การวิเคราะห์และการหาสภาวะที่เหมาะสมของกระบวนการผลิตไบโอดีเซลจากน้ำมันสบู่ดำโดยใช้หอกลั่นแบบเกิดปฏิกิริยา

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ANALYSIS AND OPTIMIZATION OF BIODIESEL PRODUCTION FROM JATROPHA OIL USING REACTIVE DISTILLATION

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ไบโอดีเซลเป็นแหล่งพลังงานทางเลือกที่น่าสนใจซึ่งสามารถนำมาทดแทนแหล่งพลังงานปิโตรเลียม โดยทั่วไปน้ำมันพืชที่รับประทานได้ เช่น น้ำมันปาล์ม น้ำมันถั่วเหลือง ถูกนำมาใช้เป็นวัตถุดิบในการผลิตไบโอดีเซล อย่างไรก็ตามการใช้น้ำมันเหล่านี้ทำให้เกิดการขาดแคลนน้ำมันพืชสำหรับการบริโภค งานวิจัยนี้จึงมุ่งเน้นการพัฒนากระบวนการผลิตไบโอดีเซลจากน้ำมันสบู่ดำซึ่งเป็นน้ำมันพืชที่ไม่สามารถบริโภคได้ เนื่องจากน้ำมันสบู่ดำมีปริมาณกรดไขมันอิสระ 14% ดังนั้นกระบวนการผลิตไบโอดีเซลที่พิจารณาประกอบด้วยสองส่วน ส่วนแรกจะเปลี่ยนไตรกลีเซอร์ไรด์ให้เป็นกรดไขมันโดยใช้ปฏิกิริยาไฮโดรไลซิส และในส่วนที่สอง กรดไขมันจะทำปฏิกิริยาเอสเทอร์ริฟิเคชันกับเมทานอลโดยใช้กรดเป็นตัวเร่งปฏิกิริยาได้ผลิตภัณฑ์เป็นเมทิลเอสเทอร์ (ไบโอดีเซล) งานวิจัยนี้ได้ประยุกต์ใช้หอกลั่นแบบมีปฏิกิริยาเพื่อเพิ่มสมรรถนะของกระบวนการเอสเทอร์ริฟิเคชัน การจำลองกระบวนการผลิตไบโอดีเซลถูกดำเนินการเพื่อหาพารามิเตอร์ที่สำคัญซึ่งมีผลต่อกระบวนการผลิต ระเบียบวิธีพื้นที่ผิวตอบสนอง (response surface methodology) โดยการออกแบบเซ็นทรัลคอมโพสิต (central composite design) ถูกใช้ในการหาสภาวะการดำเนินการผลิตไบโอดีเซลที่เหมาะสม จากการศึกษาพบว่า เพื่อให้ได้ไบโอดีเซลที่มีความบริสุทธิ์ 99.9% หอกลั่นแบบมีปฏิกิริยาต้องดำเนินการโดยมีอัตราการไหลของไบโดดีเซลที่ด้านล่างเท่ากับ 126.4 kmol/h อัตราการป้อนกลับ (reflux ratio) เท่ากับ 0.4 และอุณหภูมิของกรดโอเลอิกในสายป้อนเท่ากับ 160 °C เมทานอลและกรดโอเลอิกถูกป้อนเข้าหอกลั่นที่ชั้นที่ 12 และ 3 ตามลำดับ งานวิจัยนี้ยังได้ศึกษาการนำเมทานอลกลับมาใช้ประโยชน์และการเบ็ดเสร็จความร้อนเพื่อลดการใช้พลังงานภายในกระบวนการผลิตไบโอดีเซลโดยใช้หอกลั่นแบบมีปฏิกิริยาด้วย

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Biodiesel is considered a potential substitute of fossil fuel as it is clean and renewable. Edible oils such as palm oil and soybean oil are commonly used as feedstock in biodiesel production; however, using these feedstock cause shortage of vegetable oils for human consumption. This study was concentrated on the development of a biodiesel production process from Jatropha oil, a non-edible vegetable oil. As Jatropha oil always contains about 14% of free fatty acid, the biodiesel production process considered consists of a hydrolysis section where triglyceride is converted to fatty acid and an esterification section where fatty acid reacts with methanol in the presence of acid catalyst to produce methyl ester (biodiesel). The utilization of a reactive distillation was proposed to improve the performance of the esterification process. Simulations of the biodiesel production process using a process flowsheet simulator were carried out to identify important operating parameters. The response surface methodology (RSM) based on a central composite design (CCD) was used to determine optimal operating conditions for biodiesel production. The conditions to get optimal response with 99.9% were found to be 126.4 kmol/h of bottom rate, 0.4 for reflux ratio, 160 ºC for oleic acid feed temperature, methanol feed stage = 12 and oleic acid feed stage = 3. In order to minimize energy consumption, the pre-heated and methanol recovery of a reactive distillation process is considered.

Department : Chemical Engineering Student's Signature ....
Field of Study : Chemical Engineering Advisor's Signature ....
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LIST OF ABBREVIATIONS

CSTR	Continuous stirred tank reactor	(-)
DC	Distillation column	(-)
DEC	Decanter	(-)
E_a	Activation energy	(J/mol)
FFA	Free fatty acid	(-)
GLY	Glycerol	(-)
H2O	Water	(-)
HX	Heat exchanger	(-)
MR	Methanol recovery	(-)
N_{min}	Minimum number of plates	(-)
OIL	Triolein	(-)
OLAC	Oleic acid	(-)
RD	Reactive distillation	(-)
R_{DM}	Minimum reflux ratio	(mole)
RGibbs	Gibbs reactor	(-)
X_1	Bottom rate	(kmol/h)
X_2	Reflux ratio	(mole)
X_3	Oleic acid feed temperature	(°C)
X_4	Oleic acid feed stage	(-)
X_5	Methanol feed stage	(-)
α_{ij}	Relative volatilities	(-)

CHAPTER I

INTRODUCTION

1.1 Introduction

Since energy demands have continuously increased and petroleum-based fuels are depleted, renewable energy which can be used to replace petroleum-based fuels becomes important. Biodiesel, a clean renewable fuel, has recently been considered the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification (Leung et al., 2010). Biodiesel has several advantages over the petroleum diesel; it is safe, renewable, nontoxic and biodegradable and it contains no sulfur. Despite biodiesel and diesel fuel are different in chemical compounds, these two fuels have similar properties and performance parameters (Kiss et al., 2007).

Biodiesel is produced from natural resources such as vegetable oils, animal fats and algae. Both edible and inedible oils can be used as feedstock in the production of biodiesel. The consumption of edible oil in the world is very high, thus resulting in a shortage of oils for biodiesel production. Water and free fatty acid content in waste edible oils are relatively higher than fresh edible oil as a result of frying process. Some common physical changes observed in edible oil after frying are: increase in viscosity and specific heat, change in surface tension and color and higher tendency of fat formation (Gui et al., 2008). In order to overcome this problem, many researchers are interested in inedible oils, which are not suitable for human consumption because of the presence of some toxic components in the oils.

Jatropha curcas has been identified as inedible oil resources. *Jatropha* oil contains about 14% free fatty acid (FFA), which is far beyond the limit of 1% FFA level that can be converted into fatty acid methyl ester by transesterification using an alkaline catalyst. FFAs in the oils can react with the alkaline catalyst and form soap via the saponification reaction. This reaction not only consumes the alkaline catalyst but also causes the formation of emulsions which create difficulties in downstream recovery and purification of biodiesel (Jain and Sharmar, 2010). Accordingly, the development of an efficient process for biodiesel production from oil with high free fatty acid content is required. A two-step biodiesel production has been proposed to deal with such a problem. Following this approach, the first step involves a hydrolysis process where triglycerides in oil are hydrolyzed with water to produce fatty acids and glycerol (Chen et al., 2010). In the second step, all the fatty acids react with methanol via esterification reaction to generate fatty acid methyl ester (biodiesel product) and water. However, since the esterification is an equilibrium reaction, the conversion of fatty acid is limited. To improve the performance of biodiesel production, the application of a reactive distillation in which reaction and separation tasks are carried out in a single unit is a potential option.

This study is focused on the production of biodiesel from *Jatropha* oil. The two-step method consisting of hydrolysis and esterification processes is studied. A reactive distillation is used to improve the performance of the esterification process. Effects of key operational parameters on biodiesel production are studied and suitable operating conditions are identified using a central composite design approach with the aim to optimize the production of biodiesel. In addition, a heat integration of biodiesel production process for efficient energy usage is also considered and compared with a conventional biodiesel process.

1.2 Objectives

The objectives of this study are to analysis and optimize a biodiesel production from *Jatropha* oil using a reactive distillation.

1.3 Scopes of work

1.3.1 To simulate a hydrolysis and esterification combined process for biodiesel production from *Jatropha* oil using a reactive distillation.

1.3.2 To analyze the performance of a hydrolysis and esterification combined process for biodiesel production with respect to key operational and design parameters such as bottom rate, reflux ratio, oleic acid feed temperature, oleic acid feed stage, methanol feed stage and number of stages in a reactive distillation column.

1.3.3 To determine optimum operating conditions of a hydrolysis and esterification combined process for biodiesel production using a central composite design (CCD) approach.

1.3.4 To design the methanol recovery process for biodiesel production.

1.3.5 To improve the energy usage of a biodiesel production process by considering heat integration.

1.4 Expected benefits

1.4.1 Production of biodiesel using *Jatropha* oil as feedstock will reduce the shortage of vegetable oils for human consumption.

1.4.2 A biodiesel production process based on a reactive distillation will increase the yield of methyl ester product.

1.4.3 A suitable operating conditions and configuration of a reactive distillation for biodiesel production can be determined.

1.4.4 Design of a reactive distillation based on a heat integration and methanol recovery concept could improve the efficiency of the biodiesel production.

CHAPTER II

LITERATURE REVIEWS

2.1 Biodiesel production from vegetable oils

Presently, the price of vegetable oils as the feedstock of biodiesel production can be up to 75% of the total manufacturing cost, which makes biodiesel production costs approximately 1.5 times higher than those of diesel (Haas et al., 2002). Edible oils, such as palm oil, rapeseed oil, sunflower oil, and soybean oil have all become a major source of biodiesel production. However, there are serious concerns regarding the use of edible oil in biodiesel. This may cause an increase of edible oil prices and also biodiesel prices (Jain and Sharma, 2010). More than 95% of the biodiesel is made from edible oil, there are many claims that a lot of problems may arise. By converting edible oils into biodiesel, food resources are actually being converted into automotive fuels. It is believed that large scale production of biodiesel from edible oils may bring global imbalance to food supply and demand market. (Gui, 2008) Moreover, the use of waste vegetable oils can lower the feedstock cost significantly, complicated procedures are needed to remove the impurities, resulting in high operating costs (Lu et al., 2009). Accordingly, the high costs and limited availability of biodiesel feedstock are however critical issues in this industry.

Azapagic et al. (2006) presented a methodology for integrating sustainability considerations into process design. Designing more sustainable process is one of the key challenges for sustainable development of the chemical industry. This paper proposes a new methodology for integrating sustainability considerations into process design. Underpinned by life cycle thinking, the methodology guides the process designer through different design stages to enable integration of technical, economic, environment and social criteria to ensure that plant are fit to purpose and that the financial return are maximized. Stages in process design are as follows: project initiation, preliminary design, detailed design and final design.

2.2 Non-edible vegetable oils

The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel to the commercial filling stations. In order to overcome these drawbacks, researchers have focus on non-edible oil for biodiesel production. Non-edible oils are not suitable for human consumption because of the presence of some toxic components in the oil. Non-edible oils such as jatropha oil, castor oil, rubber seed oil and sea mango are alternative feedstock for biodiesel production. *Jatropha curcas* has been found more suitable for biodiesel production as it has been developed scientifically to give better yield and productivity (Jain and Sharma, 2010). The oil from the seeds has valuable properties such as a low acidity, good oxidation stability as compared to soybean oil, low viscosity as compared to castor oil and better cold properties as compared to palm oil. (Tapanes et al., 2007) Besides, Jatropha oil has higher a cetane number compared to diesel which makes it a good alternative fuel with no modifications required in the engine (Jain and Sharma, 2009).

Gui et al. (2008) reviewed the feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. Currently, more than 95% of the world biodiesel is produced from edible oil which is easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oil without proper planning may cause negative impact to the world, such as depletion of food supply leading to economic imbalance. Competition of edible oil sources as food vs. fuel makes edible oil not an ideal feedstock for biodiesel production. Furthermore, most of the non-edible plants can be grown in wasteland and infertile land which otherwise would not have much use. This would not only allow wasteland utilization but at the same time would also be used to produce oil crops for biodiesel production without the need to compete with food crops for limited arable land. Taking all these factors into consideration, non edible oils definitely have the advantage over edible oils as biodiesel feedstock

2.3 Production of biodiesel from *Jatropha curcas* oil

Jatropha oil contains about 14% free fatty acid (FFA), which is far beyond the limit of 1% FFA level that can be converted into biodiesel by transesterification using alkaline catalyst. Pretreatment process (esterification) was used to reduce FFA, which is far above 1% limit for satisfactory transesterification reaction. Many research studied the features of biodiesel production by using *Jatropha curcas* oil as feedstock. For example, Berchmans and Hirata (2007) have reported the biodiesel production from crude *Jatropha curcas* oil having high free fatty acids. The first step was carried out with 0.60 w/w methanol-to-oil ratio in the presence of 1% w/w H_2SO_4 as an acid catalyst in 1-h reaction at 50 °C. After the reaction, the mixture was allowed to settle for 2 h and the methanol-water mixture separated at the top layer was removed. The second step was transesterified using 0.24 w/w methanol to oil and 1.4 w/w NaOH to oil as alkaline catalyst to produce biodiesel at 65 °C. The final yield for methyl esters of fatty acids was 90% in 2 h.

Jain and Sharma (2010) reported the results of kinetics of two-step acid base catalyzed transesterification process carried out at an optimum temperature of 65 °C and 50 °C for esterification and transesterification respectively under the optimum methanol to oil ratio of 3:7 (v/v), catalyst concentration 1% (w/w) for H_2SO_4 and NaOH. The yield of methyl ester (ME) has been used to study the effect of different parameters. The results indicate that both esterification and transesterification reaction are of first order with reaction rate constant of 0.0031 min^{-1} and 0.008 min^{-1} respectively. The maximum yield of 21.2% of ME during esterification and 90.1% from transesterification of pretreated JOC has been obtained.

Chen et al. (2009) investigated supercritical carbon dioxide ($SC\text{-}CO_2$) extraction of triglycerides from powdered *Jatropha curcas* kernels followed by subcritical hydrolysis and supercritical methylation of the extracted $SC\text{-}CO_2$ oil to obtain a purity level of biodiesel. Effects of the reaction temperature, the reaction time and the solvent to feed ratio on free fatty acids in the hydrolyzed oil and fatty acid esters in the methylated oil via two experimental designs were also examined. The activation energy of hydrolysis and trans-esterified reactions were 68.5 and 45.2 kJ/mole, respectively. The hydrolysis reaction occurred at 11.0 MPa and 563 K. This study demonstrates that supercritical methylation preceded by subcritical hydrolysis of the SC-CO_2 oil is feasible two-step process in producing biodiesel from powdered *Jatropha* kernels.

2.4 Reactive distillation for biodiesel production

Kiss et al. (2007) proposed the biodiesel production by catalytic reactive distillation powered by metal oxides. The properties and use of biodiesel as e renewable fuel as well as the problems associated with its current production process are outlined. Biodiesel can be produced by esterification of fatty acid using acid catalysts. Finding catalysts that are active, selective, and stable under process conditions is the main challenge for a successful design. Catalysts based on metal oxides such as niobia, zirconia, titania, and tin oxide proved to be the best candidates. Rigorous process simulations show that combining metal oxide catalysts with reactive distillation technology is a feasible and advantageous solution for biodiesel production.

Kiss (2011) presented a novel heat-integrated process based on reactive distillation that aims to reduce furthermore the energy requirements for biodiesel production, leading to competitive operating cost. Rigorous simulations embedding experimental results were performed using computer aided process engineering tools, such as AspenTech Aspen Plus. The RD column was simulated using the rigorous RADFRAC unit with RateSep (rate-based) model, and explicitly considering three phase balances. Steady-state simulation results are given for a plant producing 10 ktpy fatty acid methyl esters (FAME) from methanol and waste vegetable oil with high free fatty acids (FFA) content, using sulfated zirconia as green catalyst. The heat-integrated RD process eliminates all conventional catalyst related operations, efficiently uses the raw materials and the reactor volume offering complete conversion of the fatty acids and allowing significant energy savings. Remarkably, compared to previously reported RD processes, the energy requirements of this process are about 45% lower – only 108.8 kWh/ton biodiesel – while the capital investment costs remains the same as no additional equipment is required.

Cossio-Vargas et al. (2011) studied the production of biodiesel using feedstock mixtures of fatty acids in complex reactive distillation columns. The production of biodiesel is explored using reactive distillation column sequences with thermal coupling. The results indicate that the complex reactive distillation sequences can produce a mixture of esters as bottom product that can be used as biodiesel. In particular, the thermally coupled distillation sequence involving a side rectifier can handle the reaction and complete separation in accordance with process intensification principles.

Fernando et al. (2011) proposes the use of reactive distillation and thermally coupled reactive distillation configurations to produce biodiesel fuel by the supercritical methanol method. First-order kinetics is used to represent the esterification reaction, obtaining high conversion in a single shell. Both of the configurations proposed reduce energy requirements when compared to conventional process. The thermally coupled reactive distillation configuration shows to be the best alternative in terms of energy consumption, CO_2 emission and thermodynamic efficiency. Further, cost estimations also show that the use of a thermally coupled scheme considerably reduces both utilities and capital costs.

2.5 Optimization for biodiesel production

Chen et al. (2008) studied the effects of enzyme concentration, temperature, molar ratio of methanol to oil and stirring rate on yield of fatty methyl ester by using central composite design (CCD) of the response surface methodology (RSM) to find the optimal conditions. The results indicated that enzyme concentration, temperature, molar ratio of methanol to oil and stirring rate were the significant factors on the yield of fatty methyl ester and a quadratic polynomial equation was obtained for methyl ester yield by multiple regression analysis. The predicted biodiesel yield was 0.915

(w/w) under the optimal conditions and subsequent verification experiments with biodiesel yield of 0.887±0.0161 (w/w) confirmed the validity of the predicted model.

Tiwari et al. (2007) used response surface methodology (RSM) based on central composite rotatable design (CCRD) to optimize the three important reaction variables; methanol quantity, acid concentration and reaction time for reduction of free fatty acid (FFA) content of the oil to around 1% and for carrying out transesterification of the pretreated oil. Using RSM, quadratic polynomials equations were obtained for predicting acid value and transesterification. Verification experiments confirmed the validity of both the predicted models. The optimum combination for reducing the FFA of Jatropha curcas oil from 14% to less than 1% was found to be 1.43% v/v H_2SO_4 acid catalyst, 0.28 v/v methanol-to-oil ratio and 88-min reaction time at a temperature of 60 °C as compared to 0.16 v/v methanol-to-pretreated oil ratio and 24 min of reaction time at a reaction temperature 60 °C for producing biodiesel. This process gave an average yield of biodiesel more than 99%.

CHAPTER III

THEORY

3.1 *Jatropha curcas* oil

The genus *Jatropha* belongs to tribe Joanneasiae of Crotonoideae in the *Euphorbiaceae* family. *Jatropha* is widely distributed in the wild and cultivated tropical areas of Central America, South America, Africa, India, South Eastern Asia, and Australia. Therefore, it typically grows between 15 and 40 ºC with rainfall between 250 and 3000 mm and is more altered by lower temperatures than by altitude or day length.

The genus Jatropha was derived from the Greek words Jatros (doctor) and trophe (food) which implies medicinal uses. It is a small tree or large shrub, which can grows between 3 to 5 meters in height, but can attain a height up to 8 to 10 meters in favorable conditions. The plant is monocious and flowers are unisexual. Pollination is by insects. The life span of the plant is more than 50 years. Jatropha is planted as a hedge by farmers all over the world around homesteads, gardens and fields, because it is not browsed by animals. The root, stem, leaves, fruit, seed, bark and latex of the plant are largely used for the treatment of many diseases in different parts of the world. (Verma and Gaur, 2009)

The plant produced capsulated fruits bearing seeds. On an average seed weight ranges from 0.53 to 0.86 g and it contains 30–40% oil or more. The oil from seeds has valuable properties such as a low acidity, good stability as compared to soybean oil, low viscosity as compared to castor oil and better cold properties as compared to palm oil. Besides, Jatropha oil has higher a cetane number compared to diesel which makes it a good alternative fuel with no modification require in the engine. Seed contain different kinds of saturated and unsaturated fatty acids. Fatty acid composition of *Jatropha* oil is shown in Table 3.1.

Table 3.1 Fatty acid composition of *Jatropha* curcas oil.

Fatty Acid	Systemic name	Formula	% Composition
Palmitic acid	Hexadecanoic	$C_{16}H_{32}O_2$	14.1
Palmitoleic acid	9-*cis*-Hexadecenoic	$C_{16}H_{30}O_2$	0.5
Stearic acid	Octadecanoic	$C_{18}H_{38}O_2$	6.8
Oleic acid	*Cis*-9-Octadecanoic	$C_{18}H_{34}O_2$	38.6
Linoleic acid	*Cis*-9,*cis*-12-Octadecadienoic	$C_{18}H_{32}O_2$	36.0
Linolenic acid	Octadecatrienoic	$C_{18}H_{30}O_2$	0.2
Arachidice acid	Eicosanoic	$C_{20}H_{40}O_2$	0.2
Gadolic acid	Eicosenoic	$C_{20}H_{36}O_2$	3.6

Table 3.2 General properties of *Jatropha curcas* (Divakara et al., 2010).

Major fuel properties	Jatropha curcas	
	Oil	Methyl-esters
Density (g/cm^3)	0.916	0.875
Flashpoint (°C)	235	186
Cetane number	46.3	57-62
Carbon Residue (%)	0.38	0.18
Sulfur content (%)	0-0.13	0.0036
Calorific value (MJ/kg)	39.63	39.65
Acid Number (mg KOH/g)	3.71	0.27
Iodine number (mg iodine/g)	101.7	95-106
Saponification number (mg/g)	195	202.6
Free glycerol (%)	-	0.015-0.030
Total glycerol (%)	-	0.088-0.100
Viscosity at 40 (°C)	40.06	4.20

Apart from being potential feedstock in the production of biodiesel as a diesel substitute, Jatropha oil has other uses such as producing soap and biocides (insecticide, molluscicide, fungicide and nematicide).

3.1.1 Kinetics of esterification of *Jatropha curcas* oil

The kinetic model used in this work relied on the following assumptions:

a) The esterification reaction was a reversible process and the rate of which under the operation conditions used was controlled by the chemical reaction.
b) The rate of the non-catalyzed reaction was negligible relative to the catalyzed reaction.
c) Fatty acid to methanol mole ratio used was high enough for the methanol concentration to remain constant throughout the process.

Under these conditions, the reaction was assumed to be first-order in the forward direction and second-order in the reverse direction, and hence conforms to the following kinetic law:

$$\frac{-d[A]}{dt} = k_1[A] - k_2[C][D] \tag{3.1}$$

Where $[A]$ denotes the concentration of FFA (acid value) in mg KOH/g oil; $[C]$ and $[D]$ are the concentrations of fatty acid methyl ester and water formed during the reaction and k_1 and k_2 are the kinetic constants for the forward and reverse reaction, respectively.

As expected, k_1 increased with increasing methanol/oil ratio and catalyst concentration; on the other hand, k_2 was negligible which indicates that the hydrolysis reaction hardly took place. The influence of temperature on the specific reaction rate was determined by fitting k_1 and k_2 data in the Arrhenius equation:

$$K = Ae^{\frac{-E_a}{RT}} \tag{3.2}$$

Table 3.3 Kinetics of Esterification of *Jatropha curcas* oil catalyzed by sulfuric acid (0.5%).

Kinetic constant	Catalyst (%)	Frequency Factor (A)	Activation Energy (J/mol)
k_1	0.5	1.37E+7	59333
k_2	0.5	3.09E12	101972

From the plot of ln K as a function of the reciprocal temperature, both the frequency factor, A, and the energy of activation, E_a, were obtained by non linear regression. The results are shown in Table 3.3.

3.2 Biodiesel

Biodiesel is a renewable diesel replacement fuel. Despite the chemical differences, these two fuels have similar properties and performance parameters (Table 3.1). An important characteristic of diesel fuels is the ability to autoignite, quantified by the cetane number (cetane index). Biodiesel not only has a higher cetane number than petroleum diesel but also has a higher flash point, meaning better and safer performance. Blends of biodiesel and petroleum diesel are designated by a “B” followed by the vol% of biodiesel. B5 and B20, the most common blends, can be used in unmodified diesel engines. Remarkably, biodiesel is the only alternative fuel currently available with an overall positive life-cycle energy balance, producing 3.2 units of fuel product energy per unit of fossil energy consumed, compared to barely 0.83 units for petroleum diesel.

3.2.1 Sources of biodiesel

Biodiesel is manufactured from natural resources such as vegetable oils, animal fats or recycled cooking oils. Vegetable oils, also known as triglycerides, are becoming one of the promising renewable feedstocks for biodiesel production and have become more attractive recently because of its environmental benefits. Edible vegetable oils like canola, soybean, rapeseed, sunflower and corn have been used for biodiesel production and found to be good as a diesel substitute. The non-edible vegetable oils such as madhuca indica, Jatropha curcas and Pongamia pinnata have also found to be suitable. Edible oils are widely used and more commonly used for biodiesel production (Koh et al., 2011). Animal fats used to produce biodiesel include tallow, lard, yellow grease and chicken fat. Recycled cooking oils are low cost feedstocks and high free fatty acid content. The biodiesel manufacturing process converts oils and fats into chemicals call long-chain mono alkyl esters, or biodiesel.

Soybeans are commonly used in the United States for food products which has led to soybean biodiesel becoming the primary source for biodiesel in the country. Malaysia and Indonesia palm oil is used as a significant biodiesel source. In Europe, rapeseed is the most common base oil used in biodiesel production. In India and Southeast Asia, the Jatropha tree is used as a significant fuel source.

Table 3.4 Petroleum Diesel vs. Biodiesel (Kiss et al., 2008).

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
Fuel composition	C_{10}-C_{21} HC[a]	C_{12}-C_{22} FAME[a]
Kinetic viscosity, mm^2/s (at 40 °C)	1.3-4.1	1.9-6.0
Specific gravity, kg/L	0.85	0.88
Boiling point, °C	188-343	182-338
Flash point, °C	60-80	100-170
Cloud point, °C	-15 to 5	-3 to 12
Pour point, °C	-35 to -15	-15 to 10
Cetane number (ignition quality)	40-55	48-65
Stoichiometric air/fuel ratio (AFR)	15	13.8
Life-cycle energy balance (energy units produced per unit energy consumed)	0.83/1	3.2/1

[a] HC, hydrocarbons; FAME, fatty acid methyl esters

3.2.2 Advantages of biodiesel

Main advantages of biodiesel are liquid nature portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number and higher biodegradability.

3.2.2.1 Availability and renewability of biodiesel

Biodiesel can be made from domestically produced, renewable oilseed crops such as soybean, rapeseed and sunflower. The risks of handling, transporting and storing biodiesel are much lower than those ones, associated with diesel. Biodiesel is safe to handle and transport because it is as biodegradable as sugar and has a high flash point compared to petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend is a mix of 20% biodiesel with 80% petroleum diesel, or B20 under recent scientific investigations.

3.2.2.2 Higher combustion efficiency of biodiesel

Oxygen content of biodiesel improves the combustion process and decreases its oxidation potential. Structural oxygen content of a fuel improves combustion efficiency due to the increase of the homogeneity of oxygen with the fuel during combustion. Because of this the combustion efficiency of biodiesel is higher than petroleum diesel as well as the combustion efficiency of methanol/ethanol is higher than that of gasoline. A visual inspection of the injector types would indicate no difference between the biodiesel fuels when tested on diesel fuel. The overall injector coking is considerably low. Biodiesel contains 11% oxygen by weight and contains no sulfur. The use of biodiesel can extend the life of diesel engines because it is more lubricating than petroleum diesel fuel. Biodiesel has got better lubricant properties the diesel.

Table 3.5 Chemical properties and higher heating values (HHVs) of biodiesel and petroleum diesel fuels (Demirbas, 2007).

Chemical property	Biodiesel	Diesel
Ash (wt %)	0.002-0.036	0.006-0.010
Sulfur (wt %)	0.006-0.020	0.020-0.050
Nitrogen (wt %)	0.002-0.007	0.0001-0.003
Aromatic (vol %)	0	28-38
Iodine number	65 - 165	0
HHV (MJ/kg)	39.2-40.6	45.1-45.6

Table 3.6 Pollutant emission from diesel engines using the biodiesel mixtures relative to standard diesel fuel (%) (Demirbas, 2007).

Mixture	CO	NO_x	SO_2	Particular matter	Volatile organic compounds
B20	-13.1	+2.4	-20	-8.9	-17.9
B100	-42.7	+13.2	-100	-55.3	-63.2

The high heating values (HHVs) of biodiesel are relatively high. The HHVs of biodiesels (39-41 MJ/kg) are slightly lower than that of gasoline (46 MJ/kg), petroleum diesel (43 MJ/kg) or petroleum (42 MJ/kg), but higher than coal (32-37 MJ/kg). Table 3.3 shows the comparison of chemical properties and HHVs between biodiesel and petroleum diesel fuels.

3.2.2.3 Lower emission by using biodiesel

Combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons (HC), and a 75-90% reduction in polycyclic aromatic hydrocarbons (PAHs). Biodiesel further provides significant reductions in particulates and carbon monoxide than petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on engine family and testing procedures.

3.2.3 Methods for biodiesel production

The conventional process for biodiesel production consists of the transesterification of triglycerides (contained in vegetable oils or animal fats used as raw materials) and a short-chain alcohol, such as methanol or ethanol, in the presence of catalyst. The more commonly used catalysts are bases (sodium hydroxide, potassium hydroxide), acids (sulfuric acid) and enzymes. However, basic catalysts are usually favored over acid catalysts because of the higher reactivity and the milder process conditions such as the lower temperature required. A disadvantage of use of a basic catalyst is the saponification reaction occurring when the raw material contains high water or free fatty acid concentrations. In the case of acid catalyst, the main disadvantage is that the reaction rate becomes very slow. In addition, the use of either kind of catalyst involves a difficult separation and high energy consumptions to obtain biodiesel and glycerin (as a by-product) with an adequate purity. In the case of enzymes as catalyst, the main disadvantage of biodiesel production is its high cost.

This transesterification involving three consecutive reversible reactions, they are the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, excess alcohol is used to shift the equilibrium toward the product (ester and crude glycerol). The overall transesterification reaction is given by three consecutive and reversible equations as shown below.

$$\begin{array}{llclll}
\text{Triglyceride (TG)} & + \ \text{ROH} & \leftrightarrow & \text{Diglyceride (DG)} & + \ \text{RCOOR}_1 & \\
\text{Diglyceride (DG)} & + \ \text{ROH} & \leftrightarrow & \text{Monoglyceride (MG)} & + \ \text{RCOOR}_2 & (3.3) \\
\text{Monoglyceride (MG)} & + \ \text{ROH} & \leftrightarrow & \text{Glycerol} & + \ \text{RCOOR}_3 &
\end{array}$$

Where R_1, R_2, R_3 are long-chain hydrocarbons, sometimes called fatty acid chains.

Alcohols are any organic compounds which have a hydroxyl function group bonded to other carbons or hydrogen atoms having. Examples are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently.

However, methanol is the most preferable because of its low cost and its physical and chemical advantages as polar and short chain alcohol. (Demirbas, 2005)

The free fatty acids (FFAs) and water contents have significant negative effects on the transesterification reaction. The high FFAs content (>1% w/w) will happen soap formation and the separation of product will be exceedingly difficult, and as a result, it has low yield of biodiesel product.

$$\underset{\text{(FFA)}}{R_1 - COOH} \quad + \quad \underset{\text{(Sodium hydroxide)}}{NaOH} \quad \rightarrow \quad \underset{\text{(Soap)}}{R_1COONa} \quad + \quad \underset{\text{(Water)}}{H_2O} \qquad (3.4)$$

3.2.3.1 Hydrolysis and Esterification

A simpler manufacturing procedure would consist in first performing the hydrolysis of triglycerides and isolating the fatty acids followed by esterification reaction in reactive distillation column. Significant advantages would be the possibility of extracting high value fatty acids from the lipid material, as well as obtaining high purity glycerol. The hydrolysis reaction can be carried out without a catalyst working in milder conditions compared to full esterification.

The acid-catalyzed esterification of the oil is an alternative, but it is much slower than the base-catalyzed transesterification reaction. Therefore, FFAs were first converted to esters in a pretreatment process with methanol using acid catalyst. The esterification reaction can be represented as follows:

Hydrolysis reaction

$$\begin{array}{lcclcl} CH_2 - OCOR^1 & & & R^1COOH & + & CH_2 - OH \\ CH - OCOR^2 & + \; 3H_2O & \leftrightarrows & R^2COOH & + & CH - OH \\ CH_2 - OCOR^3 & & & R^3COOH & + & CH_2 - OH \\ \text{Triglycerides} & \text{Water} & & \text{Fatty acids} & & \text{Glycerol} \end{array} \qquad (3.5)$$

Esterification reaction

$$\begin{array}{lllll} R_4COOH & + \quad CH_3OH & \leftrightarrows & R_4COOCH_3 & + \quad H_2O \\ \text{Fatty acid} & \quad\ \text{Methanol} & & \text{Methyl-ester} & \quad\ \text{Water} \end{array} \tag{3.6}$$

Other methods for producing biodiesel, biodiesel can also produced by using alcohols at supercritical conditions. Supercritical processes were developed to solve the problem of miscibility of oil and alcohol that hinders the kinetic of transesterification, as well as to take advantage of not using a catalyst at all. However, the operating conditions are sever (T>240 ºC, p>80 bar) and therefore require special equipment.

3.3 Distillation design

3.3.1 Minimum number of plates

Fenske's equation is used to calculate N_{min} which is the number of plates required to make a specified separation at total reflux. The Fenske total reflux equation can be written as

$$N_{\mathrm{min}} = \frac{\ln\left[\left(x_{\mathrm{Di}} / x_{\mathrm{Bi}}\right) / \left(x_{\mathrm{Dj}} / x_{\mathrm{Bj}}\right)\right]}{\ln \alpha_{\mathrm{ij}}} \tag{3.7}$$

Where i is any component and j is an arbitrary selected reference component in the definition of relative volatilities,

$$\alpha_{\mathrm{ij}} = \frac{K_{\mathrm{i}}}{K_{\mathrm{j}}} = \frac{y_{\mathrm{i}} / x_{\mathrm{i}}}{y_{\mathrm{j}} / x_{\mathrm{j}}} \tag{3.8}$$

3.3.2 Minimum reflux ratio

An approximate but fairly accurate method of determining R_{DM} was developed by Underwood. The relative volatility for each component is taken to be the same in the upper and lower invariant zones, and constant molal over flow is assumed The equations for the invariant zones are written terms of the relative volatility α_i, where $\alpha_i = K_i/K_{ref}$, with the heavy key generally generally taken as the reference component. The two equations are combined with an overall material balance and the feed quality equation to give an equation that must be solved by trial. The correct root ϕ of this equation lies between the values of α for the key. The equation is

$$1-q=\sum\frac{\alpha_i x_{Fi}}{\alpha_i-\phi} \tag{3.9}$$

The value of ϕ is then used to get R_{DM}

$$R_{DM}+1=\sum\frac{\alpha_i x_{Di}}{\alpha_i-\phi} \tag{3.10}$$

The ϕ is the common root for the top-section equations and the bottom-section equations developed by Underwood for a column at the minimum reflux with separate zones of constant composition in each section.

Then q has the following numerical limits for the various conditions:

Cold feed $q > 1$

Feed at bubble point (saturated liquid), $q = 1$

Feed partially vapor, $0 < q < 1$

Feed at dew point (saturated vapor), $q = 0$

Feed superheated vapor, $q < 0$

3.3.3 Number of ideal plates at operating reflux

The empirical correlation of Gilliland then used these values to give N for any specified. Limitations of the Gilliland correlation are discussed by Henley and Seader. The following equation, developed by Molokanov et al. satisfies the end points and fits the Gilliland curve reasonably well:

$$\frac{N-N_{\min}}{N+1}=1-exp\left[\left(\frac{1+54.4\psi}{11+117.2\psi}\right)\left(\frac{\psi-1}{\psi^{0.5}}\right)\right] \tag{3.11}$$

Where $\psi = (R - R_{DM})/(R+1)$

3.4 Reactive distillation

Reactive distillation columns (RD) incorporate both phase separation and chemical reaction in a single unit. The term catalytic distillation is also used for such systems where a catalyst (homogeneous or heterogeneous) is used to accelerate the reaction.

In conventional distillation design, tray holdup has no effect on steady-state composition. In reactive distillation, tray holdup (or amount of catalyst) has a profound effect on conversion, product composition, and column composition profiles. So, in addition to the normal design parameters of reflux ratio, number of trays, feed tray location, and pressure, reactive distillation columns have the additional design parameter of tray holdup. If there are two reactant feedstreams, an additional design parameter is the location of the second feed.

Reactive distillation is usually applied to systems in which the relative volatilities of the reactants and products are such that the products can be fairly easily removed from the reaction mixture while keeping the reactants inside the column. Considering a reversible reaction with reactants A and B reacting to form products C and D:

$$A+B \leftrightarrow C+D \tag{3.12}$$

The boiling points of the components follow sequence A, C, D and B. For the reactive distillation to be effective, the volatilities of the products C and D should be greater or less than the volatilities of the reactants A and B. Suppose the volatilities are

$$\alpha_C > \alpha_A > \alpha_B > \alpha_D \tag{3.13}$$

The conceptual layout of an RD set-up for fatty esters synthesis is presented in Figure. 3.1. From the reversible reaction, A = alcohol, B = fatty acid, C = water and D = fatty ester. A would be fed into lower section of a reactive column and rise upward. B would be fed into the upper section and flow downward. As the components reacts, product C would be distillated out the top of the column, and product D would be withdrawn out the bottom. The reactants can be retained inside the column by vapor boilup and reflux while the products are removed.

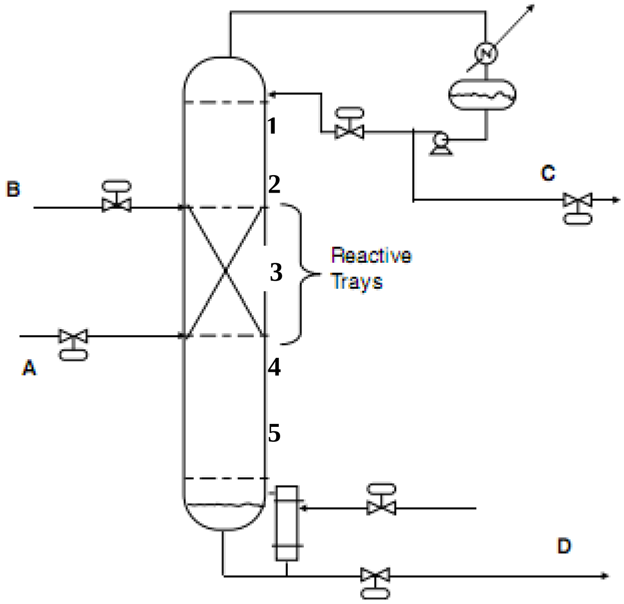

Figure 3.1 Reactive distillation.

From Figure 3.1, five zones may be distinguished, starting from the top, as follows:

(1) Rectifying section: separation of the light product C from the heavy reactant B.
(2) Recovery of un-reacted light reactant A by absorption in heavy reactant B.
(3) Reaction zone between A and B in counter current flow.
(4) Recovery of untransformed heavy reactant B by stripping with light reactant A.
(5) Stripping section: separation of the heavy product D from the light reactant A.

Reactive distillation systems are bounded by two limiting cases: (1) the non reactive case where no reaction occurs; and (2) the equilibrium reactive case where there is simultaneous vapor-liquid and reaction equilibrium.

3.4.1 Advantages of Reactive distillation

Compared to the conventional technology, Reactive distillation is attractive because it offers several advantages.

The advantages of RD can be summarized as follows:

1. Combining the reaction process and the separation into one unit. Simplification or elimination of the separation system can lead to significant capital savings.
2. Improved conversion of reactant approaching 100%. This increase in conversion gives a benefit in reduced recycle costs.
3. Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reagents can lead to reduction of the rates of side reactions and hence improved selectivity for the desired products.
4. Significantly reduced catalyst requirement for the same degree of conversion.

5. Avoidance of azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. RD conditions can allow the azeotropes to be “reacted away” in a single vessel.
6. Reduce by-product formation.
7. Heat integration benefits. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty.
8. The counter-current flow allows an excess of reactant alternatively at the top and the bottom of the reactive zone, resulting in more uniform and higher reaction rate.
9. Avoidance of hot spots and runaways using liquid vaporization as thermal fly wheel.

3.5 Response surface methodology (RSM) based on Central composite design (CCD)

Response surface methodology (RSM) is a collection of statistical and mathematical methods that are useful for modeling and analyzing engineering problems. In this technique, the main objective is to optimize the response surface that is influenced by various process parameters. RSM also quantifies the relationship between the controllable input parameters and the obtained response surfaces (Kwak, 2005). Box et al., 1951 lay the basic foundations for response surface methodology, which an integration of experimental design, regression, and optimization theory. RSM is widely used to explore and to optimize response surfaces in industrial experiments. For many industrial experiments, the response can be obtained immediately. The result from small exploratory experiments can then be used as a guide to more complicated or large follow-up experiments. In RSM, it is common to begin with a screening experiment to identify important factor or variables. Follow-up experiments seek to improve the performance of the response.

The design procedure for RSM is as follows (Aslan, 2007):

(i) Performing a series of experiments for adequate and reliable measurement of the response of interest.

(ii) Developing a mathematical model of the second-order response surface with the best fit.

(iii) Determining the optimal set of experimental parameters that produce a maximum or minimum value of response.

(iv) Representing the direct and interactive effects of process parameters through two and three-dimensional (3-D) plots.

If all variables are assumed to be measureable, the response surface can be expressed as follows:

$$y = f(x_1, x_2, x_3, \ldots, x_k)$$

Where y is the predicted response variable, and x_i the variables of action called factor.

The goal is to optimize the response variable (y). An important assumption is that the independent variables are continuous and controllable by experiments with negligible errors. The task then is to find a suitable approximation for the true functional between independent variables and the response surface. (Aslan, 2007)

The different orders of models lead to different response surface designs with different properties. Among first order designs, full factorial and fractional factorial designs are used extensively in preliminary experiments to identify potentially important factors. Central Composite Design (CCD) is a design commonly used for building a second-order (quadratic) model. CCD contains an imbedded two-level factorial design and axial (or star) points. If there are k factors, the axial number is 2^k. If the distance from the center of the design space to a factorial point is ±1 unit for each factor, the distance from the center of the design space to the axial point is $\pm\alpha$ with $|\alpha| > 1$. The choice of α is crucial to the performance of the design. The value of α depends on the number of experimental run in the factorial portion of the central composite design, which expressed as follows:

$$\alpha = \left[\text{number of factorial runs}\right]^{1/4} \tag{3.14}$$

If the factorial is a full factor

$$\alpha = \left(2^{k}\right)^{1/4} \tag{3.15}$$

Once the desired ranges of values of the variables are defined, they are coded to lie at ±1 for the factorial points, 0 for the center points and $\pm\alpha$ for the axial points. The codes are calculated as functions of the range of interest of each factor as shown in Table 3.5. When the response data are obtained from the test work, a regression analysis is carried out to determine the coefficients of the response model.

The total number of experiment trials (n_e) depends on the number of factors and the number of center points (n_c). The total number of experimental trials is expressed in Eq. (3.16). The reasonable number of the center points is usually three to five.

$$n_e = 2^k + 2k + n_c \tag{3.16}$$

The polynomial model for the yield fatty methyl ester was expressed as follows:

$$Y_{\mathrm{yield}} = \lambda_0 + \sum \lambda_{\mathrm{i}} X_{\mathrm{i}} + \sum \lambda_{\mathrm{i}} X_{\mathrm{ii}}^2 + \sum \lambda_{\mathrm{ij}} X_{\mathrm{i}} X_{\mathrm{j}} \tag{3.17}$$

Where Y_{yield} is the predicted response variable, λ_0, λ_i, λ_{ii}, λ_{ij} are constant regression coefficients of the model, and X_i, X_j represent the independent variables (the reaction conditions) in the form of code values. The accuracy and general ability of the above polynomial model could be evaluated by the coefficient of determination R^2.

3.5.1 Analysis of variance

Analysis of variance (ANOVA) is the statistical analysis used to check the significance of the equation with the experimental data. This analysis included the Fisher's *F*-test (overall model significance), its associated probability *p(F)*, correlation coefficient *R*, determination coefficient R^2 which measures the goodness of fit of regression model. For each variable, the quadratic models were represented as contour plots. The optimal combination was determined from contour plot. The statistical software was used to generate design, regression analysis, and plot abstention.

Table 3.7 Relationship between coded and actual values of a variable (Box et al., 1951).

Code	Actual value of variable
$-\alpha$	x_{min}
-1	$[x_{\text{max}} + x_{\text{min}})/2] - [(x_{\text{max}} - x_{\text{min}})/2\alpha]$
0	$(x_{\text{max}} + x_{\text{min}})/2$
+1	$[x_{\text{max}} + x_{\text{min}})/2] + [(x_{\text{max}} - x_{\text{min}})/2\alpha]$
$+\alpha$	x_{max}

x_{max} and x_{min} = maximum and minimum values of x; k = number of variables

CHAPTER IV

BIODIESEL PRODUCTION FROM JATROPHA OIL

This chapter presents a biodiesel production model by using *Jatropha* oil as feedstocks. The procedures for process simulations based on use the ASPEN Plus V7.1 consist in defining components, defining appropriate thermodynamical model, the required equipment and operating conditions. Mass and energy balances for each unit, as well as operating conditions, were obtained. The pressure drop in different equipments obviously exists but in this study it was neglected. In this work, sulfuric acid is considered as homogeneous catalyst, since kinetic data for the esterification with methanol is available from previous chapter. We first show the conventional process for biodiesel production, which shows the configuration. After that the reactive distillation process for biodiesel production is proposed, which shows the effect of operating parameters. The performance in term of biodiesel purity and fatty acid conversion is analyzed with respect to the effect key operating parameters such as methanol flow, bottom rate, reflux ratio, oleic feed temperature, oleic feed stage, methanol feed stage and number of stages. And last section, we show the comparison between conventional process and reactive distillation process.

4.1 Introduction

Biodiesel is receiving considerable attention as a renewable source of energy. One of the non-edible feedstock that has received great attention as a source of renewable energy is *Jatropha* oil. Crude *Jatropha* oil contains about 14% of FFA, which is far beyond the 1% limit for promoting transesterification reactions to occurs using alkaline catalyst. FFA can react with the alkaline catalyst and form soap, causing a difficulty in the purification of biodiesel product. It has been reported that transesterification will not occur if the FFA content in the oil is above 3% (Patil P.D and Deng S, 2009). Many pretreatment methods have been proposed and established, including steam distillation, extraction by alcohol and esterification by acid catalyst. However, the esterification of FFA with methanol in the presence of acidic catalysts is the most commonly applied method because the process is simple and acid catalysts will utilize the free fatty acids in the oil and convert into biodiesel (Leung D.Y.C et al., 2010).

4.2 Conventional process for biodiesel production

The conventional flowsheet for biodiesel process is shown in Figure 4.1. Plant capacity was specified at 46 kmol/h of *Jatropha* oil feedstock. However, a high amount of free fatty acids (FFAs) in *Jatropha* oil affects a transesterification process using alkaline catalyst to generate biodiesel. Accordingly, the development of an efficient process for biodiesel production from oils with high free fatty acid content is required. A two-step biodiesel production has been proposed to deal with such a problem. This process involves hydrolysis of triglycerides in subcritical water to produce fatty acids as the first step. The second step is the esterification of fatty acids in the continuous stirred tank reactor (CSTR) to produce the biodiesel. Significant advantages from two-step process, the impurities (water and FFA) do not interfere with the system. The biodiesel produced from this alternate two-step method is cleaner than that from the transesterification of triglyceride alone. No mono- or diglycerides or glycerol appear as by products from the esterification step since these compounds will have been removed after the hydrolysis process. The amount of glycerol in biodiesel phase can be reduced dramatically. Moreover, the hydrolysis process obtaining high purity of glycerol. These studies have simulated the *Jatropha* oil by means of triolein molecule because oleic acid is the fatty acid with the highest composition. Triolein was chosen to represent *Jatropha* oil and methyl-oleate to represent biodiesel.

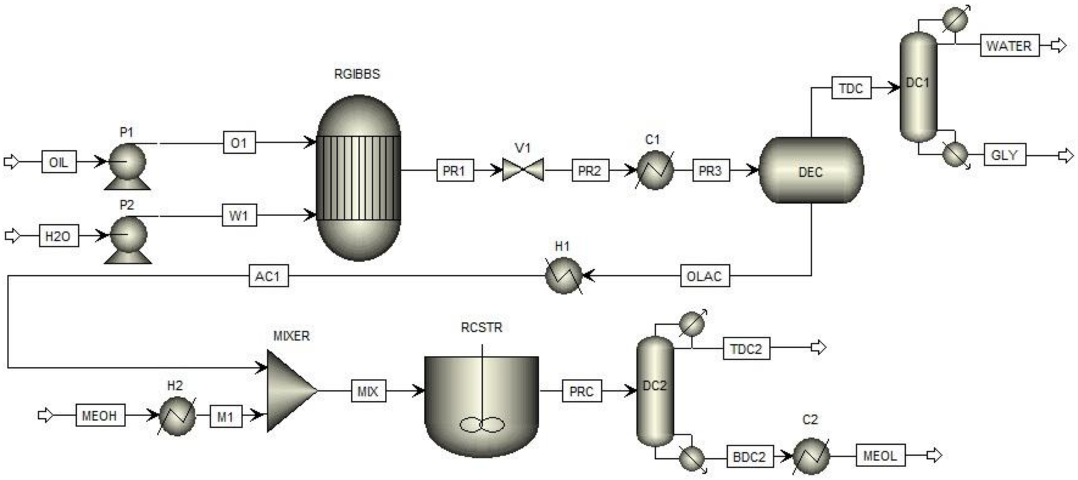

Figure 4.1 Flow diagram of biodiesel production: Conventional process.

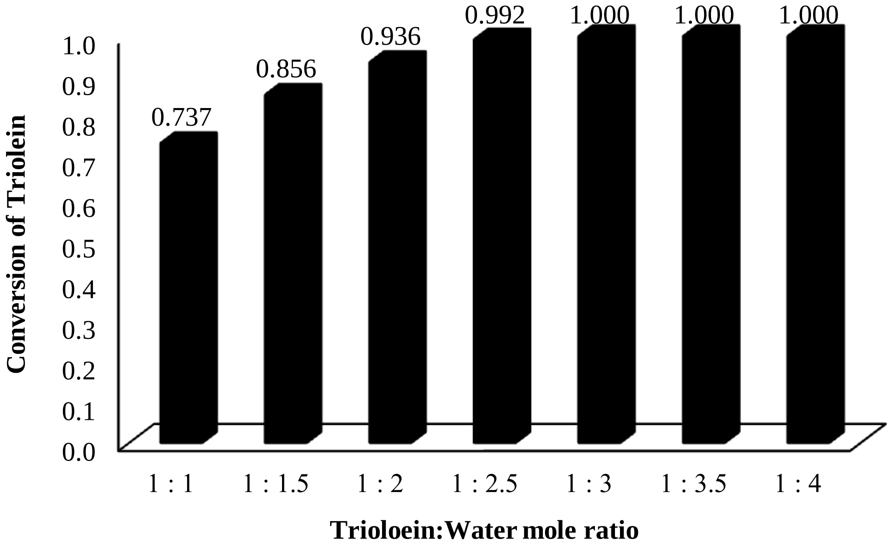

Figure 4.2 Effect of Triolein to water feed ratio on the conversion of Triolein in hydrolysis process (triolein flow rate = 46 kmol/h).

4.2.1 Hydrolysis process

Hydrolysis of triglyceride is a stepwise reaction from triglyceride to diglyceride to monoglyceride, which then produces glycerol and fatty acid. A stream of triolein (OIL) are treated with a stream of water (H2O) in chemical equilibrium reactor with the RGibbs module (RGIBBS) to get oleic acid (OLAC) and glycerol

(GLY) at 290 °C and 7 MPa. RGibbs uses Gibbs free energy minimization with phase splitting to calculate equilibrium and does not require the reaction stoichiometry.

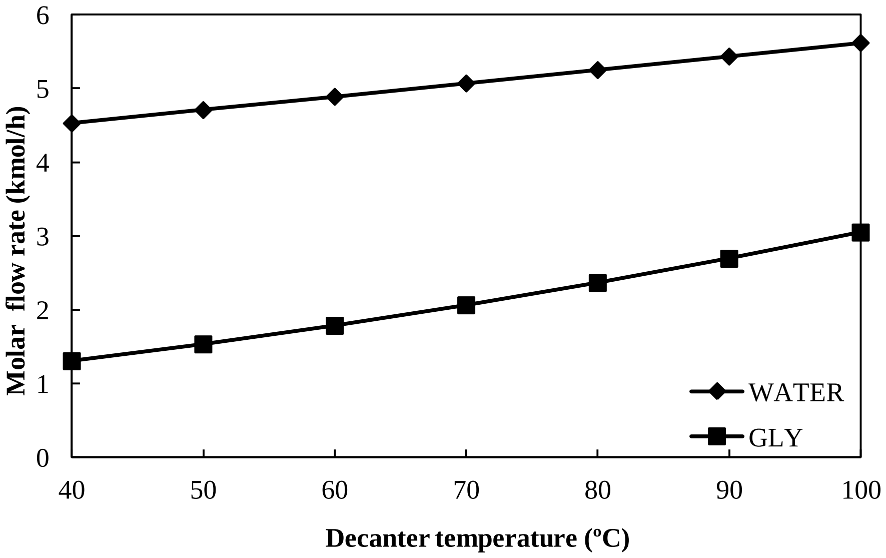

Figure 4.3 Effect of decanter temperature on the molar flow rate of glycerol and water in OLAC stream.

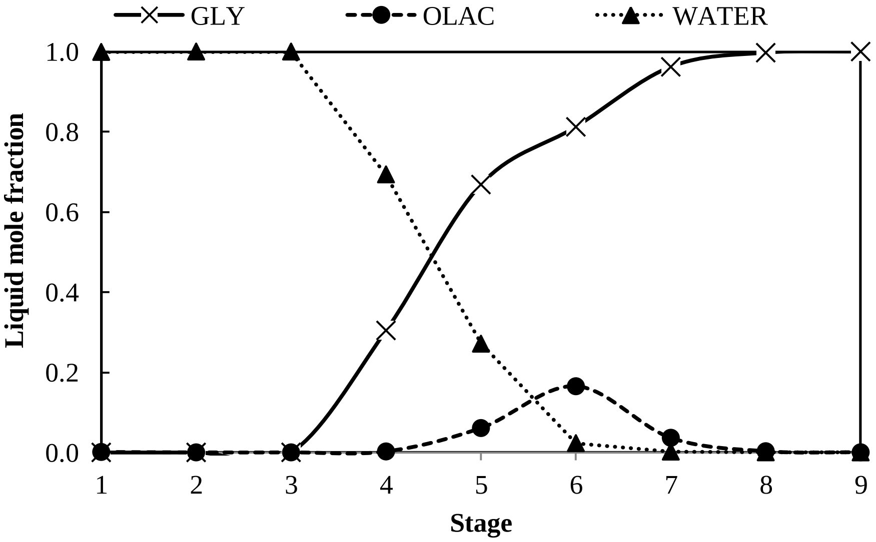

Figure 4.4 Liquid mole composition profiles along the distillation column (DC1) in conventional process.

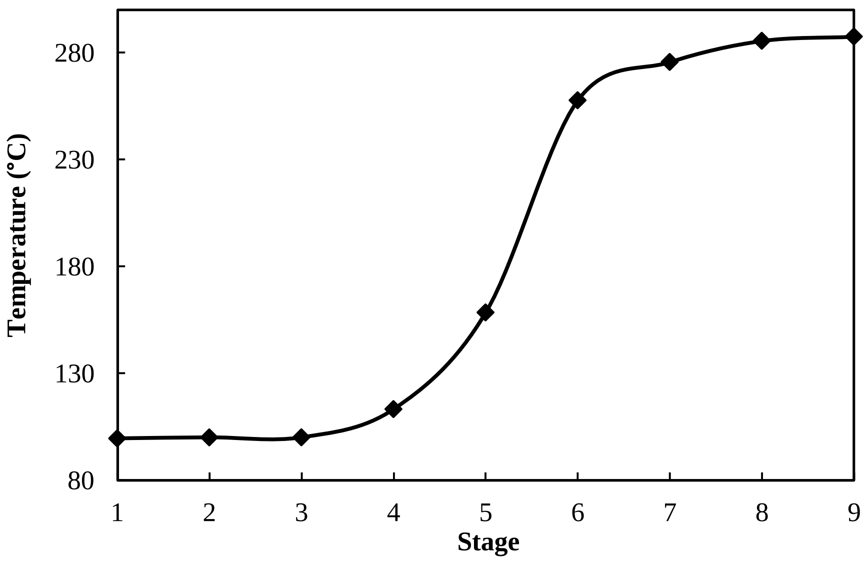

Figure 4.5 Temperature profiles along the distillation column (DC1) in conventional process.

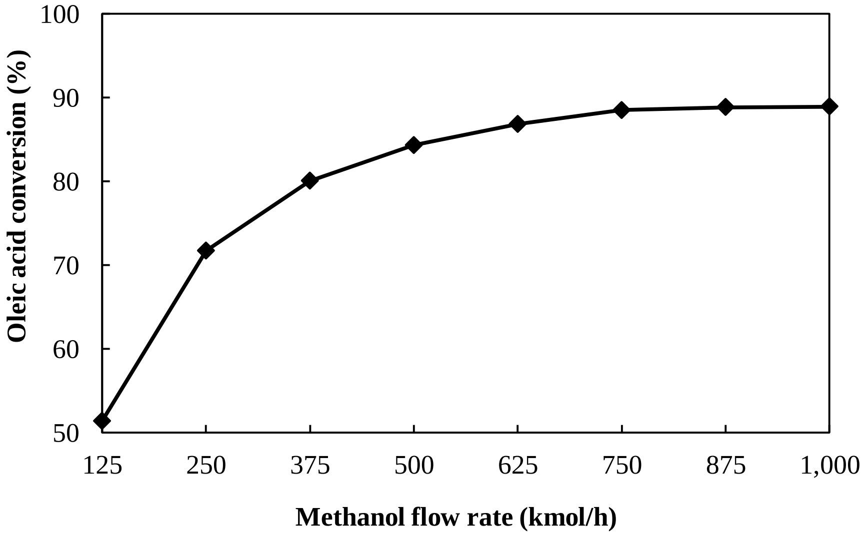

Figure 4.6 Effect of Methanol flow rate on the conversion of oleic acid in esterification process (oleic acid molar flow rate = 125.09 kmol/h and CSTR temperature = 65 °C).

Water which remains in a liquid state from 100 to 374 °C is termed subcritical water. The hydrolysis reaction can be occurred in the subcritical conditions since triolein molecules are non-polar (no dielectric constant) and water molecules are polar (high dielectric constant) and thus, triolein and water cannot mix at the normal operating conditions. Moreover, the immiscibility of oil and water causes an increase in the reaction time at low temperature.

Water in the subcritical states provides unique properties over water at ambient conditions. The dielectric constant of subcritical water (between 7 and 20 MPa; 270-350 ºC) can be adjusted from a value of 80 at ambient conditions to 5 at its subcritical point, which therefore makes it a suitable solvent for dissolving triolein.

The optimal ratio of the reactant triolein: water is the stoichiometric value of three, as illustrated by Figure 4.2. If this ratio is three then the conversion of triolein is increased to 100%. In this study, a 46 kmol/h stream of triolein enters the hydrolysis reactor and reacts with 138 kmol/h of water. After the equilibrium reaction, a decanter (DEC) was used to separate the two phases formed: an aqueous phase which contains glycerol and water and an oil phase which contains mainly the oleic acid and some water. A simple phase split by decanting can be applied at temperature of 40 to 100 ºC. From the Figure 4.3, at decanter temperature 40 ºC indicated that water and glycerol contain in OLAC stream at least. Since the glycerol content has a significant effect on fuel properties such as viscosity, pour point, and amount of carbon residue, which causes problems with deposition on the injector and combustion chamber. Then, in this study chose temperature at 40 ºC for operating decanter. After cooling and pressure reduction, the reaction mixture is separated in two phases in DEC. The oily phase containing a large majority of oleic acid is sent directly to esterification process. The results are 125.09 kmol/h of oleic acid and the 52.48 kmol/h of water/glycerol mixture.

The mixture of water/glycerol is sent to the distillation column (DC1) for obtaining high purity of glycerol. Fenske-Underwood-Gilliland shortcut method is used to design separation operations and achieve the purity of glycerol. A mixture of water/glycerol was further treated in DC1 with nine theoretical stages and a reflux ratio of 4.2575. Water was removed as distillate stream whereas pure glycerol can be obtained at bottom stream. The result is 38.42 kmol/h of glycerol. The glycerol comes out from the bottom of the column with a purity of 99.6%.

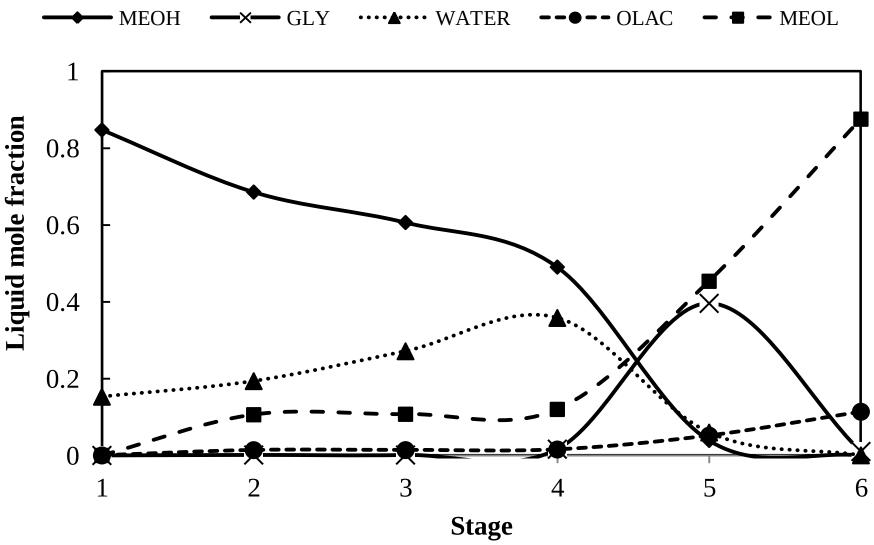

Figure 4.7 Liquid mole composition profiles along the distillation column (DC2) in conventional process.

Figure 4.4 shows the liquid mole composition profiles along DC1. In order to make high purity of glycerol, water must be evaporates into the top of column for separation glycerol from water. Water evaporates at the normal boiling point temperature (100 °C). From Figure 4.5, the temperature of the column (DC1) is increased to 279 °C at stage 5 – 9 for obtaining high purity of glycerol. It can be seen that from Figure 4.4, water was separated from methanol since the temperature of the column (DC1) is decreased at stage 4 and constant at stage 1-3 due to we obtaining 100% purity of water.

4.2.2 Esterification process

Oleic acids were converted to methyl-oleate in the esterification process with methanol by using sulfuric acid concentration 0.5% as homogeneous catalyst. Methanol is the most commonly used alcohol because of its low cost and high reactivity as compared to longer-chain alcohols. The esterification reaction was performed at the ambient pressure and temperature 65 °C. The esterification reactor was simulated as a continuous stirred tank reactor using the kinetic model previously discussed.

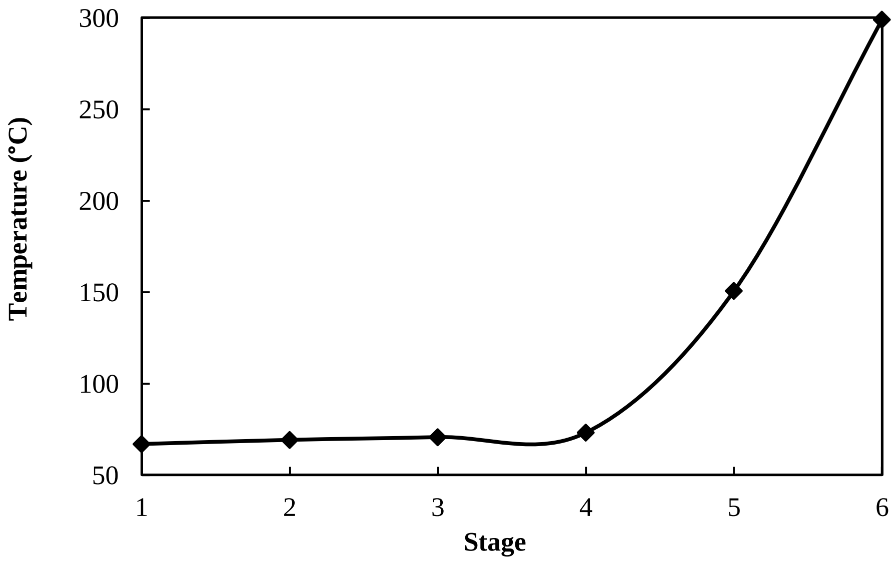

Figure 4.8 Temperatures profiles along the distillation column (DC2) in conventional process.

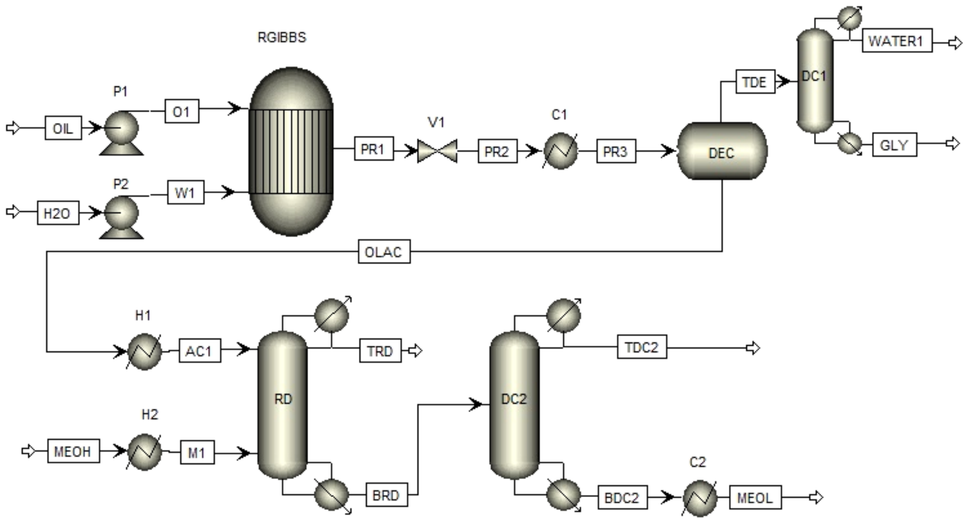

Figure 4.9 Flow diagram of biodiesel production: Reactive distillation process.

Then, the stream containing the oleic acid (OLAC) and methanol (MEOH) are preheated in heater (H1) and heater (H2), heated to 65 ºC to be suitable for the reaction. Oleic acid and methanol mixed initially in the mixture (MIXER) before entering a continuous stirred tank reactor (CSTR). An excess of methanol is necessary chiefly for shifting the chemical equilibrium. The molar ratio of methanol to oleic acid is an important variable in the esterification reaction. Since the reaction is reversible, more methanol is expected to drive the reaction to higher conversions at equilibrium. From Figure 4.6, the optimal ratio methanol: oleic acid of 6:1 is generally accepted from the limitations of kinetics data. This behavior might have occurred because the oleic acid concentration decrease as the molar ratio increased. The esterification reactor is no longer considered since the reaction and the separation take now place on the same shell.

At the completion of the reaction, the stream (PRC) leaving the reactor is then introduced into a distillation column (DC2) to eliminate the methanol and water contained on it. Fenske-Underwood-Gilliland shortcut method is used to design separation operations and achieve the purity of methyl-oleate. A mixture was further treated in DC2 with six theoretical stages and a reflux ratio of 0.8564. Water and methanol were removed as distillate stream whereas glycerol, oleic acid and methyl-oleate are bottom product. The methyl-oleate (MEOL) obtained is 87.5% (mole).

Figure 4.7 shows the liquid mole composition profiles along DC2. In order to make high purity of methyl-oleate, methanol, water and glycerol must be evaporate into the top of column for separation methyl-oleate from methanol, water and glycerol. From Figure 4.8, the temperature is increased to 300 ºC for obtaining high purity of methyl-oleate. The bottom stream (BDC2) is sent to a cooler (C2) for reducing temperature in to 25 ºC to ensure proper implementation. Table 4.1 shows the process specifications and results of the conventional biodiesel process.

4.3 Reactive distillation process for biodiesel production

Next, the performance of a reactive distillation process to produce biodiesel is presented. Reactive distillation is a valuable process intensification technique that can be applied successfully to manufacture of biodiesel, since the reactions leading to the end-product are controlled by the chemical equilibrium. This is particularly advantageous in esterification-type processes. This is the case with waste fats (cooking oil, yellow grease, tallow, etc.) or with fatty acids obtained by a hydrolysis pre-step, as in a supercritical process. By combining reaction and separation into a single unit, one can shift the reaction equilibrium toward the key product (MEOL) by continuous removal of byproduct (H2O), instead of using an excess of reactant. Reactive distillation process for biodiesel consists of two-step process. First step process is the hydrolysis section. Second step process is esterification section. The hydrolysis section is similar to a conventional process but the difference is in the esterification section. In the esterification section (see Figure. 4.9) consists of reactive distillation column (RD) and distillation column (DC2).

The relative volatilities of the component are in the following order: $\alpha_{MEOH} > \alpha_{H2O} > \alpha_{OLAC} > \alpha_{MEOL}$. The excess reactant methanol and methyl-oleate are the lightest and heaviset components, respectively. The thermodynamic behavior indicates that we should remove the product water from the distillate and obtain heavy product methy-oleate from the bottom. The feed stream MEOH is fed to the bottom, and the heavier reactant OLAC is fed to the top. Quite volatile as compare to H2O, OLAC and MEOL, the light excess reactant MEOH goes up the column and leaves in the distillate products. Likewise, the heavy reactant OLAC goes down the column, after being fed on the top and little component OLAC can be found in the bottom products.

ASPEN PLUS simulator provides different types of model for distillation options such as DSTWU, Distl, and RadFrac etc. In this case, RadFrac model has been chosen, as it provides much more rigorous calculations compared to other model. Besides, using RadFrac give more freedom to the process designer, as almost all design parameters can be specified by the designer.

4.3.1 Results and discussion

In spite of the recent progress in understanding the feasibility and design of reactive distillation, the conceptual design of RD may lead to several different process configurations and operating parameters. In this work, sensivity analysis was used as a powerful tool to evaluate the range of the operating parameters: methanol molar flow rate, bottom rate, reflux ratio, oleic acid feed temperature, oleic acid feed stage, methanol feed stage, and numbers of stage. The design parameters for simulating the biodiesel production at standard conditions are shown in Table 4.2.

Table 4.1 Specifications and simulation results of conventional biodiesel process (hydrolysis and esterification reactors).

Reactor	Hydrolysis (RGIBBS)	Esterification (CSTR)
Total mole flow (kmol/hr)	184	880.93
Conversion	100% (triolein)	88.5% (Oleic acid)
Heat duty (kW)	2715	-5687
Temperature (°C)	290	65
Pressure (MPa)	7	0.101325
Decanter		
Heat duty (kW)	-92	
Temperature (°C)	40	
Pressure (MPa)	0.101325	
Distillation column	DC1	DC2
Stages	9	6
Feed stage	4	2
Distillate to feed mole ratio	0.279	0.209
Reflux ratio	3.9693	0.8564
Condenser duty (kW)	-835	-9249
Reboiler duty (kW)	1475	14951
Top stage pressure (MPa)	0.101325	0.101325
Glycerol purity	100%	-
Biodiesel purity	-	87.5%

$$\text{Conversion} = \frac{F_{\text{OLACO}} - F_{\text{OLAC}}}{F_{\text{OLAC}}} \times 100\% \tag{4.1}$$

$$\text{Purity of MEOL} = \frac{F_{\text{MEOL}}}{F_{\text{BP}}} \tag{4.2}$$

Where F_{OLACO} and F_{OLAC} are molar flow rate of oleic acid in feed and outlet stream. F_{MEOL} and F_{BP} are molar flow rate of methyl-oleate in bottom product and total mole flow rate in bottom product.

Table 4.2 Operating conditions and design parameters for simulation of the biodiesel production.

Parameters	Value	Unit
Methanol molar flow rate	375	kmol/h
Bottom molar flow rate	255	kmol/h
Oleic acid feed temperature	145	(ºC)
Oleic acid feed stage	3	-
Methanol feed stage	10	-
Number of stages	15	-

4.3.1.1 Effect of methanol molar flow rate

Because the esterification reaction is reversible reaction, excess alcohol is used to prevent the chemical equilibrium. In the reactive distillation column, excess reactants is not necessary because of the reaction and separation takes place in just one shell, it is a positive influence on the chemical equilibrium. From the Figure 4.10 and 4.11, it is indicated that methanol molar flow rate not affect to the purity of methyl-oleate at the bottom product of the reactive distillation column and oleic acid conversion. Moreover the excess of methanol becomes a significant impurity in the top stream and thereafter in the water and methyl-oleate at the bottom product. From the Figure 4.12, it is indicated that at the methanol molar flow rate increased from 250 kmol/h to 750 kmol/h, the reboiler heat duty increased continuously because of the boilup rate in the reactive distillation column is increased at constant bottom rate for removing the excess of methanol from the column.

However, due to limitations of kinetics data, fatty acid to methanol mole ratio used was high enough for the methanol concentration to remain constant throughout the process at 375 kmol/h.

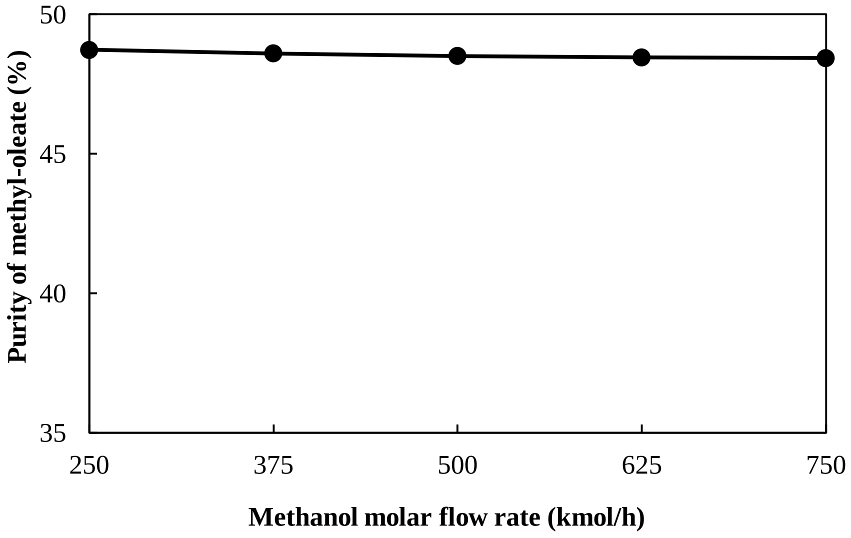

Figure 4.10 Effect of methanol molar flow rate on the purity of methyl-oleate at standard conditions.

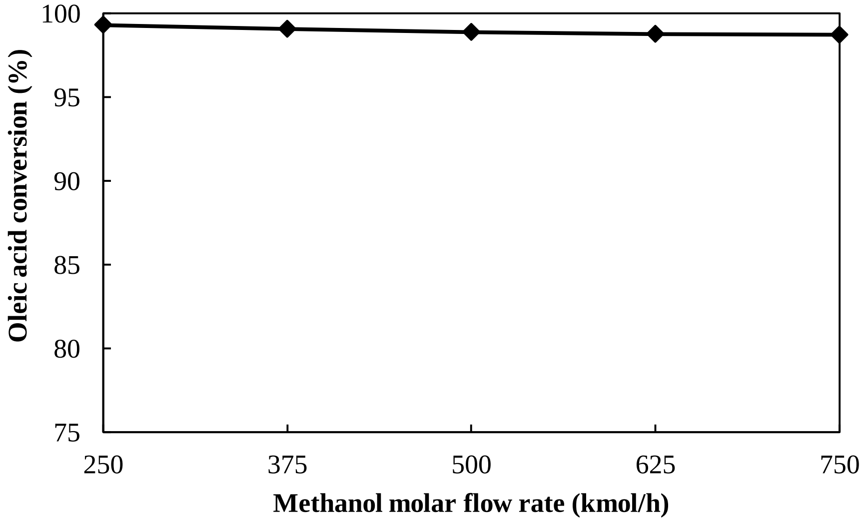

Figure 4.11 Effect of methanol molar flow rate on the oleic acid conversion at standard conditions.

4.3.1.2 Effect of bottom rate

Figure 4.13 shows the influent of bottom rate in reactive distillation column on the purity of methyl-oleate at the bottom product of the reactive distillation column. At the bottom rate increased from 150 kmol/h to 310 kmol/h, it was found that the purity of methyl-oleate decreased significantly. When the bottom rate increased (Figure 4.16), the boilup rate was decreased. Boilup rate is the vapor flow rate from bottom stage. Methanol and water is lower boiling point temperature than methyl-oleate since methanol and water must be evaporated to the top of the column as vapor flow. If boilup rate decrease, methanol and water will remain in the bottom product since the methyl-oleate is less purity. Moreover, at high boilup rate (low bottom rate), it is indicated that the reboiler heat duty is required heat duty for separation methanol and water from methyl-oleate. It can be seen that from Figure 4.15, when the bottom rate decreased, the reboiler heat duty was increased.

Figure 4.14 shows the influent of bottom rate on the oleic acid conversion. At the bottom rate decreased, it was found that the conversion of oleic acid decreased. When the bottom rate decreased at constant reflux ratio (Figure 4.16), the reflux rate was increased. Reflux rate is the liquid flow rate is returned to the column at stage 2. The top product is water, if water returns to the column, it will adversely affect to the chemical equilibrium. If boilup rate decrease, the conversion of oleic acid will decrease.

4.3.1.3 Effect of reflux ratio

Figure 4.17 shows the influent reflux ratio in reactive distillation column on the purity of methyl-oleate at the bottom product. From Figure 4.17, it is illustrated that, at high reflux ratio, the purity of methyl-oleate was decreased. The reflux ratio indicates the amount of top product to be recycled back to the top of the column (reflux rate) to the amount of liquid leaving at the top of the column (distillate rate). If the bottom rate fixes at 255 kmol/h then the distillate rate is constant at 245 kmol/h. If the reflux ratio increases at constant distillate rate, the reflux rate increases (Figure 4.20). The increasing of reflux rate influences to the increasing of the amount of water in the reactive distillation column, as returning water to the column is detrimental to the chemical equilibrium.

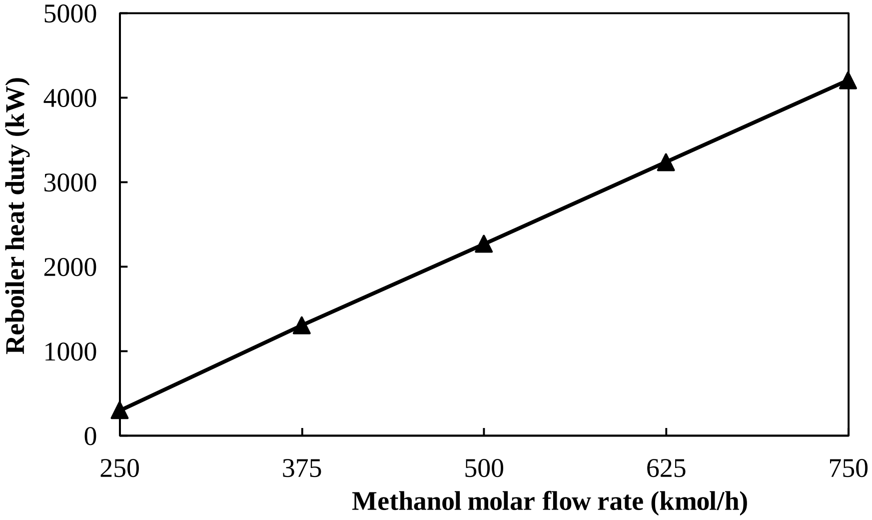

Figure 4.12 Effect of methanol molar flow rate on the reboiler heat duty at standard conditions.

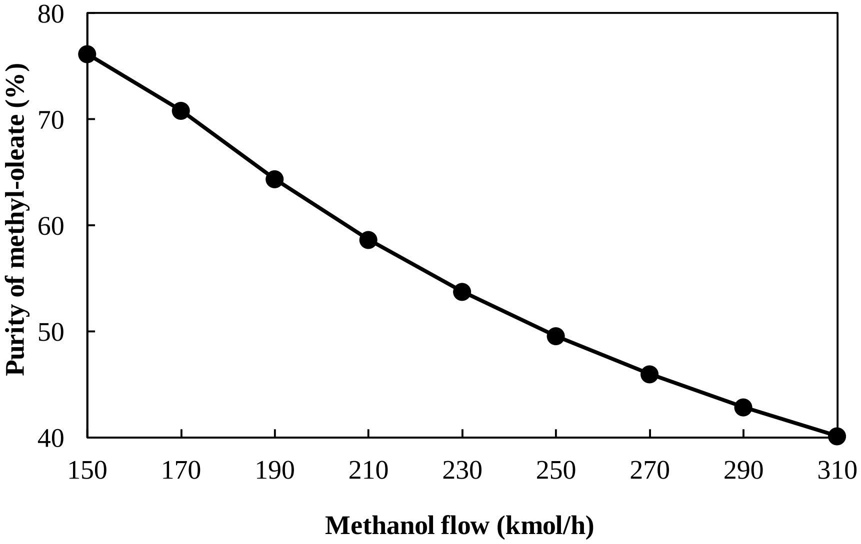

Figure 4.13 Effect of bottom rate on the purity of methyl-oleate at standard conditions.

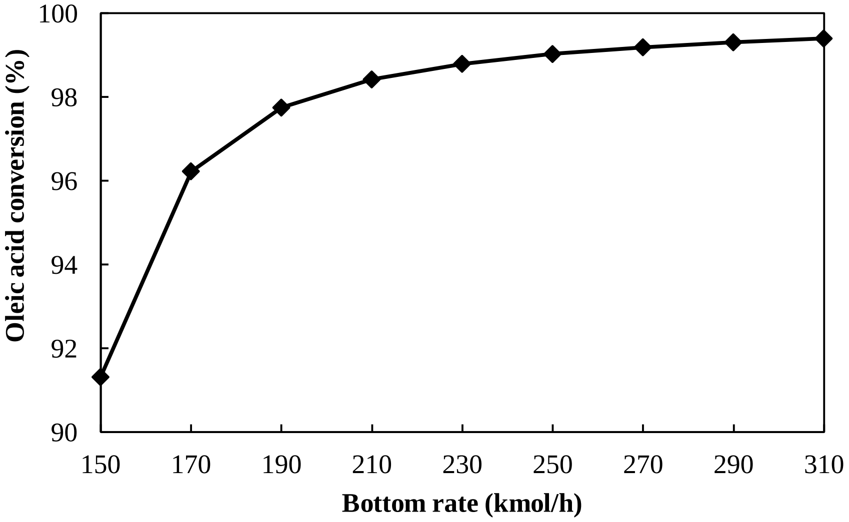

Figure 4.14 Effect of bottom rate on the conversion of oleic acid at standard conditions.

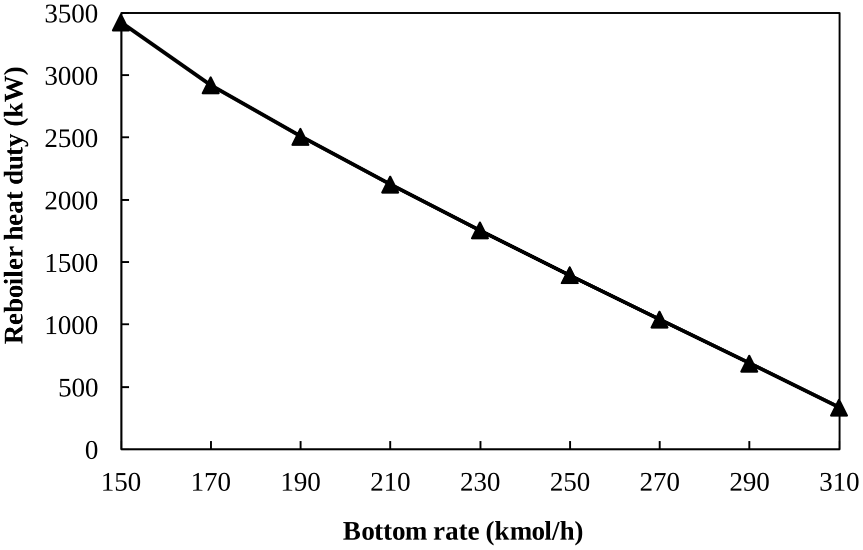

Figure 4.15 Effect of bottom rate on the reboiler heat duty at standard conditions.

Moreover, higher reflux ratio leads to an incomplete consumption of oleic acid, which passes as impurity in the bottom product; in Figure 4.18 when the reflux ratio increases, the conversion of oleic acid was decreased.

In the other hand, at high reflux ratio, some methanol and water were returned to the column that affect to the high boilup ratio (Figure 4.20). Because of methanol and water were remained along the column for obtaining high purity of methyl-oleate, methanol and water must be evaporates into the top of the column by increasing boilup ratio. As a result, the reboiler requires heat duty for evaporate methanol and water to the top of the column for obtaining purity of methyl-oleate. It can be seen that from Figure 4.19, when the reflux ratio increased, the reboiler heat duty was increased.

4.3.1.4 Effect of oleic acid feed temperature

The effect of oleic acid feed temperature on the performance of reactive distillation in terms of the purity of methyl-oletae and the conversion of oleic acid as a biodiesel product is studied. Figure 4.21 and 4.22 illustrated that when oleic acid feed temperature is increased from 60 to 200 °C, the purity of methyl-oleate and conversion of oleic acid increase until the temperature reaches to 180 °C the purity of methyl-oleate and conversion of oleic acid are constant.

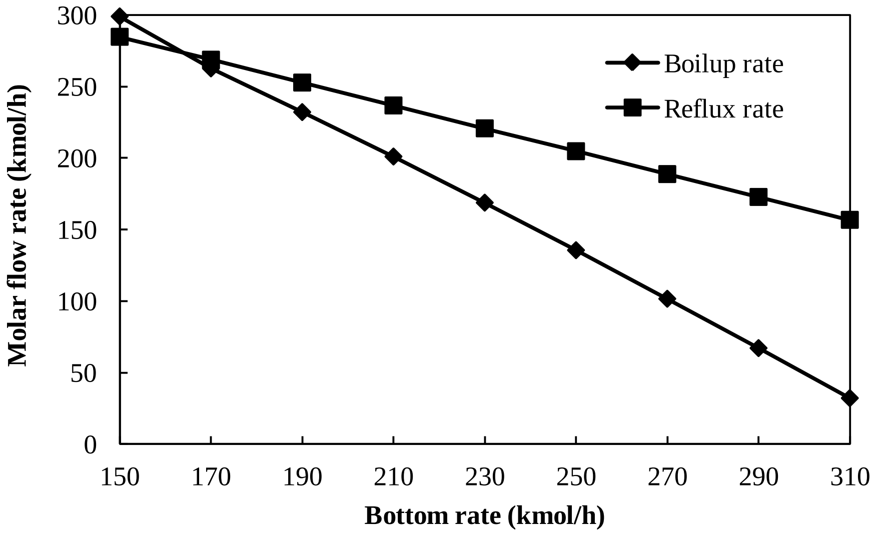

Figure 4.16 Effect of bottom rate on reflux rate and boilup ratio at standard conditions.

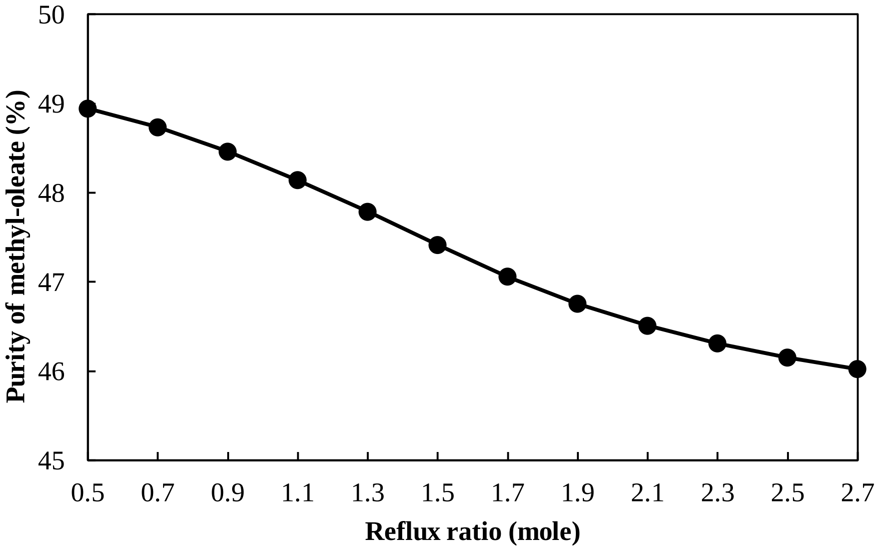

Figure 4.17 Effect of reflux ratio on the purity of methyl-oleate at standard conditions.

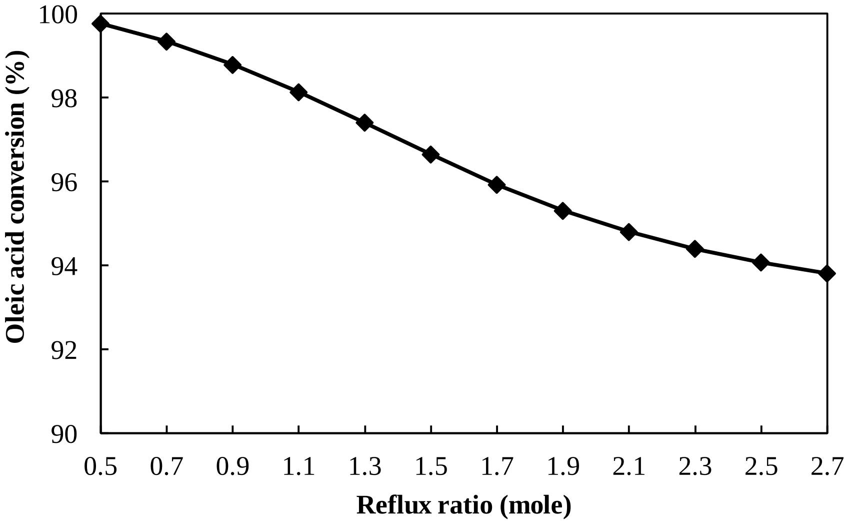

Figure 4.18 Effect of reflux ratio on the conversion of oleic acid at standard conditions.

Figure 4.23 shows the influent oleic acid feed temperature on the reboiler heat duty in reactive distillation column. The esterification reaction is the slightly exothermic reaction. When the oleic feed temperature increases as a result in more heat generated from exothermic reaction. So the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler heat duty. It can be seen that from Figure 4.23, when the oleic acid feed temperature increased, the reboiler heat duty was decreased.

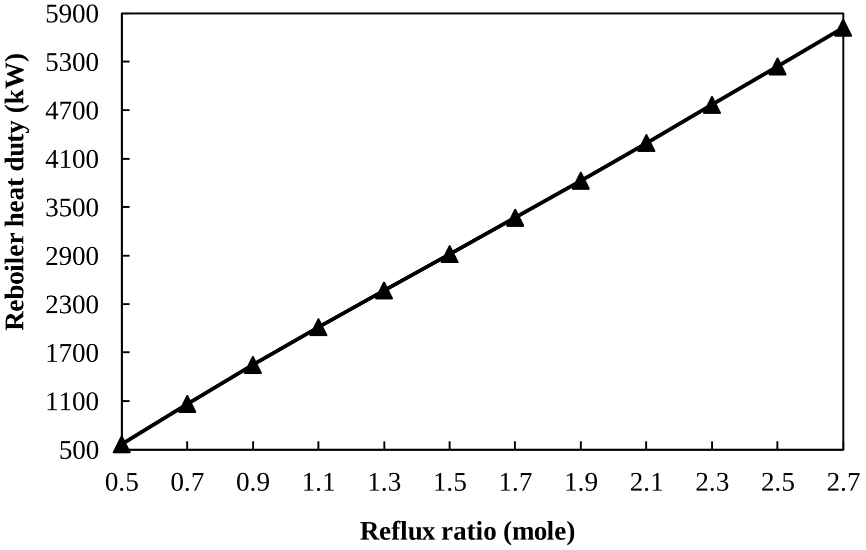

Figure 4.19 Effect of reflux ratio on the reboiler heat duty at standard conditions.

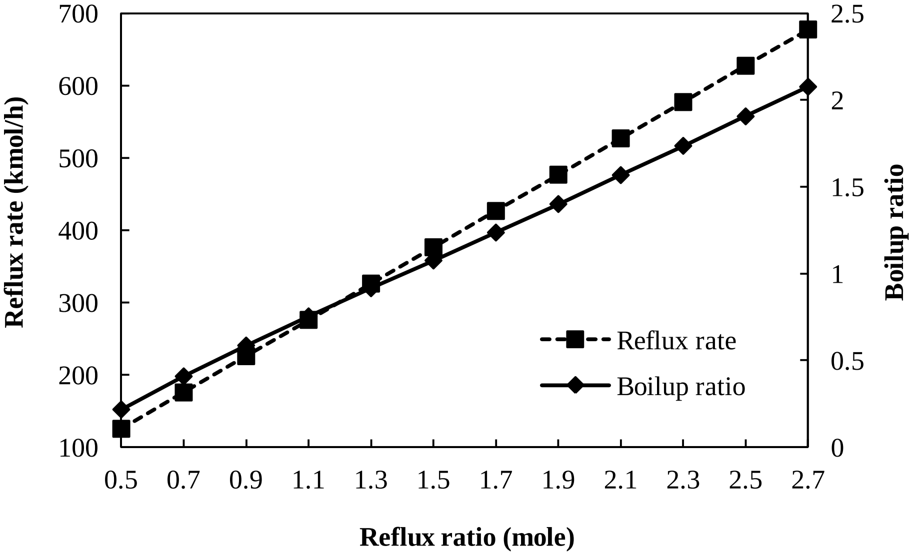

Figure 4.20 Effect of reflux ratio on the reflux arte and boilup ratio at standard conditions.

4.3.1.5 Effect of oleic acid feed stage

The effect of oleic acid feed stage on the purity of methyl-oleate is shown in Figure 4.24. The result indicates that the purity of methyl-oleate decrease with increasing the number of feed stages of oleic acid. For esterification reaction, oleic acid should be fed on the top of the column since oleic acid is fed to the column at temperature below the boiling point therefore the oleic acid is the liquid phase. Methanol should be fed on the bottom of the column because of methanol is the lighter components tend to concentrate in the vapor phase. The result is a vapor phase that becomes richer in methanol as it passes up the column and a liquid phase that flows down to the bottom of the column. When oleic acid is fed to the bottom of the column while the methanol is fed to bottom of the column, methanol will evaporate into the top of the column and does not react with oleic acid. Then there are the amounts of oleic acid remaining in the bottom product and affected on the low performance of reactive distillation column. According to the result in Figure 4.24 to 4.25, it is shown that the moving feed stage of oleic acid down near the bottom of the column decrease the purity of methyl-oleate and conversion of oleic acid.

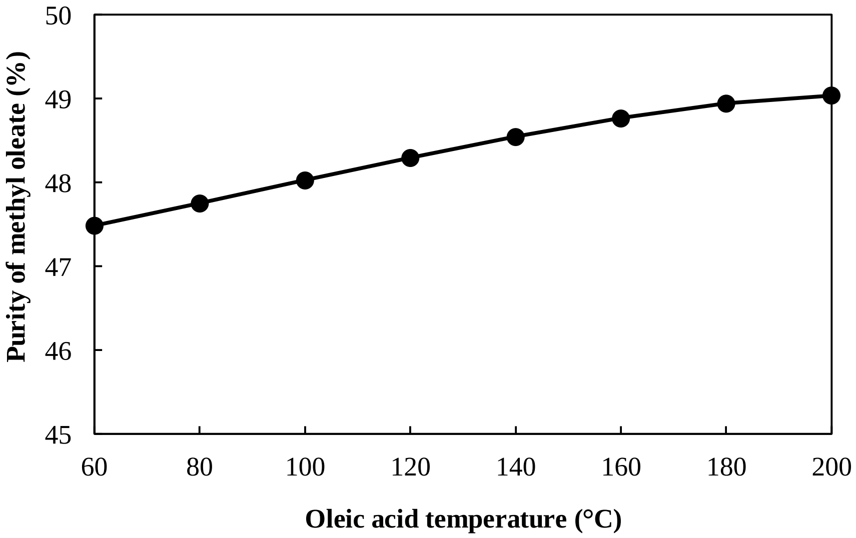

Figure 4.21 Effect of oleic acid feed temperature on the purity of methyl-oleate at standard conditions.

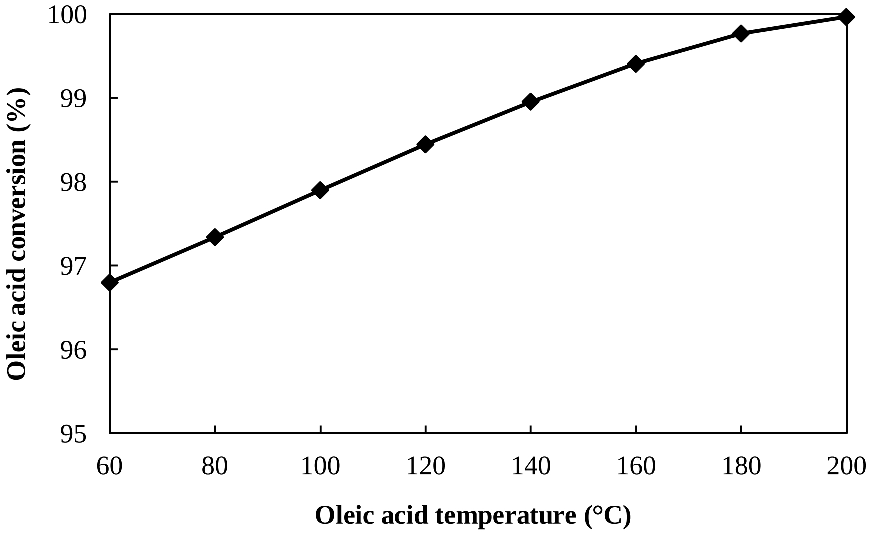

Figure 4.22 Effect of oleic acid feed temperature on the oleic acid conversion at standard conditions.

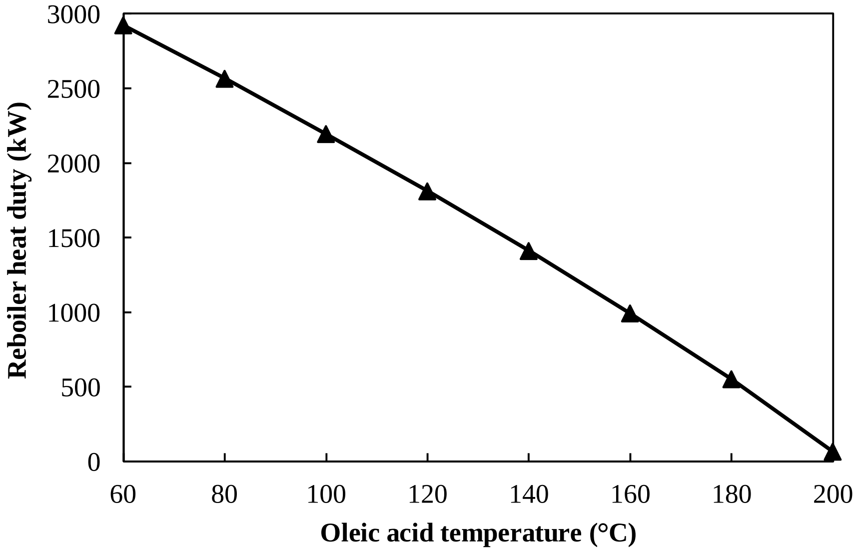

Figure 4.23 Effect of oleic acid feed temperature on the reboiler heat duty at standard conditions.

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Figure 4.26 shows the influent oleic acid feed stage on the reboiler heat duty in reactive distillation column. The moving feed stage of oleic acid up near the top of the column increase the conversion of oleic acid, it is indicated that methyl-oleate more formed from the esterification reaction. Since the reboiler requires heat duty for separation methyl-oleate from methanol and water. Figure 4.29 is shown that the reboiler heat duty increase with moving the feed stage of oleic acid near the top of the column.

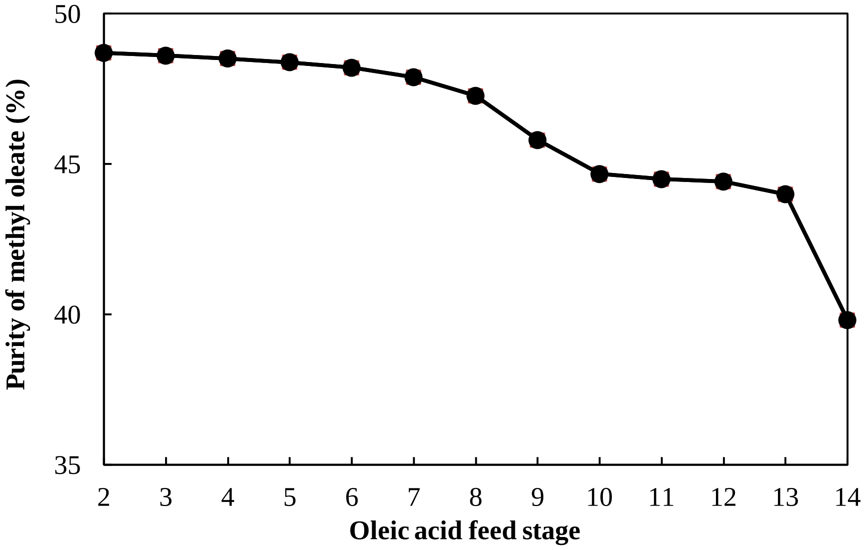

Figure 4.24 Effect of oleic acid feed stage on the purity of methyl-oleate at standard conditions.

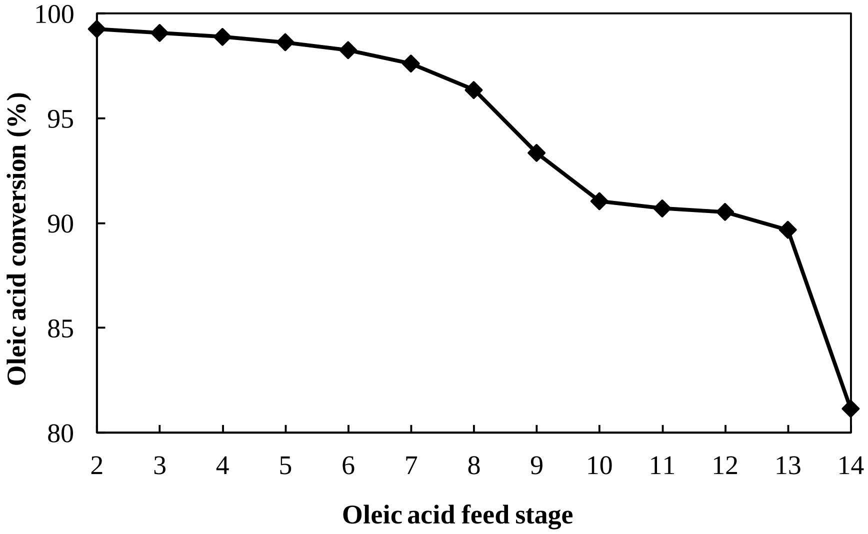

Figure 4.25 Effect of oleic acid feed stage on the conversion of oleic acid at standard conditions.

4.3.1.6 Effect of methanol feed stage

The effect of methanol feed stage on the purity of methyl-oleate is shown in Figure 4.27. The graph is indicated that the purity of methyl-oleate increase with increasing the number of feed stages of methanol. Methanol is fed to the column at the boiling point temperature therefore the methanol is the vapor phase. When methanol is fed at the top of the column, methanol will lost through vaporization and condense as the liquid phase which contaminate in the water (top product). Moreover at the upper stage of feed methanol, the reaction is not completely. According to the result in Figure 4.27 to 4.28, it is shown that the moving feed stage of methanol up near the top of the column decrease the purity of methyl-oleate and conversion of oleic acid.

Figure 4.29 shows the influent methanol feed stage on the reboiler heat duty in reactive distillation column. The moving feed stage of methanol down near the bottom of the column increase the conversion of oleic acid, it is indicated that methyl-oleate more formed from the esterification reaction. Since the reboiler requires heat duty for separation methyl-oleate from methanol and water. Figure 4.29 is shown that the reboiler heat duty increase with moving the feed stage of methanol near the bottom of the column.

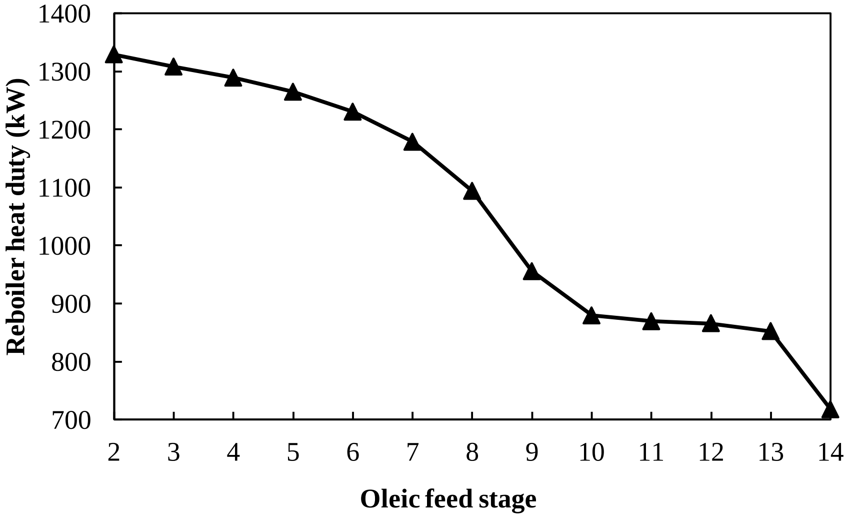

Figure 4.26 Effect of oleic acid feed stage on the reboiler heat duty at standard conditions.

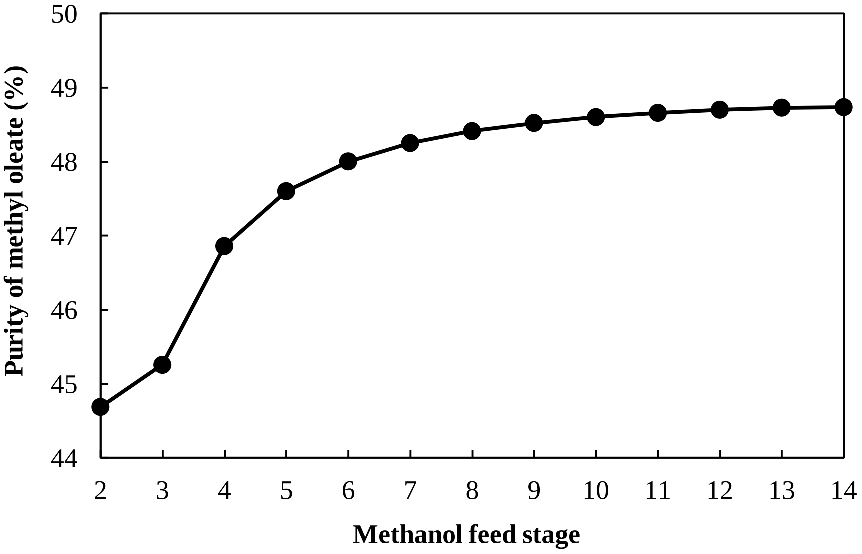

Figure 4.27 Effect of methanol feed stage on the purity of methyl-oleate at standard conditions.

4.3.1.7 Effect of number stages

The effect of number of stages on the purity of methyl-oleate and the conversion of oleic acid are shown in Figure 4.30 and 4.31. A high number of equilibrium stages are necessary to achieve simultaneous high conversion of oleic acid. If the conversion of oleic acid is incomplete, the bottom product contains un-reacted fatty acid that cannot be removed from the final by simple flashing. Since the separation of oleic acids from methyl-oleate is difficult, this situation should be avoided. The separation performance can normally be increased through increasing theoretical stages or increasing the internal vapor and liquid flows (Knapp and Doherty, 1944). The performance can be observed from the increasing purity of products. From Figure 4.30 and 4.31 the purity of methyl-oleate and the conversion of oleic acid increase as the number of stages increase. The Figure 4.32 indicated that the reboiler heat duty of reactive distillation column increases with increasing the number of stages. To ensure the esterification reaction is completely, the reactive distillation column has a total number of stages of 16.

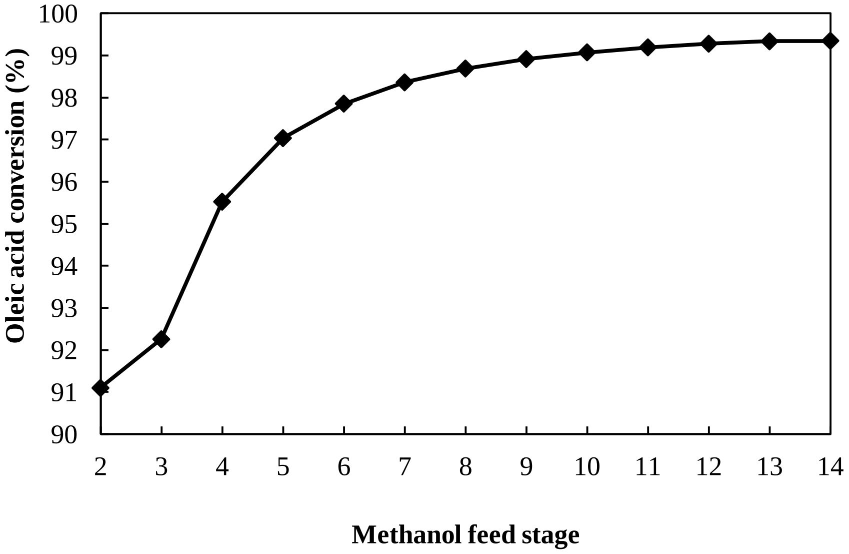

Figure 4.28 Effect of methanol feed stage on the conversion of oleic acid at standard conditions.

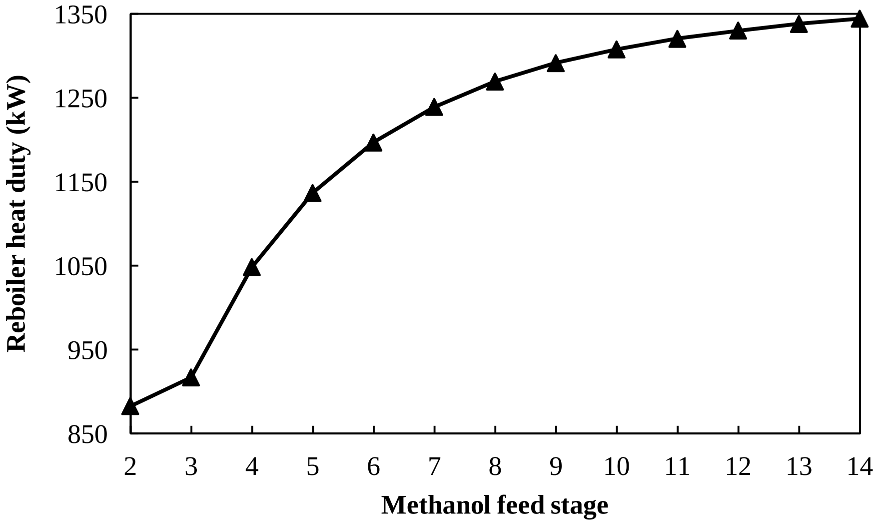

Figure 4.29 Effect of methanol feed stage on the reboiler duty at standard conditions.

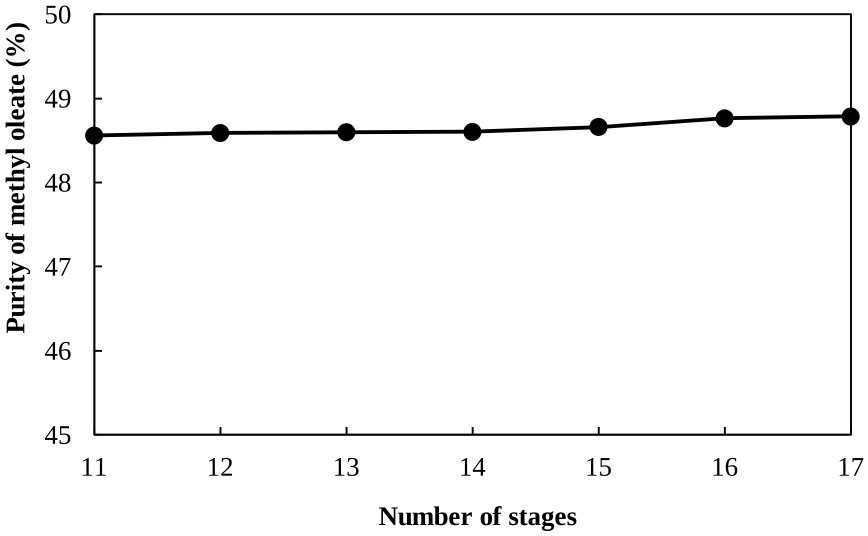

Figure 4.30 Effect of number of stages on the purity of methyl-oleate at standard conditions.

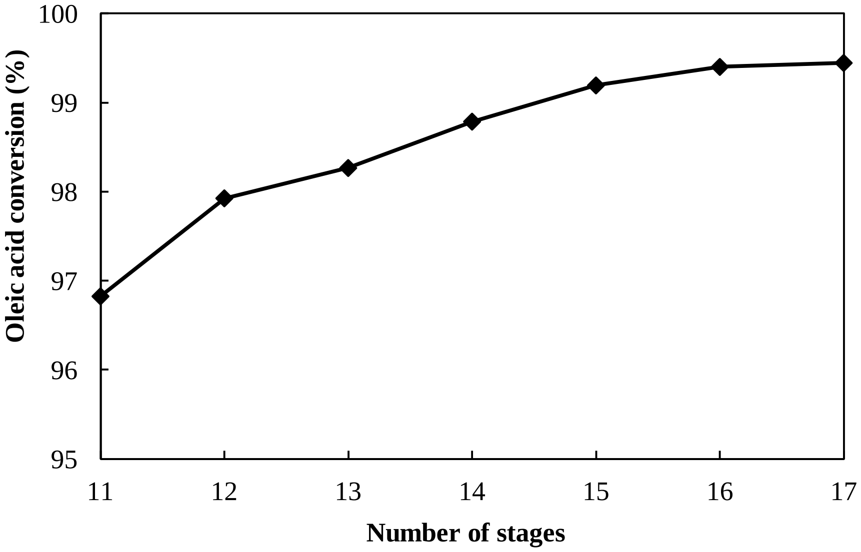

Figure 4.31 Effect of number of stages on the conversion of oleic acid at standard conditions.

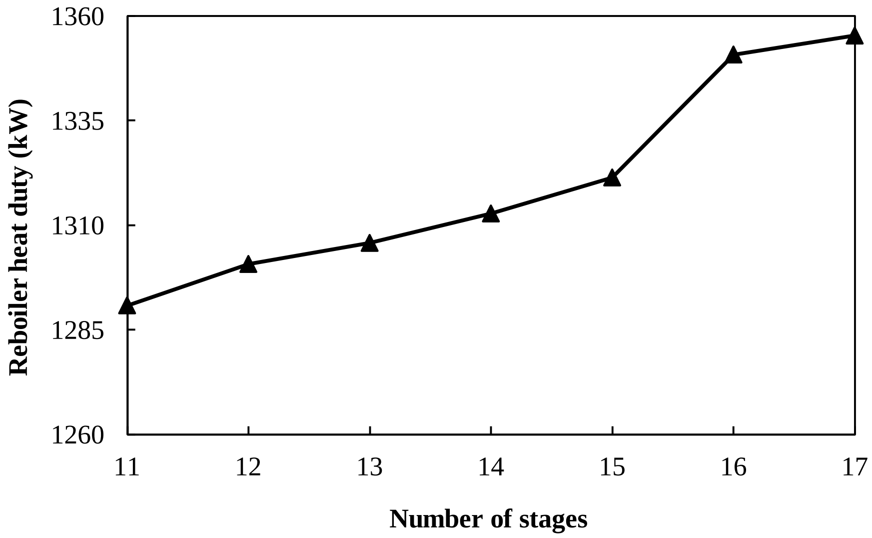

Figure 4.32 Effect of number of stages on the reboiler heat duty at standard conditions.

4.3.2 Esterification section

The reactive distillation has been implemented in the simulator, using the RadFrac model. A 125.09 kmol/h stream of oleic acid (OLAC) and 375 kmol/hr stream of methanol (MEOH) are sent to heat-exchanger1 (H1) and heat-exchanger 2 (H2), respectively. The oleic acid is pre-heated in temperature 180 °C, and then fed as hot liquid at stage 2 while a methanol is pre-heated in temperature 65 °C and then fed as hot vapor at stage 15, thus creating a counter-current vapor flow regime to contact with oleic acid along the reactive distillation column. Methanol and water are much more volatile than the methyl-oleate and oleic acid; these will separate easily in the top such that no supplementary rectifying zone is needed. Similarly, no stripping zone is necessary. In this way, the reaction zone can cover practically the whole column. The reactive distillation is operated at relatively low molar reflux ratio because the methyl-oleate product has much more higher boiling point than methanol and water, so that the separation of these substances can be easily performed. Moreover, the high reflux rates are not recommended as returning the water by-product to the column is not favorable to the chemical equilibrium. The top stream from the TRD contains water and alcohol in a proportion dictated by the reflux policy. The methyl-oleate product is removed at the bottom of the reactive distillation and then sent to a purification section in order to achieve a purity of methyl-oleate. The stream from bottom product of reactive distillation column is then introduced into a distillation column (DC2) to eliminate the methanol and water contained on it. Fenske-Underwood-Gilliland shortcut method is used to design separation operations and achieve the purity of methyl-oleate. A mixture was further treated in DC2 with twelve theoretical stages and a reflux ratio of 0.2866. Water and methanol were removed as distillate stream whereas glycerol and methyl-oleate are bottom product. The methyl-oleate (MEOL) obtained is 99% (mole).

Figure 4.33 shows the liquid mole composition profiles along DC2. In order to make high purity of methyl-oleate, methanol, water and glycerol must be evaporate into the top of column for separation methyl-oleate from methanol, water and glycerol. The normal boiling point temperature of glycerol is 285 °C. From Figure 4.34, the temperature is increased to 300 °C for obtaining high purity of methyl-oleate. The bottom stream (BDC2) is sent to a cooler (C2) for reducing temperature in to 25 °C to ensure proper implementation. Table 4.3 shows the process specifications and results of the conventional biodiesel process.

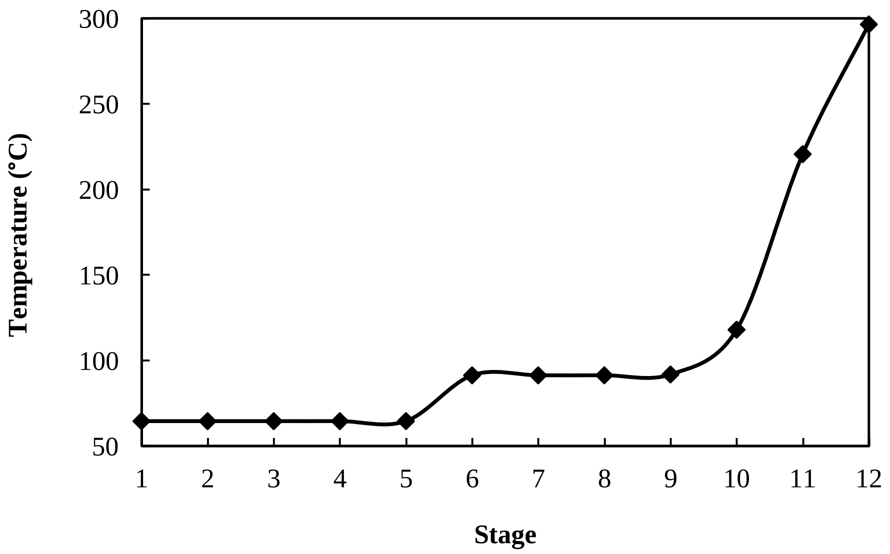

Figure 4.33 Temperature profiles along the reactive distillation column (DC2) in reactive distillation process.

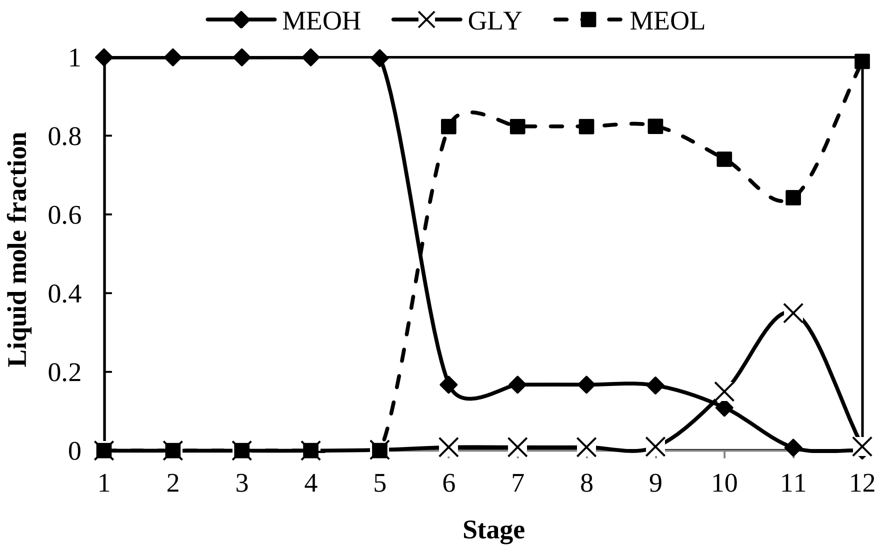

Figure 4.34 Liquid mole composition profiles along the distillation column (DC2) in reactive distillation process.

Table 4.3 Configuration and simulation results of reactive distillation column (RD).

	RD	DC1	DC2
Stage	16	9	12
Oleic acid feed stage	2	-	-
Methanol feed stage	15	-	-
Feed stage	-	4	6
Valid phases	VLL	L	L
Distillate to feed mole ratio	0.7204		0.1573
Distillate rate (kmol/h)			23.59
Reflux ratio	0.5		0.2866
Bottom rate (kmol/h)	150		126.41
Boilup ratio			1.04
Condenser duty (kW)	-5692		-296
Reboiler duty (kW)	1769		5509
Oleic acid conversion (mole)	99.99%	-	-
Biodiesel purity (mole)	83.40%	-	99%
Glycerol purity (mole)	-	100%	-

Figure 4.33 is shown the temperature profiles along the reactive distillation column. The reaction temperature must be less than the boiling point of methanol (boiling point of methanol is at 60-70 °C at the atmospheric pressure to ensure the methanol will not be lost through vaporization. The reactive distillation column is operated in the temperature range of 70 – 93 °C. The temperature almost keeps constant from the top stage to stage 15, but below stage 15, the temperature of reboiler increases to 93 °C for obtaining the purity of methyl-oleate.

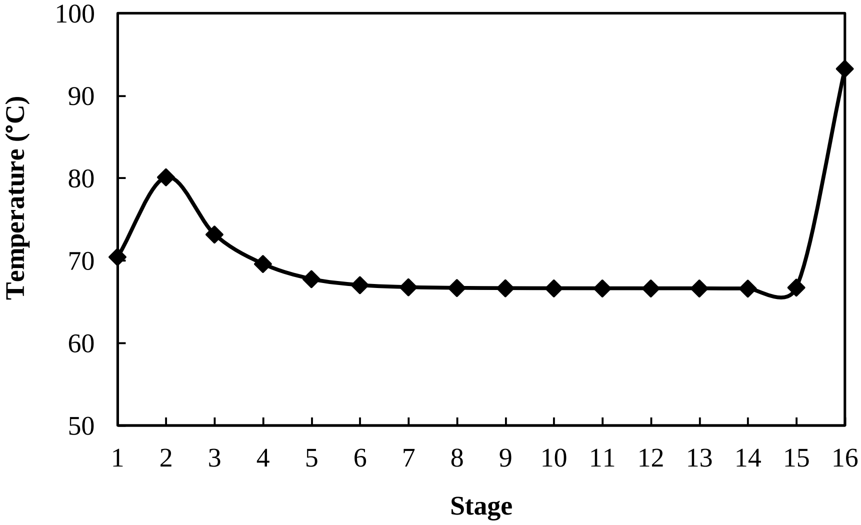

Figure 4.35 Temperature profiles along the reactive distillation column.

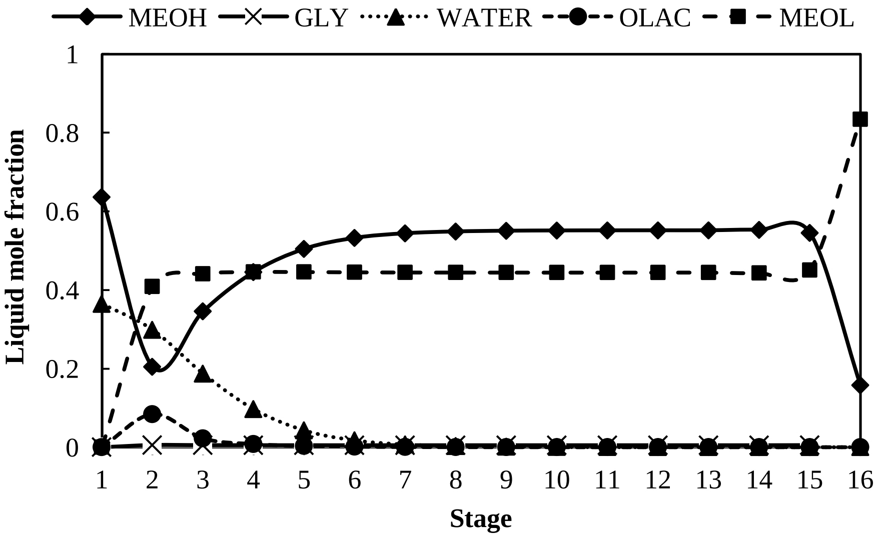

Figure 4.36 Liquid mole composition profiles along the reactive distillation column.

Figure 4.36 shows the liquid mole composition profiles in the reactive distillation column. The concentration of oleic acid in the liquid phase drops rapidly on the stage 2 (oleic acid feed stage) while the concentration of methyl-oleate increases rapidly on the stage 2, increases slowly and remain constant. Above stage 15, the liquid mole composition quickly becomes rich in methyl-oleate due to an increase in temperature. This is reflected the temperature profile as shown in Figure 4.35. Similarly, the methanol concentration decreases when reacted with oleic acid and remains constant while water concentration increases from the bottom to the top of the column.

Figure 4.37 shows the vapor mole composition profiles in the reactive distillation column. Methanol and water have the lower boiling point temperature than oleic acid and methyl-oleate. From Figure 4.35, the reactive distillation column is operated in the temperature range of 70 – 93 °C, it is indicated that methanol is the vapor phase. We fed methanol at the excess reactant at normal boiling point temperature (65 °C) so the vapor phase of methanol is rich along the column. Water has normal boiling point (100 °C) lower than methyl-oleate, it vaporize to the top of the column.

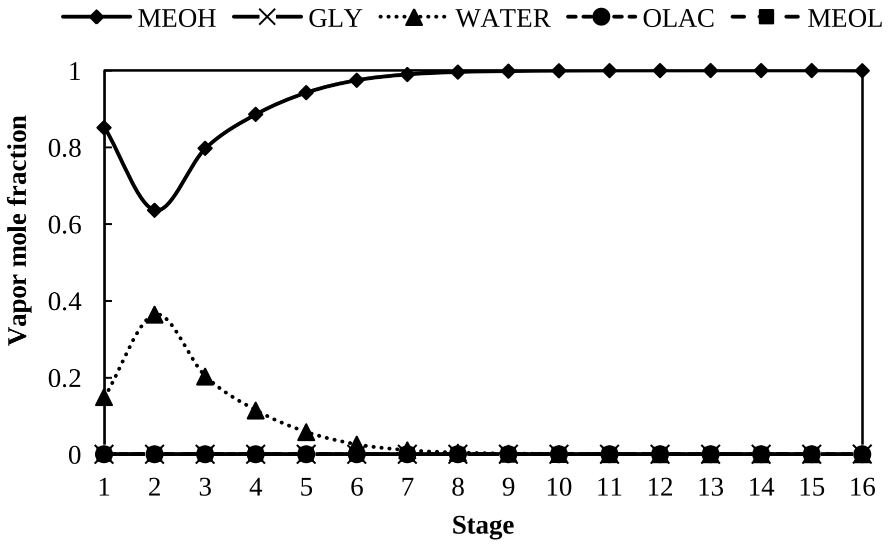

Figure 4.37 Vapor mole composition profiles along the reactive distillation column.

Table 4.4 Comparison of conventional process and reactive distillation process: Energy requirement.

Distillation column (DC2)	Conventional process	Reactive distillation process
Reboiler duty	-9249	-296
Condenser duty	14951	5510
Total energy consumption (kW)	24200	5806

4.4 Comparison between conventional process and reactive distillation process.

The design of new processes in chemical engineering takes into account policies of process intensification, which can be stated as any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology. Distillation continues being the most used separation technique in chemical industry, and it is well known that requires large amounts of energy in order to achieve a given separation. Since process intensification takes into account reduction in energy consumption, integration of several operations into one unit, safe operation and others, may be the reactive distillation is the most representative operation in process intensification because the reaction and separation are carried in the same unit leading to energy saving due to internal integration and higher conversions in equilibrium reactions since methyl-oleate and water are removed as they are formed.

Older biodiesel processes are essentially in reactor. The oleic acid is submitted to esterification in a stirred-tank reactor in the presence of a large methanol. In conventional process, we used 750 kmol/hr of methanol to ensure full solubility of oleic acid, but also for shifting the chemical equilibrium. But in the reactive distillation process, we used only 375 kmol/hr of methanol. The use of a large excess of methanol (750 kmol/h) is reflected in higher energy consumption. Moreover after the reaction in the continuous stirred tank reactor is completely, the reaction mixture is required the high energy and separation device to purity the products, by-products and remaining reactant. Table 4.3 illustrated that, the energy for separation the reaction mixture of conventional process is higher than reactive distillation process. In convention process, the economic indices are on the lower side because of lower equipment productivity and higher operation costs.

Table 4.5 Total energy requirement for different biodiesel processes.

Unit operations	Conventional process	Reactive distillation (RD) process
Reactor		
RGibbs	2715	2715
RCSTR	1629	-
Separator		
Decanter	-92	-92
Distillation column (DC1)		
Condenser duty	-835	-835
Reboiler duty	1475	1475
Distillation column (DC2)		
Condenser duty	-9249	-296
Reboiler duty	14951	5510
Reactive distillation column (RD)		
Condenser duty	-	-5692
Reboiler duty	-	1769
Additional power		
Pump	153	153
Cooler	-13563	-13512
Heater	8221	7395
Total energy consumption (kW)	52822	39445

4.5 Conclusions

The production of biodiesel by using *Jatropha* oil as feedstocks is based on reactive distillation column, powered by sulfuric acid as homogeneous acid catalyst for fatty acids esterification. The innovative process proposed in this work significantly improves biodiesel production. Compared to conventional processes, the major benefit of this unique process are:

- Efficient use of raw materials: stoichiometric reactants ratio, high conversion of oleic acid, no product recycled as reflux or boil-up vapors.
- Effective use of reactor volume leading to significantly high unit productivity than conventional biodiesel processes because both the water and methyl-oleate are continuously removed from the reaction section. This causes the reaction equilibrium shift to a product side.
- Significant reduction of the energy requirement -25.32%.

CHAPTER V

OPTIMIZATION OF BIODIESEL PRODUCTION

This chapter discusses the outcomes of simulations carried to optimize the process parameters in the esterification reaction in reactive distillation column for obtaining maximum purity of biodiesel. We first show the statistical analysis using design of simulations. The simulation data was made using central composite design (CCD) to provide data to model the effects of the independent variables. Previous section, the simulation data was analyzed by the response surface regression model using the following second-order polynomial equation. Analysis of variance (ANOVA) was applied to estimate the effects of main variables and their potential interaction effects on the purity of biodiesel. The last section, the mathematical model developed could predict the purity of biodiesel at any point in the simulation domain as well as the determination of the optimal biodiesel conditions.

5.1 Introduction

Conventionally, the optimization study for biodiesel synthesis process was performed with the variation of one component at a time and the response is a function of a single parameter (one-variable-at-a-time technique) which is time consuming and exorbitant in cost. This technique does not include interactive effects among the variables and it does not depict the complete effect of the parameters on the process (Lee et al., 2011). Response surface methodology (RSM) is a useful statistical technique, which has been applied in the research of complex variable processes (Myers and Montgomery, 2002). Multiple regression and correlation analysis are used as tools to assess the effects of two or more independent factors on the dependent variables. Furthermore, the central composite design (CCD) of RSM has been applied in the optimization of several biotechnological and chemical processes. It main advantage is the reduction in the number of experimental runs required to generate sufficient information for a statistically acceptable result. RSM has been applied successfully for optimization of biodiesel production in fat and oil feedstocks, including mahua oil (*Madhuca indica*) (Ghadge and Raheman, 2006), *Jatropha* oil (Tiwari et al., 2007), waste rapeseed oil (Yuan et al., 2008) and animal fat (Jeong et al., 2009).

5.2 Statistical analysis using design of simulations

The effects of process parameter in the esterification reaction in reactive distillation column and the optimum conditions for the purity of methyl-oleate was studied by using design of simulations. Optimization process for biodiesel production is shown in figure 5.1. In this study, the design of simulation selected was Response Surface Method (RSM) coupled with Central Composite Design (CCD) using the Design-Expert Version 8.0.7.1 (State-Ease, Inc.) software. The process parameters selected for this study are bottom rate, reflux ratio, oleic acid feed temperature, oleic acid feed stage and methanol feed stage. The design matrix of the central composite design chosen together with the results for the five optimization parameters selected. The value of α was based on the number of optimization parameters (k = 5) as follows:

$$\alpha = (2^5)^{1/4} = 2.38$$

The total number of experiment trials (n_e) as follows:

$$n_e = 2^5 + 2(5) + 1 = 43$$

The independent variables are coded to two levels namely: low (-1) and high (+1), whereas the axial points are coded as -2.38 ($-\alpha$) and +2.38 ($+\alpha$). The α value was fixed at 2.38 which is the distance of the axial point from the center and make the design rotatable. A five-level-five-factor CCD requires 43 simulations, including 32 factorial points from full factorial design CCD for five variables, ten axial points and one replicate at the center point were employed in this study.

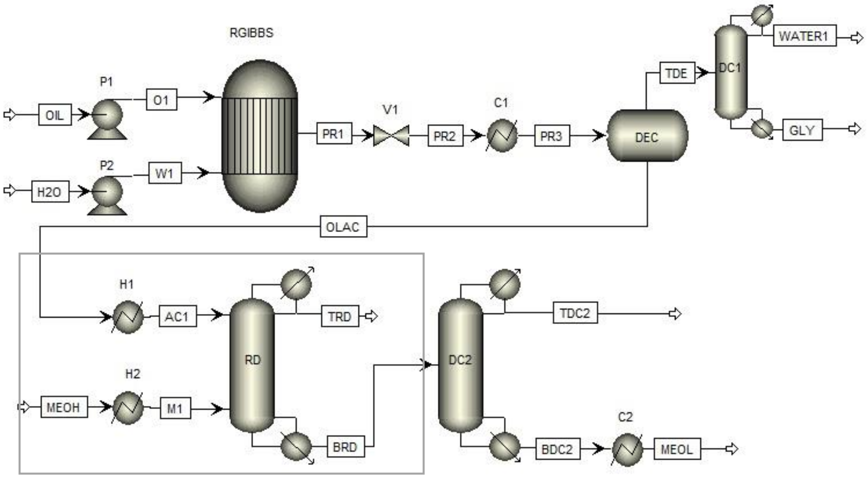

Figure 5.1 Biodiesel production process.

Table 5.1 Process parameters in the central composite design: coded and natural values.

Factors	Symbols	Units	Levels				
			-2.38	-1	0	1	2.38
Bottom rate	X_1	kmol/hr	126	176	213	250	300
Reflux ratio	X_2	mole	0.4	0.63	0.8	0.97	1.2
Oleic acid temperature	X_3	ºC	100	123	140	157	180
Oleic acid feed stage	X_4	-	2	3	4	5	6
Methanol feed stage	X_5	-	6	8	10	12	14

Table 5.1 shows the coded and actual value of the process parameters used in the design of simulations. The simulations were conducted based on the design matrix show in Table 5.2.

5.3 Development of regression model

Among the models that fitted to the response (linear, two factor interaction (2FI), quadratic and cubic polynomial), the quadratic model was selected as a best model due to its highest order polynomial with significant of additional terms and the model was not aliased (Table 5.3). The quality of the fit of polynomial model equation was evaluated by the coefficient of determination R^2, the coefficient of determination was shown as 0.9663. This indicated that, the accuracy and general availability of the polynomial model was considered to be reasonable. The predicted R^2 of 0.8469 is in reasonable agreement with the adjusted R^2 of 0.9431.

Analysis of variance (ANOVA) is a collection of statistical models, and their associated procedures, in which the observed variance in a particular variable. The ANOVA was used for checking the significance of the quadratic model equation. Table 5.4 shows analysis of variance for the fitted quadratic polynomial.

5.3.1 Mean square of error

The mean squared of error (MSE) of an estimator is one of many ways to quantify the difference between values implied by an estimator and the true values of the quantity being estimated. From Table 5.4, the mean square of the error has a little value, it is indicated that the data obtained from simulation and optimization is very little difference. Mean of square regression (MS_{SSR}) and mean of square residual (MS_{SSE}) are obtained by divining sum of square (SSR) and sum of residual (SSE) over degree of freedom (DF), respectively.

5.3.2 *F*-value

The calculated F-value is defined as the ratio between MS_{SSR} and (MS_{SSE}). The significance testing (F-test) is used as a tool to check the significance of the variables to the model. The higher F-value indicated that the variable is significant. In single parameter effect, F-value indicated that bottom rate is the most significant variable and reflux ratio, oleic acid temperature, methanol feed stage and oleic acid feed stage are significant respectively. Two interaction term show significant effect on the purity of methyl-oleate; which are X_1X_2 (bottom rate and reflux ratio) is the most significant effect on the purity of methyl-oleate, X_1X_5 (bottom rate and methanol feed stage), X_1X_3 (bottom rate and oleic acid feed temperature) and X_1X_4 (bottom rate and oleic acid feed stage) are significantly reduced, respectively.

Table 5.2 Full factorial central composite design matrix of five independent variables and the response of the dependent variable methyl-oleate purity.

RUN	Levels					MEOL PURITY	
						Simulation	Predicted
1	-1	-1	-1	-1	-1	0.6800	0.6846
2	1	-1	-1	-1	-1	0.4934	0.4917
3	-1	1	-1	-1	-1	0.6107	0.6365
4	1	1	-1	-1	-1	0.4870	0.4833
5	-1	-1	1	-1	-1	0.6993	0.7090
6	1	-1	1	-1	-1	0.4975	0.4926
7	-1	1	1	-1	-1	0.6614	0.6672
8	1	1	1	-1	-1	0.4923	0.4905
9	-1	-1	-1	1	-1	0.6323	0.6592
10	1	-1	-1	1	-1	0.4880	0.4849
11	-1	1	-1	1	-1	0.6005	0.6070
12	1	1	-1	1	-1	0.4779	0.4725
13	-1	-1	1	1	-1	0.6791	0.6842
14	1	-1	1	1	-1	0.4938	0.4864
15	-1	1	1	1	-1	0.6049	0.6382
16	1	1	1	1	-1	0.4858	0.4803
17	-1	-1	-1	-1	1	0.6966	0.7079
18	1	-1	-1	-1	1	0.4965	0.4861
19	-1	1	-1	-1	1	0.6533	0.6681
20	1	1	-1	-1	1	0.4910	0.4861
21	-1	-1	1	-1	1	0.7077	0.7296
22	1	-1	1	-1	1	0.4996	0.4843
23	-1	1	1	-1	1	0.6864	0.6961
24	1	1	1	-1	1	0.4957	0.4907
25	-1	-1	-1	1	1	0.6902	0.6961
26	1	-1	-1	1	1	0.4953	0.4930
27	-1	1	-1	1	1	0.6284	0.6523
28	1	1	-1	1	1	0.4889	0.4889
29	-1	-1	1	1	1	0.7048	0.7184
30	1	-1	1	1	1	0.4989	0.4918
31	-1	1	1	1	1	0.6758	0.6808
32	1	1	1	1	1	0.4943	0.4940
33	-2.38	0	0	0	0	0.9923	0.9159
34	2.38	0	0	0	0	0.4134	0.4642
35	0	-2.38	0	0	0	0.5856	0.5837
36	0	2.38	0	0	0	0.5529	0.5291
37	0	0	-2.38	0	0	0.5618	0.5424
38	0	0	2.38	0	0	0.5837	0.5775
39	0	0	0	-2.38	0	0.5797	0.5738
40	0	0	0	2.38	0	0.5674	0.5476
41	0	0	0	0	-2.38	0.5461	0.5283
42	0	0	0	0	2.38	0.5801	0.5723
43	0	0	0	0	0	0.5751	0.5730

Table 5.3 Model summary statistics.

Source	Standard Deviation	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	
Linear	0.0343	0.8863	0.8734	0.8439	0.0711	
2FI	0.0362	0.9023	0.8592	0.8449	0.0706	
Quadratic	0.0230	0.9663	0.9431	0.8469	0.0697	Suggested
Cubic	0.0150	0.9931	0.9759	0.1884	0.3695	Aliased

5.3.3 *P*-value

The *P*-values are used as a tool to check the significance of each coefficient, which also indicate the interaction strength of each crossproduct. The value of "*P* > F" for models is less than 0.05, indicated that the terms in the model have a significant effect on the response. The value of $P < 0.0001$ indicates that there is only a 0.01% chance that a "model *F*-value" this large could occur due to noise. *P*-values lower than 0.05 indicate that the model is considered to be statistically significant at the 95% confidence level. In this study, λ_1, λ_2, λ_4, λ_5, $\lambda_1\lambda_2$ and λ_1^2 are significant model term. **(***P*-value for each variable is less than the significant size, which was used 0.05 in this test)

5.3.4 Lack of fit

Lack of fit (LOF), this is the variation of the data around the fitted model. If the model does not fit the data well, the test will show significant. From table 5.4, lack of fit is not significance, it is indicated that the model fit the data.

5.3.5 Mathematical model

The quadratic model for the purity of methyl-oleate was regressed by considering the significant terms and was shown as below:

Table 5.4 Analysis of variance (ANOVA) for the quadratic polynomial model.

Source	Sum of Squares	df	Mean Square	*F*-value	*P*-value *(P) > F*
Model	4.40E-01	20	2.20E-02	41.62	< 0.0001
λ_1	3.90E-01	1	3.90E-01	738.76	< 0.0001
λ_2	5.69E-03	1	5.69E-03	10.77	0.0027
λ_3	2.35E-03	1	2.35E-03	4.45	0.0437
λ_4	1.31E-03	1	1.31E-03	2.49	0.1256
λ_5	3.70E-03	1	3.70E-03	7.00	0.0130
$\lambda_1 \lambda_2$	3.17E-03	1	3.17E-03	6.00	0.0206
$\lambda_1 \lambda_3$	1.10E-03	1	1.10E-03	2.08	0.1597
$\lambda_1 \lambda_4$	6.98E-04	1	6.98E-04	1.32	0.2598
$\lambda_1 \lambda_5$	1.66E-03	1	1.66E-03	3.15	0.0865
$\lambda_2 \lambda_3$	7.93E-05	1	7.93E-05	0.15	0.7012
$\lambda_2 \lambda_4$	3.38E-05	1	3.38E-05	0.06	0.8022
$\lambda_2 \lambda_5$	1.41E-04	1	1.41E-04	0.27	0.6093
$\lambda_3 \lambda_4$	6.78E-07	1	6.78E-07	0.00	0.9717
$\lambda_3 \lambda_5$	1.44E-05	1	1.44E-05	0.03	0.8699
$\lambda_4 \lambda_5$	3.71E-04	1	3.71E-04	0.70	0.4088
λ_1^2	2.38E-02	1	2.38E-02	45.04	< 0.0001
λ_2^2	4.76E-04	1	4.76E-04	0.90	0.3504
λ_3^2	2.95E-04	1	2.95E-04	0.56	0.4612
λ_4^2	2.61E-04	1	2.61E-04	0.49	0.4880
λ_5^2	8.94E-04	1	8.94E-04	1.69	0.2036
Residual	1.53E-02	29	5.29E-04		
Lack of Fit	1.53E-02	22	6.97E-04		
Cor Total	4.55E-01	49	4.55E-01		

Table 5.5 Regression analysis of a full second-order polynomial model for optimization of biodiesel production process.

Term	Regression coefficients	Standard Error	95% CI Low	95% CI High
Intercept	0.5730	0.0081	0.5565	0.5895
λ_1	-0.0949	0.0035	-0.1021	-0.0878
λ_2	-0.0115	0.0035	-0.0186	-0.0043
λ_3	0.0074	0.0035	0.0002	0.0145
λ_4	-0.0055	0.0035	-0.0127	0.0016
λ_5	0.0092	0.0035	0.0021	0.0164
$\lambda_1 \lambda_2$	0.0100	0.0041	0.0016	0.0183
$\lambda_1 \lambda_3$	-0.0059	0.0041	-0.0142	0.0024
$\lambda_1 \lambda_4$	0.0047	0.0041	-0.0036	0.0130
$\lambda_1 \lambda_5$	-0.0072	0.0041	-0.0155	0.0011
$\lambda_2 \lambda_3$	0.0016	0.0041	-0.0067	0.0099
$\lambda_2 \lambda_4$	-0.0010	0.0041	-0.0093	0.0073
$\lambda_2 \lambda_5$	0.0021	0.0041	-0.0062	0.0104
$\lambda_3 \lambda_4$	0.0001	0.0041	-0.0082	0.0085
$\lambda_3 \lambda_5$	-0.0007	0.0041	-0.0090	0.0076
$\lambda_4 \lambda_5$	0.0034	0.0041	-0.0049	0.0117
λ_1^2	0.0207	0.0031	0.0144	0.0270
λ_2^2	-0.0029	0.0031	-0.0092	0.0034
λ_3^2	-0.0023	0.0031	-0.0086	0.0040
λ_4^2	-0.0022	0.0031	-0.0085	0.0041
λ_5^2	-0.0040	0.0031	-0.0103	0.0023

*CI is confidence interval.

$$Y_{\text{yield}} = 0.574 - 0.095X_1 - 0.011X_2 + 0.007X_3 + 0.01X_1X_2 + 0.021X_1^2$$

Where Y is the purity of methyl-oleate; X_1, X_2, X_3, X_4 and X_5 are the coded independent variables. From table 5.4 shows that regression coefficients of the linear terms X_1 and X_2 are significant at 1% level as well as X_3 and X_5 are significant at 5% level. The regression coefficient of the interaction term X_1X_2 is significant at 5% level The regression coefficient of the quadratic term X_1^2 is significant at 1% level. From table 5.2, the model from CCD was considered to be accurate and reliable for predicting the purity of methyl-oleate.

5.4 Effect of process parameters

5.4.1 Effect of single parameter

5.4.1.1 Effect of bottom rate on the purity of methyl-oleate

Figure 5.3 demonstrates that the purity of methyl-oleate increases with decreasing bottom rate. When decreasing the bottom rates will result in high boilup rates. At high boilup rates, the excess reactant (methanol) and some water were evaporated into the top of the column as a result in more purity of methyl-oleate. From table 5.4, *F*- value of the parameter is 738.76 and *P*-value is <0.0001, it is indicated that this parameter has the most significant effect on the purity of methyl-oleate.

5.4.1.2 Effect of reflux ratio on the purity of methyl-oleate

Figure 5.4 demonstrates that the purity of methyl-oleate increases with decreasing reflux ratio. When decreasing the reflux ratio will result in high reflux rates. At high reflux rates, the water was recycled back into the top of the column as returning water to the column is detrimental to the chemical equilibrium.

Moreover, the oleic acids remain from the reaction as a result of the interference of chemical equilibrium and flow down to the bottom of the column. It makes the less purity of methyl-oleate due to oleic acid contaminate in the bottom product. Then at low reflux ratio, the methyl-oleate is more purity. From table 5.4, *F*-value of the parameter is 10.77 and *P*-value is 0.0027, it is indicated that this parameter has the significant effect on the purity of methyl-oleate.

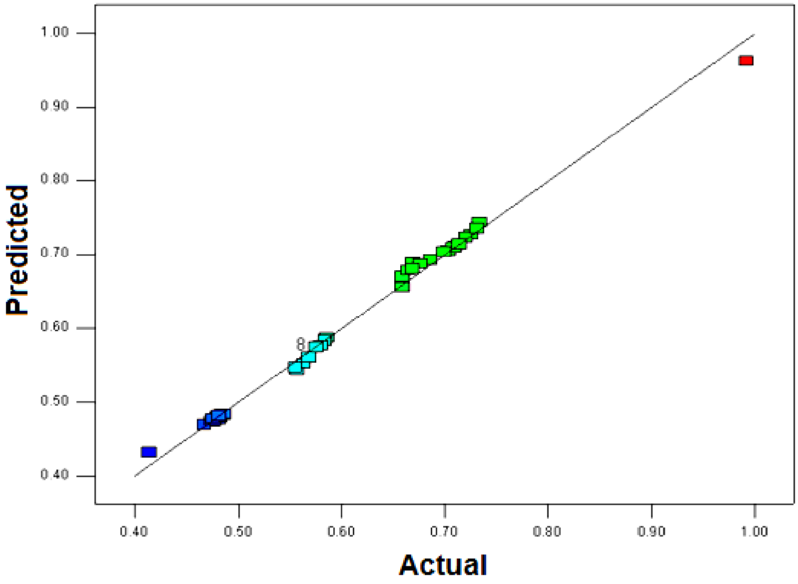

Figure 5.2 A comparative plot between simulation and predicted MEOL purity.

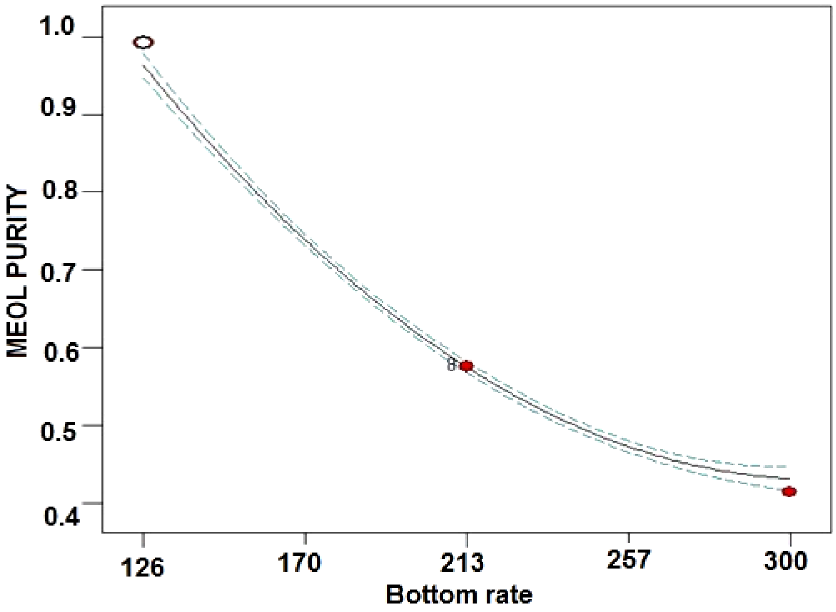

Figure 5.3 Effect of bottom rate on the purity of methyl-oleate.

5.4.1.3 Effect of oleic acid feed temperature on the purity of methyl-oleate

Figure 5.5 demonstrates that the purity of methyl-oleate increases with increasing oleic acid feed temperature. When oleic acid feed temperature increases the methyl-oleate is more generation. It is indicated that the esterification reaction in reactive distillation column is more complete as a result in high oleic acid conversion. Then we obtained the bottom product which more purity of methyl-oleate. From table 5.4, *F*- value of the parameter is 4.45 and *P*-value is 0.0437, it is indicated that this parameter has the significant effect on the purity of methyl-oleate.

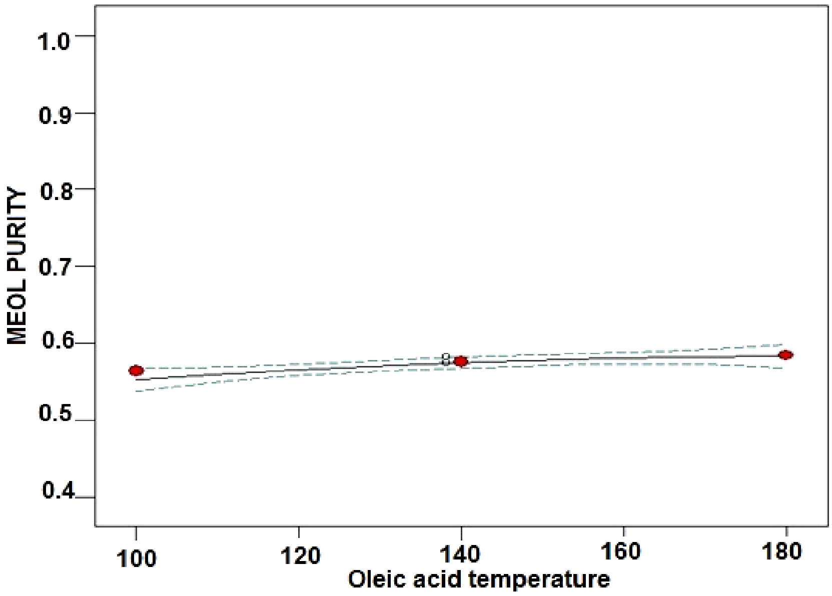

Figure 5.4 Effect of reflux ratio on the purity of methyl-oleate.

5.4.1.4 Effect of oleic acid feed stage on the purity of methyl-oleate

Figure 5.6 demonstrates that the purity of methyl-oleate increases with decreasing oleic acid feed stage. Oleic acid is fed to the column as liquid phase but methanol is fed to the bottom of the column as vapor phase. If we fed oleic acid at the bottom of the column, oleic acid will not react with methanol due to methanol evaporates rapidly to the top of the column as a result in not completely esterification reaction. From properties of pure component, oleic acid has boiling point temperature

360 °C so it is difficult to evaporate oleic acid to the top of the column. Accordingly oleic acid remaining from the esterification reaction will flow to the bottom of the column and contaminate in bottom product.

Feeding oleic acid at the top of the column is obtaining more purity of methyl-oleate. From table 5.4, *F*- value of the parameter is 2.49 and *P*-value is 0.1256. The terms shows not significant effect on the purity of methyl-oleate because *P*-value >0.05.

5.4.1.5 Effect of methanol feed stage on the purity of methyl-oleate

Figure 5.7 demonstrates that the purity of methyl-oleate increases with increasing methanol feed stage. Methanol is fed the column as vapor phase. Because of methanol have boiling point temperature 65°C and the range of operating temperature of the reactive distillation column is 65 - 93°C (from the previous chapter), so oleic acid is rich in liquid phase due to high boiling point temperature. If we fed methanol at the top of the column, methanol will vaporize to the top and not completely react with oleic acid. Feeding methanol at the top of the column is obtaining more purity of methyl-oleate. . From table 5.4, *F*- value of the parameter is 7 and *P*-value is 0.0130, it is indicated that this parameter has the significant effect on the purity of methyl-oleate.

5.4.2 Effect of interaction between parameters

The contour plots described by the regression model were drawn to display the effect of the independent variable on the response variable. From the shape of contour plots one could estimate significance of the mutual interaction between the independent variables in that an elliptical profile of the contour plots indicates remarkable interaction strength as well as the optimal values ranges of the independent variables could be observed.

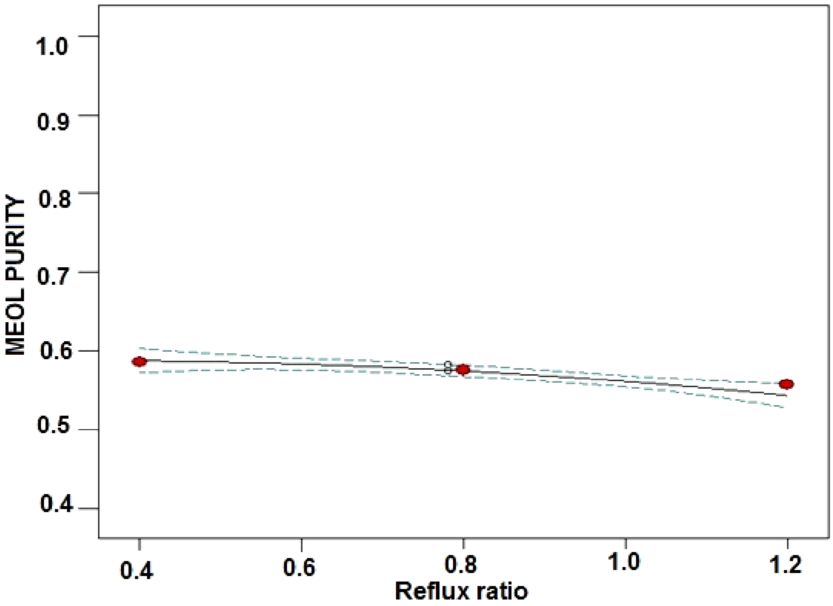

Figure 5.5 Effect of oleic acid feed temperature on the purity of methyl oleate.

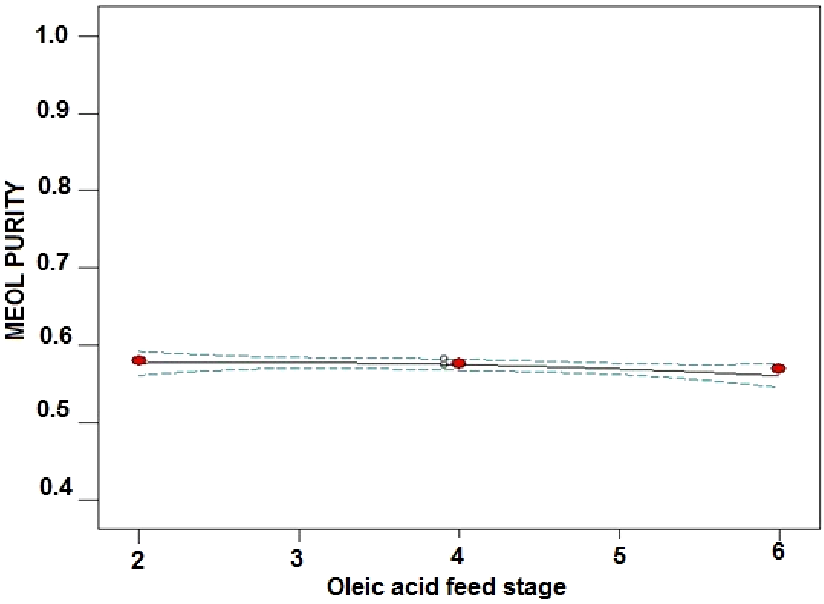

Figure 5.6 Effect of oleic acid feed stage on the purity of methyl-oleate.

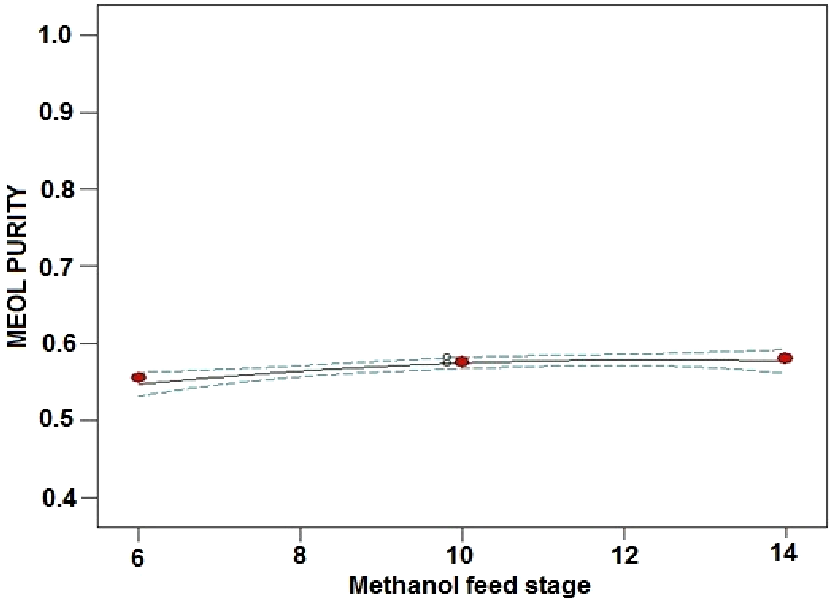

Figure 5.7 Effect of methanol feed stage on the purity of methyl-oleate.

5.4.2.1 Effect of bottom rate and reflux ratio on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_1X_2, F-value is 6 and P-value is 0.0206. Two interaction terms show significant effect on the purity of methyl-oleate. The responses corresponding to the contour plots of second-order predicted model indicated that, for low bottom rate, purity of methyl-oleate increases with reducing reflux ratio (Figure 5.8). Low bottom rate was liable for the increasing of the methyl-oleate in that reflux ratio obviously inclined to proceed at low level. If the bottom rate is low, the amount of methyl-oleate is rich in the bottom product. The reflux ratio not direct influence on the purity of methyl-oleate but it does have impact on the top water product. If the reflux ratio is increased, the amount of top product (water and excess of methanol) which returns to the column is increased. Returning water by-product to the column is not favorable to the chemical equilibrium. On the other hand, excessive reflux ratio leads to reduced product purity. For this reason, high reflux ratio that effect to the bottom rate due to the boilup ratio was increased (boilup ratio increases when bottom rate decreases) for evaporating water to the top of the column and maintain the purity of methyl-oleate. Then a minimum reflux ratio must be maintained to operate column. This can be attributed to water distillation, which otherwise would accumulate in bottom. The suitable conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at low bottom rate and reflux ratio, respectively.

5.4.2.2 Effect of bottom rate and oleic acid temperature on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_1X_3, *F*-value is 2.08 and *P*-value is 0.1597. Two interaction terms show not significant effect on the purity of methyl-oleate because *P*-value >0.05. The responses corresponding to the contour plots of second-order predicted model indicated that, for low bottom rate, purity of methyl-oleate increases with increasing oleic acid feed temperature (Figure 5.9).

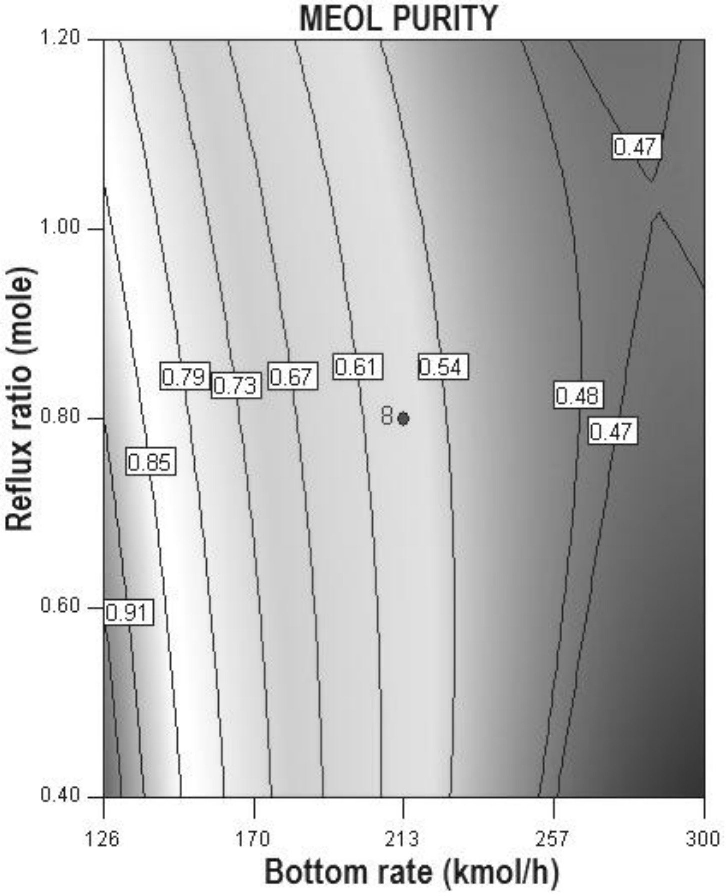

Figure 5.8 Contour plots of the combined effect of bottom rate and reflux ratio on the purity of methyl-oleate.

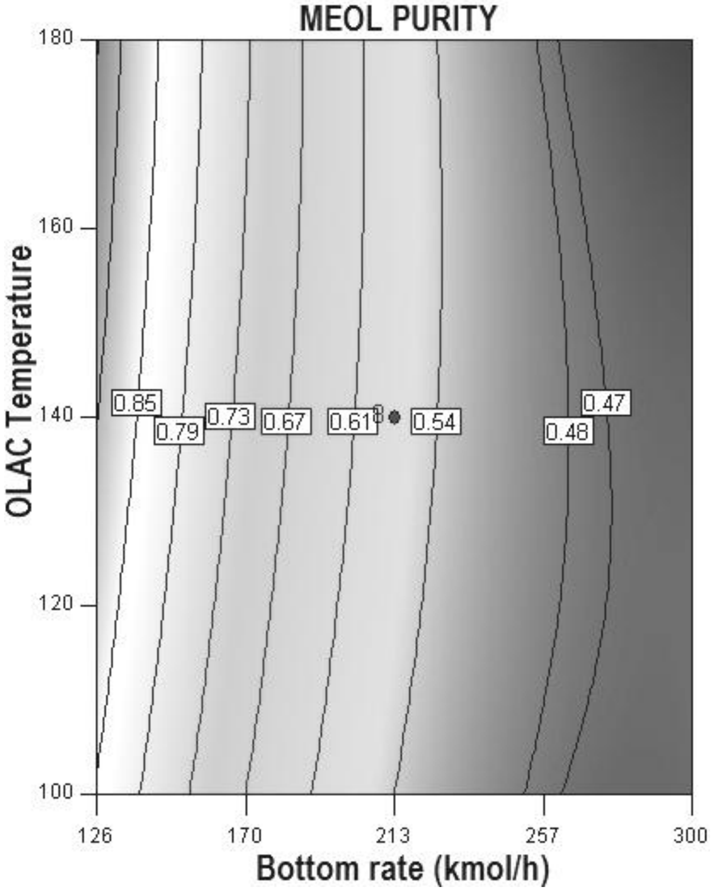

Figure 5.9 Contour plots of the combined effect of bottom rate and oleic acid feed temperature on the purity of methyl-oleate.

From the figure 5.9, at high bottom rate, graph is a straight line in y-axis and deviation toward the x-axis at high oleic acid feed temperature. Because of when temperature of oleic acid increases the amount of methyl-oleate will increases less than the bottom rate decreases. Then the influence of oleic acid feed temperature on the purity of methyl-oleate has a little when compared with bottom rate. At high oleic acid feed temperature the component of methyl-oleate is more generation than low oleic acid feed temperature, it is indicated that there are the amount of methyl-oleate rich at the bottom product. At low bottom rate, distillate rate is high according to theoretical material balances in distillation column.

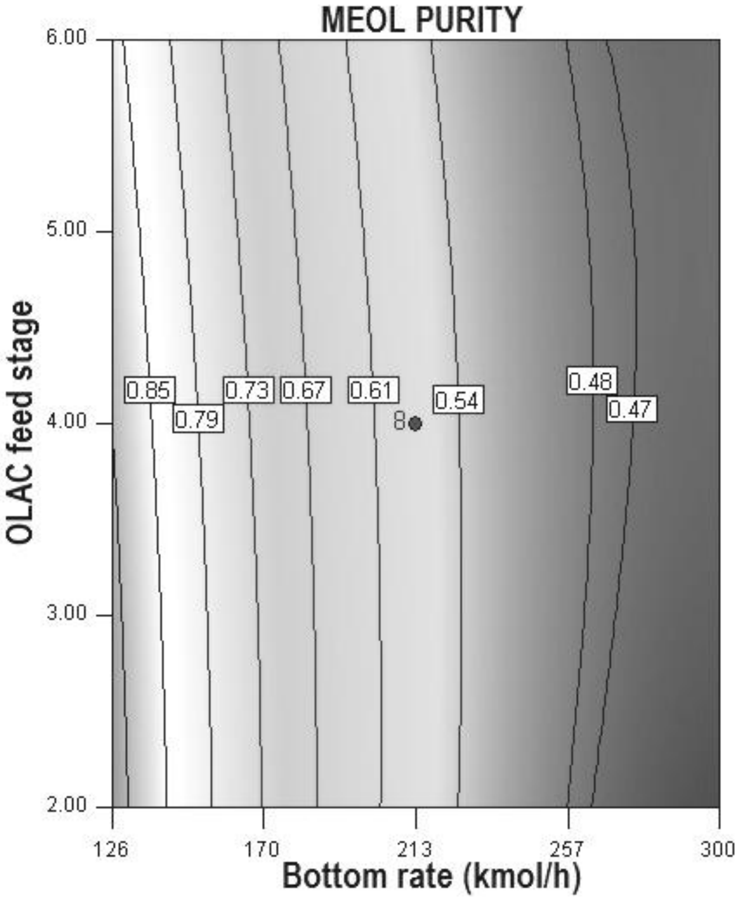

Figure 5.10 Contour plots of the combined effect of bottom rate and oleic acid feed stage on the purity of methyl-oleate.

When distillate rate is high, the water is more removal from the reactive distillation column which positive impact to chemical equilibrium. If the oleic acid feed temperature is high (140-160 °C) with the condition at low bottom rate, resulted in chemical equilibrium in reactive distillation column can be improved and more generation amount of methyl-oleate occurred.

5.4.2.3 Effect of bottom rate and oleic acid feed stage on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_1X_4, *F*-value is 1.32 and *P*-value is 0.2598. Two interaction terms show not significant effect on the purity of methyl-oleate because *P*-value >0.05. The responses corresponding to the contour plots of second-order predicted model indicated that, for low bottom rate, purity of methyl-oleate increases with feed oleic acid at the top of the colum (Figure 5.10). At high bottom rate, it is indicated that bottom rate no correlation to oleic acid feed stage due to the graph is straight line only in the y-axis. At high bottom rate, the distillate rate is very low, resulting in little amounts of methyl-oleate in bottom product. For this reason, although oleic acid feed at the top of the column but it also has a very small amount of methyl-oleate in bottom product. Due to bottom rate is a significance parameter that effects on purity of methyl-oleate more than oleic acid feed stage following the *F*-value in Table 5.4.

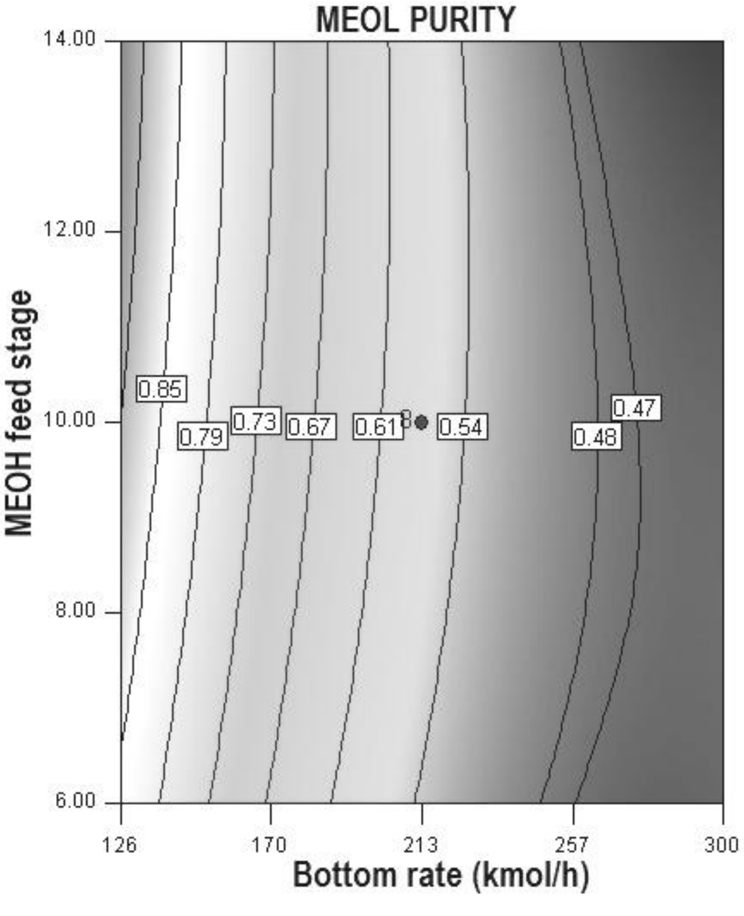

Figure 5.11 Contour plots of the combined effect of bottom rate and methanol feed stage on the purity of methyl-oleate.

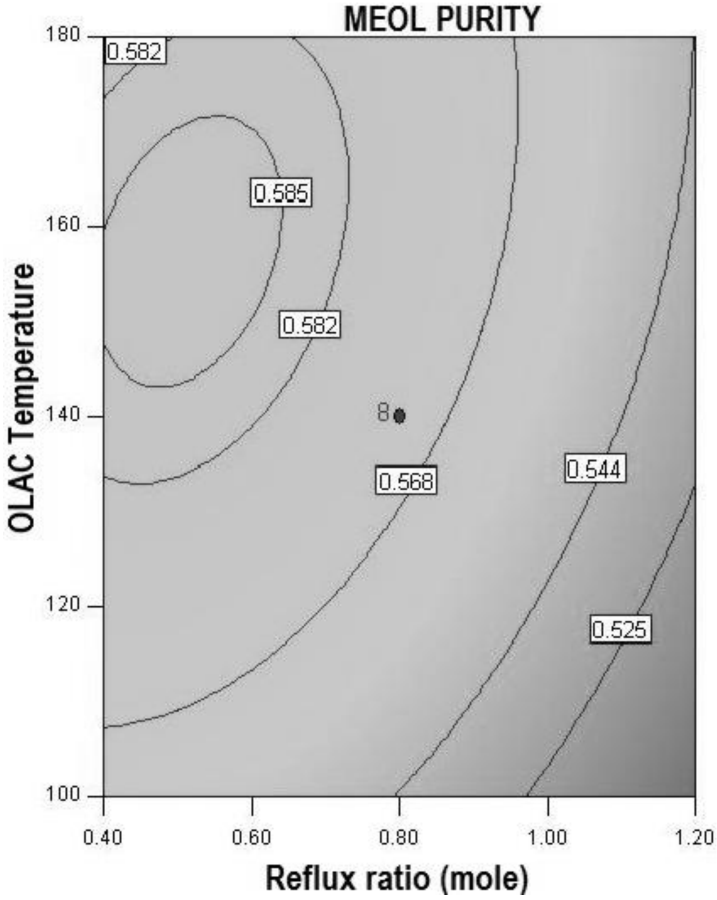

Figure 5.12 Contour plots of the combined effect of reflux ratio and oleic acid feed temperature on the purity of methyl-oleate.

At low bottom rate, the chemical equilibrium in reactive distillation is more efficiency than high bottom rate. If feeds oleic acid at the top of the column (stage 2 – 4), oleic acid can react with methanol more than feed at the bottom and makes high purity of methyl-oleate at the bottom product. Observed from the graph at low bottom rate, the line of *y*-axis deviates to *x*-axis. The suitable conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at low bottom rate and oleic acid feed stage at the top of the column.

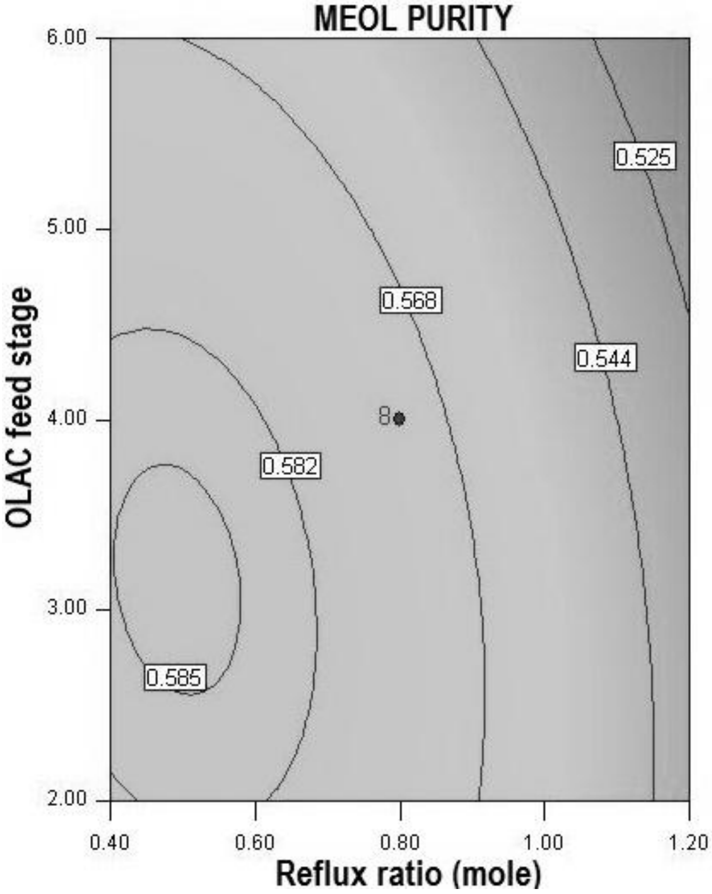

Figure 5.13 Contour plots of the combined effects reflux ratio and oleic acid feed stage on the purity of methyl-oleate.

5.4.2.4 Effect of bottom rate and methanol feed stage on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_1X_5, F-value is 3.15 and P-value is 0.0865. Two interaction terms show not significant effect on the purity of methyl-oleate because P-value >0.05. The responses corresponding to the contour plots of second-order predicted model indicated that, for low bottom rate, methyl-oleate purity increases with feed methanol at the bottom of the column. From the figure 5.11, at high bottom rate, graph is a straight line in y-axis and deviation toward the x-axis at methanol feed stage at the bottom of the column. At high bottom rate, the distillate rate is very low, resulting in little amounts of methyl-oleate in bottom product. For this reason, although methanol feed at the bottom of the column but it also has a very small amount of methyl-oleate in bottom product. Due to bottom rate is a significance parameter that effects on purity of methyl-oleate more than methanol feed stage following the *F*-value in Table 5.4. At low bottom rate, the chemical equilibrium in reactive distillation is more efficiency than high bottom rate. When methanol feed at the bottom of the column (stage 10-14), methanol was evaporated onto the top of the column and reacts with oleic acid. Then the amount of methyl-oleate is rich at the bottom product.

When bottom rate is high, resulting in the low purity of methyl-oleate. Due to there is some methanol liquid remain in the bottom product. The suitable conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at low bottom rate and methanol feed stage at the bottom of the column.

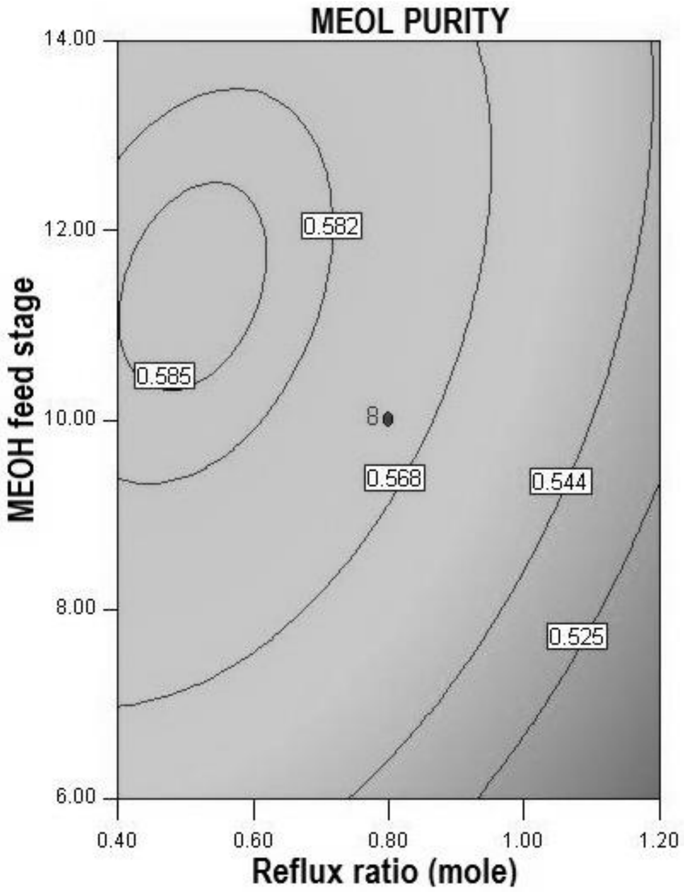

Figure 5.14 Contour plots of the combined effect of reflux ratio and methanol feed stage on the purity of methyl-oleate.

5.4.2.5 Effect of reflux ratio and oleic acid feed temperature on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_2X_3, *F*-value is 0.15and *P*-value is 0.7012. Two interaction terms show not significant effect on the purity of methyl-oleate because *P*-value >0.05. From the graph in figure 5.12, at high reflux ratio, the line of graph from y-axis deviates into the *x*-axis. It is indicated when the oleic feed temperature increases the purity of methyl-oleate increases. On the other hand, at low reflux ratio, the line of graph from *y*-axis bends toward the x-axis. It is indicated when the oleic feed temperature increases the purity of methyl-oleate increases more than the operating at high reflux ratio. The optimal conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at the elliptical nature of the contour plot at reflux ratio = 0.4 – 0.6 and oleic acid feed temperature 160 – 170 °C.

5.4.2.6 Effect of reflux ratio and oleic acid feed stage on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_2X_4, *F*-value is 0.064 and *P*-value is 0.8022. Two interaction terms show not significant effect on the purity of methyl-oleate because *P*-value >0.05. From Figure 5.13, the line from the *y*-axis bends toward the *x*-axis. The responses corresponding to the contour plots of second-order predicted model indicated that, for low reflux ratio, methyl-oleate purity increases with feed oleic acid at the top of the column. The optimal conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at the elliptical nature of the contour plot at reflux ratio = 0.4 – 0.6 and oleic acid feed stage at stage 3.

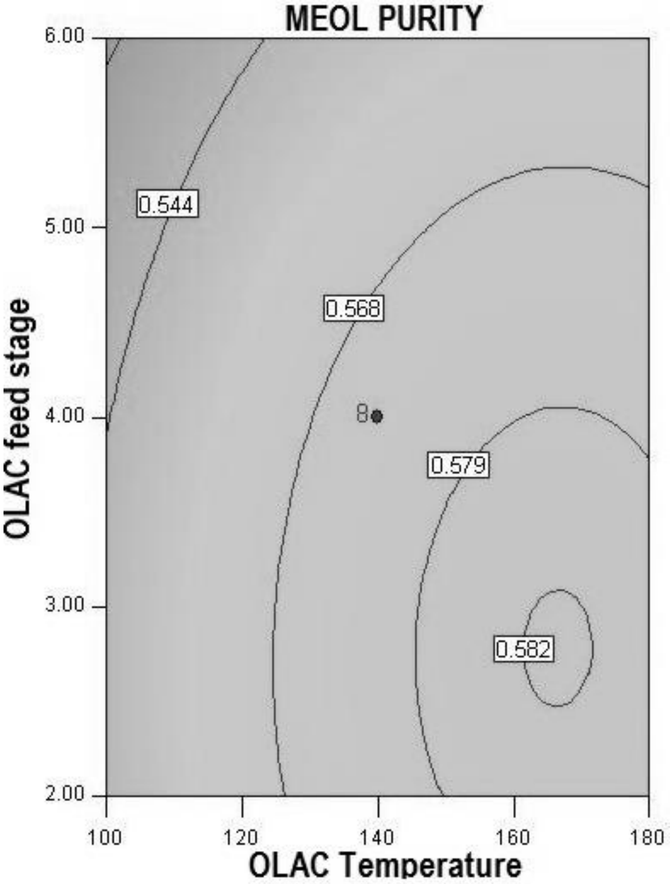

Figure 5.15 Contour plots of the combined effect of oleic acid feed temperature and oleic acid feed stage on the purity of methyl-oleate

5.4.2.7 Effect of reflux ratio and methanol feed stage on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_2X_5, *F*-value is 0.27 and *P*-value is 0.6093. Two interaction terms show not significant effect on the purity of methyl-oleate because *P*-value >0.05. From figure 5.14, the line from the y-axis bends toward the x-axis. The responses corresponding to the contour plots of second-order predicted model indicated that, for low reflux ratio, methyl-oleate purity increases with feed methanol at the bottom of the column. The optimal conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at the elliptical nature of the contour plot at reflux ratio = 0.4 – 0.6 and methanol feed stage at stage 12.

5.4.2.8 Effect of oleic acid feed temperature and oleic acid feed stage on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_3X_4, *F*-value is 0.0013 and *P*-value is 0.9717. Two interaction terms show not significant effect on the purity of methyl-oleate because *P*-value >0.05. From figure 5.15, the line from the *y*-axis bends toward the *x*-axis. The responses corresponding to the contour plots of second-order predicted model indicated that, for high oleic acid feed temperature, methyl-oleate purity increases with feed oleic acid at the top of the column. The optimal conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at the elliptical nature of the contour plot at oleic acid feed temperature = 170 ºC and oleic acid feed stage at stage 3.

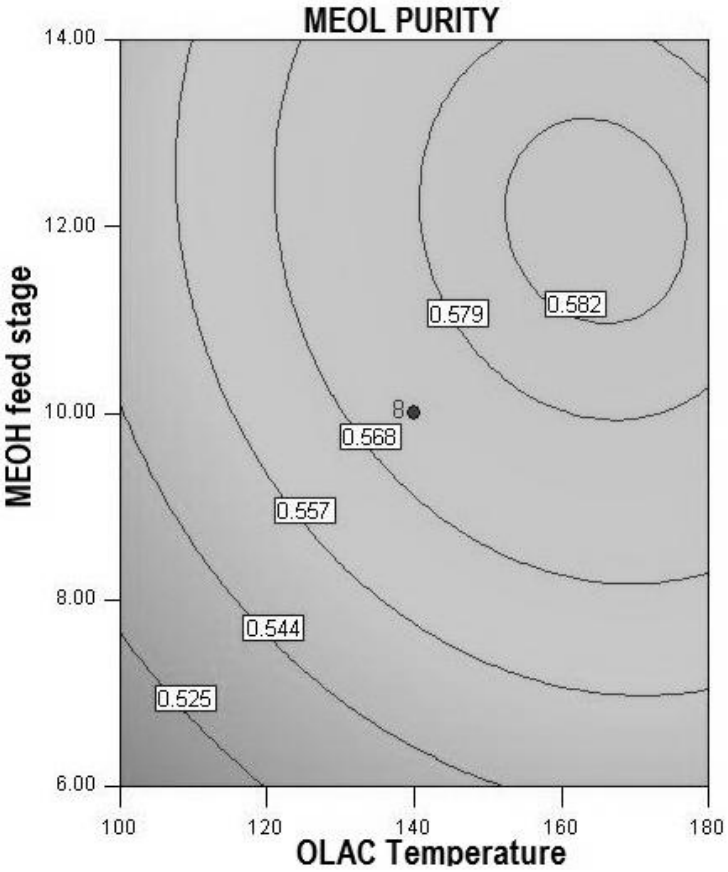

Figure 5.16 Contour plots of the combined effect of oleic acid feed temperature and methanol feed stage on the purity of methyl-oleate.

5.4.2.9 Effect of oleic acid feed temperature and methanol feed stage on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_3X_5, F-value is 0.027 and P-value is 0.8699. Two interaction terms show not significant effect on the purity of methyl-oleate because P-value >0.05. From figure 5.16, the line from the y-axis bends toward the x-axis. The responses corresponding to the contour plots of second-order predicted model indicated that, for high oleic acid feed temperature, methyl-oleate purity increases with feed methanol at the bottom of the column. The optimal conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at the elliptical nature of the contour plot at oleic acid feed temperature = 160-170 ºC and methanol feed stage at stage 12.

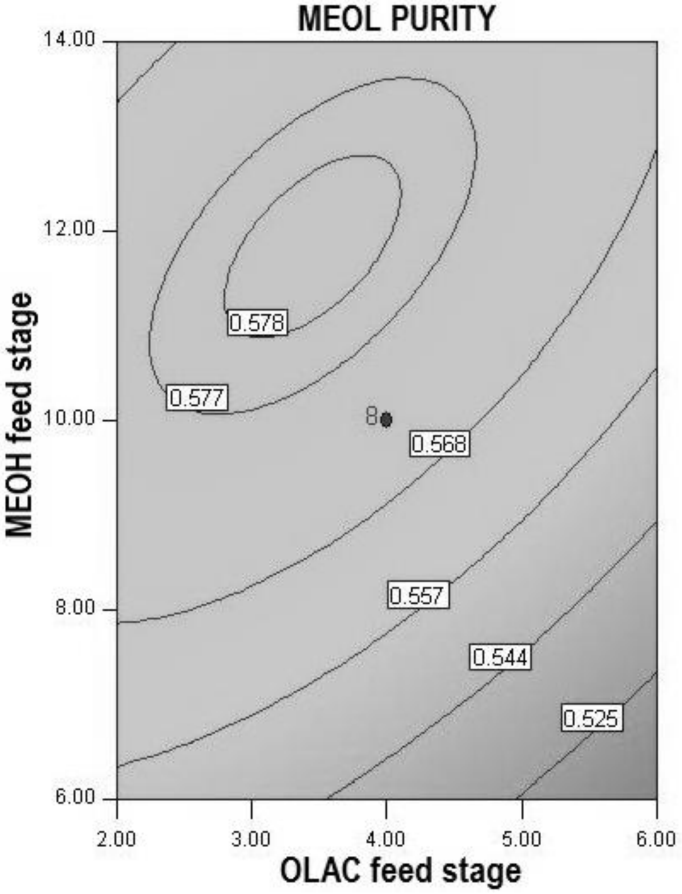

Figure 5.17 Contour plots of the combined effect of oleic acid feed stage and methanol feed stage on the purity of methyl-oleate

5.4.2.10 Effect of oleic acid feed stage and methanol feed stage on the purity of methyl-oleate

According to the ANOVA presented in Table 5.4, term X_4X_5, F-value is 0.70 and P-value is 0.4088. Two interaction terms show not significant effect on the purity of methyl-oleate because P-value >0.05. Figure 5.17 illustrate the elliptical nature of contour plot for oleic acid feed stage and methanol feed stage interaction. The responses corresponding to the contour plots of second-order predicted model indicated that, for oleic acid feed stage at the top of the column, methyl-oleate purity increases with feed methanol at the bottom of the column. Methanol was fed into the reactive distillation at the boiling point temperature (65 ºC). It is indicated that methanol has a vapor phase. Oleic acid was fed into the reactive distillation in a liquid phase and the reaction occurs on liquid phase. To ensure the appropriate distribution of liquid and vapor flow throughout the column, the liquid feed stream was fixed on the top of the column and the vapor phase methanol stream enter on the bottom of the column. For the optimal location of feed, methanol and oleic acid can reacted to maximum amount of methyl-oleate. If we feed methanol at the top of the column, methanol will evaporate to the top and does not react with oleic acid. On the other hand, if we feed oleic acid at the bottom of the column, oleic acid will flow to the bottom and methanol will evaporate rapidly to the top of the column. Therefore oleic acid and methanol are not contact to each other and no distribution of liquid and vapor flow throughout the column, as a result of low purity of methyl-oleate. The optimal conditions of two parameters for obtaining maximum purity of methyl-oleate occurred at the elliptical nature of the contour plot at oleic acid feed stage = 3-4 and methanol feed stage at stage 12.

5.5 Optimization of methyl-oleate purity

In this study, the optimization of the methyl-oleate synthesis process was performed to seek for an optimum combination of operating conditions at which the maximum methyl-oleate purity is achieved. The variables (bottom rate, reflux ratio, oleic acid feed temperature, oleic acid feed stage and methanol feed stage) were set in a range between low and high levels which coded -2.38 and +2.38 to achieve maximum response for the methyl-oleate purity (Table 5.6a). The solutions with these five variables were generated by the software for the desired response of the system based on the model obtained and the simulation data input criteria. The overall average optimized conditions for methyl-oleate purity were obtained as follows: distillate rate, reboiler heat duty, oleic acid feed temperature, oleic acid feed stage and methanol feed stage with the methyl-oleate purity of % (Table 5.7). The predicted methyl-oleate purity was %. This means that the simulation value obtained was reasonably close to the predicted value calculated from the model (% of error). It can be conclude that the generated model showed reasonable predictability and sufficient accuracy for the methyl-oleate purity in the simulation conditions used.

Table 5.6 Optimization criteria for maximum methyl-oleate purity.

Factor	Goal	Lower limit	Upper limit
Bottom rate	Is in range	126(-2.38)	300 (+2.38)
Reflux ratio	Is in range	0.4(-2.38)	1.2(+2.38)
Oleic acid temperature	Is in range	100(-2.38)	180(+2.38)
Oleic acid feed stage	Is in range	2(-2.38)	6(+2.38)
Methanol feed stage	Is in range	6(-2.38)	14(+2.38)
Methyl-oleate purity	Maximize	-	-

Table 5.7 Results of model validation at the optimum conditions.

Factors					MEOL		Oleic acid
X_1	X_2	X_3	X_4	X_5	Simulation	Predicted	Conversion
126.4	0.4	160	3	12	0.99	1.0000	99.96%

5.6 Conclusions

The mathematical model developed could predict the purity of biodiesel at any point in the simulation domain as well as the determination of the optimal methyl-oleate conditions. The high correlation in the model indicates that the second order polynomial model could be used to optimize the purity of methyl-oleate. The conditions to get optimal response with 99% were found to be 126.4 kmol/h of bottom rate, 0.4 for reflux ratio, 160 °C for oleic acid feed temperature, methanol feed stage = 12 and oleic acid feed stage = 3. These results implicate that the optimization using a response surface methodology based on central composite design was useful software in improving the optimization of methyl-oleate purity.

Figure 5.19 shows the liquid mole composition profiles in the reactive distillation column. The concentration of oleic acid in the liquid phase drops rapidly on the stage 3 (oleic acid feed stage) while the concentration of methyl-oleate increases rapidly on the stage 3 and remains constant. Above stage 13, the liquid mole composition quickly becomes rich in methyl-oleate due to an increase in temperature for separation glycerol from methyl-oleate.

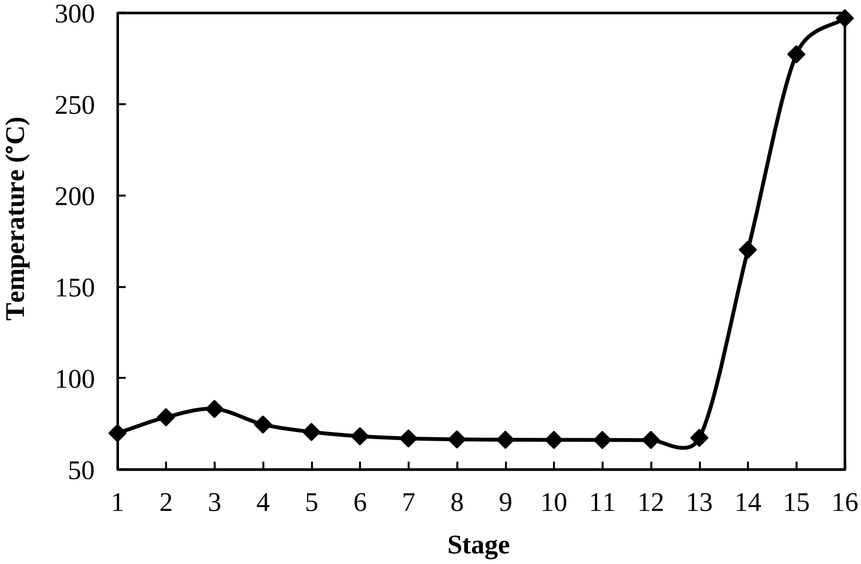

Figure 5.18 Temperature profiles along reactive distillation column in reactive distillation process.

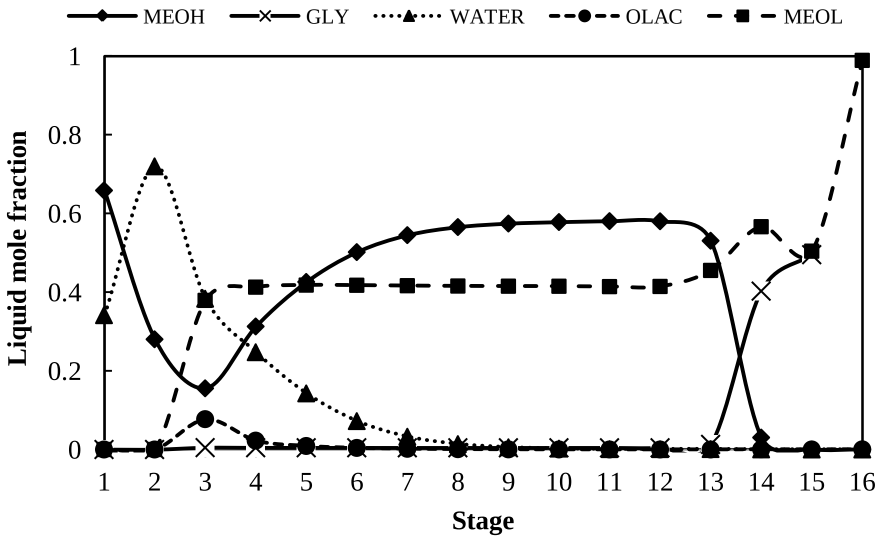

Figure 5.19 Liquid mole composition profiles along reactive distillation column in reactive distillation process.

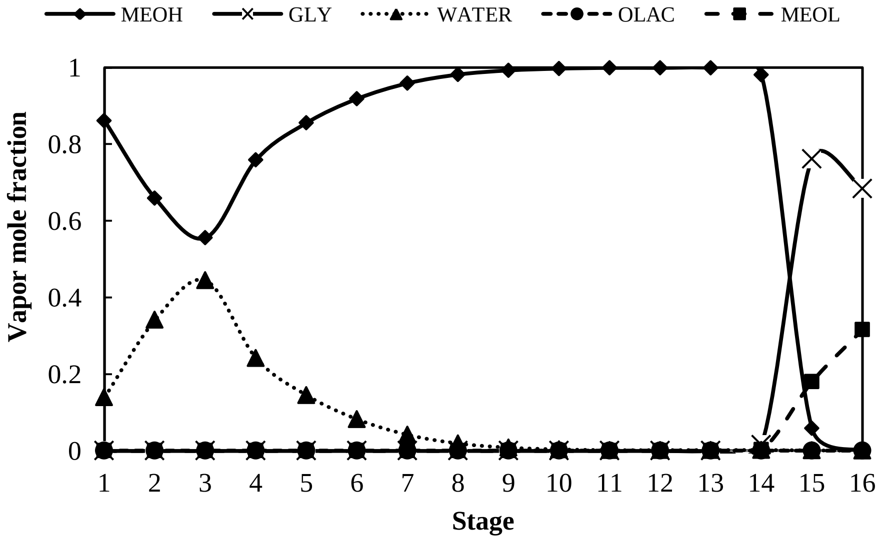

Figure 5.20 Vapor mole composition profiles along reactive distillation column in reactive distillation process.

This is reflected the temperature profile as shown in Figure 5.18. From Figure 5.18, the temperature of reboiler increases to 297 °C for obtaining the purity of methyl-oleate Similarly, the methanol concentration decreases when reacted with oleic acid and remains constant while water concentration increases from the bottom to the top of the column.

Figure 5.20 shows the vapor mole composition profiles in the reactive distillation column. Methanol and water have the lower boiling point temperature than oleic acid and methyl-oleate. From Figure 5.18, the reactive distillation column is operated in the temperature range of 65 – 70 ºC at stage 1 – 13. We fed methanol at the excess reactant at normal boiling point temperature (65 ºC) so the vapor phase of methanol is rich along the column. Water has normal boiling point (100 ºC) lower than methyl-oleate, it vaporize to the top of the column. At stage 15 the temperature increases to 297 ºC, so the vapor mole composition of glycerol is high because the normal boiling point temperature of glycerol is 285 ºC.

CHAPTER VI

METHANOL RECOVERY

From the previous chapter, we explore the optimal operating condition of biodiesel production by using *Jatropha* oil as feedstock. The biodiesel production process uses excess methanol to get high conversion of oleic acid. This excess methanol is distributed between two products (water and methyl-oleate). After the esterification process is complete, a lot of methanol is available for recovery. In this chapter, we demonstrate the methanol recovery process. Modified methanol recovery process is proposed to compare with conventional methanol recovery process in term of the energy requirements.

6.1 Introduction

Almost every biodiesel standard allows 0.2% methanol in the final product. Residual methanol in the biodiesel fuel is a major environmental and health safety issue. Methanol is toxic, and the emission of excess methanol from the use of biodiesel can be hazardous for our life and environment. Excess methanol can also make the fuel flammable and more dangerous to handle and store. Besides, Excess methanol may corrode metal components of engine. For these reasons, most conventional biodiesel manufactures waste a lot of unused methanol through washing a final product. Some biodiesel manufactures are now using distillation column for methanol recovery. Methanol recovery can make the biodiesel production process more efficient from both economical and environmental point of view, as it can save the input cost for the process as well as helps to maintain the specific standard. And in designing a cost-effective methanol recovery unit energy requirement is the most important parameter, as high energy requirements may increase the cost of biodiesel compared to petro-diesel.

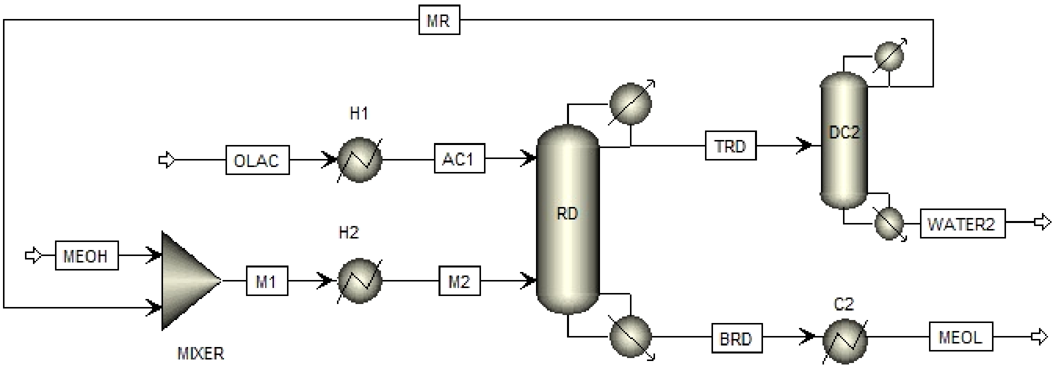

Figure 6.1 Reactive distillation process: Conventional methanol recovery process.

6.2 Conventional methanol recovery (CMR)

After the esterification reaction the excess of methanol is distributed to the mixture of the products. The distillate product of this reactive distillation column is a mixture of methanol and water. As a result an additional distillation column (DC2) is required to recover and recycle the methanol. Fenske-Underwood-Gilliland shortcut method is used to design separation operations and achieve the purity of methanol. The bottom product is 130.27 kmol/h of water (99.1%) and the top product is 250.85 kmol/h of methanol (99.6%). A 250.85 kmol/h stream of methanol are recovered as feedstock of methanol. For this reason, we only require 125 kmol/h of methanol for feedstock of biodiesel production process. The configuration of conventional methanol recovery process is shown in Table 6.1.

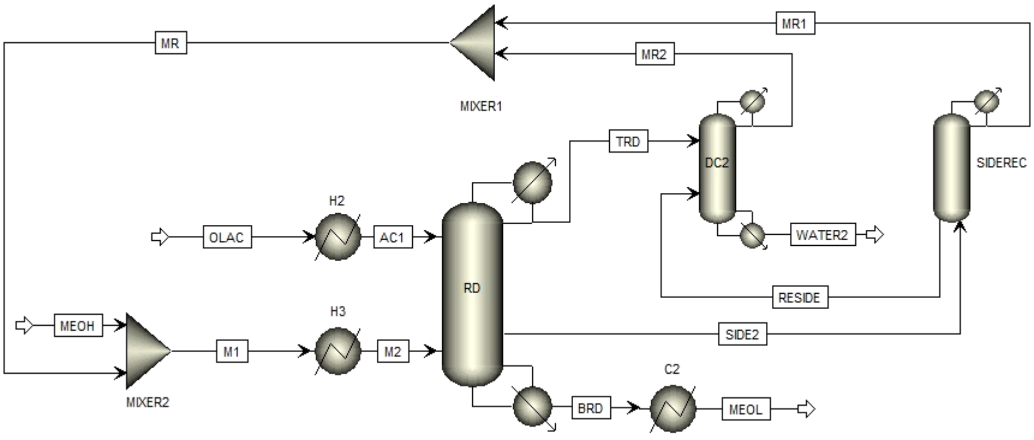

Figure 6.2 Reactive distillation process: Modified methanol recovery process.

Table 6.1 Specifications and operating condition of the reactive distillation: Conventional methanol recovery process.

	RD column	DC2
Stages	16	18
Distillate rate (kmol/h)	126.3	249.8261
Reflux ratio (mole)	0.4	1.1217
Methanol feed stage	13	-
Oleic feed stage	3	-
Feed stage	-	12
Operating pressure (atm)	1	1
Oleic acid conversion (mole%)	99.91%	-
Biodiesel purity (mole%)	99%	-

6.3 Modified methanol recovery process (MMR)

The top product of reactive distillation column is almost a binary mixture of methanol and water. From the conventional methanol recovery, it can be seen that the separation of methanol and water consumes the higher amount of energy of this step (10481kW). In order to reduce energy requirements of reboiler duty and condenser duty in reactive distillation column (RD) and distillation column (DC2), the additional side rectifier distillation is applied in the biodiesel process, as seen in Figure 6.2.

Figure 6.3 presents the reaction profiles, and it can be seen that most of the reaction takes place around the stage 3 to the bottom of the column. We considered the vapor composition along the reactive distillation in Table 6.2. So we considered the amount of water and methanol that remaining from the reaction. Stage 2, there is methanol and water vapor contain on this stage. The side vapor stream (SIDE2) from stage 2 is fed to the bottom of side rectifier column (SIDEREC). SIDEREC do not have reboiler because methanol in the vapor phase is injected directly in the bottoms part of the SIDEREC. It is important to mention that distillation requires a heat load in the reboiler to achieve the separation. In SIDEREC, the energy is supplied when the methanol stream is vaporized and the water is heated until its bubble point. The top product is pure methanol 131.38 kmol/h (99.9%). The bottom products are mixture of water and methanol, the stream RESIDE is sent to the DC2 for removing water from the reactive distillation column. From previous chapter, removing water comes out from the column can increase the performance of reactive distillation column and achieve the conversion of oleic acid because the water removal is favorable to the chemical equilibrium. Distillation column (DC2) is used to separation the top product from reactive distillation column (RD) and the bottom product from SIDEREC. The purity of the methyl-oleate is similar to that obtained in optimization process. The configuration of modified methanol recovery process is shown in Table 6.3.

Table 6.2 Vapor composition profile along the reactive distillation**.**

Stage	MEOH	GLY	WATER	OLAC	MEOL
1	0.8571	4.27E-15	0.1429	8.49E-13	4.00E-09
2	**0.6571**	**1.77E-09**	**0.3429**	**3.61E-08**	**3.53E-06**
3	0.5601	3.31E-07	0.4399	1.46E-07	5.03E-06
4	0.8196	9.91E-08	0.1804	9.61E-09	1.82E-06
5	0.9276	2.95E-07	0.0724	1.64E-09	1.22E-06
6	0.9745	7.21E-07	0.0255	4.42E-10	1.09E-06
7	0.9913	1.03E-06	0.0087	1.38E-10	1.05E-06
8	0.9971	1.17E-06	0.0029	4.49E-11	1.04E-06
9	0.9990	1.22E-06	0.0010	1.49E-11	1.04E-06
10	0.9997	1.24E-06	0.0003	4.95E-12	1.04E-06
11	0.9999	1.24E-06	0.0001	1.65E-12	1.04E-06
12	1.0000	1.22E-06	0.0000	5.38E-13	1.03E-06
13	1.0000	1.24E-06	0.0000	2.62E-13	1.04E-06
14	1.0000	8.38E-06	0.0000	1.07E-12	2.55E-06
15	0.8736	0.103875	0.0001	1.17E-07	2.25E-02
16	0.0406	0.773712	0.0000	1.34E-06	1.86E-01

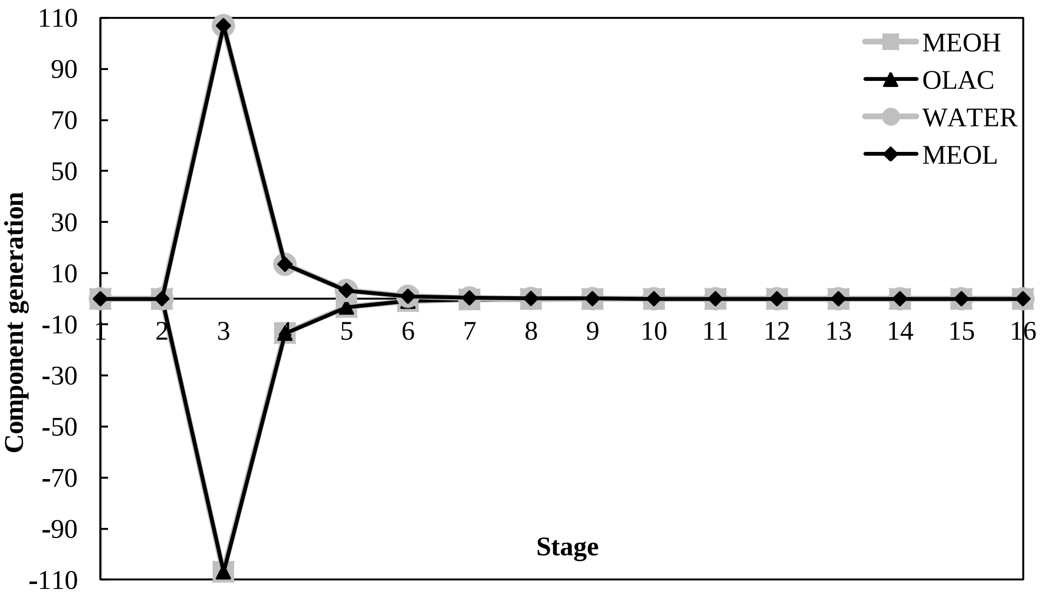

Figure 6.3 Component changes in the reactive distillation column.

6.4 Comparison between conventional and modified methanol recovery process

Figure 6.4 shows the temperature profiles between conventional and modified methanol recovery process. From figure 6.4, it is indicated that the temperature of MMR process is higher than CMR process. In CMR process methanol and water were removed at the top of the column, therefore there are methanol and water rich in vapor and liquid phases. It can be seen that from figure 6.5 and 6.6, methanol contains in the liquid and vapor phases along the column. In order to make high purity of methyl-oleate, methanol must be evaporates into the top of the column for separation methyl-oleate from methanol. Methanol evaporates at the normal boiling point temperature (65 °C) so the temperature of the reactive distillation column must be constant at the temperature around 65 °C until the stage 14, the temperature of the column rapidly increases to 276 °C. The temperature is increased to 276 °C because of in the oleic acid stream that feed to the reactive distillation column contains slightly glycerol (1.138 kmol/hr). At stage 14, there is very little methanol containing in liquid phase, for obtaining high purity of methyl-oleate, glycerol must be evaporates into the top of the column. For separation methyl-oleate from glycerol, glycerol evaporates at the normal boiling point temperature (287 °C). For this reason at stage 14-16, temperature increases to 276 °C for obtaining high purity of methyl-oleate.

In MMR process, the side rectifier column is used to increase the performance of the biodiesel process. Side rectifier removes some methanol and water comes out from the reactive distillation column. Figure 6.7 and 6.8 show the liquid and vapor composition profiles along the reactive distillation column. It can be seen that the composition profiles of methanol and water decrease obviously when compare to CMR process due to methanol and water were removed by side rectifier column. As a result, methanol and water contain in liquid and vapor phases along the column less than the CMR process. In figure 6.4, the temperature of the reactive distillation column was increased obviously and constant at stage 6-12 because of when the number of stages increases, methanol and water in liquid phase were evaporated to the top of the column. At stage 13, the vapor and liquid composition of glycerol and methyl-oleate are very high due to at this stage rarely has methanol containing, temperature increases to 267 °C. At stage 16, temperature increases to 285 °C and the liquid composition of methyl-oleate has a value close to 1.

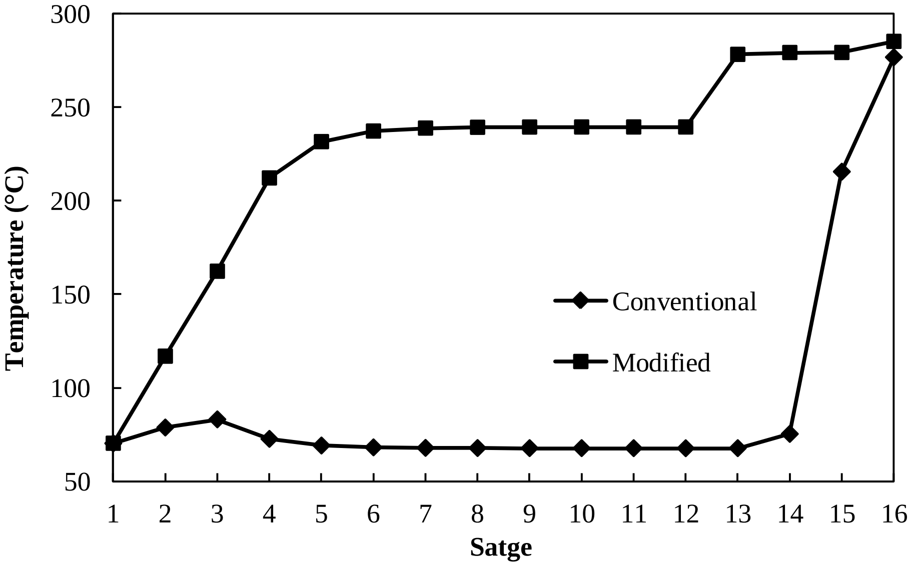

Figure 6.4 Temperature profiles in the reactive distillation column.

Table 6.4 shows the **c**omparison of energy requirements for conventional and modified methanol recovery processes. The MMR process used the less energy when compared to CMR process. Because of the side rectifier column in MMR process is the distillation column that helps the conventional distillation column (DC2) for removal methanol and water come out from the column. Side rectifier column used energy from side stream vapor from the stage 2 of reactive distillation column to separate methanol and water.

In MMR process the condenser duty in reactive distillation column was reduced due to the energy that used to supply condenser is less than the CMR process. Because of the amount of methanol and water has been divided into side rectifier column and distillation column (DC2) without passing the top of the reactive distillation column.

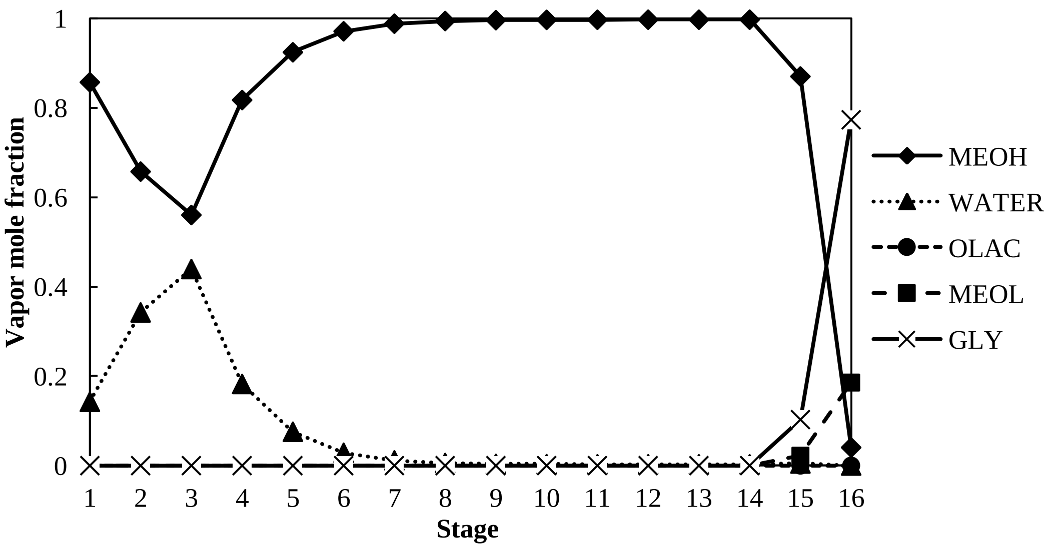

Figure 6.5 Vapor mole composition profiles in the reactive distillation column of the conventional methanol recovery process.

Table 6.3 Specifications and operating condition of reactive distillation: Modified methanol recovery process.

	RD column		DC2
	Main column	Rectificator	
Stages	16	15	17
Distillate rate (kmol/h)	126.3	131.5076	251.1173
Reflux ratio (mole)	0.4	1.56	2.11
Methanol feed stage	13	-	-
Oleic feed stage	3	-	-
Feed stage	-	16 (Above stage)	TRD=10, RESIDE=7
Side stage	2	-	-
Side stream vapor flow (kmol/h)	300	-	-
Operating pressure (atm)	1	1	1
Oleic acid conversion (mole%)	100%	-	-
Biodiesel purity (mole%)	99.3%	-	-

6.5 Heat integration of modified methanol recovery process (PMMR)

To improve energy usage, a heat integration of the reactive distillation process to produce biodiesel is considered. The methyl oleate is used as a heat source to preheat oleic acid and methanol feeds. The temperature of methyl-oleate at the bottom of the column is 285 °C, so we used as the hot feed stream to preheat oleic acid and methanol. The PMMR process is helped to reduce energy requirements for preheating feedstocks and cooling the product by using heat exchanger (HX1 and HX2) to exchange heat in the process. The major benefits of the proposed biodiesel process include increased productivity, reduced investment costs and minimum energy requirement. The results show that the heat integrated reactive distillation can save energy consumption by 35%, compared with the MMR process.

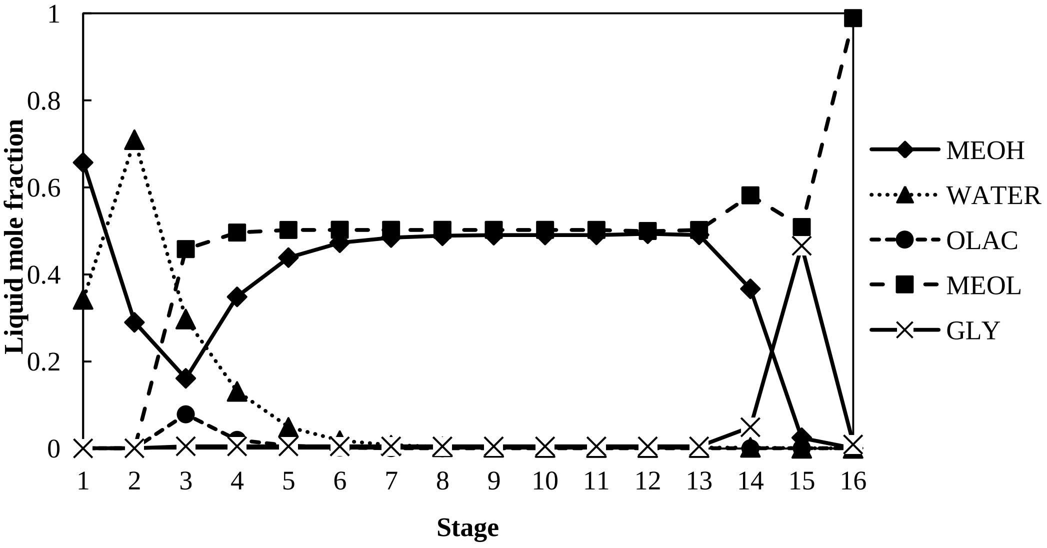

Figure 6.6 Liquid mole composition profiles in the reactive distillation column of the conventional methanol recovery process.

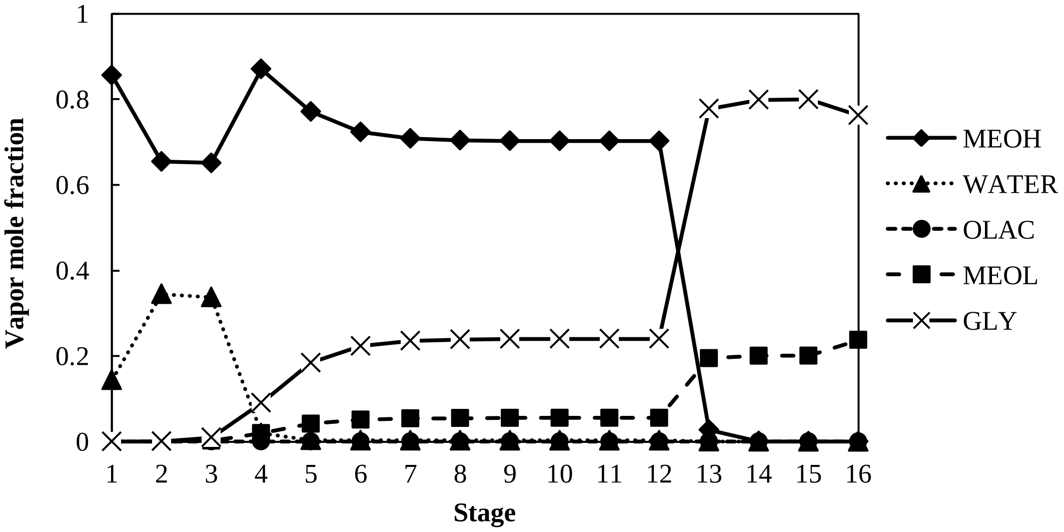

Figure 6.7 Vapor mole composition profiles in the reactive distillation column of the modified methanol recovery process.

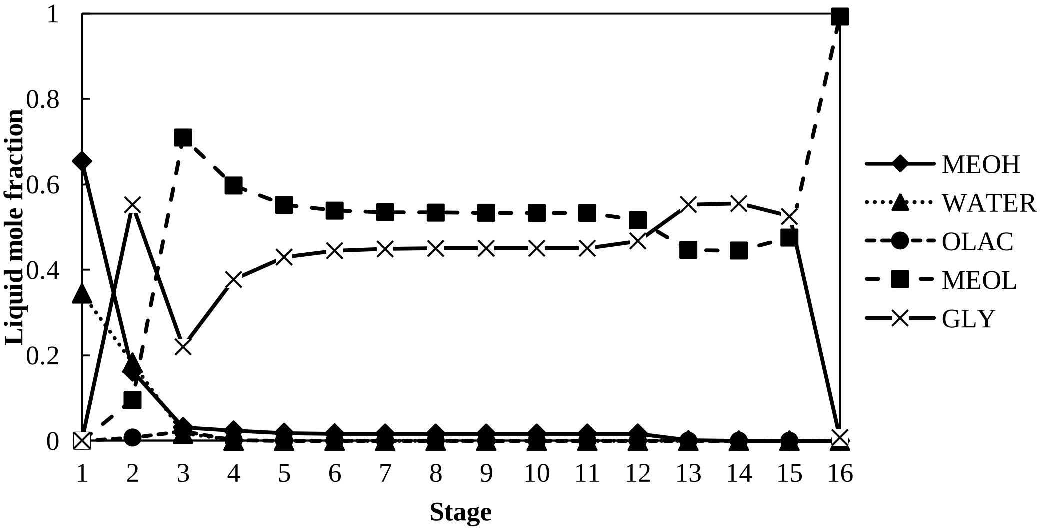

Figure 6.8 Liquid mole composition profiles in the reactive distillation column of the modified methanol recovery process.

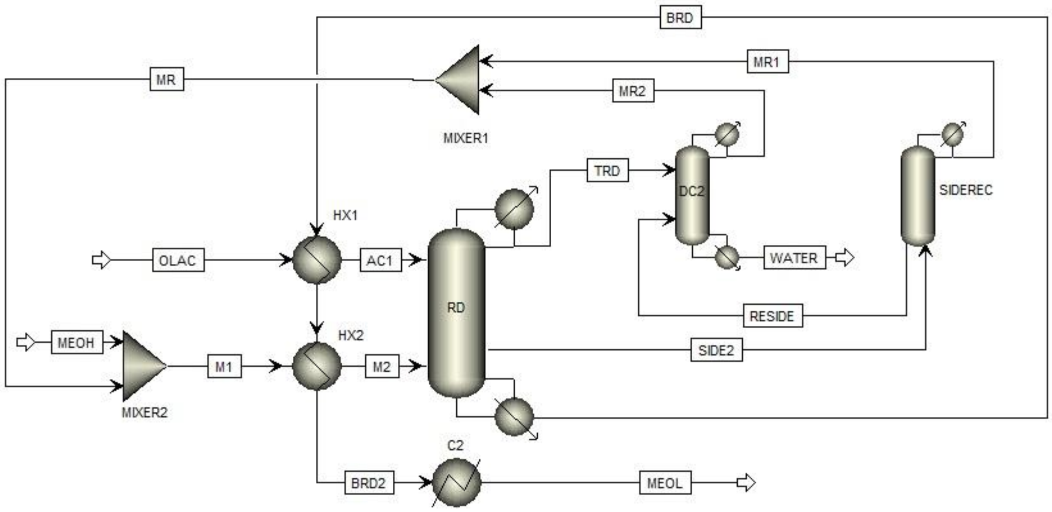

Figure 6.9 Heat integration of the modified methanol recovery process (PMMR).

6.6 Conclusions

Methanol Recovery for biodiesel is an important part of the entire biodiesel process and involves the highest cost of operation for a biodiesel plant. Only about half of the methanol used is actually consumed in the esterification process leaving the rest in the finished biodiesel. Modified methanol recovery process (MMR) has the higher performance in term of energy requirements when compared with conventional methanol recovery process (CMR). It is important to mention that the reactive distillation column with a side rectifier can handle the reaction and the complete separation. Process heat integration is considered to improve the energy usage of the biodiesel process. When compared with CMR and MMP process, the energy requirements of PMMR process are significantly reduced by 44% and 35%, respectively.

Table 6.4 Comparison of energy requirement for different methanol recovery processes.

Units operations	Conventional methanol recovery	Modified methanol recovery	Pre-heated process
Reactive distillation column (RD)			
Rebolier duty	6307	5488	7121
Condenser duty	-5626	-1254	-1254
Distillation column (DC2)			
Rebolier duty	5263	3629	3629
Condenser duty	-5218	-3622	-3622
SIDEREC			
Condenser duty	-	-3288	-3288
Heater	6884	6866	-
Cooler	-6035	-6278	-772
Total energy requirements (kW)	35333	30425	19686

CHAPTER VII

CONCLUSIONS

7.1 Conclusions

The dwindling reserve of conventional energy resources and their associated environmental problems have increased the awareness to seek other alternative renewable and sustainable resources for fuel production. Biodiesel is gaining attention as a replacement for current fossil fuels. The use of edible oils for fuel production is puzzling as more and more of the global food demand rises. *Jatropha curcas* plant oil is claimed to be a highly potential feedstock for biodiesel production.

7.1.1 Simulation of biodiesel production from Jatropha oil in the reactive distillation process

The innovative process proposed in this work significantly improves biodiesel production. The conceptual design process is based on a reactive distillation column that integrates the reaction and separation steps into a single operating unit. By combining reaction and separation, one can shift the reaction equilibrium towards products formation by continuous removal of reaction products, instead of using an excess reactant. Compared to convention process, we used 750 kmol/hr of methanol to ensure full solubility of oleic acid, but also for shifting the chemical equilibrium. But in the reactive distillation process, we used only 375 kmol/hr of methanol. Moreover after the reaction in the conventional process is completely, the reaction mixture is required the high energy and separation device to purity the methyl-oleate as a result of low unit productivity. This reactive distillation process gave a purity of Jatropha biodiesel 83.39% at the standard conditions.

7.1.2 Optimization of biodiesel production

Response surface methodology (RSM) based on central composite design was used to optimize the five important variables. The mathematical model developed could predict the purity of biodiesel at any point in the simulation domain as well as the determination of the optimal methyl-oleate conditions. The conditions to get optimal response with 99% were found to be 126.4 kmol/h of bottom rate, 0.4 for reflux ratio, 160 ºC for oleic acid feed temperature, methanol feed stage = 12 and oleic acid feed stage = 3. The coefficient of determination was shown as 96.63%. This indicated that, the accuracy and general availability of the polynomial model was considered to be reasonable. These results implicate that the optimization using a response surface methodology based on central composite design was useful software in improving the optimization of methyl-oleate purity.

7.1.3 Methanol recovery process

An excess of methanol will have as result the complete consumption of oleic acid and a drop of the oleic acid concentration at the bottom of the column. On the other hand, the excess of methanol becomes a significant impurity in the top stream and thereafter in the water by-product. Modified methanol recovery process (MMR) has the higher performance in term of energy requirements when compared with conventional methanol recovery process (CMR). The energy requirements of MMR process are reduced 14%, compared with CMR process. In addition, a heat integration of the reactive distillation process is designed for efficient energy usage. The major benefits of the proposed biodiesel process include increased productivity, reduced investment costs and minimum energy requirement. The results show that the pre-heated modified methanol recovery process (PMMR) can save energy consumption by 35%, compared with a MMR process. Figure 7.1 shows the synthesis of biodiesel by reactive distillation: Methanol recovery process and pre-heated RD flowsheet.

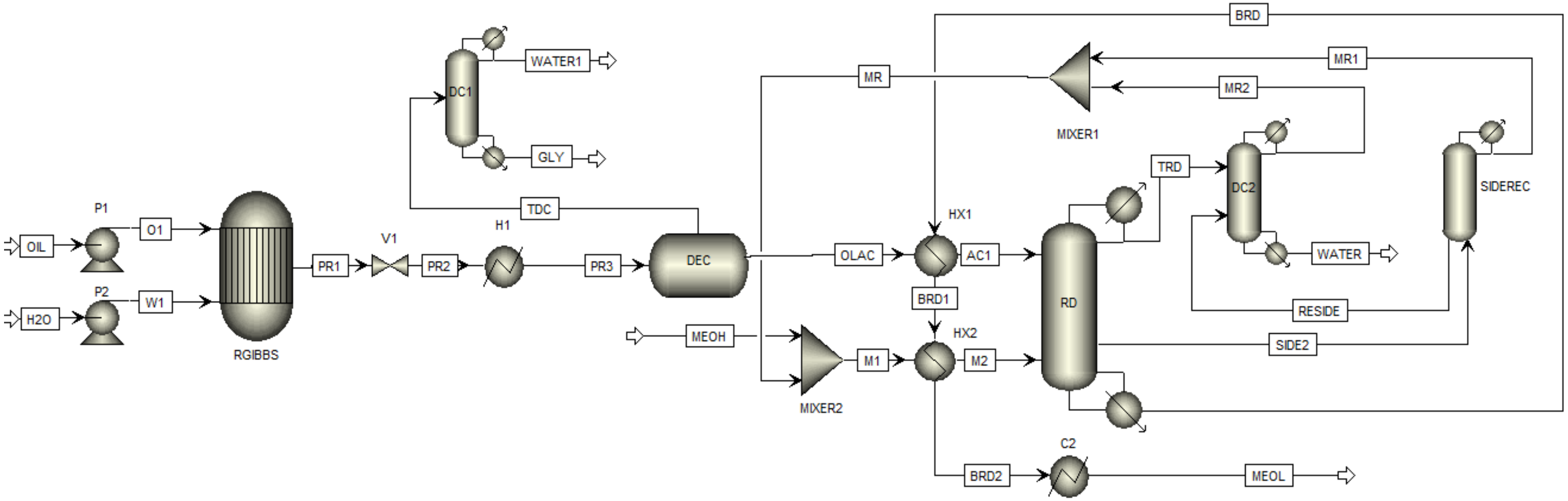

Figure 7.1 Flow diagram of the biodiesel production process a reactive distillation: Methanol recovery process and heat integration.

7.2 Recommendation

In this study, we used kinetic data instead of homogeneous sulfuric acid catalyst. It was main hindrance for production of biodiesel by homogeneously catalyzed esterification as the process involved number of washing and purification steps in order to meet the stipulated quality. Due to biodiesel specification, additional unit operations for obtaining purity of biodiesel should be further investigated. Alternative of catalyst, heterogeneous catalysis is basically a catalyst in different phase to the reactants. Heterogeneous catalysts provide a platform or surface for the chemical reaction to take place on. Separation of catalyst and products is easy. Contradict to homogeneous catalyst, heterogeneous catalyst is preferred and beneficial as the catalyst can be regenerated thus reduces the catalyst cost; utilization of lower quantity feed stocks for biodiesel production; simplification of separation process thus reduces capital cost; and as well decrease in wastewater which develops environmental friendly process.

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APPENDIX

APPENDIX

DISTILLATION DESIGN

Table A-1 Fenske-Underwood-Gilliland shortcut method

Parameters	Remarks	Equations
N_{min}	Minimum number of plates	$N_{\text{min}} = \dfrac{\ln\left[\left(x_{\text{Di}} / x_{\text{Bi}}\right) / \left(x_{\text{Dj}} / x_{\text{Bj}}\right)\right]}{\ln \alpha_{\text{ij}}}$
R_{DM}	Minimum reflux ratio	$R_{\text{DM}} + 1 = \sum \dfrac{\alpha_{\text{i}} x_{\text{Di}}}{\alpha_{\text{i}} - \phi}$
ϕ	Root	$1 - q = \sum \dfrac{\alpha_{\text{i}} x_{\text{Fi}}}{\alpha_{\text{i}} - \phi}$
N	Number of ideal plate	$\dfrac{N - N_{\text{min}}}{N+1} = 1 - exp\left[\left(\dfrac{1+54.4\psi}{11+117.2\psi}\right)\left(\dfrac{\psi - 1}{\psi^{0.5}}\right)\right]$
ψ	Psi	$\psi = (R - R_{\text{DM}})/(R+1)$

Example of calculations: Glycerol/ Water separation process

1. Minimum number of plates

$$N_{\text{min}} = \frac{ln\left[\left(0.9999/0.0001\right)/\left(0.0001/0.9999\right)\right]}{ln 58.24}$$

$$N_{\text{min}} = 4.5320$$

2. Minimum reflux ratio

$$1 - 0 = \frac{\left(58.24\right)(0.279)}{58.24 - \phi} + \frac{\left(1\right)(0.721)}{1 - \phi}$$

$$\phi = 42.2694$$

The value of ϕ is then used to get R_{DM}

$$R_{\mathrm{DM}}+1=\frac{(58.24)(0.9999)}{58.24-42.2694}+\frac{(1)(0.0001)}{1-42.2694}$$

$$R_{\mathrm{DM}}+1=3.6462$$

$$R_{\mathrm{DM}}=2.6462\;; R=1.5R_{\mathrm{min}}$$

$$R=3.9693$$

3. Number of ideal plates

$$\psi=(3.9693-2.6462)/(3.9693+1)$$

$$\psi=0.2663$$

$$\frac{N-N_{min}}{N+1}=1-exp\left[\left(\frac{1+(54.4)(0.2663)}{11+(117.2)(0.2663)}\right)\left(\frac{0.2663-1}{0.2663^{0.5}}\right)\right]$$

$$\frac{N-N_{\mathrm{min}}}{N+1}=0.4065$$

$$N=8.3162\approx 9$$

VITAE

Samaporn Phuenduang, the first sister of Kunchit and Arunee Phuenduang, was born in Samut Prakan on March 12, 1988. After graduating high school from Satreesamutprakarn School, she entered King Mongkut's University of Technology Thonburi in May 2006 and received her Bachelor of Engineering degree in Chemical Engineering in April 2010. She began her graduate study in May 2010 at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.