# Bio-diesel production using homogeneous catalyst: Product yield optimization

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# Bio-diesel production using homogeneous catalyst: Product yield optimization

by

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Teng Xiau Jeong

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| | |
|---|---|
| ANOVA | Analysis of variance |
| FA | Fatty Acid |
| FFA | Free Fatty Acid |
| FAME | Fatty Acid Methyl Ester |
| ME | Methanol |
| RSM | Response Surface Methodology |
| WCO | Waste Cooking Oil |
| WCPO | Waste Cooking Palm Oil |

# Penghasilan Bio-diesel menggunakan pemangkin Homogen : Pengoptimuman Hasil Produk

## ABSTRAK

Pengurangan bahan api fosil telah membawa kepada kebangkitan penyelidikan tenaga boleh diperbaharui. Bio-diesel merupakan antara yang paling diminati. Simulasi pengoptimuman penghasilan bio-diesel (Asid Lemak Metil Ester atau FAME) daripada sisa minyak sawit memasak (WCPO) telah dijalankan dalam Aspen Plus. Reaksi utama yang terlibat dalam menghasilkan FAME ialah pengesteran asid lemak bebas (FFA) dan trans-pengesteran asid lemak (FA) dalam WCPO. Kaedah penumpuan terbina daripada Aspen Plus ialah Programming Quadratic Sequential (SQP). Simulasi Aspen dengan penetapan tetap telah dijalankan di mana RTRANS beroperasi pada 57.74 ° C, 4 bar; RTRANS2 pada 45.15 ° C, 4 bar; dan RTRANS 3 pada 58.09 ° C, 4 bar sebagai 'kes Base' dengan hasil bio-diesel yang tinggi sebanyak 90.39%. Pengoptimuman ini memberi tumpuan kepada reaktor yang menjalani tindakbalas trans-pengesteran. Pengoptimuman suhu operasi dan tekanan operasi dilakukan secara berasingan untuk RTRANS, RTRANS2 dan RTRANS3 demi menentukan kepentingan faktor tersebut terhadap hasil bio-diesel. Suhu operasi mempunyai kesan yang lebih ketara terhadap hasil bio-diesel berbanding dengan tekanan operasi. Pengoptimuman dijalankan oleh Aspen Plus membuktikan bahawa hasil yang lebih tinggi pada 90.56% bio-diesel boleh dicapai dengan keadaan operasi yang agak rendah pada 23.34 ° C dan 2.60 bar untuk RTRANS, 20 ° C dan 2.59 bar untuk RTRANS2, 20.05 ° C dan 2.60 bar untuk RTRANS3.

# Bio-diesel production using homogeneous catalyst: Product yield optimization

## ABSTRACT

The depletion of fossil fuel has led to the rise of research of renewable energy and bio-diesel is among the most interested ones. The optimization of production of bio-diesel (Fatty Acid Methyl Ester or FAME) from waste cooking palm oil (WCPO) was simulated in Aspen Plus. The main reactions involved in producing FAME is esterification of Free Fatty Acid (FFA) and trans-esterification of Fatty Acid (FA) in the WCPO. The built-in convergence method in Aspen Plus is Sequential Quadratic Programming (SQP). Aspen simulation was run with the default setting where RTRANS operates at 57.74 °C, 4 bar; RTRANS2 at 45.15 °C, 4 bar; and RTRANS 3 at 58.09 °C, 4 bar as 'Base case' with a high yield of bio-diesel at 90.39%. The optimization is focused on the reactors undergoing the trans-esterification reaction. Optimization was done separately on operating temperature and operating pressure of RTRANS, RTRANS2 and RTRANS3 to determine the significance of impact of the variable towards bio-diesel yield. Operating temperature has a more significant impact towards yield of bio-diesel. The optimization carried out by Aspen Plus proved that a higher yield of 90.56% of bio-diesel could be achieved with a relatively lower operating conditions at 23.34°C and 2.60 bar for RTRANS, 20 °C and 2.59 bar for RTRANS2, 20.05 °C and 2.60 bar for RTRANS3.

# CHAPTER 1: INTRODUCTION

## 1.1 Fossil Fuel Depletion

It was reported that global consumption of crude oil has increased to about 3 billion barrels in 10 years from 1997 to 2007 and the number is estimated to grow higher with continuous energy demand of mankind (Shafiee and Topal, 2009). Although world fossil fuel reserves had shown constant increment as more oil field is discovered due to daily improving technology, the price of fossil fuel increased exponentially since 21st century. While most of the growing economy and populous countries' energy demand is still greatly dependent on fossil fuel resources, issues such as depletion of non-renewable fossil fuel and fossil fuel as major sources of greenhouse gas emissions have led to the arise of critical concern in power generation and utilization (Tshizanga et al., 2017; Endalew et al., 2011) . Thus, the world begins to pay attention to alternative, preferably renewable energy and bio-diesel has nevertheless become one of our interest.

Figure 1.1 shows the trend of world crude oil proven reserves and oil consumption of the period year 1980 to 2007. As shown in Figure 1.1, the world consumption of crude oil steadily increases over the years by billions of barrels. However, it takes 7 years or more for us to discover new oil reserves which is estimated to have difficulty in keeping its pace with oil consumption in the near future.

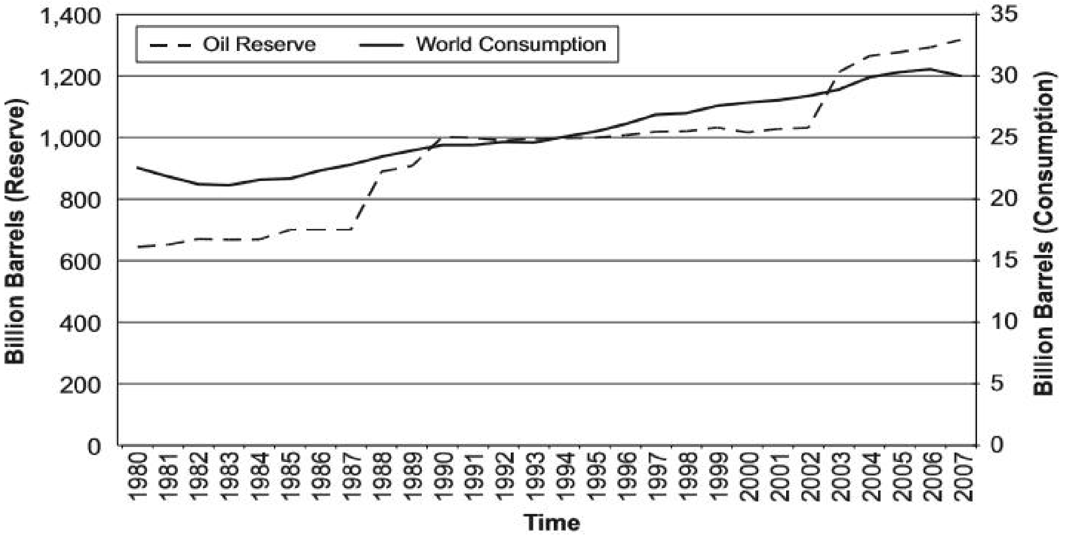


Figure 1.1 Trends of world crude oil proven reserves and oil consumption from 1980 to 2007.(Shafiee and Topal, 2009).

Figure 1.2 shows the trend of world crude oil proven reserves and oil price in the period of year 1980 to 2006. As shown in Figure 1.2, the oil price fluctuated over the years, showing a different trend than the oil reserves and the price has shown a steep increase as the 21st century started.

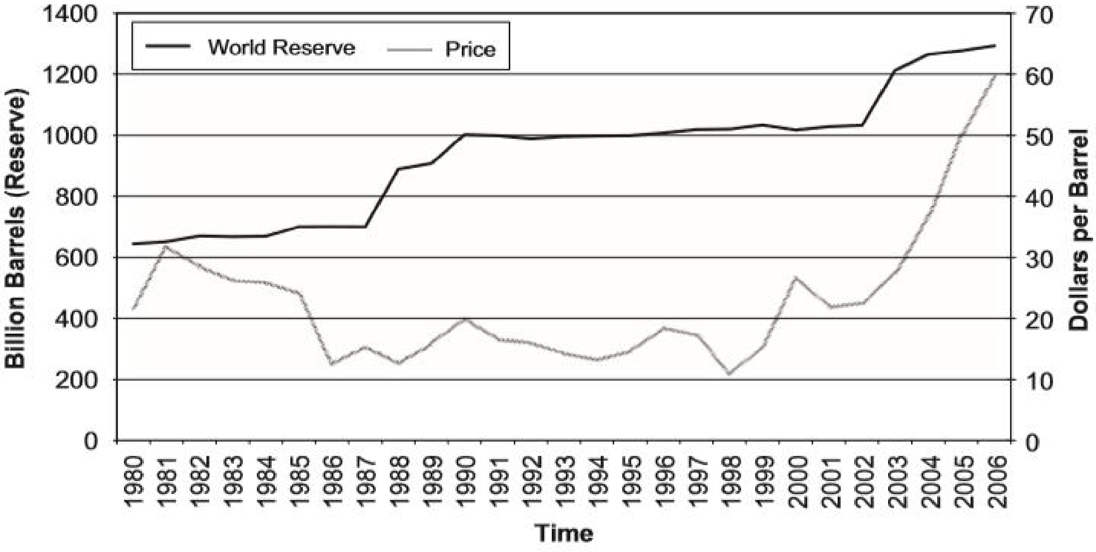


Figure 1.2 Trends of world crude oil proven reserves and oil price from 1980 to 2006. (Shafiee and Topal, 2009).

## 1.2 Biodiesel As An Alternative Energy

Bio-diesel, a fatty acid alkyl ester, or more commonly known as Fatty Acid Methyl Ester (FAME) is a type of biofuel with great potential and advantages as it is proved to be biodegradable, non-toxic and emit less carbon and sulphur to the environment than the conventional diesel  and does not contribute to global $CO_2$ and green house gas level as the carbon of the fuel is originated from photosynthesis (Chen et al., 2008; Alcantara et al., 2000).  National Renewable Energy Laboratory (NREL) revealed that through the study of the life cycle analysis of bio-diesel, $CO_2$ emission was 78% less than that of the conventional diesel. Moreover, bio-diesel works great on the conventional diesel engine and has shown improved physical properties and combustion behavior (Kirubakaran and Selvan, 2018; Alcantara et al., 2000) due to its high $O_2$ content and relatively lower carbon to hydrogen ratio, making it a perfect substitute to the conventional diesel.

## 1.3 Biodiesel Production

Researchers have found a few ways of producing FAME by catalytic (alkaline, acidic or enzymatic) or by super critical fluid method. Alkaline catalyzed method as the most common by practice in industry has a few drawbacks such as difficulty in material recovery (glycerol and alkaline metal). On the other hand, super critical fluid method is not favored as its high energy consumption due to high temperature and pressure, and high methanol consumption in the trans-esterification process are main concerns and burden to industries (Chen et al., 2008).

Generally, the raw materials used to produce bio-diesel can be catheterized into 3 generations. The first generation bio-fuel is associated with edible oils as raw material to produce FAME but has raised global concern due to its competition with the food industries. The high cost of the raw material is another main problem for the first generation bio-fuel (Kirubakaran and Selvan, 2018). The second generation bio-fuel utilizes non-edible crops as raw material and does not endanger the food industries. However, the third generation bio-fuel, with micro-algae oil as its raw material is currently researched with some problems to be solved for it to be applicable in industries such as sensitive to weather for open cultivation, size limitation for circular ponds and low biomass productivity for raceway ponds (Farieda et al., 2017).

As early as 2000, FAME production from 3 different oils was studied(Alcantara et al., 2000) : soy-bean oil, used frying oil and tallow. In 2005,  a non-edible crop namely *Jatropha curcus* or Linnaeus was used to produce FAME. *Jatropha curcus* is a kind of perennial shrub which non-edible oil can be extracted from its seed to be further processed to produce FAME (Chitra et al., 2005). To avoid the “food-fuel competition” and high production cost problem, Kirubakaran and Selvan, (2018) studied FAME production from waste chicken fat from market’s waste disposal which is low in price, abundant and easy to process, turning waste into wealth.

## 1.4 Problem Statement

Implementation of blending bio-diesel with conventional diesel with a ratio of as much as 30% of bio-diesel or more could greatly dampen the consumption speed of diesel and so does its reserve. Thus, the increase of biodiesel production will come inversely proportional to the fossil fuel consumption.

According to Loh et al., (2006), annually 50000 tonnes of used frying oil were disposed as waste in Malaysia. This problem can further lead to tons of environmental problems when these used oils were discharged into the river (Chen et al., 2008). Previously, methods like membrane technology and adsorption were used to process the used oil to solve the problem but were rather costly and were subjected to further treatment.

Therefore, utilizing waste cooking oil (WCO) to produce bio-diesel becomes a subject in interest. The product yield can be optimized by adjustment of process parameters. To make it cost effective to industries, the energy conservation must be optimized too.

## 1.5 Objectives

1. To determine significant parameters for production of bio-diesel.

2. To determine the optimum conditions for bio-diesel production yield.

3. To determine the energy conservation in the optimization of yield of bio-diesel production

# CHAPTER 2: LITERATURE REVIEW

## 2.1 Introduction

Process optimization had been established for bio-diesel production date back in 1998 by Vicente et al., (1998). The effectiveness of catalyst by yield by trans-esterification process were compared. It was found that NaOH best all the others including anion exchange resin, cation exchange resin, immobilized lipase and Lewis acid ($SnCl_2$). Factorial design of experiments and response surface methodology (RSM) developed by Box and Wilson (1951) were employed.

This literature chose temperature, $X_T$, and catalyst concentration, $X_C$ as factors with stirring fix at 600 rpm to avoid limitations by mass transfer . Pressure was not taken into account as the high cost and energy consumption seemed impractical for industrial use at that moment.

Effects from the factors and their interaction were significant with the factors having positive influence while their interaction having negative influence towards FAME yield (Y). The negative influence was discussed to be soap formation side reaction. The statistical model converts temperature into factor $X_T$ and concentration into factor $X_C$ .Meanwhile, T represents temperature and C represents concentration in their respective unit in the technological model.

Statistical model is shown as follow (Vicente et al., 1998):

$$Y = 97.77+2.098X_T+3.894X_C-2.95X_TX_C+0.094X_T^2-1.73X_C^2 \quad (2.1)$$

Technological model is shown as follow:

$$Y = 65.54+0.379T+34.914C-0.295TC+2.3\times10-4T^2-6.925C^2 \quad (2.2)$$

Equations 2.1 and 2.2 were obtained through multiple regression to explain relations between FAME yield and mentioned factors. The positive coefficient indicates that catalyst has a most significant impact on FAME yield. Increasing temperature beyond optimum value does not increase FAME yield. The negative concentration quadratic coefficient was claimed to be caused by soap formation side reactions.

## 2.2 Common Factors Affecting Fatty Acid Methyl Ester (FAME) Yield

### 2.2.1 Temperature

Process reaction temperature has been found to be an important parameter affecting FAME yield. As agreement to previous research, it is reported that temperature has a positive influence on FAME yield (Bautista et al., 2009). FAME yield was found to be the highest at 40°C (Garcia-Moreno et al., 2014) but fatty acid (FA) conversion was high at 60°C. Others found FAME yield optimum at 65°C (Buasri et al., 2014; Tshizanga et al., 2017).

Lower temperatures were reported to be optimum for FAME yield. 35°C was reported by Sirajunnisa and Surendhiran, (2016); 40 °C by Yucel, (2012), 50°C by Vishal et al., (2017), 55°C by Gurunathan and Ravi, (2015) and 60°C by El-Gendy et al., (2015). All at slightly different conditions with different raw materials, catalyst and other reaction conditions. Generally, all the research results fall under the scope of below methanol's boiling point of 65°C (Vicente et al., 1998).

However, there are a few exceptions that do not fall in the mentioned range: it is reported by Lam et al., (2009) that increasing reaction temperature from 100°C to 150°C caused FAME yield to increase but yield remained unchanged beyond 150°C; another reported by Saeidi et al., (2016), optimum temperature at 113.7°C and 115.5°C by two different optimization analysis, FAME production by supercritical methanol obtained 253.5°C as optimum temperature (Omar et al., 2017). Through 2 different optimization approaches( Response Surface Methodology or RSM and Taguchi method), it is found that both approaches agree that temperature is the most important factor to FAME production (Tan et al., 2017).

### 2.2.2 Catalyst Loading

Catalyst loading as an important factor in reaction has always been the topic of interest. Commonly used catalysts include conventional alkaline catalyst NaOH (Almeida et al., 2015), KOH (Onukwuli et al., 2017), solid acid catalyst (Lam et al., 2009), CaO from eggshells (Tan et al., 2017), bio-catalyst (Sirajunnisa and Surendhiran, 2016) or nanocatalyst (Gurunathan and Ravi, 2015) and (Pandit and Fulekar, 2017). 0.5 wt% NaOH catalyst produced higher yield than that of 1 wt% is due to formation of soap (Almeida et al., 2015). Only catalyst derived from scallop shells and eggshells

(Buasri et al., 2014, Tshizanga et al., 2017) can have loading up to 3.5 wt% or even 8 wt%. Catalyst loading higher than its optimum value did not contribute to FAME yield because when more FAME was being produced, the reaction rate was limited by reactants' diffusion to active site (Lam et al., 2009) . Thus further catalyst loading does not show significance in yield of FAME.

### 2.2.3 Methanol To Oil Ratio

Overloading of methanol would cause inactivation of catalyst and reverse reaction might occur (Wan and Nor Aishah, 2011) as trans-esterification and esterification both are reversible reactions, methanol to oil ratio seems to be always higher than its stoichiometry ratio (3).Various optimal methanol to oil ratios have been reported: 9:1 (Garcia-Moreno et al., 2014) , 6:1 (El-Gendy et al., 2015) even as high as 70:1 (Amin Talebian-Kiakalaieh et al., 2013).

### 2.2.4 Reaction Time

The reaction time has always been an important factor of a wide range and is important because longer reaction time allows complete trans-esterification. Various optimum time have been obtained for FAME production: 14 h (Amin Talebian-Kiakalaieh et al., 2013); 3h (Lam et al., 2009) ; 1.5h (Garcia-Moreno et al., 2014) . (Onukwuli et al., 2017), (Tan et al., 2017), (Vishal et al., 2017) all reported reaction time below 3h. Even optimal reaction time as short as 14.8 minutes was reported (Omar et al., 2017) to obtain yield >90%.

## 2.3 Other Factors

### 2.3.1 Fatty Acid (FA) Content In Waste Cooking Oil (WCO)

FA content has negative influence on FAME purity due to catalyst loss to neutralization, incomplete methanolysis causing increase in glycerol level and hence the drop in purity (Bautista et al., 2009). The quadratic term has a positive influence on FAME yield but at the same time has positive influence on yield loss.

### 2.3.2 Calcination Of Metal Oxide Catalyst

Catalyst $SO_4^{2-}/SnO_2$ used for tranesterification at 300°C was found to be optimum for its calcination (Lam et al., 2009). The optimum calcination period was 2h as yield of FAME shows slight increment.The effect of mixed metal oxide($SiO_2$ and $Al_2O_3$) catalyst with weight ratio of 3 sulphated Tin to 1 metal oxide gave a higher yield than ratio 1:1 and 5:1.

### 2.3.3 Pressure

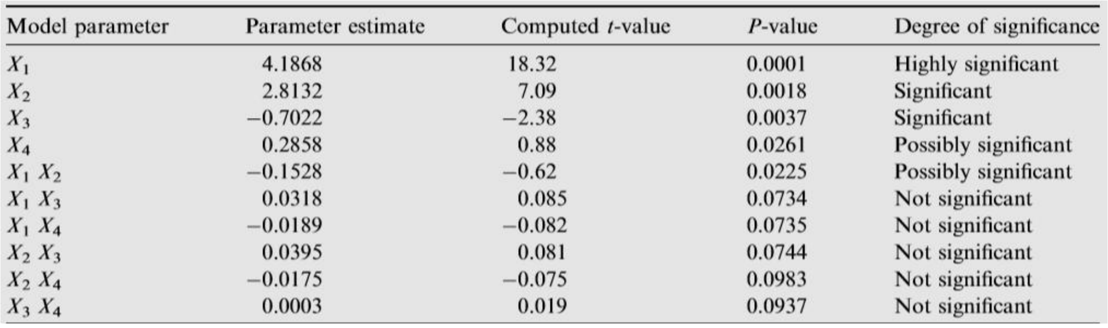
For supercritical methanol reaction, Carbon dioxide was used to pressurize the reaction and at the same time acted as co-solvent to increase methanol solubility in oil (Omar et al., 2017). Increasing pressure from 180-230 bar increased FAME yield. Further increase in pressure beyond 230 bar gave no effect on FAME yield.

Optimum FAME yield of 91% by quadratic model with 0.54% error to that of 91.5% by experiment can be achieved at 37:1 methanol to oil ratio, 253.5°C of reaction temperature,198.5 bar reaction pressure and 14.8 minutes reaction time.

### 2.3.4 Mixing Rate

The rate of mixing was found to be not so significant as compared to the common factors (El-Gendy et al., 2015, Soufia et al., 2017) . Table 2.1 shows analysis of variance (ANOVA) of 4 parameters of bio-diesel production process:

Table 2.1 Significance of regression parameters (coefficients) (El-Gendy et al., 2015)



| Model parameter | Parameter estimate | Computed $t$-value | $P$-value | Degree of significance |
|---|---|---|---|---|
| $X_1$ | 4.1868 | 18.32 | 0.0001 | Highly significant |
| $X_2$ | 2.8132 | 7.09 | 0.0018 | Significant |
| $X_3$ | −0.7022 | −2.38 | 0.0037 | Significant |
| $X_4$ | 0.2858 | 0.88 | 0.0261 | Possibly significant |
| $X_1$ $X_2$ | −0.1528 | −0.62 | 0.0225 | Possibly significant |
| $X_1$ $X_3$ | 0.0318 | 0.085 | 0.0734 | Not significant |
| $X_1$ $X_4$ | −0.0189 | −0.082 | 0.0735 | Not significant |
| $X_2$ $X_3$ | 0.0395 | 0.081 | 0.0744 | Not significant |
| $X_2$ $X_4$ | −0.0175 | −0.075 | 0.0983 | Not significant |
| $X_3$ $X_4$ | 0.0003 | 0.019 | 0.0937 | Not significant |

Y is the yield of bio-diesel. The independent variables are: methanol to oil ratio $X_1$, catalyst concentration $X_2$, reaction time $X_3$ and mixing rate $X_4$.

Regression model obtained:

$$Y= 40.157 + 4.1868 X_1 + 2.8132 X_2 - 0.7022 X_3 + 0.2858 X_4 - 0.1528X_1X_2 + 0.0318X_1X_3 - 0.0189X_1X_4 + 0.0395 X_2X_3 - 0.0175 X_2X_4 + 0.0003 X_3X_4 \quad (2.3)$$

### 2.4 Interaction Of Factors

It is reported that by Bautista et al., (2009) the interaction between fatty acid (FA) content and catalyst concentration has significant positive impact on FAME. Maximum FAME purity is observed at lowest FA conc in the oil (0.76%). At this point, the interaction is not significant. Temperature-catalyst interaction is obvious on yield of

FAME. But increasing only one of these 2 factors is good on FAME yield, increasing both will increase soap formation tendency.

Some similar trends were found by Wan and Nor Aishah, (2011) , where interaction between methanol-oil ratio and reaction time show no significance towards yield. Interaction between methanol-oil ratio and reaction temperature is significant for both methanol (ME) yield and conversion. Interaction between reaction time and catalyst loading is not significant for ME yield but is significant for free fatty acid (FFA) conversion. Interaction between catalyst loading and reaction temperature is not significant for both ME yield and conversion. Interaction between reaction time and reaction temperature shows the most significance for both ME yield and conversion.

## 2.5 Optimization In Fatty Acid Methyl Ester (FAME) Production

FAME yield in reactive distillation column depended on 4 independent variables: total feed flow, reboiler duty, feed temperature and methanol/oil ratio (Noshadi et al., 2012) (Linear terms: Inlet temperature (C), total feed flow (A) and methanol/oil ratio (D)). The obtained experimental yields were lower than actual due to fraction of FAME lost in water washing for purification for analytical purpose. This model used ANOVA to identify significant factors for the yield like many previous reported work. Reboiler duty(B) has a relatively less significance on FAME yield but its quadratic term ($B^2$ ) was reported to be the most significant quadratic term of all while others remained relatively small or insignificant towards FAME yield. Interaction between inlet temperature and methanol/oil ratio was reported to be the only significant coupling term (CD).

FAME production in baffled reactor was studied by Soufia et al., (2017). Some rare and specific factors like baffle space distance and oscillation frequency were used to optimize FAME yield. Unfortunately, the work reported dissatisfying yield results all below 82%.

Two alternative processes altering sequence of washing and product separation were also studied (Patle et al., 2014). Data like reaction kinetics, oil composition were taken from literature while physical properties from Aspen in simulation. With careful precautions such as temperature control to avoid biodiesel degradation, the simulated results were proven to agree with reported data. Process optimization was done for profit, heat duty and organic waste with variation in oil used, feed stage of distillation column, temperature and residence time in reactor as decision variables.

The result revealed that there was trade-off between profit and heat duty in the first process where increase in annual profit of around 8 million USD is accompanied by increase in heat duty of 1.5M. The findings also showed that smaller reactor volume and residence time with high temperature was enough for a certain required conversion. For the second process, trade-off happened between profit and organic waste where increase in annual profit of around 10 million USD was accompanied by increase in 0.04 kton of organic waste.

# CHAPTER 3: METHODOLOGY

## 3.1 Introduction

A few variables with significant impact on FAME yield,heat and energy conservation of the process should then be chosen as decision variables such as temperature of reaction or unit operation, reaction time, retention time, inlet temperature of separation unit, catalyst loading. Optimization of process is done on FAME yield, heat and energy conservation by taking profit and waste production into consideration. This process is proposed to be carried out with aid of Aspen Plus as a useful simulation tool with its built-in optimization feature.

The project was carried out in terms of overall plant yield and energy conservation, or scoped down to specified units if there is such needs. The project will be focused on esterification and trans-esterification process as these has direct and significant impact towards final yield of FAME.

Undesired simulation results required adjustments of decision variables. After fine adjustments of variables, careful analysis should be carried out on the simulated data to choose reasonably optimal operating conditions.

## 3.2 Research Flow Chart

Figure 3.1 shows the research flow chart of this research. As a start, the simulation of FAME production plant is run by Aspen Plus simulation. Then, objectives of optimization is determined to be bio-diesel yield and bio-diesel production energy conservation. The objective choosing is followed by the choosing of independent variables for optimization. Due to some limitations, a few common factors of interest are eliminated and will not be discussed in this research.

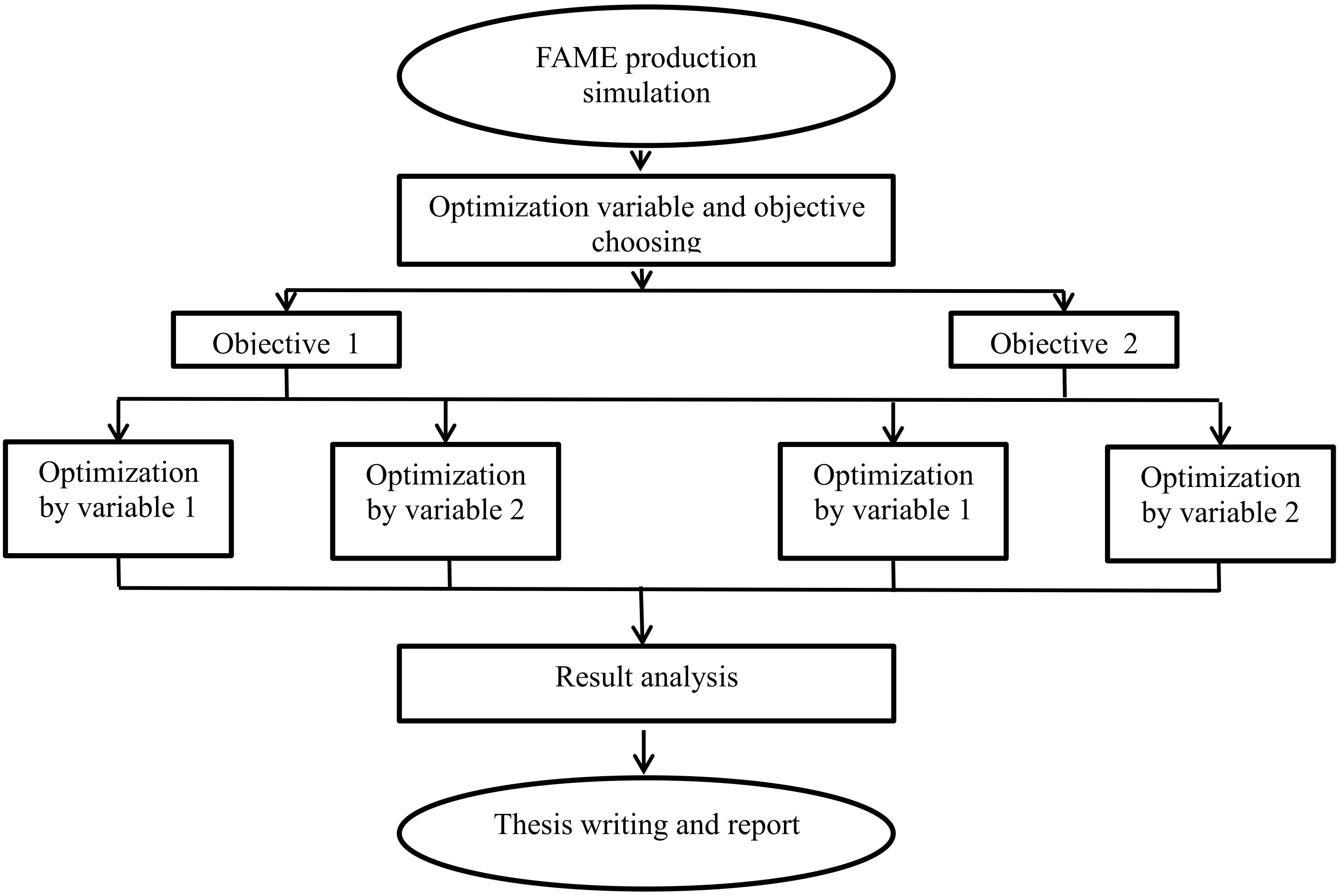


Figure 3.1 Research Flow Chart

## 3.3 Optimization objectives and variables

Through study of literature from Chapter 2, the independent variables for the optimization is determined. Due to limitations from Aspen Plus data base and the software operation, the catalyst factor is eliminated to not be one of the independent variables. This is because lack of reaction kinetics input which is necessary if there is a change in catalyst loading which in turn will affect the reaction kinetics. Since the production plant is well completed with recycle streams and having a high methanol to oil ratio, the methanol to oil ratio factor is also eliminated.

The chosen variables for optimization in this research are operating temperature and operating pressure of reactors for the reaction trans-esterification. As mentioned in Chapter 2, reaction temperature has a positive and significant impact towards yield of bio-diesel. Therefore, operating temperature of reactor is chosen as 1 of the variables. Another possible influencing parameters affecting the reaction is pressure. Previous research report reacting temperature under 65°C due to limitation of the boiling point of methanol. Reaction pressure could contribute to increase of bio-diesel yield. This is because increasing pressure increases boiling point. Thus operating pressure of reactor is chosen as another variable.

### 3.3.1 Variable 1: Operating temperature

There are 3 reactors involved in the trans-esterification reaction in FAME production: RTRANS, RTRANS2 and RTRANS3. RTRANS as the first reactor to undergo the trans-esterification reaction has the largest amount of methanol and waste cooking palm oil (WCPO) to be reacted while the main function of RTRANS2 and RTRANS3 is to increase the yield by more complete reaction of the raw materials.

With a fixed reaction kinetics input to Aspen Plus, the operating temperature is now 1 of the most significant factor in affecting the reaction in the reactor. However, through

Chapter 2, survey study tells that the trans-esterification process should not be carried out under temperature higher than 80°C which in the presence of alkaline catalyst will favor the production of soap instead of FAME.

### 3.3.2 Variable 2: Operating pressure

Operating pressure as 1 of the factor that affects reaction is not commonly discussed by researchers in the production of bio-diesel except for supercritical cases. Although the operating pressure might not have effect as significant as temperature, raw material ratio and catalyst loading, operating pressure of reactor is chosen as an independent variable in this research to study its effect and significance towards the yield of bio-diesel production and energy conservation in the production.

## 3.4 Design

### 3.4.1 Base Case

The Aspen Plus simulation of the bio-diesel production (Patle et al., 2014) was run to validate the availability of the bio-diesel plant production process. The operating temperature, operating pressure and net duty of reactor RTRANS, RTRAMS2 and RTRANS3, and yield of bio-diesel were recorded and tabulated for comparison purpose. Image 3.1 shows the flow sheet of bio-diesel production plant.

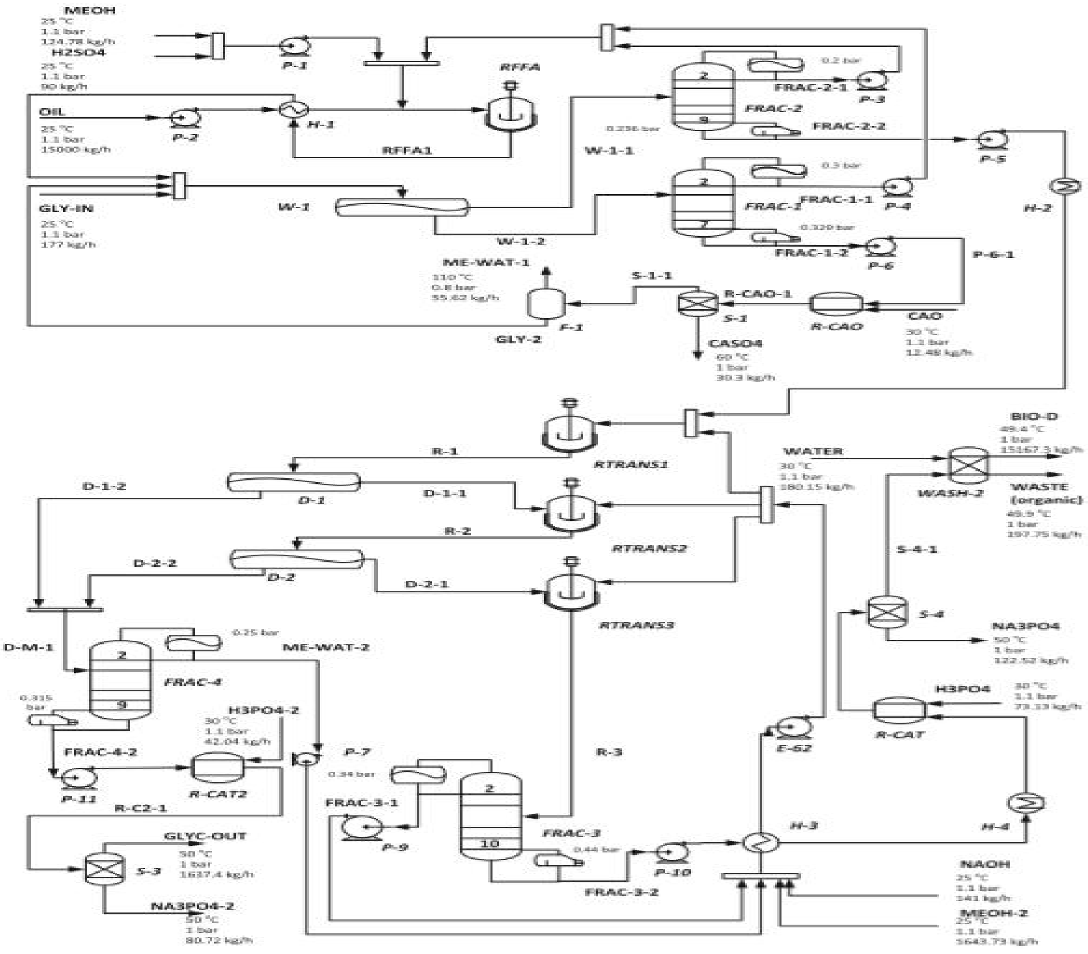


Image 3.1 Bio-diesel production plant flow sheet(Patle et al., 2014)

### 3.4.2 Constrains

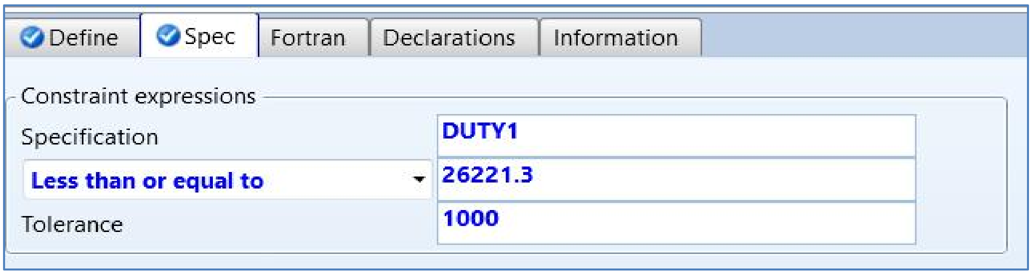
The Aspen Plus simulation was run with RTRANS, RTRANS2 and RTRANS3 all set at 70°C and 8 bar. The net duty of each reactor was obtained from the result from their respective block and later set as the maximum net duty of the reactors. as The reported optimum temperature from previous research are all below 65°C due to boiling point of methanol. However, this is subjected to change with higher operating pressure. Thus, 70°C was chosen as the maximum temperature. The base case simulation was run with the reactors RTRANS, RTRANS2 and RTRANS3 all set at 4 bar. To study the effect of operating pressure around the base case value, the maximum operating pressure of the reactors was set at 8 bar.

The optimization process would go on forever if no constrain is set. Proper constrains are determined by literature survey done in Chapter 2. To set the constrains for the reactors, the maximum heat duty set for the reactors are of operating conditions of 70°C and 8 bar. The respective maximum heat duty of the reactors are listed in Table 3.1 as follow:

Table 3.1 Constrains set for optimization

| reactor | constrain | Spec | Heat duty(W) | Tolerance |
|---|---|---|---|---|
| RTRANS | DUTY1 | Less than or equal to | 26221.3 | 1000 |
| RTRANS2 | DUTY2 | Less than or equal to | -108029 | 1000 |
| RTRANS3 | DUTY3 | More than or equal to | -46033.3 | 1000 |

Figure 3.2, 3.3 and 3.4show the constrains input into the Constrain block in Aspen Plus. The specification of the constrains defer depend on the difference between of the maximum duty achieved by the condition of 70 °C, 8 bar and the duty of the reactors by default simulation's operating condition as mention in Section 4.2.



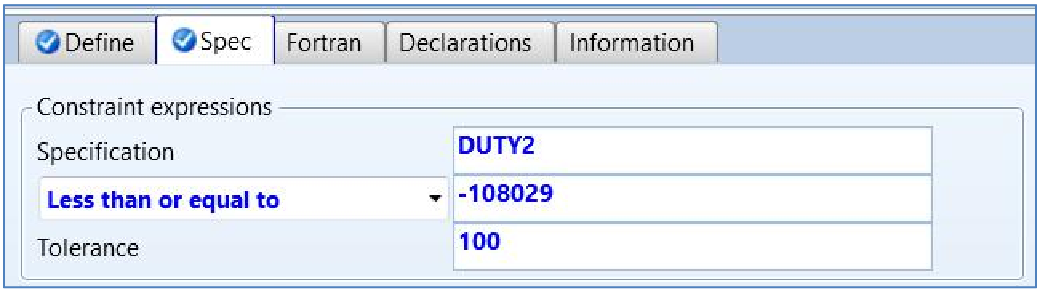
Constraint expressions

Specification DUTY1

Less than or equal to 26221.3

Tolerance 1000

Figure 3.2 Constrain "DUTY1"



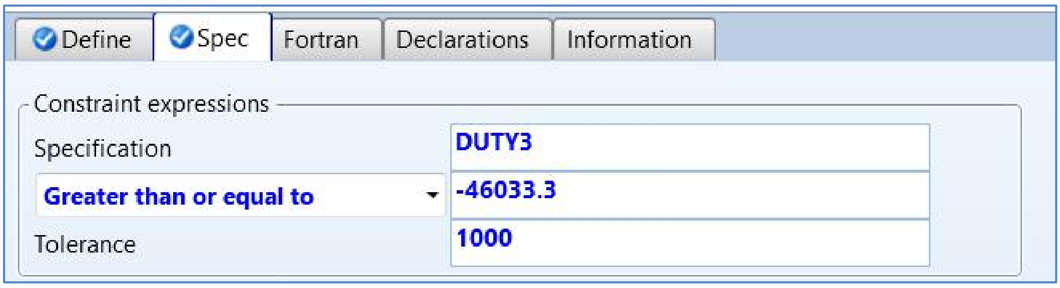
Constraint expressions

Specification: DUTY2

Less than or equal to: -108029

Tolerance: 100

Figure 3.3 Constrain "DUTY2"



Constraint expressions

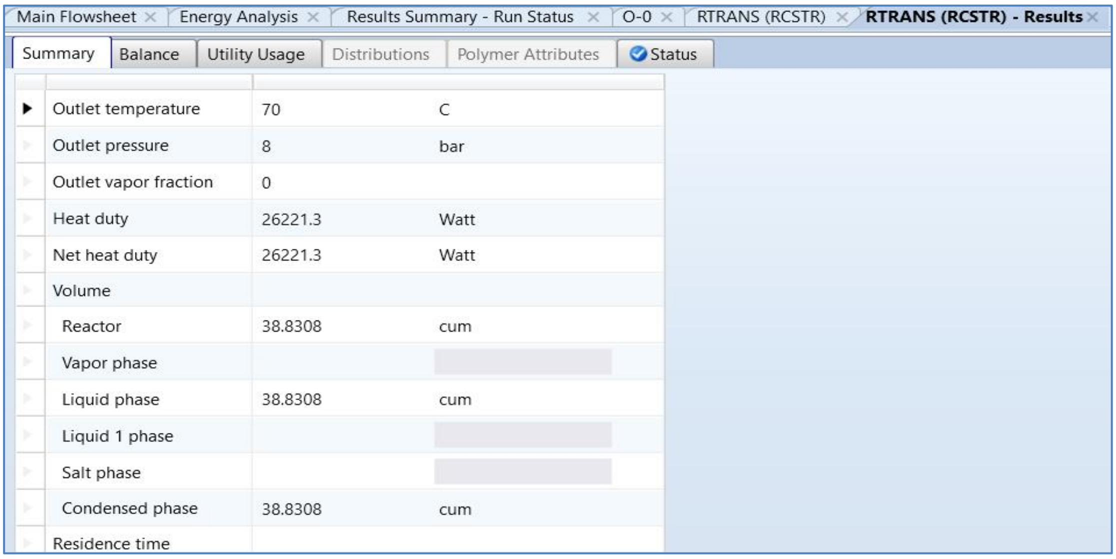
Specification: DUTY3

Greater than or equal to: -46033.3

Tolerance: 1000

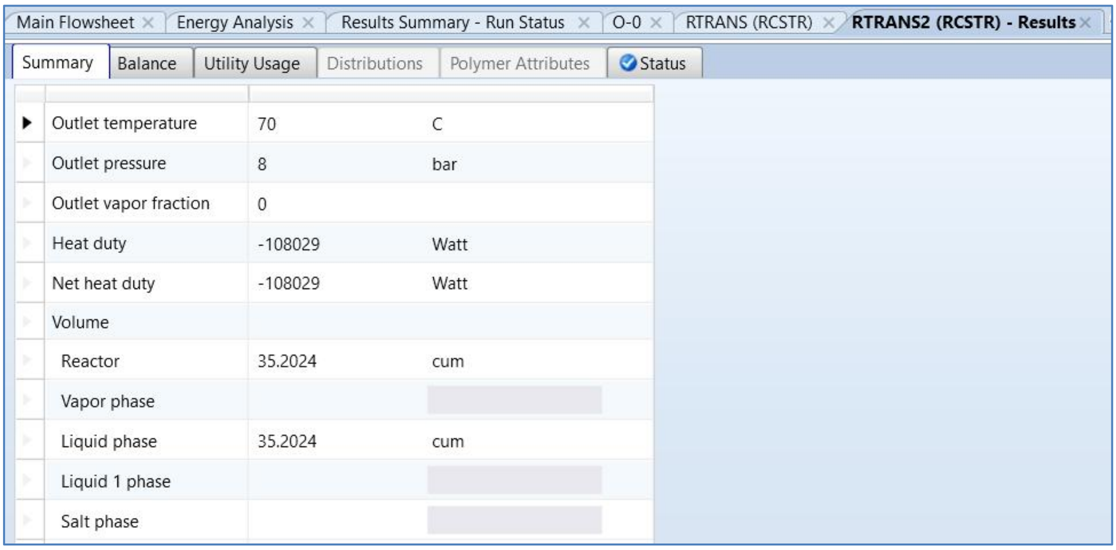
Figure 3.4 Constrain "DUTY3"

Figure 3.5, 3.6 and 3.7 show the duty of RTRANS, RTRANS2 and RTRANS3 at the operating condition of 70 °C, 8 bar. The operating conditions were changed via the input of the unit operations' block under the 'Blocks' block and the Aspen Plus simulation is run. The duty of reactors can be obtained through results under 'Blocks'.



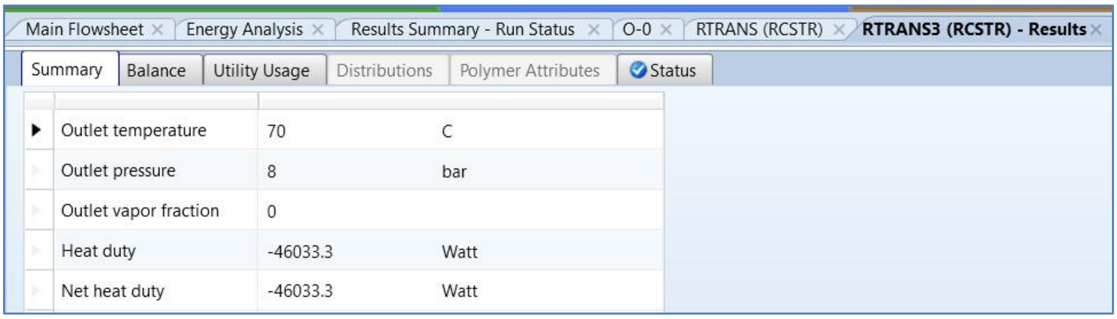
| | | |
|---|---|---|
| Outlet temperature | 70 | C |
| Outlet pressure | 8 | bar |
| Outlet vapor fraction | 0 | |
| Heat duty | 26221.3 | Watt |
| Net heat duty | 26221.3 | Watt |
| Volume | | |
| Reactor | 38.8308 | cum |
| Vapor phase | | |
| Liquid phase | 38.8308 | cum |
| Liquid 1 phase | | |
| Salt phase | | |
| Condensed phase | 38.8308 | cum |
| Residence time | | |

Figure 3.5 Duty of RTRANS at 70 °C, 8 bar



| | | |
|---|---|---|
| Outlet temperature | 70 | C |
| Outlet pressure | 8 | bar |
| Outlet vapor fraction | 0 | |
| Heat duty | -108029 | Watt |
| Net heat duty | -108029 | Watt |
| Volume | | |
| Reactor | 35.2024 | cum |
| Vapor phase | | |
| Liquid phase | 35.2024 | cum |
| Liquid 1 phase | | |
| Salt phase | | |

Figure 3.6 Duty of RTRANS2 at 70 °C, 8 bar



| | | |
|---|---|---|
| Outlet temperature | 70 | C |
| Outlet pressure | 8 | bar |
| Outlet vapor fraction | 0 | |
| Heat duty | -46033.3 | Watt |
| Net heat duty | -46033.3 | Watt |

Figure 3.7 Duty of RTRANS3 at 70 °C, 8 bar

### 3.4.3 Set up

Simple equation to calculate yield of bio-diesel was input in the Fortran tab in the optimization block. The variables were defined via the same block under the tab ‘Define’. The objective was specified in the tab ‘ Objective and Constrain’ to maximize the yield. The variable to be varied was input in the tab ‘Vary’.

Constrains were set in the block ‘Constrain’ to prevent endless calculation by Aspen due to lack of boundaries. The net duty obtained from section 3.4.2 for RTRANS, RTRANS2 and RTRANS3 were set as constrains.

The dependent variable is set to be the yield of the bio-diesel. Due to limitations from the software, only 2 main parameters or independent variables are chosen to be optimized:

I) operating temperature and

II) operating pressure

Since the simulation was done for a complete plant for bio-diesel production, several unit operations are available for the mentioned factors.

The input waste cooking palm oil (WCPO) mass flow rate is fixed at 18000 kg/h as default. 2 main reaction are involved in the production of bio-diesel: esterification of free fatty acid(FFA) and trans-esterification of WCPO by methanol. The reactors that are involved includes RTRANS, RTRANS2 and RTRANS3 for trans-esterification of WCPO and RFFA for esterification of FFA.

### 3.4.4 Objective & Fortran

In the optimization block of model analysis tool in Aspen Plus, the Objective block is the parameter in interest or the dependent variable which we are interested to maximize or minimize. In this case, the Objective input is yield( yield of bio-diesel in %) which is later being defined in Fortran. A Fortran equation can be input which is defined by the user. Having bio-diesel yield as the parameter of interest to be maximized, the Fortran input is

$$\text{yield} = \text{BIOD}/(\text{OIL}+\text{MEOH}+\text{MEOH1})*100 \tag{3.1}$$

Where

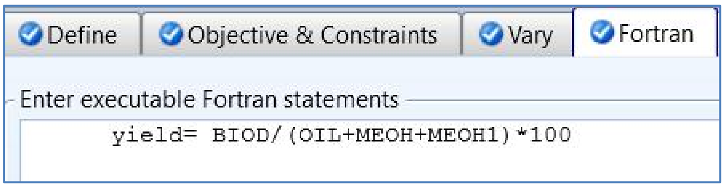
BIOD = mass of bio-diesel produced (kg)

OIL = mass of waste cooking palm oil input (kg)

MEOH and MEOH1= mass of methanol input (kg)

Yield= yield in %

The stream where the bio-diesel is measured which is taken as BIOD is well treated with only trace amount of contaminant. Thus it is fine to take the mass flow rate of the stream BIOD as the mass flow rate of bio-diesel produced. The default methanol input in stream MEOH and MEOH1 are 3.97 kmol/h at 25°C, 5.1 bar and 1500.22 kg/h at 25 °C,4 bar. Figure 3.8 shows the Fortran equation input to the optimization block of model analysis tool in Aspen Plus.



```
      yield= BIOD/(OIL+MEOH+MEOH1)*100
```

Figure 3.8 Fortran equation