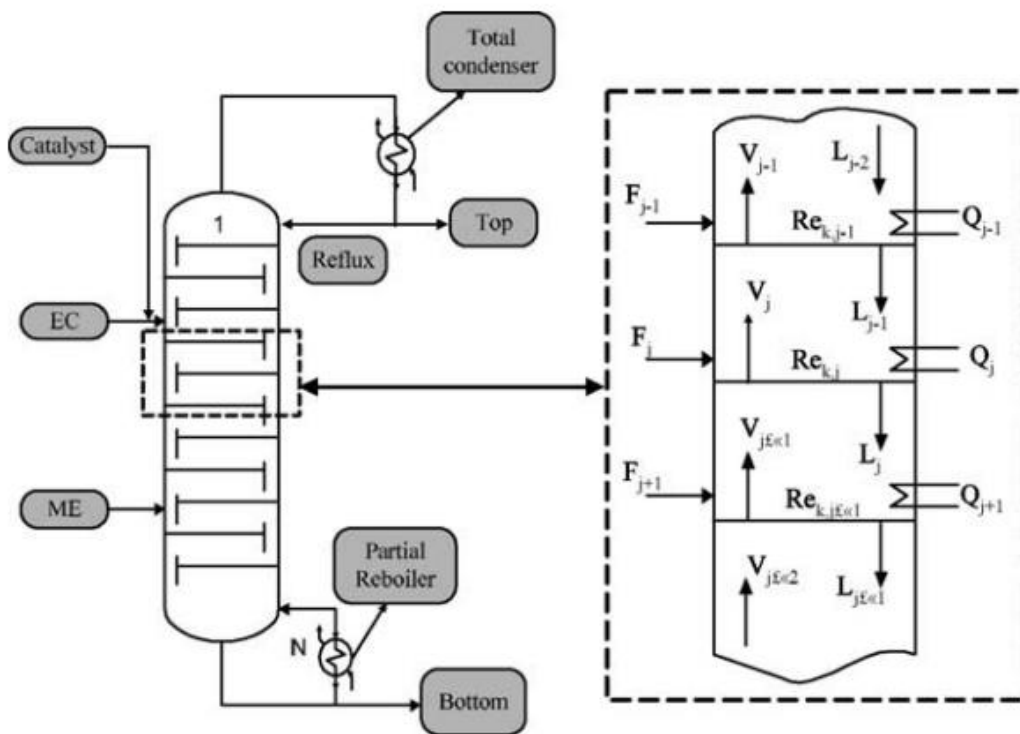


Figure 3.1 Schematic configuration of the reactive distillation column

Distillation is considered as a complex process where it consists of the process of mass transfer and separation. However, the reactive distillation also depends on the reactive process.

3.2 SIMULATION AND SOLUTION STRATEGY

Simulation defined as a process of running a model. Hence, before running a simulation, a model with complete parameters should be developed first. A computer simulation was applied to compare the result of real or established result data.

3.2.1. Simulation Procedures

Step 1: Data collection

All the necessary information regarding the modeling and simulation of reactive distillation column for the production of DMC were collected from literature. The required data such as synthesis of DMC, kinetic model and column specifications were also collected.

Step 2: Mathematical modeling study

The VLE is described by the use of UNIQUAC model for liquid phase and RK model for vapor phase. The traditional process of the DMC synthesis system at operating pressure of 101.3kPa is shown in Figure 3.2.

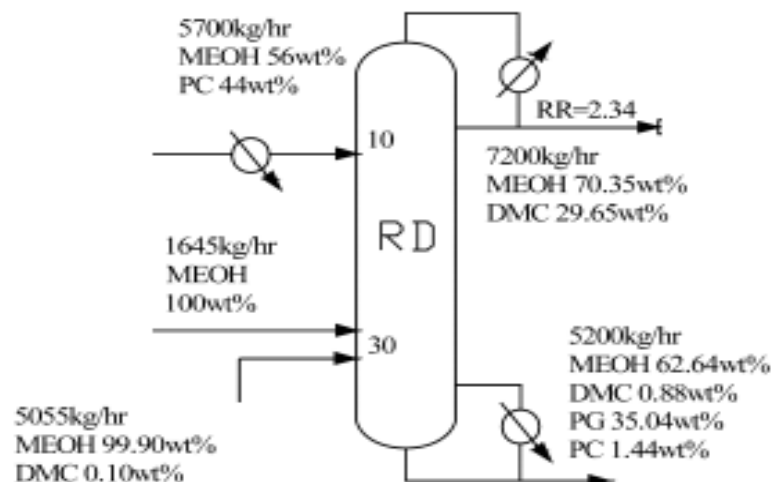


Figure 3.2 Flowsheet of the traditional process of DMC synthesis system.

Step 3: Simulation methodology flowchart

Figure 3.3 shows the methodology flowchart for Aspen Plus RADFRAC simulation.

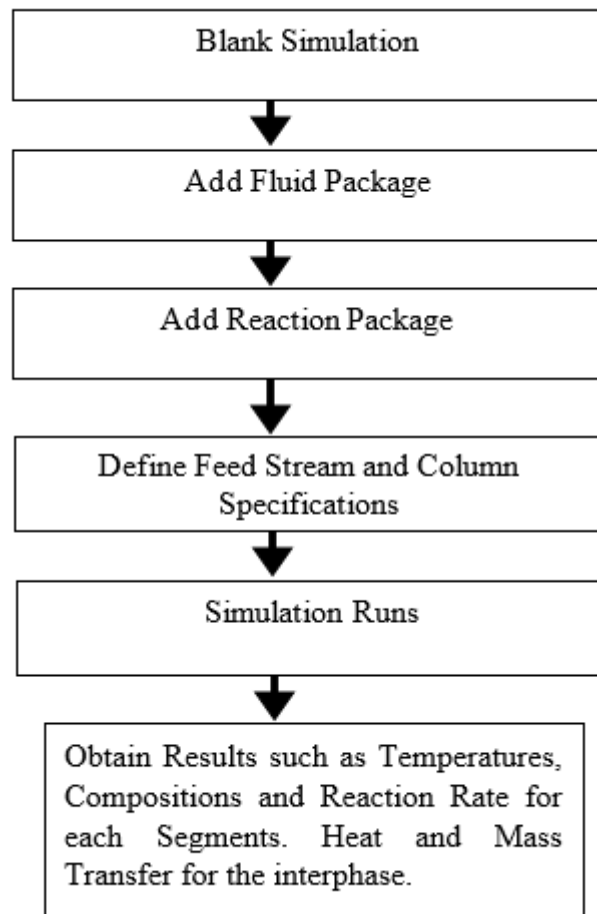


Figure 3.3 Aspen Plus RADFRAC simulation methodology flowchart (Chim et al., 2004).

Firstly, the appropriate module should be chosen for simulation. In Aspen Plus, the RADFRAC module was developed based on the rigorous equilibrium stage model which is used to describe the multistage vapor liquid transfer in the columns (Huang et al., 2014). In this research, the model was developed by selecting the RADFRAC

module to the flowsheet and add stream (inlet and outlet streams) to it. Then, entering all the process conditions and make sure the required input are filled.

Step 4: Simulation study and model verification

After presenting the model using Aspen Plus, run the simulation with the same conditions or parameters used by the published simulation work by other researchers from the literature. Error should be avoided when running the simulation. Then, compare the results from simulation with the published simulated values. If the simulated data obtained are on the acceptable range, thus the model equations are considered verified. Other conditions are then simulated by changing the parameters of the column specifications.

Step 5: Result analysis

The results obtained from the simulation with various conditions are then analysed it by plotting the graph and compare with the results from the literature. The reactive distillation column simulations are carried out using RADFRAC steady state model in Aspen Plus. The problem may have encountered during simulation in Aspen Plus include fatal error, severe error and warning with results.

3.2.2. General Thermodynamic Data for DMC System

The simulation can be done when all the required information and data are readily available. The general thermodynamic data needed in simulation can obtained from journal. The thermodynamic properties of components in DMC synthesis are presented in Table 3.1. Symbol of $h^{\circ}_{f,i}$ indicates the standard heat of formation of component and $\Delta h^{\circ}_{v,i}$ is values of the standard heat of vaporisation.

Table 3.1 Thermodynamic Properties for DMC synthesis at 298K, 1atm

Quantity	Unit	Component			
		MeOH	PC	PG	DMC
$h^{\circ}_{fL,i}$	kJ/mol	-238.40	-613.00	-500.30	-482.27
$\Delta h^{\circ}_{v,i}$	kJ/mol	37.34	61.30	62.20	37.70

Table 3.2 shows the critical and physical properties of components in DMC synthesis which collected from Perry and Green (1997), Thomas E. Daubert, R. P. Danner (1989) and Haynes (2014). T_c is the critical temperature, P_c is the critical pressure and T_b is the normal boiling point. Due to the unavailable data of critical temperature and critical pressure of propylene carbonate, Joback method is used to predict the critical temperature and critical pressure of propylene carbonate.

Table 3.2 Critical Properties and Boiling Points of Components in DMC synthesis

Component	T_c (K)	P_c (kPa)	T_b (K)
Methanol	512.40	814.00	337.70
Propylene Carbonate	650.09	5065.79	514.60
Propylene Glycol	626.00	604.00	460.30
DMC	545.00	4500.00	363.00

3.2.3. Design Guidelines for Reactive Distillation Column

The design of column specification become the important criteria to be discussed. The design guidelines are used to generate the initial estimation so that the design is within the optimum and relevant operating condition with respect to the production of DMC.

3.2.3 (a) Selection of Operating Pressure

The range of column pressure depends on condenser pressure and reboiler pressure (determined by condenser coolant temperature). In general terms, the operating pressure depends upon the reaction temperatures, relative volatility and the effect of pressure upon azeotropes (Almeida-Rivera et al., 2004). Based on the previous work, many researchers reported the operating pressure of reactive distillation column for the transesterification reaction as at atmospheric pressure (101.3kPa or 1 atm).

3.2.3 (b) Reactive Zone Location

The reactive zone location depends on the relative volatilities of reactant and product (Hoshang and James, 1999). The reactive zone section should be located where the concentration of at least one reactant (preferably the limiting reactant) is the maximum. Almost pure DMC can be obtained at the top of the RD column where PG is heavier component (less volatile product) and DMC is the most volatile product. For DMC synthesis, it is a four-component system with two intermediate-boiling reactants where the reactive zone should be located at the center of the RD column (Hoshang and James, 1999).

3.2.3 (c) Reactant Ratio and Feed Location

A right choice of feed location guarantees high concentrations of reactants in the reactive zone. A pre-reacted product containing feed enters the column ensuring the separation between reactants and products takes place on stages between the feed point and the reactive zone. The desirable requirement of reactants can be calculated from

product specifications and desired conversion at different operating pressures (Almeida-Rivera et al., 2004).

3.2.3 (d) Catalyst Mass

Inadequate catalyst volume reduces the residence time and gives poor conversion while excess value of catalyst may cause the product decomposition when it is not located appropriately (Hoshang and James, 1999). Some of the literature ignored the catalyst composition in simulation due to the very low catalyst concentration. However, an initial estimation value of catalyst mass is taken from Johannes (2013) who conduct the experiment of catalyst screening using batch reactor at atmospheric pressure.

3.2.3 (e) Number of Theoretical Stages

The number of stages can be estimated by using shortcut methods such as Fenske Underwood, especially for the non-reactive stripping and rectifying zones (Almeida-Rivera et al., 2004). The minimum number of stages proposed by researcher is 35 stages while maximum number of stages is 45 stages for the synthesis of DMC by transesterification of PC and methanol in the reactive distillation column.

3.3 ASPEN PLUS SIMULATION

Aspen Plus is a sequential modular simulation package which containing an extensive model library that lets most of the unit operations to be simulated easily and correctly (Kiran and Bhaskar, 2007). In additional, Aspen Plus also allow us to predict the behaviour of a process using basic engineering relationships. The purpose of the simulation is to model and predict the performance of a proposed model equation of a

process. Meanwhile, the results obtained from the Aspen Plus simulation are compared with the proposed model equations from the literature to get a verification of the proposed model. The RADFRAC module was chosen to describe the multistage vapour-liquid separation as the complexity of distillation and reactive distillation (Huang et al., 2014). In addition, RADFRAC can solve both equilibrium reactions and kinetically limited reactions. The effect of various operating conditions and parameters also can be detected. Aspen Plus also provide a wide range of tasks for us to perform by changing the specifications in the system.

Different from homogeneously catalysed simulation, the heterogeneously catalyst simulation is done in Aspen Plus by adding the packing section. Before simulating, the calculation type in Aspen Plus is set as “Rated-Based” to obtain the HETP value.

However, in this thesis, our focus will be on the production of DMC inside the reactive distillation column. Simulation is done only on the RD column with the flowrate from bottom of the low pressure (LP) column as the third feed (recycle feed) to the RD column.

3.4 HOMOGENEOUSLY CATALYSED DMC SYNTHESIS

A set data of basis for simulation has been set first to simulate the reactive distillation process for DMC synthesis. Those basis data include operating pressure, reactive zone location, feed stage location, number of theoretical stages, bottom flow rate and reflux ratio. For homogeneously catalysed system, the catalyst is assumed to be mix with reactants throughout the whole column.