SIMULATION OF METHYL ETHYL KETONE (MEK) PRODUCTION IN A FIXED BED REACTOR

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by

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FATIN NUR LIYANA BINTI MOHD IDRIS,

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LIST OF SYMBOL

Symbol	Description	Unit
d_p	Length	m
ρ_p	Particle density	kg/m^3
λ_s	Thermal conductivity	W/(m.K)
c_p	Heat capacity	kJ/(kg.K)
$\varepsilon_в$	Porosity of the bed	-
X	Conversion	%

LIST OF ABBREVIATIONS

Al_2O_3	Aluminium oxide
BET	Brunauer–Emmett–Teller
CDS	Chemical Data System
C_4H_8	Butene
CH_2O_2	Formic acid
$C_3H_6O_3$	Lactic acid
$C_4H_6O_4$	Succinic acid
$C_4H_8O_2$	Acetoin
$C_4H_{10}O_2$	2,3-Butanediol
$C_6H_{12}O_6$	Glucose
CO_2	Carbon dioxide
COPRE	Co-precipitation
Cr_2O_3	Chromium oxide
Cu	Copper
CuO	Copper oxide
DRUV-Vis	Diffuse Reflectance UV–Vis
EDTA	Ethylenediaminetetraacetic acid
H_2	Hydrogen gas
H_2O	Water
H_3PO_4	Phosphoric acid
IM	Impregnation
ICP	Inductively coupled plasma
La_2O_3	Lanthanum oxide
MEK/ C_4H_8O	Methyl Ethyl Ketone

MgO	Magnesium oxide
O_2	Oxygen
PFR	Plug Flow Reactor
RPLUG	Plug Flow Reactor
RSM	Response Surface Method
SBA/ C_4H_9OH	Sec-Butanol Alcohol
SG	Sol-gel
SiO_2	Silicon dioxide
TEA	Triethanolamine
TPR	Temperature-Programmed Reduction
UNIQUAC	Universal QuasiChemical
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray diffraction
Zn	Zinc
ZnO	Zinc oxide

SIMULASI PENGELUARAN METIL ETIL KETON (MEK) DALAM REAKTOR KATIL TETAP

ABSTRAK

SBA atau sec-butanol alkohol merupakan produk perantaraan untuk menghasilkan metil etil keton (MEK) yang merupakan pelarut untuk ejen dan pembuang cat pembersihan. Proses nyahhidrogenan SBA telah disimulasi, dianalisis dan dioptimumkan dengan simulator Aspen Plus versi 8.8. SBA model nyahhidrogenan dihasilkan dan disimulasi di Aspen Plus. Reaktor katil tetap merupakan reaktor berbilang tiub dimodelkan oleh reaktor aliran palam (PFR). Hasil yang diperolehi bagi pengesahan menunjukkan keputusan simulasi hampir mengikuti trend data literasi pada SBA penukaran di mana ralat yang paling tinggi ialah 18% dan yang paling rendah ialah 0.1%. Selain itu, analisis sensitiviti dilakukan dengan menggunakan model alat analisis dalam Aspen Plus untuk mengkaji kesan tindak balas tekanan, suhu dan kadar aliran suapan SBA ke penukaran SBA. Nilai optimum diperolehi dalam analisis sensitiviti adalah 0.5 bar, 400 ° C dan perubahan yang terlalu kecil untuk kadar aliran suapan SBA. Dalam seksyen pengoptimuman, tujuannya adalah untuk mengurangkan kadar aliran molar SBA di aliran produk untuk mencapai tertinggi dioptimumkan penukaran SBA. Pengoptimuman itu dapat dioptimumkan nilai SBA kadar aliran molar sebanyak 13.4911 kmol / jam dengan tertinggi dioptimumkan SBA penukaran yang merupakan 99.96% apabila suhu optimum dan tekanan masing-masing adalah 550 ° C dan 0.5 bar.

SIMULATION OF METHYL ETHYL KETONE (MEK) PRODUCTION IN A FIXED BED REACTOR

ABSTRACT

SBA or sec-butanol alcohol is an intermediate product in order to produce methyl ethyl ketone (MEK) which is a solvent for cleaning agents and paint removers. SBA dehydrogenation process has been simulated, analysed and optimized with the Aspen Plus software version 8.8. SBA dehydrogenation model is developed and simulated in Aspen Plus. The fixed bed reactor which is multi-tubular reactor are modelled by plug flow reactor (PFR). The result obtained for the validation shows the simulation results almost follow the trend of the literature data on SBA conversion whereby the highest error is 18% and the least is 0.1%. Besides, sensitivity analysis is performed in model analysis tool in Aspen Plus to study the effect of reaction pressure, temperature and SBA feed flow rate towards the SBA conversion. The optimum values obtained in sensitivity analysis are 0.5 bar, 400°C and insignificantly changes for the SBA feed flow rate. In optimization section, the objective is to minimize the molar flow rate of SBA at the product stream in order to achieve highest optimized SBA conversion. The optimization is able to optimized the value of SBA molar flow rate at 13.4911 kmol/hr with highest optimized of SBA conversion which is 99.96% when the optimum temperature and pressure are 550°C and 0.5 bar respectively.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Butanol can be considered as an important industrial chemical which is useful as a fuel additive, feedstock chemical in the plastic industry and food grade extractant in the food and flavor industry. Every year, 10 to 12 billion pounds of butanol are produced by petrochemical implies and the requirement for this commodity will probably increase (Bramucci, et al., 2013). Sec-butanol alcohol (SBA) is an intermediate product in order to produce methyl ethyl ketone (MEK) which is a solvent for cleaning agents and paint removers. Since SBA is an isomer of butanol it is anticipated to have similar fuel properties. Besides, volatile esters of SBA are used in perfumes and artificial flavors. It is a chiral compound, and hence it exists as two enantiomers (Waldron, 2010).

MEK is a volatile, highly flammable liquid, colorless organic liquid with acetone-like odor (Foxall, 2010). MEK can form azeotropes with a number of organic solvents since it is partially miscible with water and many conventional organic solvents (Melorose, et al., 2015). In safety and health, methyl ethyl ketone does not cause a significant threat to the environment except in cases of major spills or discharges. It is also a relatively safe organic solvent (Organization, 2014) and there are no prove on methyl ethyl ketone causing cancer to humans (Foxall, 2010). The production of MEK is important for automotive, construction, electronic and furniture industries based on local and global demand.

MEK is produced by dehydrogenation of sec-butanol with the presence of a catalyst. The catalyst used in this reaction is a copper based catalyst with the production

of hydrogen as the by-product. In most of the production plant, the production involves two reaction steps. Firstly, it will start with n-butene whereby the n-butene will be hydrated to produce sec-butanol. Then, the hydrated n-butene (SBA) will undergo dehydrogenation reaction to produce MEK. This production route dominates the MEK production industry in which 90% of the world production plant has chosen this route (Schulze and Homann, 1989) and it is the second largest method of utilizing n-butene produced by refinery of butane and butene in oil and gas industry (Kent, 2007). Due to the rapid development of the oil and gas industry, these production routes is considered to be comparatively cheaper.

Usually, complicated problems in industry may not be solved by hand because of two reasons which is human error and time constraints. There are various simulation programs used in industry depending on the field, application and desired simulation products such as for entire process unit or one piece of equipment. Aspen can be a very powerful tool when used to its full capabilities for a Chemical Engineer in a different of fields including oil and gas production, refining, chemical processing, environmental studies and power generation (Bernards and Overney, 2004). The advantages of modelling using by Aspen plus are it can reduce plant design as well as allows designer to quickly test various plant configurations. Besides, it also helps in improve current process as determines optimal process conditions within given constraints and assists in locating the constraining parts of a process that will be carried out using model analysis tools such as sensitvity analysis and optimization tool. Furthermore, the use of a process flowsheet simulator is beneficial in research and development (R&D), design and production. In R&D, it helps to cut down on laboratory experiments and pilot plant runs while in design, it enables a speedier development with simpler comparisons of various

alternatives. Meanwhile, in production it can be used for risk-free analysis of various what-if-scenario (Sylvia and Orchanian, 2001).

1.2 Problem Statement

The demand of methyl ethyl ketone (MEK) has been expanding throughout the years as there is a positive interest viewpoint in the paints and coating industry, where it is broadly utilized as a solvent. However, the present issue confronted is that the use feedstock from butane refined in oil and gas industry to deliver MEK. This clearly pictures the assets are restricted because of its non-renewable properties. Therefore, depletion of fuels can occur overtime and can lead to their constrained supply. Additionally, extracting and blazing oil produces hurtful gases that adds to natural contamination and consequently, to a dangerous atmospheric deviations. This means that degradation of our ecosystems will be made faster since our feedstock to produce MEK is based on refined oil and gas industry. Besides, there is lack of studies on optimization of this production by simulation, thus an optimization of the production of MEK in a fixed bed reactor using ASPEN plus is introduced in this paper to enhance the yield and selectivity of the MEK production. Furthermore, in order to maximize the amount of MEK, some parameters such as operating temperature and pressure are needed to be controlled because it will affect the reaction process.

1.3 Research Objective

The conversion of SBA into MEK has been known for long and the reaction is applied industrially. Considering the importance of the present process, the simulation of the dehydrogenation of SBA in a fixed bed reactor is done by using Aspen plus. Tubular

reactor of fixed bed reactor is chosen and it will be modelled as plug flow reactors with heterogeneous catalytic reactions. The objectives of the present project are following.

i) To simulate the production of MEK in a fixed bed reactor and validate the literature data.

ii) To study the effect of pressure, temperature and SBA feed flow rate to the SBA conversion by using sensitivity analysis tool.

iii) To optimize the SBA conversion based on the variables involve in the sensitivity analysis part.

1.4 Organization of the Thesis

Chapter 1: Introduction

This chapter outlines the general information about research background for example explanation of the raw material used, product and the reaction process occur in order to produce the product. It also contains information on sensitivity analysis and optimization. Besides, the problem statement is elaborated about past research study while research objectives will be considered about the validation of the simulated and literature data, the sensitivity of the variables such as pressure, temperature and flow rate affect the SBA conversion. The last objective is optimization of the SBA conversion based on the variables in the sensitivity part.

Chapter 2: Literature review

This chapter outlines literature review regarding from previous researcher's paper that is related to this project which is a simulation on MEK production in a fixed bed reactor. The type of MEK production include bio-based and petroleum-based are also be discussed. The issues on modelling and analysis tools will be discussed too.

Chapter 3: Methodology

This chapter presents the methodology of the research. Aspen plus is used to develop the simulation flowsheet for the RPLUG model in dehydrogenation process. Sensitivity analysis on pressure, temperature and SBA feed flow rate is analysed in Aspen plus. Then, the analysis is proceed by optimization of the SBA conversion. All the steps are represent in a methodology flow chart and it is clearly explained for each of steps involve.

Chapter 4: Results and Discussion

This chapter presents the results and discussion of the simulation results. The simulated data is compared to the literature data. From sensitivity analysis result, the most significant effect on the SBA conversion will be used in optimization part. The optimization is carried out to further increase the SBA conversion as well MEK produce.

Chapter 5: Conclusion and Recommendation

This chapter concludes the research for each of the objectives that have been carried out in this study. Recommendation is a suggestion or proposal as to the best course of action. Thus, the recommendation for this paper is made in order to improve or optimize the SBA conversion.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter will provide the review from previous researcher's study that is related to this project which is a simulation on MEK production in a fixed bed reactor. Each of the previous research will be discussed on the issues raised from the papers, the methods used and the results from the experimental works. Besides, this chapter also will be explained about the type of processes involved and reason for chosen the particular process. Since, this paper is concerned on software such as simulator, thus the issues on the modelling and the analysis tools will be discussed too.

2.2 Dehydrogenation of 2-butanol

The researchers of Dehydrogenation of 2-butanol over copper-based catalyst are studied about the effect of support type (MgO and SiO_2) and copper loading on methyl ethyl ketone (MEK) yield. Besides, they also covered the effect of reaction temperature, 2-butanol feed flow rate and particle size of catalyst. This copper-based catalyst can be unsupported or supported catalyst and mostly they are supported catalyst where provides a large surface area compared to the unsupported type. The dehydrogenation reaction will be favoured if the acidity support has high pH. The 4 basic techniques for preparing copper-based catalyst are precipitation, urea hydrolysis, electroless plating and impregnation. Thus, in this study, it used a porous support impregnated copper-based and kinetic parameter for 2-butanol at atmospheric pressure and 190 to 280°C is determined. The dehydrogenation of 2-butanol is modelled in a catalytic membrane reactor that is

required pure kinetic data. The catalyst is performed in two stages where for the first stage it will determine the optimum catalyst and for second stage, the optimum catalyst will determine the kinetic parameter. The result of the reaction of 2-butanol over MgO and SiO_2 shown MEK as the main product and butene as the by-product. MgO supported catalyst has low BET surface area, so the MEK yield also will low while the silica supported catalyst gave highest yield of MEK since it has an optimum copper concentration on the support which is 15wt% and it particles is in the range of 300-850 μm. The amount of butene increased either smaller or larger particles produced. The selectivity of MEK for a 15wt% Cu on silica catalyst is closed to 100% at 240°C while at 390°C the selectivity is decreased between 83 and 86%. The catalyst is deactivated at 310°C and it stable at 250°C over 24 hours. The MEK adsorption coefficient is the main concern compared to 2-butanol and hydrogen coefficient. There is a little interphase mass transfer resistance for this 2-butanol dehydrogenation reaction (Keuler, et al., 2001) .

In another research, they are studied about the chemical activation of olive stone with phosphoric acid that is prepared for the catalytic conversion of 2-butanol on a carbon-based acid catalyst. The activated carbon catalyst is found from olive stone residues. The catalyst activities are measured by the decomposition of 2-butanol that is operated at 1 atm by using quartz fixed bed reactor placed inside the furnace with temperature control. From result, the chemical activation of olive stone with H_3PO_4 produced an activated carbon with a high apparent of surface area and a wide microporous structure. The mechanism for the activated carbon to be formed is through formation of phosphate and polyphosphate bridges that connect crosslink biopolymer fragments that is avoid the contraction of structure from effect of the temperature. Decomposition of 2-butanol is occurred at 413 to 573 K but in the absence of catalyst there is no reaction takes place below than temperature of 750 K. The carbon catalyst is active in produce olefin by

dehydration of 2-butanol rather than production of MEK by dehydrogenation of 2-butanol especially at high conversion. This paper proposed of two 2-butanol decomposition mechanisms for dehydration and dehydrogenation as A and B models. E2 elimination mechanism is for dehydration reaction of model A while in model B the dehydration reaction is assumed to take place through an E1 elimination mechanism. The dehydrogenation reaction occurs from both cases by an E2 mechanism. The rate expressions derived from both models fit properly with the experimental results that shown the two mechanisms occur simultaneously (Bedia, et al., 2010).

Next is investigated the catalytic performance tests in vapor-phase dehydrogenation of 2-butanol to MEK. Two types of copper-based dehydrogenation nanocatalyst which are $Cu/ZnO/Al_2O_3$ and Cu/SiO_2 prepared from various precursors by impregnation method (IM), sol-gel (SG) and co precipitation (COPRE) methods. The objective of this study to investigate the influences of the preparation method and reaction conditions on the catalytic properties of copper-based nanocatalysts in MEK production. The nanocatalyst prepared by co precipitation has the general form of $Cu/ZnO/Al_2O_3$ while the Cu/SiO_2 is general form for prepared by impregnation and sol-gel methods. Vapor-phase dehydrogenation of 2-butanol is carried out by CDS (Chemical Data System) unit. The reactor used is fixed bed reactor that is loaded by 3 g of nanocatalyst in the middle section of the reactor. To prevent the product from condensate, the transfer line from reactor outlet to the separated vessel is externally heated and maintain at 120°C. From the result, impregnation method shown the highest total surface area and pore volume while the lowest value for the total surface area is co precipitation method and pore volume for sol-gel method. The COPRE method is obtained the highest selectivity to MEK and conversion of 2-butanol. Meanwhile, the IM method obtained the lowest value of MEK selectivity and 2-butanol conversion. The optimization is done by using

response surface method (RSM) to optimize the response based on the factors studied. According to statistical results, the optimum level of parameters that can maximize the selectivity to MEK is precipitation temperature at 65°C, aging temperature at 68.75°C, pH of precipitation stage is 7.27 and Cu/Zn molar ratio is 1.38 (Geravand, et al., 2015).

Furthermore, another research is study about the Cu-ZnO-Cr_2O_3/SiO_2 catalysts that are prepared by impregnation which shown high activity for the dehydrogenation of 2-butanol to 2-butanone. The catalytic activity test is carried out in a 0.6 cm diameter of a stainless reactor with pressure of 1 atm. The catalyst loaded for each experiment is 0.3 g. From the result, the specific surface area of all the catalysts are smaller that means some small pores of SiO_2 were blocked during impregnation. Furthermore, the specific surface areas of the catalyst inversely proportional to the increasing of reduction temperature. This occur might be because of microcrystalline metallic copper sintering. The conversion of 2-butanol over the catalyst calcined at 673 K for 3 h is very high at the beginning but it becomes slowly decreasing. The catalyst reduced at 723 K shows a relatively low conversion because the reduction at high that leads to sintering and to decrease the amount of active sites on the surface. CuO exhibits high catalytic activity for dehydrogenation of 2-butanol however it is not stable at the beginning of the reaction. Thus, with reduction of CuO, the amount of Cu^0 increases so the catalytic activity becomes stable. The selectivity to 2-butanone increases since the catalyst reduced at higher temperature and the selectivity to 5-methyl-3-heptanone which is the by-product is decreases. The reduction temperature shown the decreasing of CuO amount and consequently the selectivity of condensation product 5-methyl-3-heptanone is decreases because of the reaction reaches a stable state. The condensation of 2-butanone is occurred due to existence of CuO in the catalyst (Wang, et al., 2002).

The other research using co-precipitation, the copper-based catalysts, supported on γ-Al_2O_3, La_2O_3 and γ-Al_2O_3- La_2O_3, respectively, are prepared and tested in the continuous dehydrogenation of 2-butanol to methyl ethyl ketone. The objective of this paper is to examine the effect of support acid-base properties and the catalytic activity and stability on the copper-based catalysts and correlate both of them. The 2-butanol dehydrogenation is carried out in a tubular, fixed bed reactor with internal diameter of 20 mm and 5 g catalyst is loaded into the reactor. The catalysts are characterized by using XRD, ICP, XPS, TPR, DRUV-Vis. From the results, the actual Cu contents of the three catalysts are slightly lower than nominal content which is 30wt%, with Cu-Al_2O_3- La_2O_3 having highest amount of Cu. The Cu-Al_2O_3 had the maximum surface area and pore volume while Cu-La_2O_3 is conversely. Conversion of 2-butanol for Cu-Al_2O_3 is 93.1% but MEK selectivity is only 83.5% while for Cu-La_2O_3 the 2-butanol conversion is only 84.1% and 96.4% is the MEK selectivity. For Cu-Al_2O_3- La_2O_3 the conversion of 2-butanol and MEK selectivity is the highest which are 92.2% and 95.8% respectively. Thus, the catalytic performance of copper-based catalysts are dependent on acid-base properties of the support in dehydrogenation of 2-butanol. Cu-Al_2O_3- La_2O_3 shows the best activity and stability (Bai, et al., 2013).

Besides, another research is studied about the EDTA and TEA chelating agents that are used to prepare seven Cu/γ-Al_2O_3 catalysts of different copper contents, 8.44 - 2.56wt% and 7.09 – 25.92wt% respectively. The activities of these catalysts are tested using dehydrogenation of 2-butanol as model reaction. The aims of this paper is to study the effect of the effects of the chelating agents on the surface morphology and dispersion of copper on the alumina substrate and on the dehydrogenation activity of 2-butanol. The copper surface area and acidity of these catalysts are measured using volumetric chemisorption method. The dehydrogenation reactions are carried out in a microreactor

and operated under atmospheric pressure. The activities are measured in the range of 473 – 573 K and the reactant flow rate is maintained at 10.93 mL/hr. Based on the result of this paper, for both chelating agents, the BET surface are gradually decreased which indicates that the micropores of the support might be blocked by some copper crystallites. The preparation of Cu/Al_2O_3 catalyst with TEA took 5 minutes and with EDTA it took 30 minutes to complete the plating process. The rate of dehydrogenation of 2-butanol increased proportional to the temperature as well as the number of exposed copper atoms. The complexing capability on the properties of the chelating agent dominates the copper crystallites particle size, thus, the copper dispersion on the alumina support. The Cu-TEA chelate enhanced the formation of bulky copper clusters occurring even at low copper loading. The catalysts prepared by Cu-EDTA chelates had smaller copper crystallites, higher copper dispersion and higher activity than those prepared by Cu-TEA chelates. The acidity of the catalyst could be reduced more effectively for the EDTA series (Chang, 1997).

2.3 Current industrial process

Currently, MEK is commercially produced using the two step of n-butene technique which is hydrating butene to produce SBA and dehydrogenating the SBA. Besides, there are two methods to produce MEK via dehydrogenation of SBA, first, gas dehydrogenation and second, liquid dehydrogenation. However, gas dehydrogenation is widely used in the industry because it is comprise a simpler process flow sheet and its investment is low.

By this process, it can give high conversion of SBA and high selectivity of MEK of about 95%. The key to technical development is the improvisation of the catalyst

activity, selectivity and operation cycle (Zhenhua, 2006). Furthermore, the commercial alcohol dehydrogenation catalyst are copper, brass or zinc based. The copper based catalysts are found to be quite effective in dehydrogenation of SBA because of their lower operation temperatures and minimum side reactions. Hence, the advantages of this process are better yield, longer catalyst life, simple production separation and lower energy consumption.

2.3.1 Bio-based

The production of MEK also can be done through biological path by using lignocellulosic biomass as the substrate. Lignocellulosic biomass which is rice straw and bagasse is one of the most abundant waste found on earth that were composed by cellulose, hemicelluloses and lignin (Wong, et al., 2012). Firstly, alkaline pretreatment is done to reduce the lignin content then the treated biomass will be subjected to enzymatic hydrolysis to convert the cellulose and hemicelluloses to fermentable sugar and this process is costly (Weerasai, et al., 2014) . The hydrolysate that contains fermentable sugar (i.e glucose) will be sent to the bioreactor for batch fermentation.

Microorganisms such as *Klebsiella oxytoca*, *Klebsiella pneumonia* and *Saccharomyces cerevisiae* are used to produce 2,3-butanediol from fermentation of glucose. Since the process will undergo a series of biochemical path through pyruvate formation, thus there will be other product produced as well such as acetoin, lactic acid, succinic acid, ethanol, carbon dioxide and hydrogen. The process also will take up to three days at temperature between 30°C to 37°C with an initial pH of 6 to 6.5 and no control will be done on the pH throughout the fermentation period (Wong, et al., 2012) (Wong, et al., 2014) (Cho, et al., 2015). The formation of these products from glucose is deduced as follow (2.1) to (2.5):-

$$\text{Glucose } (C_6H_{12}O_6) \rightarrow \text{2,3 Butanediol } (C_4H_{10}O_2) + 2CO_2 + H_2 \quad (2.1)$$

$$\text{Glucose } (C_6H_{12}O_6) \rightarrow \text{Acetoin } (C_4H_8O_2) + 2CO_2 + 2H_2 \quad (2.2)$$

$$\text{Glucose } (C_6H_{12}O_6) + O_2 \rightarrow \text{Succinic acid } (C_4H_6O_4) + 2 \text{ Formic acid } (CH_2O_2) + H_2 \quad (2.3)$$

$$\text{Glucose } (C_6H_{12}O_6) \rightarrow 2 \text{ Lactic acid } (C_3H_6O_3) \quad (2.4)$$

$$\text{Glucose } (C_6H_{12}O_6) + O_2 \rightarrow 2 \text{ Acetic acid } (C_2H_4O_2) + 2 \text{ Formic acid } (CH_2O_2) \quad (2.5)$$

The fermentation broth will be subjected to a series of separation process to obtain 2,3-butanediol. Then, when the 2,3-butanediol is purified, it will undergo catalytic dehydration process that take place in liquid phase. The reaction operated at temperature of 300°C to 400°C with pressure range from 0 to 50 bar. The dehydration reaction is shown below (2.6):-

$$C_4H_{10}O_2 \rightarrow \text{MEK}(C_4H_8O) + H_2O \quad (2.6)$$

Based on the reaction, apart from MEK, 1,3-butanediene also be produced as the side product (Soo, et al., 2016). In this section, the separation will involve azeotropic compound of MEK and water.

2.3.2 Petrochemical-based

Production of MEK can be synthesized by the dehydrogenation of sec-butanol (2-butanol) process. In most of the production plant, the production involves two reaction steps. Firstly, it will start with n-butene whereby n-butene will be hydrated to produce sec-butanol. After that, the hydrated n-butene (sec-butanol) will undergo dehydrogenation reaction to produce MEK. This production route dominates the MEK production industry in which 90% of the world production plant has chosen this route

(Schulze and Homann, 1989). Besides, the proposed production route is the second largest method of utilizing n-butene produced by refinery of butane and butane in oil and gas industry (Kent, 2007). Due to the rapid development of the oil and gas industry, these production routes is considered to be comparatively cheaper. The two reactions involved in this process is summarized in the following stoichiometry equation:-

$$\mathrm{n-butene(C_4H_8) + H_2O \rightarrow Sec-butanol(C_4H_9OH)} \tag{2.8}$$

$$\mathrm{C_4H_9OH \rightarrow MEK(C_4H_8O) + H_2} \tag{2.9}$$

Ion exchange catalyst has the advantage in terms of safety and environmental friendly characteristics because liquid strong acid is not used and less hazardous waste water will be generated. Moreover, less by product will be generated by the direct hydration route too. Up to the date of publication, Deutsche Texaco plant in Meerbeck is the only plant that utilizes direct hydration (Schulze and Homann, 1989). Followed the hydration process will be the dehydrogenation of sec-butanol. The hydrogen product produced in this reaction can be recovered for sale or utility purpose. Even though this route of production is considered to be easier, its separation may be tedious as the upstream product and reactant will form azeotrope. The unreacted water may form azeotrope with the unreacted sec-butanol and MEK. Overall there are two azeotropes involve.

Controversial been raised on the MEK production using n-butene since n-butene is considered as a non-renewable source which will depleted sooner and later. However, instead of waiting the resource to be depleted, scientist been divert their attention to create the n-butene from renewable source. Recently, research been carried out to produce n-butene can by the dehydration of butanol that derived from fermentation approach (West, et al., 2009). Bio-1,3-butadiene hydration could also be another butane production

alternative (Umpierre, et al., 2005). Hence, the feedstock sustainability should not be a large problem in future.

Based on the bio-based and petrochemical-based, this paper is proposed to choose the petrochemical-based rather than bio-based due to higher cost for the enzymatic hydrolysis process for the bio-based. Besides, there will be other product produced as well such as acetoin, lactic acid, succinic acid, ethanol, carbon dioxide and hydrogen while the petrochemical-based only produce MEK as the main product and hydrogen. The catalyst used in petrochemical based has the advantage in terms of safety and environmental friendly characteristics and the production route is cheaper.

2.4 ASPEN model

The importance of having simulation in predicting reaction process model by using basic engineering relationships, such as mass and energy balances, and phase and chemical equilibrium. Given reliable thermodynamic data, realistic operating conditions, and rigorous equipment models, the actual plant behaviour can be simulated (Aspen Technology, 2001). The Aspen plug flow reactor is used to simulate the dehydrogenation of SBA in a fixed bed reactor because the reaction kinetic of this reaction is known. In this step, SBA is converted to MEK and hydrogen. Other reactions are possible, but their reaction mechanisms are still not clear. RPlug handles kinetic reactions, including reactions involving solids, since the kinetic is given in the literature, so the RPlug is chosen as the reactor model. The reaction kinetics must be determined before using RPlug to model a reactor.

Sensitivity analysis is a tool for determining how a process changes with varying key operating and design variables. It can be used to vary one or more flowsheet variables and study the effect of that variation on other flowsheet variables. It is a valuable tool for

carrying out “what if”’ studies. The flowsheet variables are inputs to the flowsheet. Besides, sensitivity analysis also can be used to verify whether the solution to a design specification lies within the range of the manipulated variable. The optimization process is carried out to achieve the optimum output variables.

CHAPTER THREE

METHODOLOGY

3.1 Introduction

In order to achieve the objectives as stated in Chapter 1, a process model is developed for SBA dehydrogenation in a fixed bed reactor using Aspen plus version 8.8 software. First, a suitable reactor block in Aspen plus is chosen to simulate the data. Next, suitable information and assumption were taken into account for the reactor block. By using the model developed, the three parameters which are pressure, temperature and SBA flow rate towards reactor were studied. The data were simulated by using sensitivity analysis in Aspen plus. Regarding to validate the simulation results, experimental data from literature is used. The experimental data from case study is used to validate the model in order to determine the model fits with the experimental data. If the validation succeeded, the optimization of the model can be performed by using optimization tool in Aspen plus.

There are few steps involved before creating a simulation model. First, open the software, the menu will display the Properties. Select the Specifications and fill the components used for this simulation. Then, click Methods in order to choose the Base method before select the Simulation part. The Figure 3.1 shows the flow for the Properties section in Aspen Plus.

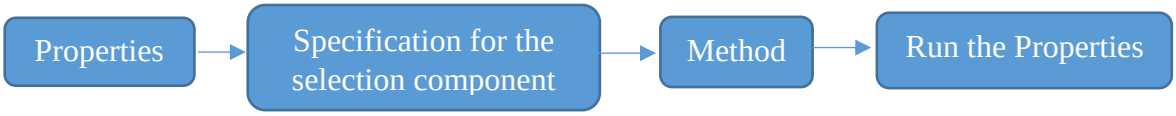

Figure 3.1: Flow for Properties section

3.1.1 The research methodology steps

A general flow of the methodology is shown in Figure 3.2.

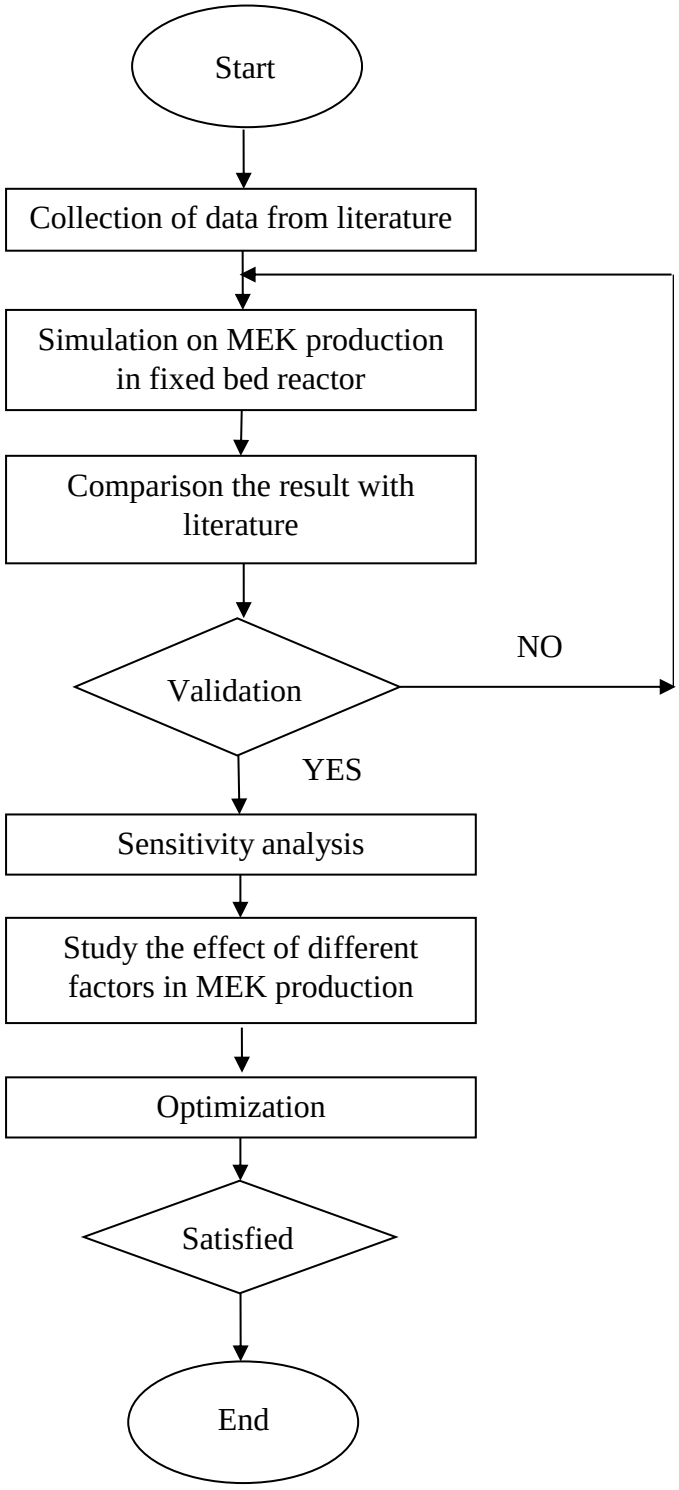

Figure 3.2: Schematic flow diagrams of methodology

3.2 Methodology flow chart

The detail information based on the flow diagrams in Figure 3.2 will be explained as below.

3.2.1 Data collection

Aspen plus simulator is used to model and predict the performance of a process which involves the decomposition of the process into its constituent elements for individual study of performance. It is widely used to study and investigate the effect of various operating parameters on various reactions. The fixed bed reactor which is tubular reactor were modelled by PFR in Aspen plus according to the data that found from case study provided (Olsson, 2013). UNIQUAC (Universal QuasiChemical) is used as the property method for the Aspen model. A PFR model in the Aspen plus is known as RPLUG. In the case study setup the reactant which is SBA is fed to the RPLUG at 12.08 tons/hr. The mass fraction of feed solution is 1. Temperature and pressure of feed stream are set as 500 °C and 300 kPa respectively. Length of the reactor is 0.46 m from calculate by interpolation and the diameter of the tube is 32 mm.

There are some assumptions used:

1. There is no accumulation of impurities in the process.
2. The simulation does not take into account the heat loss that is present throughout the process.
3. In the SBA dehydrogenation process, the main component for the output is MEK and the by-product is hydrogen gas.
4. No other reaction is occurred others than main reaction.

5. Mole of hydrogen gas in output is ignored in calculation for conversion, selectivity and yield in order to get accurate results of calculation.
6. Since there is no fixed bed reactor in Aspen model, RPLUG is chosen as the model to simulate the reaction.

Table 3.1 to Table 3.4 are the data obtained from the literature. The Table 3.1 shows the MEK plant specifications. Table 3.2 is the properties of the catalyst bed meanwhile the Table 3.3 is reactor specifications. The Table 3.4 is reactor length for the first reactor for different conversions.

Table 3.1: MEK plant specifications

MEK production	90000 tons/year
Raw material	SBA
Conversion in the reactor	96%
Purity of produced MEK	99 wt% MEK
Loss of MEK from the plant	1 wt% based on feed
Operation time	8000 hr/year
Flue gas stack temperature	150 °C

Table 3.2: Properties of the catalyst bed

Length	d_p	0.0032 m
Particle density	ρ_p	8500 kg/m^3
Thermal conductivity	λ_s	125.4 W/(m.K)
Heat capacity	c_p	0.38 kJ/(kg.K)
Porosity of the bed	ε_B	0.39

Table 3.3: Reactor specifications

Given values from the course project	
Fluid viscosity	1.89×10^{-5} Pa.s
Wall thickness	4 mm
Thermal conductivity	15 W/(m.K)
Overall heat transfer coefficient	50 W/(m^2.K)
Minimum temperature difference for heating the reactor	50 °C
Calculated values	
Tube diameter	32 mm
Number of tubes	1156
Wall heat transfer coefficient	100 W/(m^2.K)

Table 3.4: Reactor length for the first reactor for different conversions

Conversion (%)	Length (m)
85	0.35
90	0.38
95	0.42

3.2.2 Run simulation

To run a simulation:

1. Click the Next button to confirm that you have finished entering all required input. The Required Input Complete dialog box appears.
2. Click OK. A Control Panel appears and shows the run progress.
3. As the run proceeds, status messages appear in the Control Panel. When the calculations are completed, the message Result Available appears in the status bar at the right corner of the Aspen Plus main window.

3.2.3 Examine simulation results

When the message Results Available appears in the status bar simulation results can be examined.

To examine the results:

1. From the Menu Tree, double-click the Results Summary folder.
2. In the Results Summary folder, click Run Status.
3. The Summary sheet appears.
4. The Aspen Plus version, run starting time and run status are summarized on this sheet.
5. From the Results Summary folder, click Streams.
6. The Material sheet appears with the stream results.

The summary result of the simulation by Aspen plus will be compared with the result from literature data (Olsson, 2013) especially the effect of temperature towards the SBA conversion. Figure 3.3 shows the literature data for the reaction.

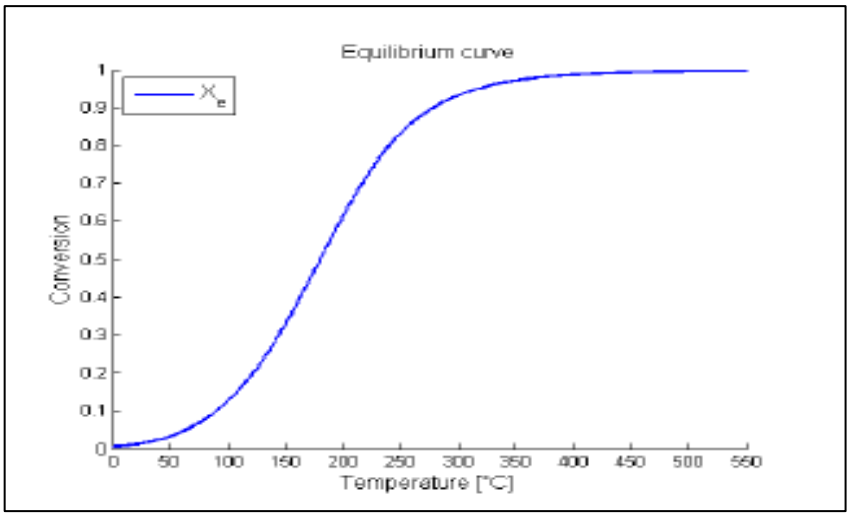

Figure 3.3: Equilibrium curve for MEK (Olsson, 2013)

The determination of the conversion in the SBA dehydrogenation is related to the SBA conversion. The definition of conversion (X) is the relation between the related amount of SBA and the initial amount of SBA. In terms of moles (3.1) is:

$$X_{SBA} = \frac{(Mole_{SBA})_{inlet} - (Mole_{SBA})_{outlet}}{(Mole_{SBA})_{inlet}} \times 100 \quad (3.1)$$

3.2.4 Sensitivity analysis

A sensitivity analysis is carried out for the SBA dehydrogenation reactor. The effects of operating condition on the product will be analysed below. By using sensitivity analysis tool at Aspen plus, the reactor pressure is varied from 0.5 to 3.5 bar in case 1, reactor temperature is varied from 50°C to 600°C in case 2. SBA feed flow rate is varied from 1000 kg/hr to 13000 kg/hr in case 3. Table 3.5 shows the range operating variables used for sensitivity analysis.

Table 3.5: Range operating variables used for sensitivity analysis

Parameter	Lower range	Upper range	Increment
Temperature (°C)	50	600	50
Pressure (bar)	0.5	3.5	0.5
SBA feed (kg/hr)	1000	13000	1000

The steps for sensitivity analysis:

1. Select Model Analysis Tools and then select Sensitivity from the submenu.
2. Click New and a dialog box of Create New ID will appear. It will display an automatically generated S-1. Rename the Enter ID in that box or just use as the default.
3. Click OK to accept the Create New ID dialog box.
4. The Sensitivity Input Vary sheet for S-1 appears and click New.
5. Variable labelled with 1 will display for the Manipulated variable.
6. Edit the selected variable for the Type such as Stream-Var, then click the S1 and TEMP for variable that are needed to manipulate.
7. Specify the limits for the manipulated variable limits and put the number points, increment or list of values.
8. Repeat the step 4 to 7 for another parameters which are pressure and SBA feed flow rate.
9. Click Next for Input Define sheet and edit selected variable by click New and name it by BUTIN for feed stream of SBA. Add in the variable for BUTOUT which is product stream of SBA.
10. Choose any of the category and the reference.