BIODIESEL PRODUCTION USING REACTIVE DISTILLATION: OPTIMIZATION AND COMPARATIVE SIMULATION STUDY USING ASPEN

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2021

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by

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Project report submitted in partial fulfilment of the requirement for the degree of Bachelor of Chemical Engineering

June 2021

ACKNOWLEDGEMENT

First and foremost, I would like to express my heartfelt gratitude to my supervisor, Associate Professor Dr. Syamsul Rizal Abd Shukor for his precious encouragement, guidance, and support throughout this project.

I would also convey my gratitude towards all USM Engineering librarian for their kindness, cooperation and helping hands in providing us thesis template and teaching us on Mendeley reference to ease our work. It is much appreciated that they are willing to share their thoughts, idea, information, skills, and knowledge.

Apart from that, I would like to express my deepest gratitude to everyone, including my friends and technician in school. All of their contributions are very much appreciated. Lastly, not to forget my family members who gave their mental support that allowed me to pull through all the hardship and challenges. Thank you very much.

Chuah Jing Xuan

January 2021

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LIST OF SYMBOLS

X	Conversion of triolein through transesterification
T_0	Reference environment temperature (298.15K)
ΔS_{irr}	Entropy production [J/(K.s)]
E_d	Exergy destruction [W]
T_j	Temperature of heat source [K]
Q_j	Heat transfer flow [W]
W_i	Work transfer flow [W]
n_i	Molar flow rate of stream [kmol/s]
e	Specific exergy of a stream [kJ/mol]
h	Molar entalphy [J/kmol]
s	Molar entropy [J/kmol]
V	Velocity [m/s]
g	Gravitational acceleration [m2/s]
z	Height [m]
e^{ch}	Molar chemical exergy of a stream [J/kmol]
Q	Heat Duty
m	Flowrate of process stream
C_p	Heat capacity of process stream
ΔT	Changes in temperature
λ	Latent heat of vaporization or condensation

LIST OF ABBREVIATIONS

FAME	Fatty Acid Methyl Ester
PI	Process Intensification
RD	Reactive Distillation
FFA	Free Fatty Acid
CSTR	Continuous Stirred Tank Reactor
VOC	Volatile Organic Compounds
MBA	Malaysian Biodiesel Association

ABSTRAK

Pengurangan bahan bakar fosil dalam beberapa tahun kebelakangan ini telah menyebabkan perhatian penyelidik untuk mengembangkan tenaga diperbaharui yang berpotensi sebagai pengganti bahan bakar fosil. Oleh itu, biodiesel dicadangkan kerana ia adalah penggantian bahan bakar fosil yang baik sebagai 'sumber tenaga bersih'. Namun, disebabkan kos bahan mentah dan perbelanjaan operasi yang tinggi dalam pengeluaran biodiesel konvensional, biodiesel dianggap tidak kompetitif secara ekonomi dibandingkan dengan bahan bakar berasaskan petroleum. Halangan ini dapat diatasi dengan teknologi intensifikasi proses (PI). Teknologi PI diterapkan dalam pengeluaran biodiesel yang diperkuat dengan menggunakan reactive distillation column untuk menggantikan reaktor dan distillation column pemulihan metanol. Reactive Distillation (RD) adalah teknik intensifikasi proses yang cekap yang menggabungkan tindak balas kimia dan penyulingan dalam satu alat. Untuk meminimumkan penggunaan tenaga di lajur RD, analisis kepekaan dan pengoptimuman dilakukan untuk mengkaji kesan parameter operasi seperti suhu makanan dan nisbah refluks pada tugas panas reboiler. Hasil analisis sensitiviti menunjukkan bahawa tugas haba reboiler berkadar langsung dengan suhu suapan tetapi berbanding nisbah refluks terbalik. Hasil yang dioptimumkan menunjukkan bahawa keadaan optimum untuk pengeluaran biodiesel yang cekap dengan penggunaan tenaga minimum adalah pada suhu 145^{o}C feed dan nisbah refluks pada 1. Selain itu, keuntungan proses yang diperoleh melalui intensifikasi kilang biodiesel konvensional dengan penambahan lajur penyulingan reaktif dikaji. Didapati bahawa proses yang diperhebat mempunyai penukaran minyak Jatropha menjadi biodiesel yang lebih tinggi berbanding dengan proses konvensional dengan kadar penukaran

yang dilaporkan masing-masing pada 48.19% dan 32.52% untuk proses intensif dan konvensional. Dari aspek analisis tenaga, keperluan utiliti panas dalam proses intensif adalah 60.70% lebih rendah daripada yang diperlukan untuk proses konvensional dengan keperluan utiliti panas yang dilaporkan masing-masing pada 7.702×10^4 cal/s dan 1.96×10^5 cal/s untuk proses intensif dan konvensional. Selain itu, tugas haba reboiler dalam proses intensif adalah 21.84% lebih rendah daripada proses konvensional dengan tugas reboiler yang dilaporkan masing-masing pada 69034.1kW dan 88327.1kW untuk proses intensif dan konvensional. Dari aspek analisis eksergi, hasil menunjukkan perubahan eksergi merentas kolom reaktor dan pemulihan metanol dalam proses konvensional masing-masing -10.39kW dan -25.54kW. Manakala perubahan eksergi di lajur penyulingan reaktif dalam proses yang dipergiatkan adalah 91.15kW. Ini menunjukkan bahawa eksergi hilang atau disia-siakan dalam proses konvensional, sedangkan dalam proses yang dipergiatkan eksergi diperoleh dalam ruang penyulingan reaktif. Oleh itu, ruang penyulingan reaktif ini menggunakan sepenuhnya tenaga yang diperoleh dari sumber lain.

ABSTRACT

Depletion of fossil fuels in the recent years had led to attention of researcher to develop potential renewable energy as the fossil fuel substitute. Thus, biodiesel is suggested since it is a good replacement of fossil fuels as a ‘clean energy source’. However, due to high cost of raw material and operating expenses in conventional biodiesel production, biodiesel is considered not economically competitive compared to petroleum-based fuel. This limitation can be overcome by process intensification (PI) technology. PI technology is applied in intensified biodiesel production by using reactive distillation column to replace methanol recovery column and reactor. Reactive distillation (RD) is a process intensification technique that combines chemical reaction and distillation in a single equipment. To minimize the energy consumption in RD column, sensitivity and optimization analysis are conducted to study the effect of operating parameters such as feed temperature and reflux ratio on reboiler heat duty. Results from sensitivity analysis showed that reboiler heat duty is directly proportional to feed temperature but inversely proportional to reflux ratio. Optimized results showed that optimum condition for efficient production of biodiesel with minimum consumption of energy is at 145^{o}C of feed temperature and reflux ratio at 1. Besides, the process gains obtained through intensification of a conventional biodiesel plant by addition of a reactive distillation column is studied. It is found that intensified process has higher conversion of Jatropha oil into biodiesel compared to conventional process with reported conversion rate at 48.19% and 32.52% for intensified and conventional process, respectively. From aspect of energy analysis, hot utility requirement in intensified process is 60.70% less than that required for conventional process with reported hot utility requirement at 7.702×10^{4}cal/s and

1.96×10^5cal/s for intensified and conventional process, respectively. Besides, reboiler heat duty in intensified process is 21.84% less than in conventional process with reported reboiler duty at 69034.1kW and 88327.1kW for intensified and conventional process, respectively. From aspect of exergy analysis, result showed exergy change across reactor and methanol recovery column in conventional process are -10.39kW and -25.54kW, respectively. Whereas exergy change across reactive distillation column in intensified process is 91.15kW. This implies that exergy is lost or wasted in conventional process, whereas in intensified process exergy is gained within reactive distillation column. Thus, this reactive distillation column utilizes fully exergy gained from other sources.

CHAPTER 1

INTRODUCTION

This study proposes biodiesel as an alternative to replace fossil fuel since biodiesel has enormous possibility in reducing the side effect of fossil fuel in future. Besides, process intensification (PI) is applied on conventional biodiesel production plant with an addition of reactive distillation column. The application of process intensification is to maximize the energy, capital, and environmental benefits through reduction of plant size and maximal usage of feedstock available. In this chapter, biodiesel production through conventional and intensified process are discussed, providing a framework for the objectives of this study. This chapter covers the depletion and drawback of fossil fuel, introduction of biodiesel as alternative energy, biodiesel production, problem statement and finally the objectives of this study.

1.1 Depletion and Drawback of Fossil Fuel

Mitigation of climate change, economic growth, and the continuing depletion of reserved oil are all significant factors for development of renewable energy. Due to detailed modelling of climate change consequences, national economic repercussions, and other factors, the need of finding CO_2-neutral fuel sources has been emphasised. Among these, climate change is the most significant factor for the development of renewable energy technology. This is because, as stated at the 2009 Copenhagen Climate Change Summit, it is necessary to reduce CO_2 emissions by 25-40% by 2020 and 80-90% by 2050 in order to keep global warming below the 2°C limit (Stephens *et al.*, 2010). The apparent problem of reducing CO_2 emissions is exacerbated by the prediction that the world's population will grow from 6.6 billion in 2008 to 9.2 billion by 2050, followed by the reality that the resulting increase in fuel consumption will be exacerbated further by the increasing energy demands of certain countries' rapidly growing economies (Stephens *et al.*, 2010).

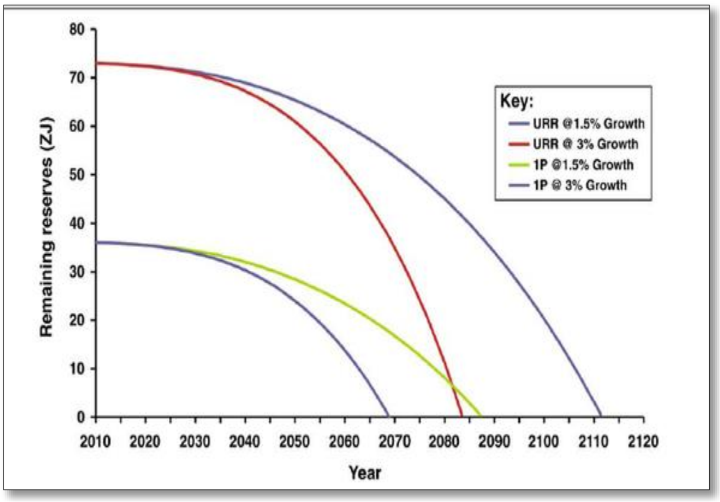

Figure 1-1:Predicted rates of global fossil fuel depletion (Stephens *et al.*, 2010)

Figure 1-1 depicts the compounding impacts of rising world population and economic growth (1.5-3% per year) on total fossil fuel depletion (oil, gas, coal, and uranium). These calculations consider a 1% gain in energy efficiency per year. Based on the calculations, it is estimated that fossil fuels would be totally depleted between 2069 and 2088 if we rely primarily on them to meet global energy consumption (Alkhateeb *et al.*, 2016).

Fossil fuels also generate plenty of environmental problems that endanger our ecosystem's long-term viability. The production of greenhouse gases and other types of air pollutants such as sulphur dioxide and volatile organic compounds (VOCs) is one of the most pressing concerns. As shown in Figure 1-2 below, since 1998, Malaysia's total carbon dioxide emissions from fossil fuels have risen every year. Massive carbon dioxide accumulation in our atmosphere will eventually result in dramatic climate changes, acid rain, and smog (Steven and Lee, 2010). Thus, biodiesel, a renewable energy source, has grown in popularity in recent years and is on the approach of overtaking fossil fuels.

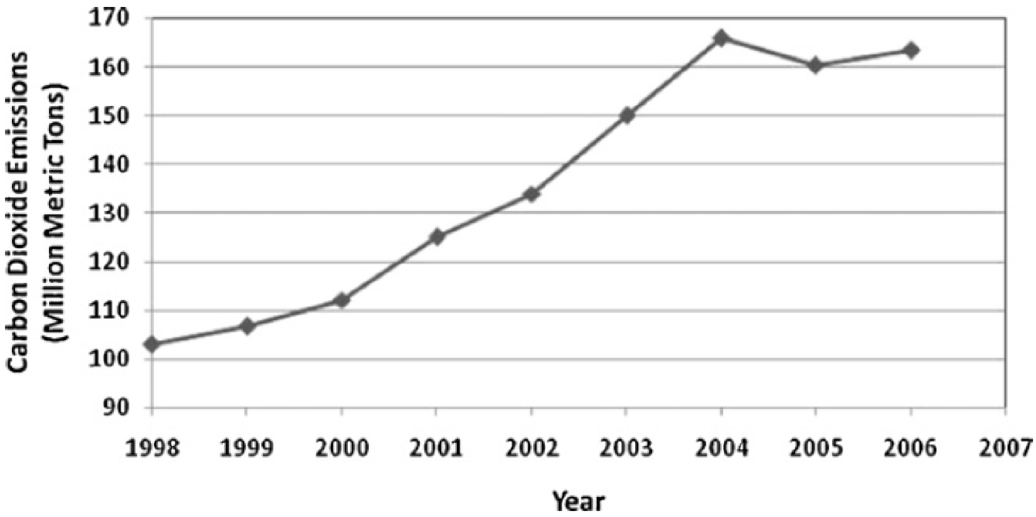

Figure 1-2: Malaysia total carbon dioxide emission from consumption of fossil fuels (Steven and Lee, 2010)

1.2 Biodiesel as Alternative Energy

Due to the depletion of world petroleum reserves, increased energy demand, rising environmental concerns, and growing petroleum prices, alternative and renewable energy sources have become more appealing in recent years (Kumar *et al.*, 2015). As a result, biofuels, particularly biodiesel, are gaining popularity around the world because they have several advantages, including: 1) the ability to be derived from a domestic renewable source (vegetable oils), and 2) the ability to reduce greenhouse emissions (carbon dioxide) by 78% over the lifecycle of a crude-based diesel fuel. 3) It is biodegradable, making it a more environmentally friendly fuel, and 4) it has been shown to reduce engine exhaust pollutants dramatically (Poddar *et al.*, 2015).

Biodiesel is a good replacement for fossil fuels as a ‘clean energy source’ since it reduces CO_2, SO_2, CO, HC emission. Biodiesel's carbon cycle is dynamic due to the photosynthesis process, as seen in Figure 1-3. The amount of carbon dioxide absorbed by plants is more than the amount of carbon dioxide released by the biodiesel combustion process. When compared to the usage of fossil fuel, biodiesel may efficiently reduce CO_2 emissions, conserve the natural environment, and maintain ecological equilibrium. Furthermore, due to the low sulphur content in biodiesel, SO_2 emissions in the combustion process of biodiesel are substantially lower than in the combustion of regular diesel oil. As a result, substituting biodiesel for regular diesel oil will effectively reduce acid rain, which poses a serious threat to the environment and human infrastructure in the form of soil acidification, surface and ground water pollution, forest and vegetation damage, and increased corrosion of buildings and historical monuments made of calcium-containing stones Furthermore, due to biodiesel's ester components contain oxygen, which promotes clean burning, CO, HC, and particulate matter emissions will be reduced (Fan *et al.,* 2016). As a result, it can be claimed that utilising biodiesel can significantly reduce air pollution by reducing hydrocarbons, aromatic hydrocarbons, carbon monoxide, alkenes, aldehydes, ketones, and particulate matter (Huang *et al.*, 2012).

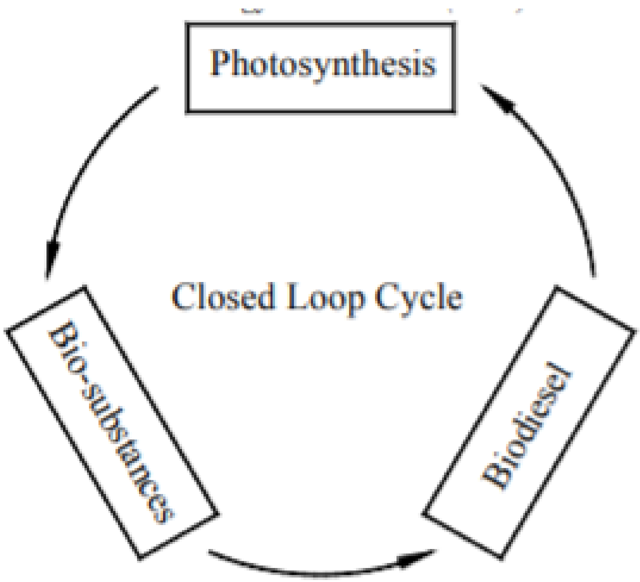

Figure 1-3: Closed loop cycle of biodiesel (Huang *et al.*, 2012)

Malaysian government has recognised the long-term value of promoting biodiesel since the early 1980s. Malaysia has established itself as a pioneer in the palm biodiesel business. Until now, according to the Malaysian Biodiesel Association (MBA), our country has 10 operating biodiesel plants with a total yearly installed capacity of 1.2 million tonnes, as shown in Table 1-1 (Steven and Lee, 2010).

Table 1-1: List of operating biodiesel plants in Malaysia 2008 (Steven and Lee, 2010)

No.	Name of production company	Plant location	Plant capacity (tonnes/year)
1	Carotino Sdn. Bhd.	Pasir Gudang, Johor	200,000
2	Malaysia Vegetable Oil Refinery Sdn. Bhd.	Pasir Gudang, Johor	110,000
3	PGEO Bioproducts Sdn. Bhd.	Pasir Gudang, Johor	100,000
4	Vance Bioenergy Sdn. Bhd.	Pasir Gudang, Johor	200,000
5	Mission Biotechnology Sdn. Bhd.	Kuantan, Pahang	200,000
6	Carotech Bio-Fuel Sdn. Bhd.	Ipoh, Perak	150,000
7	Lereno Sdn. Bhd.	Setiawan, Perak	60,000
8	Golden Hope Biodiesel Sdn. Bhd.	Teluk Panglima Garang, Selangor	150,000
9	Global Bio-Diesel Sdn. Bhd.	Lahad Datu, Sabah	200,000
10	SPC Bio-Diesel Sdn. Bhd.	Lahad Datu, Sabah	100,000

1.3 Biodiesel Production

Due to similar qualities and properties to those of petroleum-based diesel, biodiesel has arisen as a feasible alternative fuel to replace petroleum-based fuels (Salvi and Panwar, 2012). Biodiesel is mono alkyl ester of fatty acid generated through transesterification or esterification process. Glycerol and fatty acid methyl esters are produced via transesterification of triglycerides with methanol in the presence of an alkaline catalyst (FAME). The FAME product can be refined and purified to make biodiesel fuel, while the secondary product glycerol is typically used in soap manufacturing. Fatty acid methyl ester (FAME) and water (by-product) are produced via esterification of fatty acid with methanol (Kick *et al.*, 2013) (Kiss, 2014). The following equations represent both transesterification and esterification reactions:

$$Triglycerides + 3\ Methanol \rightleftharpoons 3\ Methyl\ Ester + Glycerol$$

$$Fatty\ Acid\ +\ Methanol\ \rightleftharpoons\ Methyl\ Ester\ +\ Water$$

Transesterification to generate biodiesel is commonly catalysed by a homogenous alkaline catalyst such as NaOH or KOH. Although ethanol can be used to make biodiesel, it is better to utilise methanol because it is less expensive and has a larger supply of available feedstock. (Borges and Díaz, 2012). The transesterification mechanism is made up of three reversible processes. These processes require a significant amount of surplus alcohol to achieve high conversion of triglycerides and produce biodiesel. The three relevant steps take place in transesterification are assumed as below:

$$\text{Triglyceride} + \text{Methanol} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Diglyceride} + \text{Methyl ester}$$

$$\text{Diglyceride} + \text{Methanol} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{Monoglyceride} + \text{Methyl ester}$$

$$\text{Monoglyceride} + \text{Methanol} \underset{k_6}{\overset{k_5}{\rightleftarrows}} \text{Glycerol} + \text{Methyl ester}$$

Due to high cost of raw material and operating expenses for biodiesel production, they are considered not economically competitive compared to petroleum-based fuel (Kick *et al.*, 2013). However, this limitation can be overcome by process intensification technology. Process intensification (PI) is a concept of process design that enhances process flexibility, product quality, speed to market, and inherent safety while reducing environmental impact (Tao, 2014). It is also a professional approach of chemical engineering that comprises shrinking the size of a chemical plant by integrating many unit processes or unit operations into a single unit. Reactive distillation (RD) is an example of a multifunctional reactor, which combines a reactor with a unit operation (Narasimhan *et al.*, 2016). Reactive distillation (RD) is a process intensification technique that combines chemical reaction with distillation in a single apparatus, allowing reactants to be converted while products are separated simultaneously (Oh *et al.*, 2012). This reactive distillation technology has several benefits, including a lower capital investment and significant energy savings. Biodiesel production based on the PI concept, such as reactive distillation technology, focuses on shorter reaction times but higher conversion, a low molar ratio of alcohol to oil, low catalyst concentration, and, most importantly, lower operating costs and energy consumption for biodiesel purification, as well as the recovery of glycerol, catalyst, and excess alcohol. Eventually, limitations faced by biodiesel production can be overcome by applying reactive distillation based on PI technology.

In this study, there will be a comparison between conventional and intensified biodiesel plants through energy and exergy analysis to evaluate their efficiency. The quantity of energy in a system is determined by an energy analysis, whereas the quality of the energy is determined by an exergy analysis. Exergy is a sort of available or useable energy. It is also the maximum useful work that can be done during a process to bring the system into balance with a heat reservoir and achieve maximum entropy. Exergy analysis is a powerful analytical tool based on thermodynamics' first and second laws. It is useful for determining the amount and quality of energy used in a process (Wiki, 2021). This analysis can be used to determine location, source, and amount of exergy losses in the process (Seyitoglu *et al.*, 2017). Hence, it is used in this research to determine an energy-efficient process.

1.4 Energy and exergy analysis

Energy and exergy analysis are tools that can be applied to evaluate efficiency in a chemical process. Energy analysis can be implemented through identification of energy inputs, energy wastes, energy-recovery capabilities, and energy-efficiency possibilities. Energy analysis is significant in reduction of energy requirement and leads to reduction of capital cost and environmental impact. According to the First Law of Thermodynamics, energy cannot be generated or destroyed and it is a system of constant mass, yet it can be transformed from one form to another (Bhatia, 2014). At present, most chemical processes in industry are now optimised using the first law of thermodynamics which allows for the identification of energy requirements. However, this does not help to determine whether the energy is being used effectively. By using second law of thermodynamics, it is possible to analyse the energy quality and indicate the efficiency of energy consumed (Amelio *et al.*, 2016).

The quality of energy is the subject of the Second Law of Thermodynamics. It claims that as energy is transported or converted, a greater proportion of it is dissipated. It further claimed that any isolated system has a natural propensity to degrade into a more chaotic state (Lucas, 2015). The second law of thermodynamics explains the configuration of energy and entropy in a system, as well as how they are exchanged between systems. The second law of thermodynamics gives rise to the concept of exergy. “The ability to accomplish work” or “the amount of work that can be extracted from a substance” is how exergy is defined (Gray, 2019). Exergy can be lost due to irreversibility in real-world processes. Exergy can also be obtained by the reception of energy from other sources. Exergy loss typically refers to waste or by-product streams in which exergy is not included in the product but is recoverable in theory, whereas exergy destruction refers to an irrecoverable loss (Rocco *et al.*, 2014). For example, a heated wastewater stream directed to a holding pond, might be considered a lost exergy because it could theoretically be used to heat another part of the process, but heat released to the atmosphere from a piece of equipment might be considered a destroyed exergy because there is no way to use it.

1.5 Problem Statement

The key obstacles that conventional biodiesel sector faces are refining prices, production capacity, and feedstock flexibility. These production factors make biodiesel cannot compete with petroleum fuels which is cheaper in cost. Until today, when compared to petroleum-based diesel fuel, biodiesel's high production cost has remained a major hindrance to commercialization. It is reported that feedstock costs account for 70-95% of overall biodiesel manufacturing costs (Oh *et al.*, 2012). This is due to pre-treatment is needed for animal fats, used oil and greases which consists of high content of free fatty acid (FFA). Without pre-treatment steps, the presence of FFA in alkali-catalysed biodiesel production will promote soap formation. Formation of this soap will partially consume the alkali catalyst, reduce product yield, and interferes with the separation of glycerol. Therefore, pre-treatment step become crucial when feedstock with high content of FFA is used in the production of biodiesel and this leads to high production cost of biodiesel. Besides that, conventional biodiesel production commonly uses a continuous stirred tank reactor which will reduce conversion rate of transesterification reaction. Since transesterification is a reversible reaction, thus it is difficult to have complete conversion of vegetable oil and achieve high yield of biodiesel in a single step process without removing the reaction products such as FAME and glycerol. Therefore, product refining process is necessary. This post-treatment of products, by-products and waste will lead in significant manufacturing cost and a challenging wastewater treatment problem. From literature, it is recognised that improving biodiesel process modelling and optimization is the key to lowering biodiesel production costs without using a lot of oil (Kick *et al.*, 2013). Hence, reactive distillation has been proposed for process intensification for biodiesel production process since it is favourable to tackle the issue faced by conventional biodiesel production process. At the same time, optimization is essential in reactive distillation column as it reduces energy consumption and makes intensified process cost effective.

1.6 Objectives

The objective of this research:

i. To investigate the effect of feed inlet temperature and reflux ratio on energy consumption based on reboiler heat duty in RD column.

ii. To study the optimum operating condition for RD column through sensitivity and optimization analysis.

iii. To compare the performance of conventional and intensified process based on energy and exergy analysis.