SIMULATION OF REACTIVE DISTILLATION COLUMN OF METHYL TERT- BUTYL ETHER PRODUCTION

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by

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ABSTRAK

Penyulingan reaktif adalah teknik gabungan antara tindak balas dan pemisahan yang berkesan dalam satu unit yang bermanfaat untuk reaksi terhad keseimbangan, menjimatkan kos, mengurangkan tenaga dan meningkatkan kemurnian produk. Penggunaan lajur penyulingan reaktif telah mendapat perhatian yang lebih banyak kerana berpotensi tinggi untuk intensifikasi proses dan oleh itu proses ini perlu dikaji sepenuhnya sehingga penukaran reaksi dan kemurnian produk terjamin sebelum pelaksanaannya dalam skala industri. Dalam karya ini, Aspen Plus digunakan untuk simulasi tiang penyulingan reaktif di mana metanol dan butena mengalami reaksi esterifikasi untuk menghasilkan metil tert-butil eter (MTBE) dan menjalani proses pemisahan berterusan. Pertama, hasilnya dibandingkan untuk kajian eksperimen dan simulasi. Hasil simulasi yang diperoleh oleh Aspen Plus menunjukkan bahawa rentang yang dapat diterima kerana nilai simulasi mematuhi literatur dengan kesalahan kemurnian atas dan bawah untuk MTBE masing-masing 0.0048% dan 0.0026**%.** Dalam ketagihan, hasil simulasi telah dilakukan untuk analisis kepekaan. Analisis kepekaan pada model RadFrac yang sama menunjukkan bahawa nisbah refluks, bilangan tahap reaktif, dan reboiler mempunyai kesan yang signifikan terhadap penukaran metanol dan kemurnian MTBE. Analisis kepekaan yang dilakukan menunjukkan bahawa kesucian mtbe dan penukaran metanol adalah maksimum pada nisbah refluks 7. Lokasi suapan terbaik untuk butena pada tahap 3 manakala metanol memberi makan pada tahap 12.

ABSTRACT

Reactive distillation is an efficient technique of combination of both reaction and separation in a single unit beneficial for equilibrium-limited reactions, cost-effective , reduce energy and improvement purity of the product**.** The usage of reactive distillation column has increased attention because of its high potential for process intensification and therefore this process needs to be studied fully so that the reaction conversion and purity of the product are assured before its implementation in industrial scale. In this work, Aspen Plus was used for simulation of reactive distillation column where methanol and butene undergo esterification reaction to produce Methyl tert-butyl ether (MTBE) and undergo continuous separation process. Firstly, the results are compared for both literature and simulation studies. The simulated results obtained by Aspen Plus showed that it is acceptable range since the simulation values obeyed that of the literature with a purity errors of top and bottom for MTBE is 0.0048% and 0.0026% respectively**.** In addiction, simulation results have been performed for sensitivity analysis. Sensitivity analysis on the same RadFrac model showed that reflux ratio of 7, number of reactive stages at 10, and reboiler of 11.45 have significant effects on met MTBE purity. Sensitivity analysis conducted shows that the MTBE purity were maximum at reflux ratio 7. The best feed location for butene at stage 3 while methanol feed at stage 12.

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CHAPTER ONE

INTRODUCTION

1.1 REACTIVE DISTILLATION

Reactive distillation (RD) is an efficient process intensification where it involves instantaneous chemical reaction and distillation process in a same unit operation. Reactive distillation consists of reactive section, non-reactive rectifying and stripping section in a column. The conversion limits for reversible reactions are difficult to surpass towards the highest product purity as no further reactants can be transformed into products once the equilibrium is reached. But, RD act as a process intensification in which reaction and separation of product take place simultaneously in a single column. (Ahmed & Ahmad, 2020).By considering an example of a reversible reaction as shown in equation 1.1,

$$A + B \Leftrightarrow C + D \qquad \text{eq1}$$

This process consists of reactor followed by a sequence of distillation column if the process run in the conventional figure 1.1.The mixture of A and B is fed to the reactor with a specific flow rate, where the reaction takes place in the present catalyst and reaches equilibrium. Catalyst is a substances that increase a chemical reaction without itself undergoing any permanent chemical change. Distillation column in a series is required to produce pure products C and D. The unreacted components, A and B are recycled back to the reactor to increase the production selectivity. The 3 section which is reaction section in the middle, rectifying section in the top, and stripping section at the bottom of the column. In the rectifying section is to recover reactant B from the product stream C. The reactant A is stripped from the product stream D in the stripping section. In the reactive section the products are separated in situ, driving the equilibrium to the right preventing any undesired side reactions between the reactants A or B with the product C or D. In perspective on

this load of limitations, reactive distillation emerged as a novel procedure of process where reaction and separation of product occur all the while in a single column.(Sakhre, 2019)

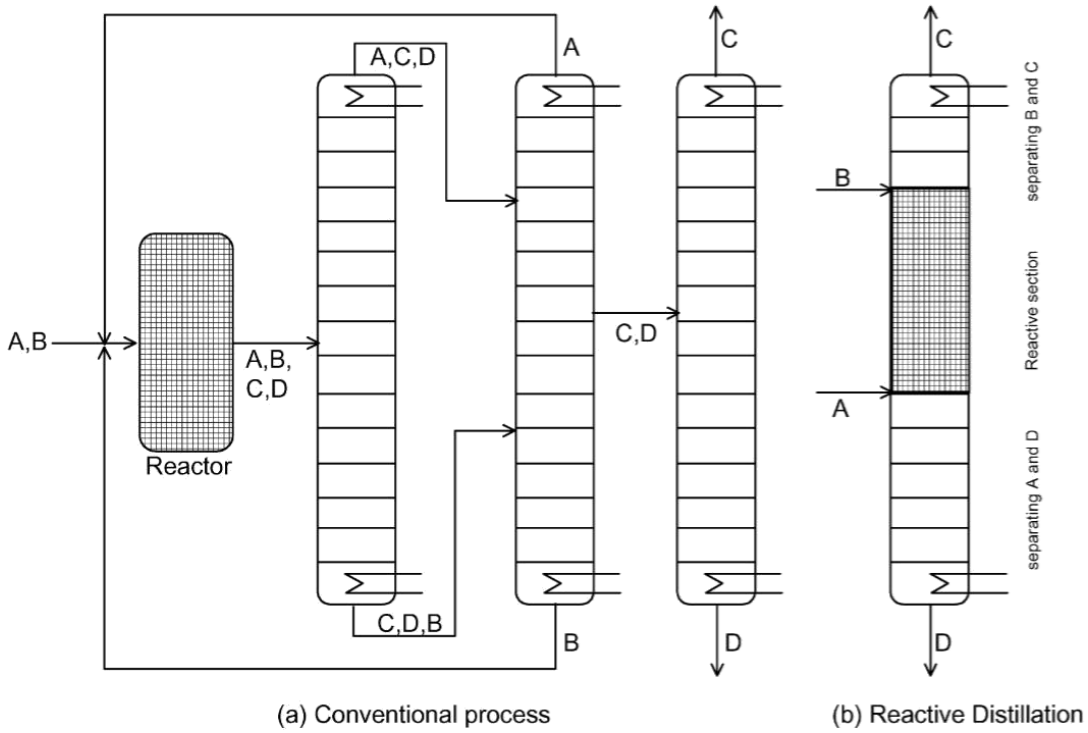

Figure 1.1: Schematic diagram of reactive distillation column (RDC).

(a) typical configuration of a conventional process (b) the reactive distillation configuration

The synthesis of MTBE using reactive distillation is in the best and biggest utilization of process intensification.(Gautam et al., 2013). It can improved reaction rates, increased conversion, upgraded reaction selectivity, and decreased operating expenses are a few of the benefic in reaction distillation. This elements adds to the developing commercial significance of reaction distillation. In any case, the necessary consideration regarding reducing the energy usage and increased the effectiveness of the current reactive distillation column is focused in this work.

1.2 METHYL TERTIARY BUTYL ETHER (MTBE)

Methyl tertiary butyl ether (MTBE) is a super charged fuel addictive organic compound with structural formula (CH3)3COCH3. MTBE highly flammable, volatile, colorless liquid that sparingly soluble in water. Primarily used as a fuel addictive and it is blended into gasoline to reduce unwanted emissions.(Hömmerich & Rautenbach, 1998).MTBE is a clean air component in gas, and is reputed to be the world's quickest developing chemical.

MTBE is produced by reacting isobutene with methanol over a catalyst bed. The isobutene can be obtained from C4 stream from a steam cracker with the butadiene removed known as Raffinate-1 which is a mixture of isobutene and 1- and 2-butenes. The butane fractions from a catalytic cracker and n-butane which is isomerized to isobutane and then dehydrogenated to isobutene. The reaction of methanol and isobutene can take place in a liquid phase reactor containing an acidic ion exchange resin. The reaction mixture is distilled to produce high purity MTBE.

1.2 INDUSTRIAL APPLICATION OF METHYL TERTIARY BUTYL ETHER (MTBE)

MTBE is utilized as a fuel component in fuel for gasoline engines. The blending research octane number of MTBE is 105-123. MTBE commonly known as oxygenates because it increases the oxygen content of gasoline. In the U.S MTBE has been used in gasoline at low levels since 1979, replacing tetraethyllead (TEL) as an antiknock to prevent engine knocking. Oxygenates also help gasoline burn more completely, decreasing tailpipe emissions and dilute or displace gasoline components such as aromatics (benzene). Before the introduction of other oxygenates and octane enhancers, refiners chose MTBE for its blending characteristics and low cost. Furthermore, MTBE is extensively used in industry as a safer alternative to diethyl ether which is commonly used in

academic research as the tert-butyl group prevents MTBE from forming potentially explosive peroxides..

1.3 PROBLEM STATEMENT

Reactive distillation is a well-established process that can build the production of MTBE. Even though, it is still exceptionally complicated process and difficult to control due to the complexities in the design, synthesis and robustness of RD processes resulted from reaction and distillation interactions. As the parameters of reaction kinetics in continuous RD process is unknown, researches use parameters of reaction kinetics of batch process. So, it is very important to study the reaction kinetics parameters of batch process to match the continuous reaction of reaction distillation and other operating condition of RD as well to identify accurate and precise methods to ensure that the operation of the reactive distillation for MTBE.

1.4 OBJECTIVES

1. To simulate for reactive distillation for production of Methyl Tertiary-Butyl Ether and compare with literature.
2. To study the effect of reflux ratio, reboiler duty, reaction stages towards the conversion of methanol and MTBE fraction by using Sensitivity Analysis Tool in Aspen Plus V10

1.6 ORGINISATION OF STUDY

The contents for each chapter in this study is explained as below:

Chapter 1 summaries the overall details of this research about reactive distillation, MTBE, issue proclamation, objectives, and extent of study.

Chapter 2 clarify literature review on reactive distillation, MTBE, industrial reactive distillation process, reactive distillation measure modeling, Aspen Plus programming and reaction distillation process thermodynamics

Chapter 3 clarifies the methodology of the research. It includes measures to make simulation flows for the RadFrac model of reactive distillation for MTBE production followed by sensitivity on operating variables like reflux ratio, number of reactive stages, and reboiler duty and furthermore measure process optimization Aspen Plus version 10.

Chapter 4 discuss the outcome and analyze the results of the simulation. First and foremost, the simulated results were contrasted with those in literature. Then, at that point, the effects of the selected variables were examined and studied. Finally, this section also discussed about the outcomes got from sensitivity analysis.

Chapter 5 concludes every one of the findings got in this study. This part additionally gives recommendations to enhancing the current results of the study.

CHAPTER TWO

LITERATURE REVIEW

2.1 CONCEPT OF REACTIVE DISTILATION

Reactive distillation (RD) is a process where the separation of the product from the reaction mixture does not effects with a different distillation step which saves energy (for heating) and materials. The reactive distillation innovation for MTBE production has been created in the mid 80's (Smith and Huddleston, 1982). Reactive distillation process couple chemical reactions and physical separations into a single unit operation.(Gautam et al., 2013).The in-situ removal of products for an equilibrium limited chemical reaction in RD helps in acknowledging improved conversion, increased selectivity, and diminished recycles. (Krishna et al., 20. Consequently, the advantages of the MTBE reactive distillation can fill in as a significant tool in predicting and analyzing the ideal production for MTBE without the need to run the actual analysis, so the enhancement of the MTBE reactive distillation is fundamental to stimulate the process which can cause high MTBE production. (Sudibyo et al., 2011).. The benefits of using reactive distillation are as (Kanse, 2019):

1. Lesser wastes and less by-products and reaction conversions can be increased by overcome chemical balance limitations through the evacuation of reaction products.
2. Lower capital and operational expense since the quantity of equipment utilized have been decreased, along these lines the lower energy utilization and least equipment dealing with required. This kind of combination lessens costs in pumps, piping, and instrumentation.
3. Chemical equilibrium limitation can be overcome to build the conversion of the reaction moving toward 100 %. As indicated by Le Chatelier's guideline, the removal of product

from a system at equilibrium cause more product to produce. Along these lines, RD builds the change of a equilibrium-limitations reaction beyond its thermodynamic limit.

4. Non-reactive azeotropes may vanish under reaction distillation conditions. Azeotropic mixture constraint can be overwhelmed by reaction. RD measure is especially gainful when the reactor product is a combination of species that can form a few azeotropes with one another. RD conditions can permit the azeotropes to be "responded away" through reaction.
5. Improved product quality-reducing opportunity for degradation, considering less heat, heat duty can be diminished by using the heat of reaction. For exothermic response, the heat released during the reaction can be utilized for vaporization of liquid during separation. This saves energy costs by the decrease of reboiler duties
6. Increased speed and improved effectiveness and better temperature control. The maximum temperature in the response zone is typically restricted to the limit of the response combination to stay away from boiling of mixtures, with the goal that the risk of problem area development on the catalyst is decreased essentially. Thusly, a basic and dependable temperature control can be accomplished.
7. An equilibrium reaction can be headed to completion by separation of the products from the reacting mixture. Distillation columns operate at higher liquid and vapor flow rates than conventional reactors. Accordingly, faster removal of products from the reaction zone of the column is conceivable and may diminish the likelihood of consecutive reactions occurring. Eliminating one of the products from the reaction mixture or keeping a low concentration of reagents will prompt diminished side reaction rates and along these lines improved selectivity for the desired products and decreased by-product development. As such more modest measures of waste and by-product are produced.

2.2 THERMODYNAMICS OF REACTIVE DISTILLATION

Thermodynamics considered a significant part in understanding and planning this process. As like conventional processes, thermodynamics properties and equilibrium are fundamental for RD process. However it is more complicated as reaction and separation happen at the same time. This process combination can be generously streamlined through the implementation of a counter-current column, in which both the reaction and distillation happen.. Furthermore, thermodynamics gives the essential relations, for example, energy balance of equilibrium condition, utilized all the process, model, which again are the way to reactive distillation design (Sundmacher and Kienle, 2006).

2.3.1 MODEL DESCRIPTION

The RD column comprises of 17 stages, including an total condenser and a partial reboiler. Reactive stages are situated in the middle of column, stage 4 down to and including stage 11. In Aspen , the numbering of the stages is top descending, the condenser is stage 1 and reboiler is last stage. MTBE is produced by reaction of butene and methanol.

2.3.2 EQUILIBRIUM MODAL

The equilibrium stage model expects that the vapor and liquid stream leaving at given stage are in thermodynamic equilibrium (Krishna and Taylor, 1985). In EQM model, with legitimate beginning estimates, the simulation converges to a high mole fraction of MTBE in the bottom product. In EQM, vapor and liquid accepts to be in thermodynamic equilibrium in a stage.(A., 2014).Vapor liquid equilibrium model (VLE) is used to calculate the liquid phase activity coefficient of a liquid

mixture. There several VLE model that used in for production MTBE usually used such as that explained in the **(**Pereira, 2018**):**

- UNIQUAC (Universal Quasi-Chemical) model

  UNIQUAC is relevant in the analysis of VLE, LLE and vapor-liquid equilibrium cases. UNIQUAC model additionally offers another critical benefit because of the way that the component concentrations are a function of volume and area portions rather than mole fractions. Likewise, the UNIQUAC model can be applicable to wide scope , including small and large molecule.

2.3.3 REACTION KINETICS AND CHEMICAL EQUILIBRIUM

MTBE synthesis process takes place in the liquid phase, commonly occurring at a temperature range between 50 °C and 100 °C from methanol and isobutene, where the liquid-phase reaction is catalyzed by ion exchange resin (heterogeneous reaction).

The reaction scheme is :

$$\text{i-C4H8} + \text{CH3-OH} = \text{C5H12O} \qquad \text{eq2}$$

N-butene is inert for the reaction, the mixed butene feed for MTBE synthesis consists of about 40% isobutene and 60% n-butene. Methanol is fed in excess to increase the conversion of isobutene into MTBE. MTBE forms azeotropes with methanol and isobutene, so to get high purity of MTBE become more complex. However, reactive distillation can handle this problem because reactive distillation process allows for “reacting away” the azeotropes.

2.4 ASPEN PLUS SOFTWARE

Specialists from MIT's Energy Laboratory have made a model for process simulation and they named it as Advanced System for Process Engineering which is generally known as ASPEN PLUS. It gives a thorough incorporated explanation to handle design and a appropriate selection of thermodynamic models, AP utilizes numerical models to predict the performance of the interaction.(Ortega, 2019).Many interaction designing parts includes this product from design and benefit analysis. It additionally offers worked in model library for unit operations such reactors, distillation columns, separators, heat exchangers and others. It can likewise deal with exceptionally complex cycles, for example,

- Multiple-column separation systems
- Chemical reactors
- Distillation of chemically reactive compounds
- Electrolyte solutions such as in Chlor-Alkali Industry
- Complex Recycle – Bypass Stream in Processes

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CHAPTER THREE

METHODOLOGY

3.1 RESEARCH METHODOLOGY

Overall, this project will be focused on the simulation of reactive distillation of methanol and butene stream to produce MTBE. ASPEN PLUS is utilized to stimulate the reaction and separation processes and compare with literature review. After successfully compared with literature the simulated model is used for sensitivity analysis

Process Description

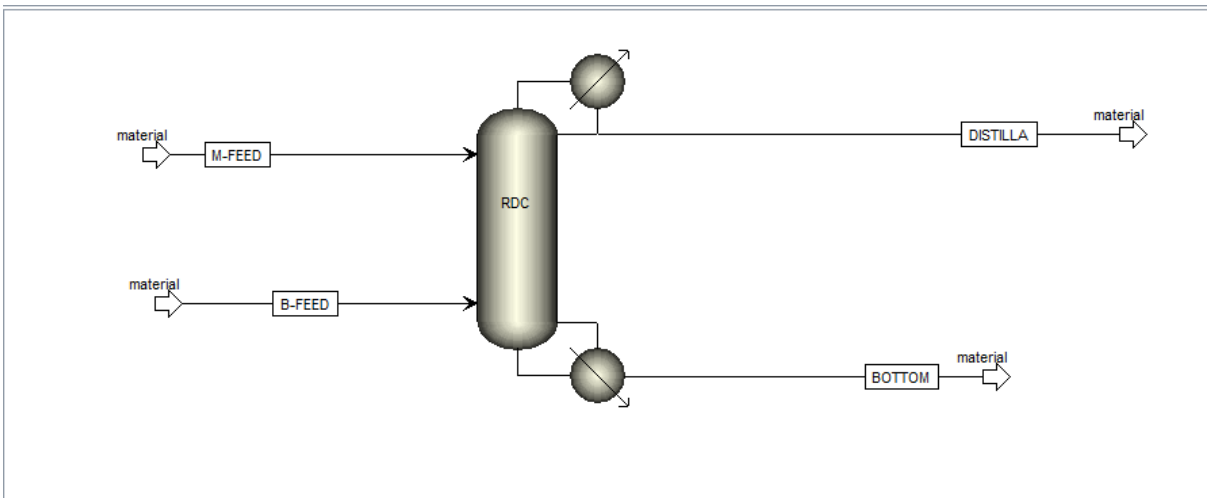


Figure 3.1: Reactive distillation model or 'RadFrac' Column used in the simulation

Firstly, a proper reactive distillation column (Radfrac segment) was chosen for simulation with suitable property method which is UNIQUAC. Two feed streams are defined which are butene stream which consists of 40% isobutene and 60% N-butene and methanol stream. Butene stream

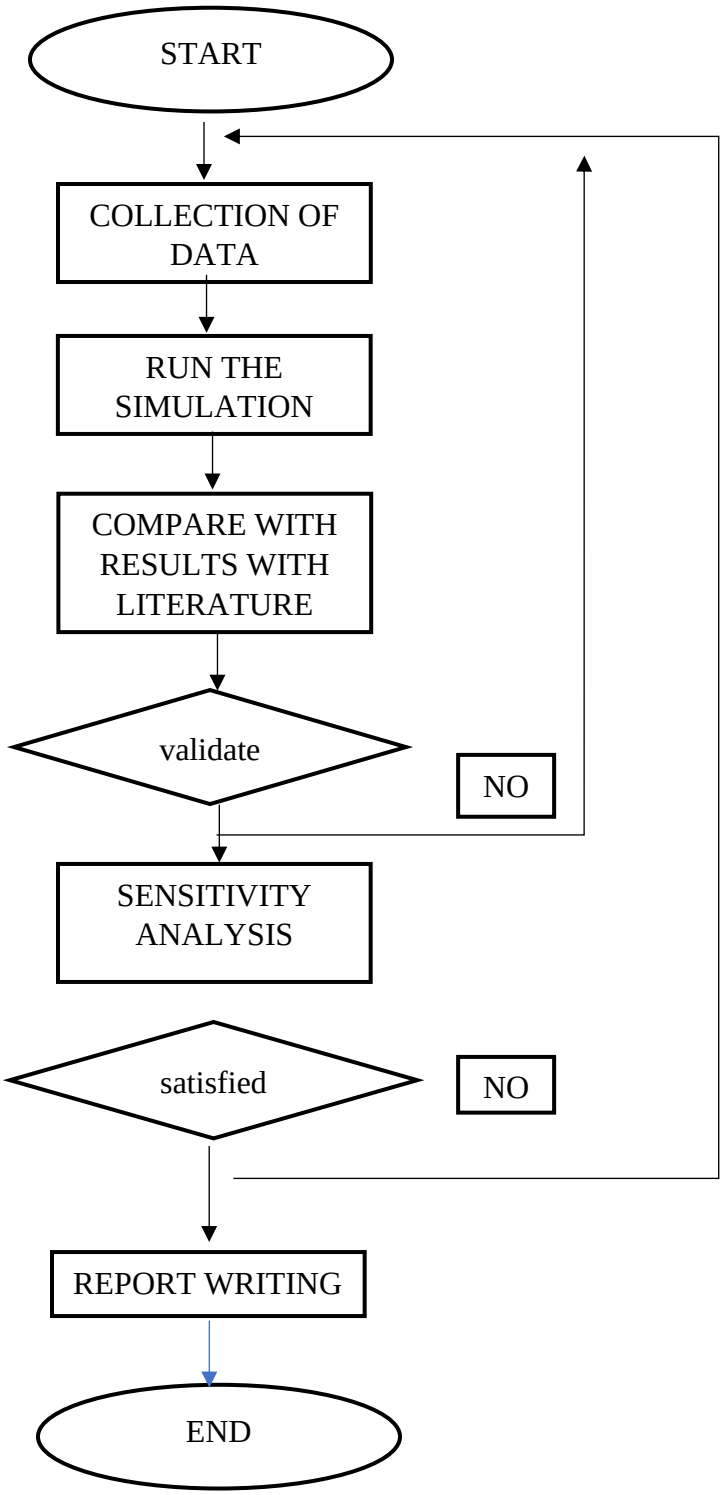
with temperature of 350 K and pressure of 12 atm while methanol stream with temperature of 320K and pressure of 12 atm. As for specifications of chosen RDC, the reflux ratio is set to 7 and the boilup ratio is set to 11.45 with calculation type is defined as equilibrium. For column internals, from stage 2-3 (rectifying section), from 4-11 (reaction stages) and 12-16 (stripping section). The stream results obtained where MTBE as bottom product and N-butene as top product. If the validation satisfactory, operating variables like the reflux ratio, number of reactive stages, and reboiler duty were analyse in the Sensitivity Analysis Tool in Aspen Plus.

Assumption made in the simulation of MTBE production through reactive distillation process are stated below:

- Butene and methanol is feed to the RD column.
- No accumulation in the RD column.
- No side reaction of dehydration of methanol to dimethyl ether (DME) and water since most studies do not consider it because it is usually can be ignored
- Backward reaction is negligible since continuous product removal from the system.

3.2 RESEARCH METHODOLOGY STEPS

Figure 3.2 shows the summary of methodology steps involved in this research work.



3.2.1: Step1: DATA COLLECTION

The simulation work was continued when identified variables and parameters extracted from main literature.

Parameters	**Values**	
Number of stages	17, including reboiler and condenser	
Reactive stage	4-10 (reactive zone)	
Rectifying stage	2-3	
Stripping stage	11-16	
Input condition	Methanol (stage 3)	butene (stage 6)
Temperature	320 K	350 K
Flow rate	215.5 mol/s	549 mol/s
Reboiler heat duty	11930900 cal/sec	
Reflux ratio	7	
Condenser temperature	350 K	
Distillate rate	1340 kmol/hr	
Reflux rate	9382 kmol/hr	
Reboiler temperature	420 K	
Bottom rate	708 kmol/hr	
Boil up rate	8113 kmol/hr	

Table 3.1 of Data Collection (Sakhre, 2019)

3.2.2: STEP 2 RUN SIMULATION

The reactive distillation process model was run using the steps are shown in Figure 3.1 and the steps explained in detail.

a) Define the Flow sheet

1. A new blank simulation was chosen on Aspen Plus.
2. A process flow sheet window was selected once a new blank simulation is chosen. RadFrac model under Column's tab was chosen and named as RD block in the process flow sheet window as demonstrated in Figure 3.1.
3. Four material streams were associated with the RD block and named as 'M-FEED'' and 'B-FEED' for feed streams and 'DIST' and 'BOT' for item streams.

b) Define the components

Three components associated with for example, butene, methanol and MTBE were defined. Every one of the 3 components and their physical properties data are presents in aspen information.

c) Define the Property Method

The UNIFAC model was selected which were readily available for use in simulation.

d) Define Stream Data

All the necessary stream information were defined in the feed stream M-FEED and feed stream B-FEED.

e) Column specification

In the setup option, the computation type was set to Equilibrium. The total number of stages are 17 numbered top-down. Stage 1 is condenser and stage 17 is the reboiler. The wide range of various info conditions that recorded in Table 3.1 were entered.

f) Run Simulation

Simulation was run and the results were obtained under the Results Summary tab.

3.2.3: COMPARISION OF LITERATURE WITH ASPEN RESULTS

The results from the Aspen Plus simulation compared with the results from the literature. In this progression, mole fraction, temperature top and bottom, reflux ratio, reboiler heat duty, and MTBE purity are compared with literature and the errors were determined. The simulated model is viewed as approved and acknowledged as the percentage error of MTBE is 0.0048% and 0.0026% at top and bottom respectively.

3.2.4: SENSITIVITY ANALYSIS

Sensitivity analysis is a useful procedure that allows the users to analyze the effect on process outputs of changes in input variable. It was utilized to control at least one flow sheet variables and to analyze their impact on other stream sheet variables. In this work, sensitivity analysis is done for the MTBE reactive distillation system by analyzing reflux ratio, number of reaction stages and reboiler duty and study the impacts of the variables on the reactive distillation operation predominantly focused on the MTBE purity.

CHAPTER FOUR

RESULTS AND DISCUSSION

MTBE fraction in the reactive distillation column have been simulated depend on the information from the literature and from AspenPlus10 to produce MTBE. The simulation is to observe the process lastly to analyze using sensitivity analysis. The column consists of 17 stages including a total condenser and a partial reboiler. The column consists of three zones: rectification section stage 2, in which separation of inert takes place from unreacted components, reactive zone (4-11) in which methanol and isobutene react to form MTBE, stripping section (12-17) in which separation of product from unreacted components takes place. In the production of MTBE, the mole fraction of MTBE should be high in the bottom stream.(Ahmed & Ahmad, 2020).Total number of stages, feed stages and column and feed specifications are kept constant for both the temperature profiles and composition profiles under steady state simulation. All further simulation were finished utilizing a reflux ratio equivalent to 7. Reflux ratio of 7 was chosen as optimum as beyond this value the increased reflux had little impact on MTBE purity in the distillate. The product composition constantly increased and when concentration of reactants diminishes, the composition likewise diminishes. For continuous process, continuous supply of reactants is needed to keep up the product composition synthesis. We have set the reboiler temperature at 343K which is close to boiling point of methanol. Anyway, it differs as the reaction continues. The composition of MTBE got experimentally is 95%.(Sakhre, 2019).This chapter is divided into two parts. The first section is process validation. Comparisons of results obtained from the from literature and results from ASPEN Plus V10 simulation are discussed . The second section is related to sensitivity analysis.