# ENVIRONMENTAL ASSESSMENT OF ALKALI-CATALYSED BIODIESEL PROCESS USING WAR ALGORITHM

SITI FAIZNUR BINTI DAUD

UNIVERSITI MALAYSIA PAHANG

| SITI FAIZNUR BINTI DAUD | BACHELOR OF CHEMICAL ENGINEERING | 2013 | UMP |

ENVIRONMENTAL ASSESSMENT OF ALKALI-CATALYSED

BIODIESEL PROCESS USING WAR ALGORITHM

SITI FAIZNUR BINTI DAUD

Thesis submitted in fulfillment of the requirements for the award of the

degree in Bachelor of Chemical Engineering

Faculty of Chemical and  Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

## SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature                :

Name of supervisor  :      DR. ING. MOHAMAD RIZZA BIN OTHMAN

Position               :

Date                  :      FEBRUARY 2013

# STUDENT'S DECLARATION

I declare that this thesis entitled "Homogenous Alkali-Catalysed Biodiesel Process: Environmental Assessment Using WAR Algorithm" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature   :

Name        :   SITI FAIZNUR BINTI DAUD

ID number   :   KA09167

Date        :   FEBRUARY 2013

*Special dedication to my supervisor, Dr. Ing. Mohamad Rizza bin Othman for your time, guidance and support*

*And,*

*my beloved parents (Daud bin Yusoff and Ramlah binti Ibrahim)*
*my friends, my fellow colleagues and all faculty members*
*that encouraged and fully supports me throughtout completing this thesis.*

# ACKNOWLEDGEMENT

Praise to God with His blessings, my Undergraduate Research Project (URP) is finally completed. I would like to take this opportunity to express my appreciation to those who helped me during completing this project. First and foremost, I would like to express my sincere gratitude to Dr. Ing. Mohamad Rizza bin Othman as my supervisor for the guidance, comments, supporting, commitment and advice in overseeing the progress of my URP from the initial phase until the completion of this project.

Next, I also would like to acknowledge my sincere indebtedness and gratitude to my parents for their love, dream and sacrifice throughout my life. Last but not least, special thanks also should be given to my fellow colleagues especially As Eleyana binti Ali for her comments and suggestions, which was crucial for the successful completion of this study. From this project, I did learn a lot of new things and gain valuable knowledges that hopefully will be give benefits towards my career in future.

# ENVIRONMENTAL ASSESSMENT OF ALKALI-CATALYSED BIODIESEL PROCESS USING WAR ALGORITHM

## ABSTRACT

A continuous homogenous chemical process flow sheet for biodiesel production from waste cooking oil under alkaline conditioning was developed. The process simulation was conducted by using Aspen Plus software simulator since it can optimize the simulation process. Details on the operating conditions and equipment designs for the process were obtained from the previous research. By defining suitable indicators from the result obtained, the potential environmental impact (PEI) of the process towards the environment can be conducted. Hence to determine the PEI value, WAR Algorithm is then introduced. It is used to evaluate the environmental friendliness of a process and was carried out by using the developed Microsoft Excel spread sheet.  There are four PEI indexes involved (TRO, TOP, TRG and TGP) as the comparative manner. To evaluate in PEI indexes, eight PEI categories are used (HTPI, HTPE, ATP, TTP, GWP, PCOP and AP). The result of PEI value obtained was compared with the heterogeneous chemical process. As conclusion, heterogeneous catalysed is desirable chemical process since it was produced lower PEI value and had lower chemical impact towards the environment compared to homogenous chemical process.

# PENILAIAN TERHADAP ALAM SEKITAR BERDASARKAN PROSES PEMANGKIN ALKALI BIODIESEL DENGAN MENGGUNAKAN WAR ALGORITHM

## ABSTRAK

Sebuah pengeluaran prosess kimia homogen yang berterusan daripada minyak sayuran telah dibuat. Proses simulasi telah dijalankan dengan menggunakan perisian Aspen Plus kerana ia boleh mengoptimumkan proses simulasi. Keadaan proses operasi dan rekabentuk peralatan yang lengkap telah diambil daripada penyelidikan yang lepas. Dengan mendefinisikan petunjuk daripada keputusan yang diberikan, potensi impak alam sekitar (PEI) daripada proses kepada alam sekitar, telah diperkenalkan. Untuk mendapatkan nilai PEI, Algorithm WAR telah diperkenalkan. Untuk mengira tahap mesra alam proses tersebut, perisian Excel yang telah diformulasi telah digunakan. Terdapat empat indeks PEI yang terlibat (TRO, TOP, TRG dan TGP) sebagai perbandingan pengiraan. Untuk mengira indeks PEI, lapan PEI kategori telah digunakan (HTPI, HTPE, ATP, TTP, GWP, PCOP dan AP). Keputusan daripada nilai PEI yang dikeluarkan telah dibandingkan dengan proses kimia heterogen. Kesimpulannya, proses kimia heterogen adalah lebih baik kerana mempunyai nilai PEI yang rendah dan bahan kimia yang digunakan kurang memberi kesan kepada alam sekitar berbanding proses homogen.

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

**Page**

# LIST OF ABBREVIATIONS

| AP | Acidification Potential |
|---|---|
| ASTM | The American Society For Testing and Material |
| ATP | Aquatic Toxicity Potential |
| $C_{19}H_{36}O_2$ | Methyl Oleate |
| $C_3H_8O_3$ | Glycerol |
| $C_{57}H_{104}O_6$ | Triolein |
| $CH_4O$ | Methanol |
| CSTR | Continuous Stirred-Tank Reactor |
| FAME | Fatty Acid Methyl Ester |
| GWP | Global Warning Potential |
| $H_2O$ | Water |
| $H_2PO_4$ | Phosphoric Acid |
| HTPE | Human Toxicity Potential by Inhalation/ Dermal Exposure |
| HTPI | Human Toxicity Potential by Ingestion |
| MT | Metric tonne |
| $Na_3PO_4$ | Sodium Phosphate Salt |
| NaOH | Sodium Hydroxide |
| ODP | Ozone Depletion Potential |
| PCOP | Photochemical Oxidation Potential |
| PEI | Potential Environmental Impact |
| PFD | Process Flow Diagram |
| TGP | Total Rate Generation/Product |
| TGR | Total Rate Generation |
| TOP | Total Rate Output/Product |
| TOR | Total Rate Output |
| TTP | Terrestrial Toxicity Potential |
| WAR | Waste Reduction Algorithm |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Proposed Study

As stated by Banarjee and Chakraborty (2009), high consumption of diesel used in transport can lead towards major deficit of the resources in future. Therefore, other alternatives should be taken as the replacement. Recently, researchers have been found that there are many resources can be used as the alternatives. Here, the usage of biodiesel considered as the replacement recently. Lam *et al.,* (2009) defined biodiesel as the transesterification reaction of triglycerol with alcohol to produce fatty acid methyl ester and glycerol as the byproduct. In this research we are interested to used waste cooking oil as raw material because of the low cost consumption. Beside, alkali catalysed reaction system is choose because of its transesterification reaction is more rapid than acid catalysed reaction (Zhang, 2002). Later on, production of 8000 MT/annum of biodiesel will be simulated by using Aspen Plus software simulator. Othman (2011) stated that the basic steps involved in

process simulation are defining chemical components, selecting thermodynamic model and method, designing process flowsheet by choosing proper operating units, determining plant capacity, and setting up input parameters. Then, in order to describe the flow and the generation of potential environmental impact through a chemical process, the Waste Reduction Algorithm (WAR) has been developed (Young *et al.,* 2000). WAR algorithm is based on the conventional mass and energy balance from the process or Potential Environmental Impact. The lowest PEI value is preferable.

## 1.2 Problem Statement

Recently, the production of biodiesel seems significant due to the decreasing of the sources of diesel. However, the high emission of chemical; from chemical process design actually could lead towards health and environmental problem. Hence, the simulation of biodiesel production and environmental assessment of the process must be conducted.

## 1.3 Research Objective

1.3.1 To simulate and modeling the biodiesel production from alkali catalysed transesterification of waste cooking oil by using Aspen Plus.

1.3.2 To perfom the environment analysis of biodiesel production from vegetable oil using WAR algorithm.

## 1.4 Scope of Proposed Study

We need to perform simulation and modeling of biodiesel production from virgin vegetable oil. Later on, the research will proceed to the environmental analysis of the process by using WAR algorithm.

## 1.5 Significance of Proposed Study

By conducting this research, a model of biodiesel production from waste cooking oil can be generated. From the simulation result, the environmental analysis of the process also will be conducted by using WAR algorithm method. Hopefully by this research, the result obtained can open the new paradigm of engineers by bringing another perspective in analyse the process design.

## 1.6 Thesis Outline

In this chapter we are focusing on the general background of the research, problem statement, research objective, scope of proposed study, expected outcome, and also the significance of the proposed study. The next chapter will discuss further on the literature review of the simulation process together with the environmental assessment of the process design.

# CHAPTER 2



# LITERATURE REVIEW



## 2.1    Introduction to Biodiesel



Lam, Lee and Mohamed (2010) stated that the consumption of diesel fuel is increasing from days to days. It is estimated that the world wide's consumption of biodiesel especially in transport usage is nearly achieved until 934 million tonnes per year. The huge consumption by mankind can make the natural resources will be deficit in future (Banerjee *et al.*, 2009). Besides, the high usage of diesel can cause the greenhouse effect increase significantly resulting from the high emission of carbon monoxide to the air. Because of it, some other alternatives rather need to be replaced in order to full fill the mankind demanding beside yet keep the positive

environment values (Zhang *et al.,* 2003a). Hence because of these factors, biodiesel is introduced as the replacement.
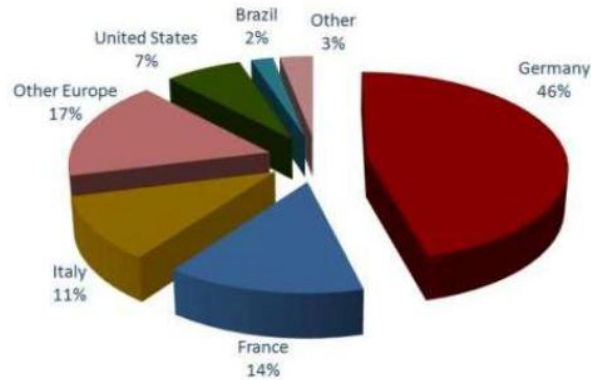


**Figure 2.1**    World production of biodiesel
(Source: Guerro, Romerro & Sierra, 2005)

As defined by The American Society for Testing and Materials (ASTM), biodiesel fuel is a mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock. The raw materials of biodiesel can be vegetable oil, animal fats, canola seeds and many organic and any biodegradable sources (Rice, Frohlich & Korbitz, 1997). However, the expensive raw material is the great barrier in the production of biodiesel. As reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw material (Ariffin, 2009). Hence, waste cooking oil is used as the interest because it is having low cost of material and can reduce to almost zero (Zhang, 2002).

Besides, Jacobson et al (2008) also stated that the usage waste cooking oil as biodiesel actually can reduce the environmental pollution by disposed it. Currently large quantity of waste cooking oil can be easily obtained from household and restaurants. 'Thus, waste cooking oil offers significant potential as an alternative

low–cost biodiesel feedstock which could partly decrease the dependency on petroleum-based fuel' (Jacobson, 2008).

**Table 2.1**      Physical and chemical properties of biodiesel
(Source: American Standard Test Material, 2001)

| Vegetable oil methyl ester | Kinematic viscosity (mm$^2$/s) | Cetane number | Lower heating value (MJ/l) | Cloud point (°C) | Flash point (°C) | Density (g/l) | Sulfur (wt %) |
|---|---|---|---|---|---|---|---|
| **Peanut**[a] | 4.9 (37.8°C) | 54.00 | 33.60 | 5.00 | 176.00 | 0.88 | - |
| **Soybean**[a] | 4.5 (37.8°C) | 45.00 | 33.50 | 1.00 | 178.00 | 0.89 | - |
| **Soybean**[b] | 4.0 (40°C) | 45.7-56 | 32.70 | - | - | 0.880 (15°C) | - |
| **Babassu**[a] | 3.6 (37.8°C) | 63.00 | 31.80 | 4.00 | 127.00 | 0.88 | - |
| **Palm**[a] | 5.7 (37.8°C) | 62.00 | 33.50 | 13.00 | 164.00 | 0.88 | - |
| **Palm**[b] | 4.3-4.5 (40°C) | 64.3-70 | 32.40 | - | - | 0.872-0.877 (15°C) | - |
| **Sunflower**[a] | 4.6 (37.8°C) | 49.00 | 33.50 | 1.00 | 183.00 | 0.86 | - |
| **Tallow**[a] | - | - | - | 12.00 | 96.00 | - | - |
| **Rapeseed**[b] | 4.2 (40°C) | 51-59.7 | 32.80 | - | - | 0.882 (15°C) | - |
| **Used rapeseed**[c] | 9.48 (30°C) | 53.00 | 36.70 | - | 192.00 | 0.90 | 0.00 |
| **Used corn oil**[c] | 6.23 (30°C) | 63.90 | 42.30 | - | 166.00 | 0.88 | 0.00 |
| **Diesel fuel**[b] | 12-3.5 (40°C) | 51.00 | 35.50 | - | - | 0.830-0.840 (15°C) | - |
| **JIS-2D**[c] **(Gas oil)** | 2.8 (30°C) | 58.00 | 42.70 | - | 59.00 | 0.83 | 0.05 |

[a] Ref.10.
[b] Ref. 20.
[c] Ref. 19.

Later, in order to convert the raw materials to the main product, catalysed transesterification reaction has been proposed. Zhang (2002) claimed that it is called 'transesterification' because it is involving the conversion of one ester (triglyceride) to another ester (alkyl ester) with a presence of catalyst. In this research proposal, we are interested to focus on the homogenous catalysis reaction because it provides

much faster reaction rates compared to the heterogeneous catalyst reaction (Arifin, 2009).

## 2.2    Process Description

Transesterification process is the most common process that used to yield the biodiesel. It is a catalysed chemical reaction which involved the triglyceride and an alcohol to produced fatty acid methyl ester (FAME) with glycerol as the byproduct (Wang, Ou, Liu, Xue & Tang, 2006). In order to produce the highest conversion of FAME, large amount of methanol is used as the solvent. Instead of other alcohol, methanol is commonly used due to its low cost and easy to get (Zhang *et al.,* 2003a; Zhang *et al.,* 2003b).
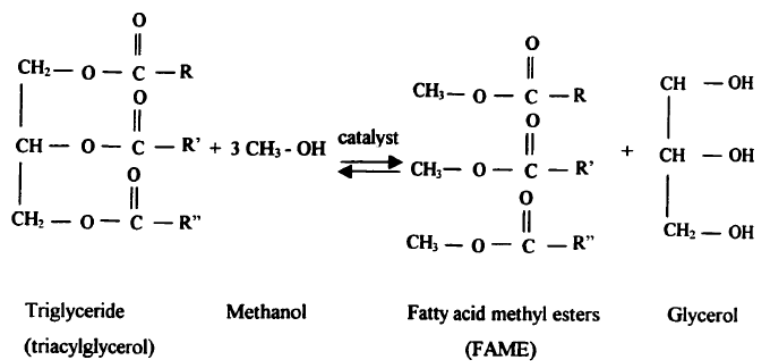
**Figure 2.2**    The transesterification of triglyceride with methanol to
produce fatty acid methyl esters
(source: Zhang, 2002)

Homogenous catalysed reaction is used because it produced high conversion of product in shorter time. It is also provides faster reaction rate compared to heterogenous catalysed reaction (Lam *et al.,* 2010; Ariffin, 2009). Instead of types of phases, transesterification reactions also can be either alkali catalysed, acid catalysed or enzyme catalysed (Zhang *et al.,* 2003a). However, alkali catalysed is the most preferable one because its transesterification reaction was more rapid than the acid catalysed reaction (Zhang, 2002). Due to this reason, together with the fact that the alkaline catalysts are less corrosive that acidic compounds, industrial processes usually favour base catalyst such as alkaline metal alkoxides, and hydroxides, as well as sodium and potassium carbonates (Braz, 1998).

For basic catalyst, alcohol-oil molar ratio 6:1 is the most used ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol (Khalid 2011). Under this condition, conversion of oil to esters could reach 95% within one hour. The construction material for the process equipment in the alkali catalysed system is also important. Zhang (2002) stated that the alkali catalysed transesterification was less corrosive to process equipment than the acid catalysed process.

Helwani, *et.al.,* (2009) stated that normally, the alkaline catalyst show high performance when vegetable oil with high quality is used. However, when the oils contain significant amounts of free fatty acids, they cannot be converted into biodiesels but to a lot of soap. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of biodiesel, glycerine and wash water. Triglycerides are readily transesterified batch wise in the presence of alkaline catalyst at atmospheric pressure and at a temperature of approximately 60–70 ° C with an excess of methanol. It often takes at least several hours to ensure the alkali

(NaOH or KOH) catalytic transesterification reaction is complete. The removal of these catalysts is technically difficult and it brings extra cost to the final product. Because of it, the reaction of free fatty acid with alkaline catalyst will not be considered in this research.

**Table 2.2** Fatty acid composition for various feedstock
(source: Othman, 2011)

| Vegetable oil | Fatty acid composition % by weight | | | | | | | | | Acid value | Phos (ppm) | Peroxide value |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 16:1 | 18:0 | 20:0 | 22:0 | 24:0 | 18:1 | 22:1 | 18:2 | 18:3 | | | |
| Corn | 11,67 | 1,85 | 0,24 | 0,00 | 0,00 | 26,16 | 0,00 | 60,60 | 0,48 | 0,11 | 7 | 18,4 |
| Cottonseed | 28,33 | 0,89 | 0,00 | 0,00 | 0,00 | 13,27 | 0,00 | 57,51 | 0,00 | 0,07 | 8 | 64,8 |
| Crambe | 20,7 | 0,70 | 2,09 | 0,80 | 1,12 | 18,86 | 58,51 | 9,00 | 6,85 | 0,36 | 12 | 26,5 |
| Peanut | 11,38 | 2,39 | 1,32 | 2,52 | 1,23 | 48,28 | 0,00 | 31.95 | 0,93 | 0,20 | 9 | 82,7 |
| Rapeseed | 3,49 | 0,85 | 0,00 | 0,00 | 0,00 | 64,4 | 0,00 | 22,30 | 8,23 | 1,14 | 18 | 30,2 |

$$
\begin{array}{lll}
\overset{\displaystyle O}{\underset{||}{CH_2-O-C-R_1}} & & CH_3-OH \\
| & & | \\
\overset{\displaystyle O}{\underset{||}{CH-O-C-R_2}} + H_2O & \rightarrow & \overset{\displaystyle O}{\underset{||}{CH_3-O-C-R_2}} + \overset{\displaystyle O}{\underset{||}{HO-C-R_1}} \\
| & & | \\
\overset{\displaystyle O}{\underset{||}{CH_2-O-C-R_3}} & & \overset{\displaystyle O}{\underset{||}{CH_3-O-C-R_3}} \\
\text{Triglyceride} \quad \text{Water} & & \text{Diglyceride} \quad \text{Fatty acid}
\end{array}
$$
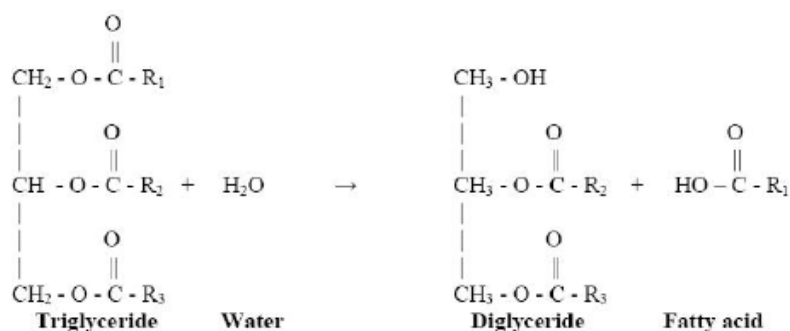
**Figure 2.3** FFA formation with presence of water
(source: Othman, 2011)

Zhang *et al.,* (2003a) stated that a 6:1 molar ratio of alcohol to oil was recommended at a temperature which is near to the boiling point of methanol. Based on this ratio, about 90-98% of oil conversion to methyl esters was observed within 90 min. The oil and a mixture of methanol and sodium hydroxide were fed into the transesterification reactor. Inside the reactor, the temperature and pressure of the process was set at $60^{o}C$ and 1 bar respectively (Othman, 2011).
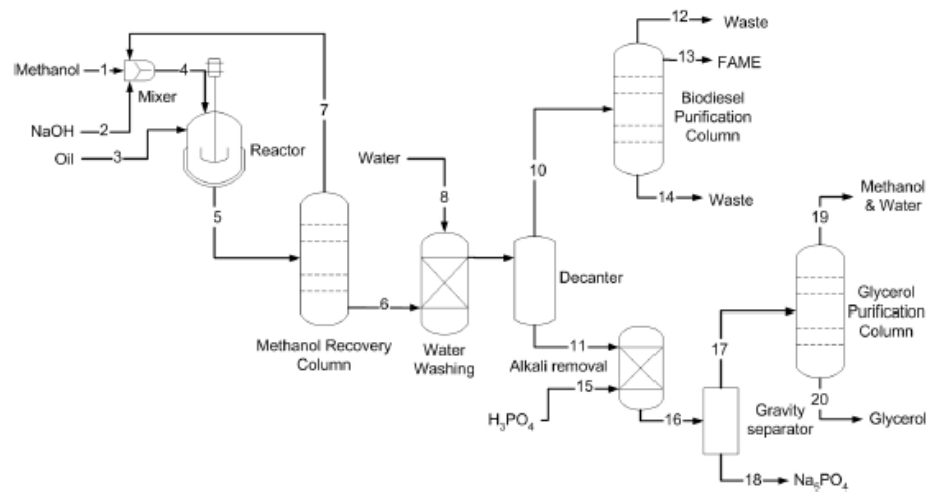
**Figure 2.4**    Biodiesel flowsheet (alkali based transesterification)

(source: Othman, 2011)

Zhang *et al.,* (2003a & 2003b) also claimed that an effluent stream of the transesterification reactor is contained FAME, glycerol, methanol, unconverted oil and sodium hydroxide. Then, they were entered methanol distillation column by setting 100% distillate rate of methanol. The distilled methanol mixed with the fresh methanol stream, then proceeded to the reactor. In order to purify the product, a multi-stage water washing was employed in the process (Zhang *et al.,* 2003a). Cited by Zhang (2002), using the waste water washing at $50^{o}$C was the best way to separate and purify the biodiesel product. The effluent product was then forwarded to a distillation column to further remove methanol and water.

From the top of the column, high purity FAME was obtained in the distillate. The bottom stream of the water washing column, containing sodium hydroxide, glycerol, methanol, and water were entering the neutralization reactor to remove the catalyst (sodium hydroxide) by adding phosphoric acid (Zhang *et al.,* 2003b). To

remove the excess alkali catalyst, neutralization reactor was used by adding phosphoric acid into the feed reactor. From the reaction, $Na_5PO_4$ solid was produced. The neutralization reaction below was followed:

$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$$
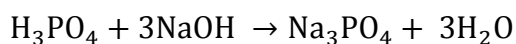
After the sodium is removed, the stream was then sent to gravity separator to separate the solid sodium phosphate salt (Othman, 2011). Then, liquid stream was proceeded into glycerol purification column where the bottom stream contained high quality byproduct (glycerine).

However, some process assessment will be discussed in the next topic in order to verify whether these factors having significant impact towards on acid catalysed reaction process of biodiesel production.

## 2.3    Process Assessment

In sustainability assessment, environmental analysis is one of the crucial assessments in a plant design. The environmental analysis of the alkali transesterification of biodiesel production from waste cooking oil will be conducted later on in order to explore the impact the biodiesel manufacture towards the environment.

### 2.3.1 Environmental Assessment

Young and Cabezas (1999) stated that the concept of implementing pollution prevention techniques into process design has received more attention in recent years. Hence, environmental analysis is also conducted in this research. This is to make sure that the sustainable biodiesel strategy is followed, which to ensures that biofuels are produced and consumed in a sustainable manner, as well as the environmental (Zyl & Barbour, 2010). Recently, there too many massive growth of plant company that very success in their products. However later, they could not realised that actually the process reaction that produced by them can lead towards the decreasing of environmental value (Othman, 2011).

So here, Waste Reduction algorithm (WAR algorithm) is being used in order to investigate the life cycle assessment and also assessment of waste reduction from the acid catalysed reaction process. The WAR algorithm is simply a tool to be used by design engineers to aid in evaluating the environmental friendliness of a process (Young et al., 2009). WAR algorithm is first introduced by Young and Cabezas in 1999 but 'the concept of pollution prevention was first presented in the 1970s via heat exchange networks (HENs) which first introduced by El-Halwagi and Manou-Siouthakis'( Young, Scharp & Cabezas 2000).

Young et al., (2000) also claimed that the WAR algorithm is a methodology used to evaluate the relative environmental impact of a chemical process. It will consider only the manufacturing aspect of product's life cycle. From Potential Environmental Impact (PEI) balance, 'PEI indexes are calculated which provide a

relative indication of the environmental friendliness or unfriendliness of the chemical process' (Young *et al.,* 2000).

This kind of algorithm is rather to be used because it is deal with the component-specific potential environment impact (PEI). PEI is based on the conventional mass and energy balance which is conducted at the manufacturing level (Othman, 2011). Here, 'PEI indexes are calculated which provide a relative indication of the environmental friendliness or unfriendliness of the chemical process' (Young *et al.,* 2000)

The following equation will be used in this research in order to determine the environmental impact from the process (Othman, 2011; Young *et al.,* 2000).

$$I_{gen}^{t} = I_{out}^{cp} - I_{in}^{cp} + I_{out}^{ep} - I_{in}^{ep}$$

(2.1)

Then, for the mass expression below equation will used

$$I_{in}^{cp} = \sum_{h}^{Streams} \sum_{c}^{Comps} M_{h,in} \sum_{c}^{Comp} \left( x_{c,h} \psi_{c,i}^{s} \right)$$

(2.2)

$$I_{out}^{cp} = \sum_{h}^{Streams} \sum_{c}^{Comps} M_{h,out} \sum_{c}^{Comp} \left( x_{c,h} \psi_{c,i}^{s} \right)$$

(2.3)

Where $I_{in}^{cp}$ is the potential environment impact of the energy conversion process while $I_{out}^{cp}$ is the summation of all gaseous output stream. The unit used is PEI/h. To calculate the product basis PEI/kg, following formula is being used.

$$\hat{I}_{gen}^t = \frac{I_{out}^{cp} - I_{in}^{cp} + I_{out}^{ep}}{\sum M_p} \qquad (2.4)$$

$$\hat{I}_{out}^t = \frac{I_{out}^{cp} + I_{out}^{cp}}{\sum M_p} \qquad (2.5)$$

All the formulas that will be used are included all the products and non-product streams. High value of PEI is not considerable because the lower the PEI values the desirable the process (Othman 2011)

The TRO values that generated in Microsoft Excel flow sheet is based on the specific PEI of each chemical over certain impact category. The indicators that involved in this impact factors are human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation/dermal exposure (HTPE), aquatic toxicity potential (ATP), terrestrial toxicity potential (TTP), global warning potential (GWP), photochemical oxidation (smog formation) potential (PCOP), acidification potential (AP) and ozone depletion potential (ODP).

**Table 2.3**    Impact factors (process) for each component
(Othman, 2011)

| No. | Component | HTPI | HTPE | ATP | TTP | GWP | PCOP | AP | ODP |
|-----|-----------|------|------|------|------|------|------|------|------|
|     |           | LD50 | TWA-TLV | LC50 | LD50 |      |      |      |      |
| 1 | TG | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | MEOH | 5628 | 200 | 29400 | 5628 | 0 | 0.123 | 0 | 0 |
| 3 | NAOH | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | GLY | 12600 | 10 | 58.5 | 12600 | 0 | 0 | 0 | 0 |
| 5 | FAME | 0 | 0 | 0 | 0 | 0 | 0.223 | 0 | 0 |
| 6 | WATER | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 7 | H3PO4 | 1530 | 1 | 0 | 1530 | 0 | 0 | 0 | 0 |
| 8 | NA3PO4 | 4150 | 15 | 220 | 4150 | 0 | 0 | 0 | 0 |

## 2.4    Concluding Remark

In conclusion, there are many routes that be used in order to produced biodiesel from waste cooking oil. But as stated above, homogenous alkali catalysed reaction processes is the most preferable one. This is due to the most economic process compared to others. The environmental analysis of the process also will be performed later on. For the next chapter, we will discuss more on methodology of the research so that we can have a clearer vision on how this research will be conducted.

# CHAPTER 3

# SIMULATION PROCESS

## 3.1 Introduction

For the research methodology, most of the information and parameters involved in simulation and reaction process later on was taken from Zhang (2002) and Othman (2011).

Before start with the simulation process, the suitable process flow diagram (PFD) for the reaction need to be constructed. PFD is very important in order:

i)    To get the overview of the whole process.

ii)   To get the mass and energy balance of the process.

iii)  To determine equipment involves in the reaction process.

Furthermore, all the equipment involved in PFD also will be considered in the calculation of environmental analysis later on.

The most common way to produce biodiesel is through the transesterification process. For this research proposal, the homogenous alkali catalysed reaction process will be carried on because it provides much faster reaction rate compared to the heterogeneous catalysis reaction process. There are many types of catalysts that can be used in the transesterification process. Here, NaOH is used as catalyst to speed up the rate reaction of the process.
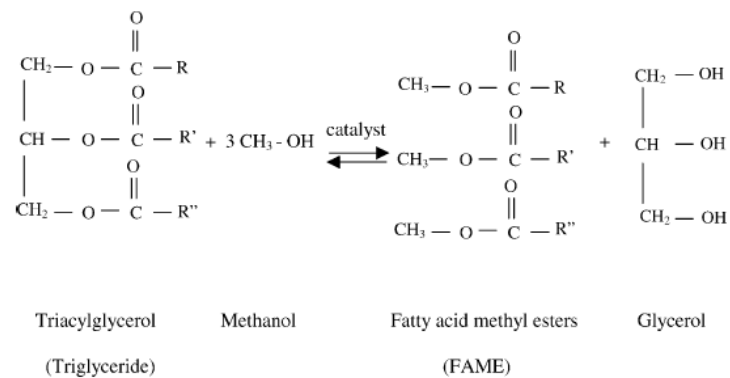


**Figure 3.1**     Transesterification of triglyceride
( Source: Zhang, *et al.,* 2003)

## 3.2     Process Simulation

In order produce the process model of biodiesel production of alkali catalysed reaction, Aspen Plus software simulation is used. The process simulation is based on the production of 8000tonnes/year of biodiesel by using transesterification process. Vlad *et al.,* (2010) had stated that the procedures for process simulation is mainly

involve in defining chemical components, selecting a thermodynamic model, checking up properties required, choosing proper operating units and setting up input condition. Information on most components, such as methanol, glycerol, sulphuric acid, sodium hydroxide and water is available in the component library. Because of methanol and glycerol are highly polar products, NRTL model is recommended for predicting the activity coefficient of the components in a liquid phase (0thman, 2011).

Table below shows the chemical compounds used in the simulation work. Most of the compound properties are available in the Aspen Plus component library. Then the process flow diagram of the chemical process design is generated.

**Table 3.1**     Compounds Defined in Aspen Plus

| Component ID | Type | Component name | Formula |
|---|---|---|---|
| C3H8O-01 | Conventional | GLYCEROL | C3H8O3 |
| CH4O | Conventional | METHANOL | CH4O |
| C19H3-01 | Conventional | METHYL-OLEATE | C19H36O2 |
| H2O | Conventional | WATER | H2O |
| C57H1-01 | Conventional | TRIOLEIN | C57H104O6 |
| H3PO4 | Conventional | ORTHOPHOSPHO | H3PO4 |
| NA3PO-01 | Conventional | TRISODIUM-PHOS | NA3PO4 |
| NAOH | Conventional | WATER | H2O |

## 3.3    Result of Biodiesel Process
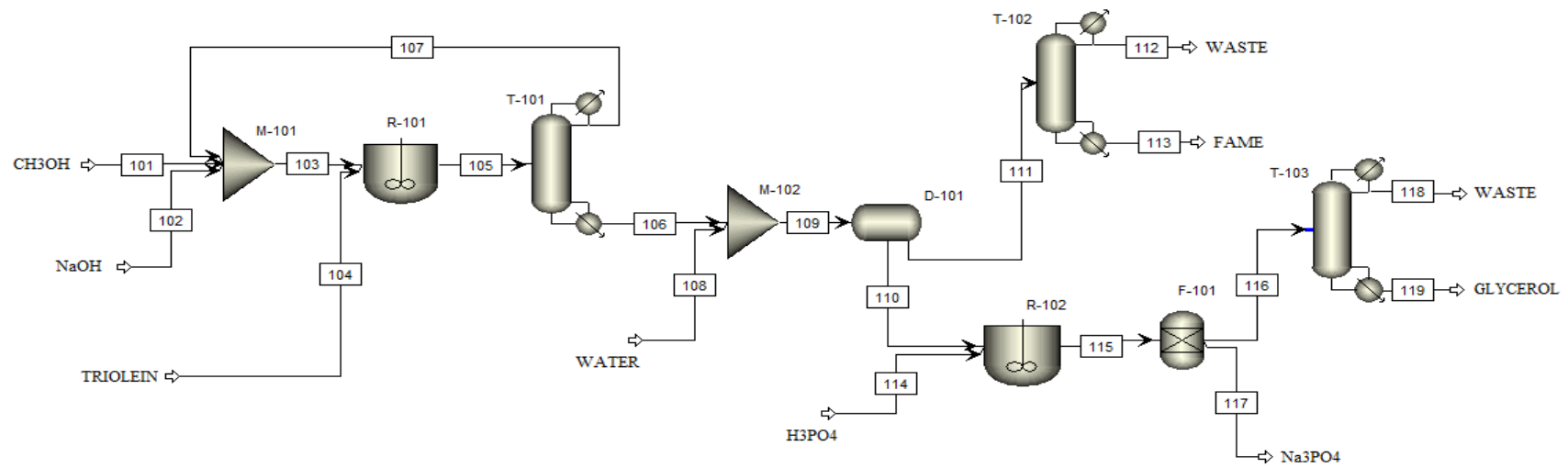


**Figure 3.2**    Biodiesel process flowsheet (alkali transesterification)

**Table 3.2**     Result summary of simulation process

| Stream ID | 101 | 102 | 104 | 106 | 107 | 108 | 110 | 111 | 113 | 114 | 119 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp ($^{o}$C) | 30 | 30 | 30 | 126.9 | 32.9 | 30 | 30 | 30 | 280.1 | 30 | 260.1 |
| Pressure (bar) | 1.0 | 1.0 | 1.0 | 0.30 | 0.25 | 1.0 | 1.0 | 1.0 | 0.20 | 1.0 | 0.50 |
| Total Mass flow (kg/hr) | 227.982 | 10.0 | 1050.0 | 1173.9 | 113.99 | 10.0 | 126.768 | 1057.22 | 1052.95 | 11 | 108.790 |
| Mass Flow (kg/hr) | | | | | | | | | | | |
| $C_3H_8O_3$ | | | | 109.21 | trace | | 108.791 | 0.418 | trace | | 108.737 |
| $CH_4O$ | 227.982 | | | 0.673 | 113.32 | | 0.395 | 0.278 | trace | | trace |
| $C_{19}H_{36}O_2$ | | | | 1054.8 | trace | | 0.033 | 1054.75 | 1052.95 | | <0.001 |
| $H_2O$ | | | | | | 10.0 | 9.080 | 0.920 | trace | | 0.046 |
| $C_{57}H_{104}O_6$ | | | 1050.0 | | | | | | | | |
| $H_3PO_4$ | | | | | | | | | | 11 | |
| $Na_3PO_4$ | | | | | | | | | | | |
| NaOH | | 10.0 | | 9.327 | 0.673 | | 8.469 | 0.858 | trace | | 0.007 |
| Mass Frac | | | | | | | | | | | |
| $C_3H_8O_3$ | | | | 0.093 | trace | | 0.858 | 396ppm | trace | | 1.00 |
| $CH_4O$ | 1.00 | | | 573ppm | 0.994 | | 0.003 | 263ppm | trace | | 10ppb |
| $C_{19}H_{36}O_2$ | | | | 0.898 | trace | | 259ppm | 0.998 | 1.00 | | 268ppb |
| $H_2O$ | | | | | | 1.00 | 0.072 | 870ppm | trace | | 422ppm |
| $C_{57}H_{104}O_6$ | | | 1.00 | | | | | | | | |
| $H_3PO_4$ | | | | | | | | | | 1.00 | |
| $Na_3PO_4$ | | | | | | | | | | | |
| NaOH | | 1.00 | | 0.008 | 0.006 | | 0.067 | 811ppm | trace | | 67ppm |

### 3.3.1 Process Description

The alkali catalysed process will be set up at the reaction temperature of $60^{\circ}$C and pressure of 1 bar. The reaction was carried out with the molar ratio of methanol to oil, 6:1. The feed flowrates of catalyst and methanol were 10kg/hr and 227.982 kg/hr respectively. In the transesterification reactor, 114.663 kg/h of fresh methanol from stream 101 was mixed up with 113.991 kg/h of recycle methanol. 10 kg/hr of NaOH also was supplied into M-101 through stream 102. Then, about 1050 kg/h of waste cooking oil was fed into the R-101. The reaction was occurred at temperature $60^{\circ}$C and pressure 1 bar. About 99.8% of oil was converted to biodiesel. Then, all the effluents were discharged from R-101.

Because of the large excess of methanol was used in the reaction, methanol recovery step was considered. Methanol distillation column T-101, was introduced in this reaction process. 113.991 kg/h of methanol was obtained in stream 107 and was recycled back to the main entrance. By recycled the unconverted methanol, it can reduced much cost. Then, the bottom product of T-101 which consists of 89.8% of methyl oleate (FAME), 9.3% of glycerol, 0.8% of NaOH, and also traces of methanol was then forwarded to F-101.

10 kg/hr of water was entered the M-102 through stream 108 at $30^{\circ}$C and 1 bar. As stated from the literature, water washing is used in order to purify the product. Then, the effluent was preceded to D-101. Here, decanter was used to separate the main product (FAME and glycerol) from the other components. The upper part of the decanter contained biodiesel was the forwarded to the biodiesel

purification column, T-102. By using seven theoretical stages with a reflux ratio of two, 100% of FAME was obtained at the bottom part of the distillation column.

However, the bottom stream of the decanter, 110 was forwarded to the neutralization process in R-102. Here, the reaction was occurred at temperature $60^{o}$C and pressure 1 bar respectively. This process was conducted in order to remove the excess catalysed alkali that was used in R-101. It was removed by adding phosphoric acid to produced solid waste of $Na_3PO_4$ and $H_2O$. Then, filter F-101 was introduced to remove the solid waste ($Na_3PO_4$) out from the process. The neutralization process reaction can be described as below:

$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$$
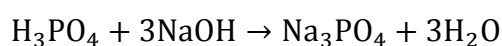
Next, the remaining compound in the reactor was forwarded to the glycerol purification, T-103 through stream 116. By using four theoretical stages with a reflux ratio of 1, almost 100% of glycerol by product has been produced from the bottom part of the distillation column while the others product were traces.

Tables below show the summaries of parameters used in the simulation process:

**Table 3.3**     Summary of parameters used in transesterification  reactor

| Transesterification Reactor | |
| --- | --- |
| Catalysts | NaOH |
| Reactor type | CSTR |
| Temperature, $^{o}$C | 60 |
| Pressure, bar | 1 |
| Residence time, min | 60 |
| Volume, m$^3$ | 9.72 |
| Conversion, % | 99.8 |
| Reaction | $C_{57}H_{104}O_6 + 3CH_3OH \rightarrow 3C_3H_8O_2 + C_{19}H_{36}O_2$ |

**Table 3.4**     Summary of parameters used in neutralization reactor

| Neutralization Reactor | |
| --- | --- |
| Reactor type | CSTR |
| Temperature, $^{o}$C | 30 |
| Pressure, bar | 1 |
| $H_3PO_4$ flowrate, kg/hr | 11 |
| Volume, m$^3$ | 0.40 |
| Conversion, % | 100 |
| Reaction | $H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$ |

**Table 3.5**      Summary of Parameters used in Methanol Recovery Column

| Methanol Recovery Column | |
| --- | --- |
| Reflux ratio, mass | 1 |
| No. of stages | 7 |
| Distillate temperature, $^{o}C$ | 30 |
| Condenser/reboiler pressure, kPa | 25/30 |
| Distillate flowrate, kg/hr | 113.991487 |

**Table 3.6**      Summary of Parameters used in Biodiesel Purification Column

| Biodiesel Purification Column | |
| --- | --- |
| Reflux ratio, mass | 2 |
| No. of stages | 7 |
| Distillate temperature, $^{o}C$ | 30 |
| Condenser/reboiler pressure, kPa | 15/20 |
| Distillate flowrate, kg/hr | 4.26918578 |

**Table 3.7**      Summary of Parameters used in Glycerol Purification Column

| Glycerol Purification Column | |
| --- | --- |
| Reflux ratio, mass | 1 |
| No. of stages | 4 |
| Distillate temperature, $^{o}C$ | 30 |
| Condenser/reboiler pressure, kPa | 40/50 |
| Distillate flowrate, kg/hr | 19.978 |

**3.4 Concluding Remarks**


In this chapter, Aspen Plus software simulator is used to simulate 8000 MT/annum of the biodiesel from waste cooking oil with 7600 hours of operating working condition. The reaction was carried out with the feed flowrates of waste cooking oil (triolein) to methanol with molar ratio 1:6. However, the flowrate for each reactant were set at 1050 kg/hr and 227.982 kg/hr respectively. NaOH catalyst is used in order to assist the process reaction. From the result, almost 100% of FAME is produced with flowrate of 1052.953 kg/hr or 8002.443 MT/annum. Then, the potential environmental impact of the process will be conducted by using some specific formula that will be developed in Microsoft Excel. The next chapter will discuss further on PEI of the simulation process.

# CHAPTER 4

# ENVIRONMENTAL ASSESSMENT

## 4.1    Introduction

In order to assess the impact of the process towards the environment, the total rate of PEI generated were developed in Microsoft Excel spread sheet. The comparison between homogenous and heterogeneous transesterification also had been conducted. The result for heterogeneous process is taken from Eleyana, (2012).

Some of parameters obtained in Aspen Plus are used in WAR Algorithm to determine the environmental impact of the chemical process. The results generated for both processes had been discussed based on Total Rate Output (TOR), Total Rate Output/Product (TOP), Total Rate Generation (TGR), and Total Rate

Generation/Product (TGP). For both processes, the comparison of these parameters is made. Lower PEI value indicates the best process.

## 4.2 Result of Potential Environment Impact (PEI)

Based on the parameters needed in Microsoft Excel spread sheet, the environmental impacts of the process (Table 4.1 and Table 4.2) are generated.

From the result obtained with product, it is showed that the TRO value for homogenous process is 1736.20 whereas the heterogeneous process is 1552.33. However without product, homogenous and heterogeneous processes values are 37.68 and 0.19 respectively. Heterogeneous process gives lower TRO value compared to homogeneous process. Lower TRO means the chemical process' site should be located in an ecologically sensitive area. Hence, heterogeneous chemical process is preferable.

Next, the TOP value for both processes is compared. From the result generated, the TOP values for homogenous and heterogeneous processes with product are 1.49 and 1.48 respectively. Hence, heterogeneous chemical process is desirable. When a production rate of process is increased, the TOP value will be increased. Since TOP measures the efficiency of material utilization by a specific process per unit mass of product, it will reduce the TRO value. This means that improving material utilization efficiency through process modification tends to lower the PEI output per unit mass of products.

On the other hand, selection of process for the operating conditions will be affecting the TRG values of the process itself. It is based on how fast they generate the impact during comparing the processes. However, if the comparing is based on the amount of new potential environmental impact generated in product manufacturing, TGP parameter is used. From the result generated with product, the TRG values for homogeneous and heterogeneous process are 241.09 and 999.29 respectively. While the TRG values without product are -1457.42 and -552.84 respectively. Hence, homogenoues chemical process is preferable because of lower PEI values generated. Same goes with TGP values. Homogenoues chemical process also is desirable in TGP values because it gives lower values compared to heterogeneous chemical process.

**Table 4.1**        Overall PEI result for homogenous process

Overall PEI

| Indicator | Input stream | Output stream | | Energy consp (output) | With product stream | | | | | | Without product stream | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Product stream | Non-prod. stream | | Output/ prod. | Energy/ prod. | TRO | TOP | TRG | TGP | Output/ prod. | Energy/ prod. | TRO | TOP | TRG | TGP |
| HTPI | 165.67 | 29.99 | 3.14 | 0.00 | 0.03 | 0.00 | 33.13 | 0.03 | -132.55 | -0.11 | 0.00 | 0.00 | 3.14 | 0.00 | -162.54 | -0.14 |
| HTPE | 1000.59 | 23.86 | 4.77 | 0.00 | 0.02 | 0.00 | 28.63 | 0.02 | -971.96 | -0.84 | 0.00 | 0.00 | 4.77 | 0.00 | -995.82 | -0.86 |
| ATP | 1.07 | 257.41 | 23.89 | 0.00 | 0.24 | 0.00 | 281.30 | 0.24 | 280.23 | 0.24 | 0.02 | 0.00 | 23.89 | 0.02 | 22.82 | 0.02 |
| TTP | 165.67 | 29.99 | 3.14 | 0.00 | 0.03 | 0.00 | 33.13 | 0.03 | -132.55 | -0.11 | 0.00 | 0.00 | 3.14 | 0.00 | -162.54 | -0.14 |
| GWP | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| PCOP | 162.09 | 1357.27 | 2.73 | 0.00 | 1.17 | 0.00 | 1360.00 | 1.17 | 1197.91 | 1.03 | 0.00 | 0.00 | 2.73 | 0.00 | -159.36 | -0.14 |
| AP | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| ODP | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Total | 1495.10 | 1698.52 | 37.68 | 0.00 | 1.49 | 0.00 | 1736.20 | 1.49 | 241.09 | 0.21 | 0.03 | 0.00 | 37.68 | 0.03 | -1457.42 | -1.25 |

**Table 4.2:**        Overall PEI result for heterogeneous process

(source: Eleyana, 2012)

Overall PEI

| Indicator | Input stream | Output stream | | Energy consp (output) | With product stream | | | | | | Without product stream | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Product stream | Non-prod. stream | | Output/ prod. | Energy/ prod. | TRO | TOP | TRG | TGP | Output/ prod. | Energy/ prod. | TRO | TOP | TRG | TGP |
| HTPI | 141.99 | 60.76 | 0.00 | 0.00 | 0.06 | 0.00 | 60.76 | 0.06 | -81.23 | -0.08 | 0.00 | 0.00 | 0.00 | 0.00 | -141.99 | -0.14 |
| HTPE | 195.63 | 9.37 | 0.00 | 0.00 | 0.01 | 0.00 | 9.37 | 0.01 | -186.26 | -0.18 | 0.00 | 0.00 | 0.00 | 0.00 | -195.63 | -0.19 |
| ATP | 0.41 | 196.40 | 0.00 | 0.00 | 0.19 | 0.00 | 196.40 | 0.19 | 196.00 | 0.19 | 0.00 | 0.00 | 0.00 | 0.00 | -0.41 | 0.00 |
| TTP | 141.99 | 60.76 | 0.00 | 0.00 | 0.06 | 0.00 | 60.76 | 0.06 | -81.23 | -0.08 | 0.00 | 0.00 | 0.00 | 0.00 | -141.99 | -0.14 |
| GWP | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| PCOP | 73.02 | 1224.83 | 0.19 | 0.00 | 1.17 | 0.00 | 1225.03 | 1.17 | 1152.01 | 1.10 | 0.00 | 0.00 | 0.19 | 0.00 | -72.83 | -0.07 |
| AP | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| ODP | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Total | 553.04 | 1552.13 | 0.19 | 0.00 | 1.48 | 0.00 | 1552.33 | 1.48 | 999.29 | 0.95 | 0.00 | 0.00 | 0.19 | 0.00 | -552.84 | -0.53 |

**Table 4.3:**     Result Summary of homogenous process

| | Homogenous Process | | | |
|---|---|---|---|---|
| Environmental indicator | TRO ( $I_{out}^t$ ) | TOP ( $\hat{I}_{out}^t$ ) | TRG ( $I_{gen}^t$ ) | TGP ( $\hat{I}_{gen}^t$ ) |
| With product | 1736.20 | 1.49 | 241.09 | 0.21 |
| Without product | 37.68 | 0.03 | -1457.42 | -1.25 |

**Table 4.4:**     Result Summary of heterogeneous process

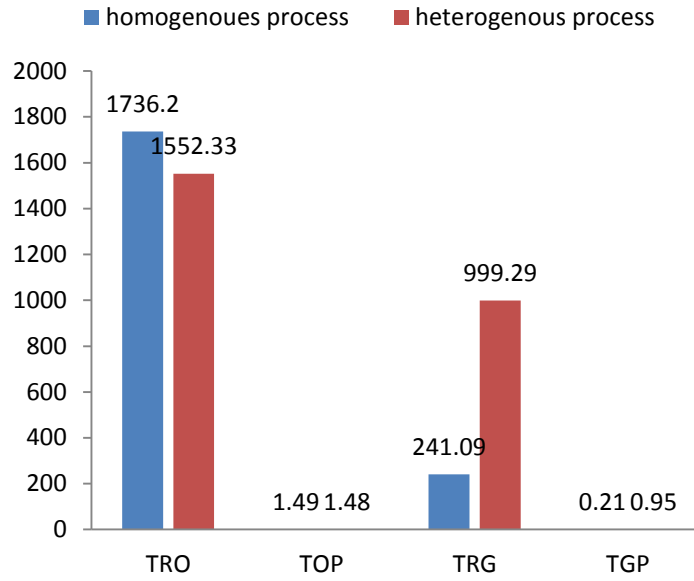| | Heterogenous Process | | | |
|---|---|---|---|---|
| Environmental indicator | TRO ( $I_{out}^t$ ) | TOP ( $\hat{I}_{out}^t$ ) | TRG ( $I_{gen}^t$ ) | TGP ( $\hat{I}_{gen}^t$ ) |
| With product | 1552.33 | 1.48 | 999.29 | 0.95 |
| Without product | 0.19 | 0.00 | -552.84 | -0.53 |

**Figure 4.1**　Comparison of environmental assessment for homogenous and heterogeneous processes with product
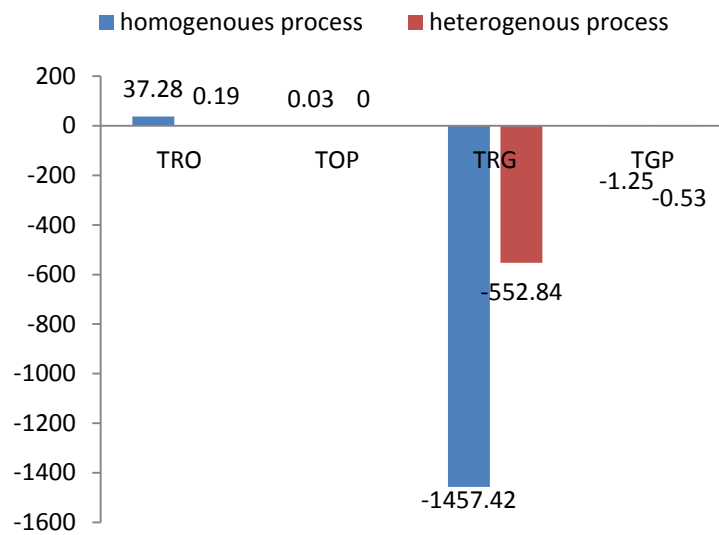


**Figure 4.2**　Comparison of environmental assessment for homogenous and heterogeneous processes without product

## 4.3    Specific PEI value of Chemical Components

### 4.3.1   Introduction

A summary table result (Table 4.1 and Table 4.2) is generated from the developed Microsoft Excel spread sheet. From the summary table, details value for each indicator is obtained and the respective graph is plotted.

### 4.3.2   Homogenous and Heterogeneous Chemical Processes: With Product

The HTPI values for homogenous and heterogeneous chemical process are 0.058 and 0.029 respectively. These values indicate that homogeneous consists of higher chemical that exist as a liquid or solid at temperature of $0^{o}C$ and at atmospheric pressure than heterogeneous chemical process. Hence, the human toxicity especially in dermal exposure is higher compared to the heterogenous process.

However, the HTPE value for homogenous chemical process is higher with 0.009 compared to the heterogeneous chemical process with 0.025. These values indicate that in the chemical process, the chemical is exists as a gas at $0^{o}C$ and at atmospheric pressure. Hence, the higher HTPE value is non-preferable chemical process as it will lead to the human toxicity especially during inhalation and ingestion.

Next, from the result generated showed that the ATP value for homogenous is lower than heterogeneous chemical process with 0.187 and 0.242 respectively. Lower ATP value indicates the lower exposure of toxicity level to human. Hence, homogeneous chemical process is preferable. However, TTP value in homogenous is higher compared to the heterogeneous chemical process with 0.058 and 0.029 respectively which also indicates the toxilogical level exposure to human.

Then, the PCOP value for homogenous is slightly lower than heterogeneous chemical process with 1.168 and 1.171 respectively. By comparing the rate of unit mass of chemical reacts with a hydroxyl radical (OH$^.$) to the rate at the unit mass of ethylene reacts with OH$^.$, the PCOP or smog potential is determined. However for both processes, GWP, AP and ODP are not considered since the indicators do not give any impact during the process.

By adding all the available indicator parameters in homogenous and heterogeneous chemical with product (FAME and glycerol), hence, it is concluded that heterogeneous is most preferable compared to the homogenous chemical process. This is due to the lower PEI value with 1.48 compared to homogenous chemical process with 1.49 with slightly different PEI value.
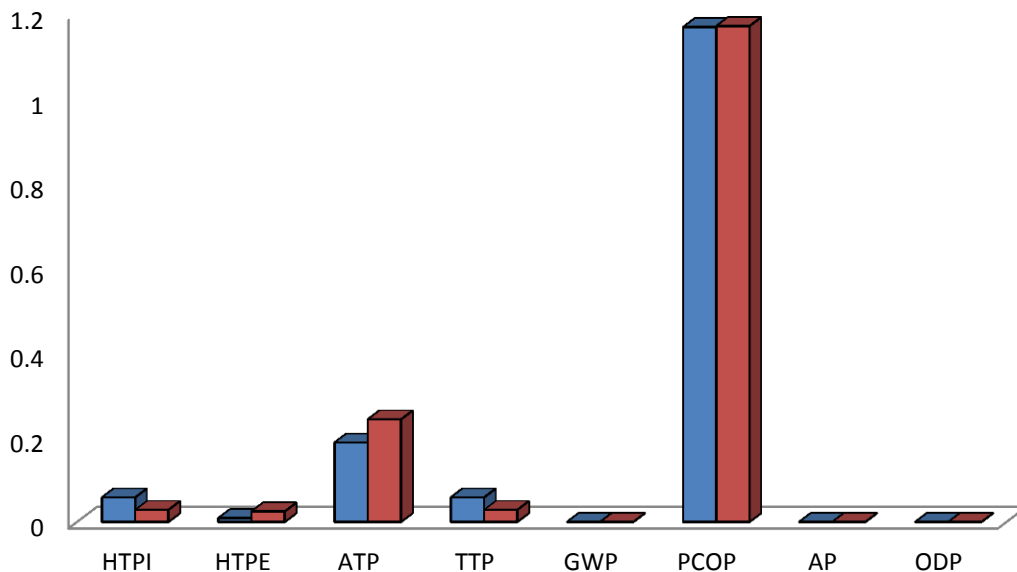
**Figure 4.3** TOP of environmental impact categories with product
( ■ indicates homogenous catalysed while ■ indicates heterogenous catalysed of
chemical process)

### 4.3.3 Homogenous and Heterogeneous Chemical Process: Without Product

The HTPI and HTPE values for homogenous chemical process without product are 0.003 and 0.004 respectively compared to the heterogeneous chemical process which is zero. This means that for HTPI; at a temperature $0^{o}C$ and atmospheric pressure, the chemical is exists as liquid or solid phase in homogenous chemical process while for HTPE, the chemical exits as gas phase at the same operating conditions. Hence, the existing values of HTPI and HTPE in Table 4.1 indicate that the homogenous provides higher exposure level to human compared to the heterogeneous chemical process.

Next, the ATP and TTP values for homogenous chemical process are 0.021 and 0.003 respectively. These indicators are also indicating the toxilogical level exposure to human. Higher values are non-preferable

However in heterogeneous chemical process, zero values are seems to appear for all indicators. This is due to the 100% conversion of triolein to produce product (FAME). Hence, the waste from the heterogeneous chemical processes can be neglected.

The PCOP value in homogenous is higher than heterogeneous chemical process with 0.002. Higher the PCOP value indicates that the higher smog formation will be produced by the process. Hence, heterogeneous chemical process is preferable. But the other indicators such as GWP, AP and ODP are not considered in both processes since they not give any impact during the process.

In conclusion, it is conclude that heterogeneous is preferable chemical process due to its lower PEI value with 0.00 compared to the homogenous chemical process which gives higher PEI value with 0.03.

For both with and without product, heterogenous chemical process is preferable because the impact of the chemical produce from the process does significant towards the environment compared to the homogenous chemical process. This is due to the removal of solid $Na_3PO_4$ in homogenous catalysed during the alkali catalyst removal process. This means that the solid product produce from reaction of NaOH and $H_3PO_4$ does affected the impact towards the environment.
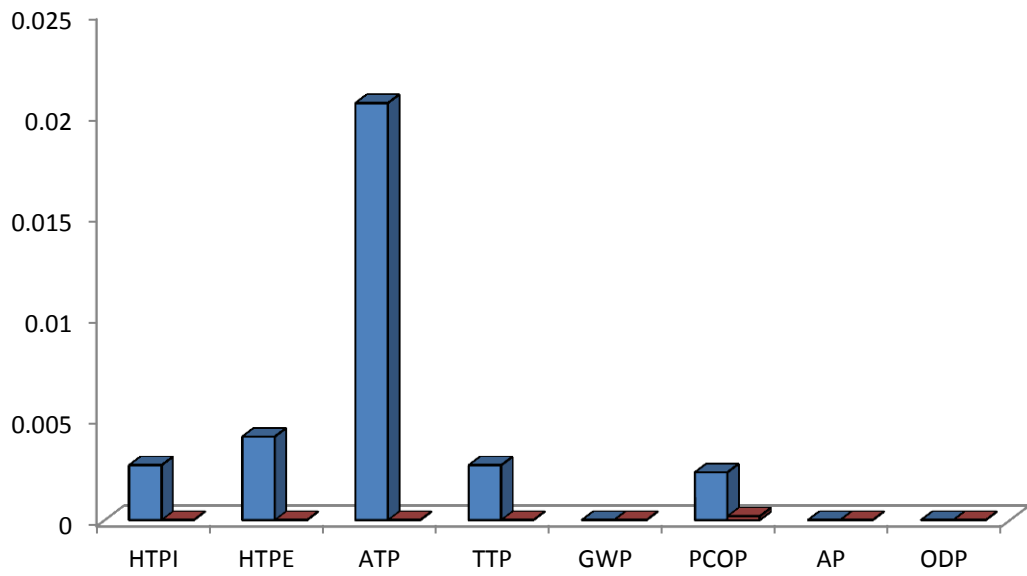
**Figure 4.4** TOP of environmental impact categorieswithout product
( ▪ indicates homogenous catalysed while ▪ indicates heterogenous catalysed of chemical process)

## 4.4    Concluding Remarks

In this chapter, details parameters that obtained from simulation process by Aspen Plus simulator was used in developed Microsoft Excel spread sheet. It is used to study the potential environmental impact of the process towards the environment. From the result, it is conclude that heterogeneous is preferable compared to the homogenous chemical process since it gives lower PEI values either with or without product. Lower PEI value indicates the preferable chemical process.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1    Conclusion

Due to the abundance of waste cooking oil yet it is easier to get, it has become the alternative way to replace diesel in future. It is desired to produce 8000 MT/annum of FAME with 7600 hours of operating working condition by using Aspen Plus software simulator. The process is conducted with molar ratio of waste cooking oil to methanol by 6:1. Alkali catalysed is used to assist the chemical process reaction. Then, the impact of the chemical process towards the environment is conducted by using WAR Algorithm. The PEI values between homogenous and heterogeneous chemical process is desired to compare. Since this report is only covered for homogenous chemical process, the result simulation and WAR algorithm

of heterogeneous chemical process had been taken from Eleyana (2012). From the result, it is concluded heterogeneous chemical process is preferable since it gives lower PEI value.

## 5.2    Difficulties and Recommendation

Throughout the research, some difficulties were faced especially during conducting the software itself. Some guidance from the expertise is sometimes needed. Since some of the software is quite new to student, it will time for student to explore and get familiar with it. So, longer time will be taken before they can get start up with the project. As the recommendation, faculty should provide a basic class on how to use the software for the beginner. For sure, this class will give much benefit to the students.

Besides for this research, it is quite difficult to remove the excess catalysed used in the reaction process. Many researchers also had faced the same difficulties in their papers when it is deals with neutralization process. This may due to the ionic chemical reaction between acid and alkali. In order to overcome these difficulties, the alkali catalyst's component name had been changed to water during defining the chemical properties in Aspen Plus. Hence, the difficulties of ionic equation for neutralization of alkali and acid equation can be prevented since the molecular structure is also changed and become water. Hence, the process simulation can be run easier without generating any error from the process.

# REFERENCES

A.H., W., Posarac, D., & Ellis, N. (2008). Assessment of Four Biodiesel Production Processes Using HYSYS.Plant. *Bioresource Technology 99*, 6587–6601.

Arifin, S. (2009). *Production of Biodisel From Waste Cooking Oil and RBD Palm Oil Using Batch Transesterification Process.* Kuantan: Universiti Malaysia Pahang.

B. Rice, A. F. (1997). *Bio-diesel Production based on Waste Cooking Oil : Promotion of the Establishment of an Industry in Ireland.* Carlow, Ireland.

Banerjee, A., & Chakraborty, R. (2009). Parametric Sensitivity In Transesterification of Waste Cooking Oil For Biodiesel Production—A Review. *Resources, Conservation and Recycling 53*, 490–497.

Bautista, L., Vicente, G., Rodriguez, R., & Pacheco, M. (2009). Optimisation of FAME Production From Waste Cooking Oil For Biodiesel Use. *Biomass and Bioenergy 33*, 862-872.

Braz, J. (1998). Transesterification of Vegetable Oils: A Review. *Chemical Society Vol. 1,* 199-210.

Cardona, C., Rincón, L., & Jaramillo, J. (2011). Integral Analysis of Feedstocks and Technologies For Biodiesel Production In Tropical and Subtropical Countries. *World Renewable Energy Congress 2011* (pp. 216-223). Sweden: Bioenergy Technology.

Ali, A., E. (2012). Heterogeneous Transesterification of Biodiesel from Waste Cooking Oil: *Environmental Analysis by Using WAR Algorithm*. Kuantan: Universiti Malaysia Pahang.

Helwani, Z., Othman, M. R., Fernando, W. J. N., & Kim, J. (2009). Technologies for Production of Biodiesel Focusing on Green Catalytic Techniques: A Review. *Fuel Processing Technology,* 1502-1514.

Howe, L., Dennis, Konda, N., & Rangaiah, G. (2005). Synthesis and Design of Chemical Processes. *Journal of The Institution of Engineers*, 39-49.

Jacobson, K., Gopinath, R., Meher, L., & Dalai, A. (2008). Solid Acid Catalysed Biodiesel Production From Waste Cooking Oil. *Applied Catalysis B: Environmental 85*, 86–91.

Khalid, K., & Khalid, K. (2011). Transesterification of Palm Oil for the Production of Biodiesel. *American Journal of Applied Science 8*, 804-809.

Lam, M., Lee, K., & Mohamed, A. (2010). Homogeneous, Heterogeneous and Enzymatic Catalysis For Transesterification of High Free Fatty Acid Oil (Waste Cooking Oil) To Biodiesel: A Review. *Biotechnology Advances 28* , 500-518.

McManus, M. (2011). An Environmental Assessment of The Production of Biodiesel From Waste Oil : Two Case Studies. *World Renewable Energy Congress 2011* (pp. 455-462). Sweden: Bioenergy Technology.

Othman, M. (2011). *Sustainability Assessment and Decision Making.* Berlin: University Technical of Berlin.

Phan, A., & Phan, T. (2008). Biodiesel Production From Waste Cooking Oils. *Fuel 87*, 3490–3496.

Pokoo-Aikins, G., Nadim, A., El-Halwagi, M., & Mahalec, V. (2010). Design and Analysis of Biodiesel Production From Algae Grown Through Carbon Sequestration. *Clean Techn Environ Policy*, 239–254.

Rice, B., Frohlich, A., Leonard, R., & Korbitz, W. (1997). *Bio-diesel Production based on Waste Cooking Oil: Promotion of the Establishment of an Industry in Ireland.* Carlow: Agriculture Food and Environment Authority.

Vlad, E., Bildea, C.D.,Plesu, V,. Morton Brozga (2010).  Process Design of Biodiesel Production from Rapeesed Oil: *Chemical Engineering Transaction,* Romania: Universiti of Bucharest.

Wang, Y., Ou, S., Liu., P., Xue, F., & Tang, S. (2006). Comparison of Two Different Processes to Synthesize Biodiesel by Waste Cooking Oil: *Journal of Molecular Catalysis A: Chemical 252*, 107-112

Wright, M., Satrio, J., Brown, R., Daugaard, D., & Hsu, D. (2010). *Techno -Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels* . Colorado: National Renewable Energy Laboratory.

Young, D., & Cabezas, H. (1999). Designing Sustainable Processes With Simulation: The Waste Reduction (WAR) Algorithm. *Computers and Chemical Engineering 23*, 1477–1491.

Young, D., Scharp, R., & Cabezas, H. (2000). The Waste Reduction (WAR) Algorithm: Environmental Impacts, Energy Consumption, and Engineering Economics. *Waste Management 20*, 605-615.

Zhang, Y. (2002). *Design and Economic Assessment of Biodisel Production From Waste Cooking Oil.* Ottawa: Faculty of Graduate and Postdoctoral Studies, University of Ottawa.

Zhang, Y., Dube, M., McLean, D., & Kates, M. (2003). Biodiesel Production From Waste Cooking Oil: 1. Process design and Technological Assessment. *Bioresource Technology 89*, 1-16.

Zhang, Y., M.A, D., McLean, D., & Kates, M. (2003). Biodiesel Production From Waste Cooking Oil: 2. Economic Assessment and Sensitivity Analysis. *Bioresource Technology 90*, 229–240.

Zyl, H., & Barbour, T. (2010). *Strategic Environmetal Assessment (SEA) For Biofuel Production In The Caprivi And Kavango Regions of Namibia.* Windhoek: Ministry of Environment and Tourism.

**APPENDIX A** shows the process flowsheet of homogenous alkali-catalysed biodiesel from virgin vegetable oil**.**
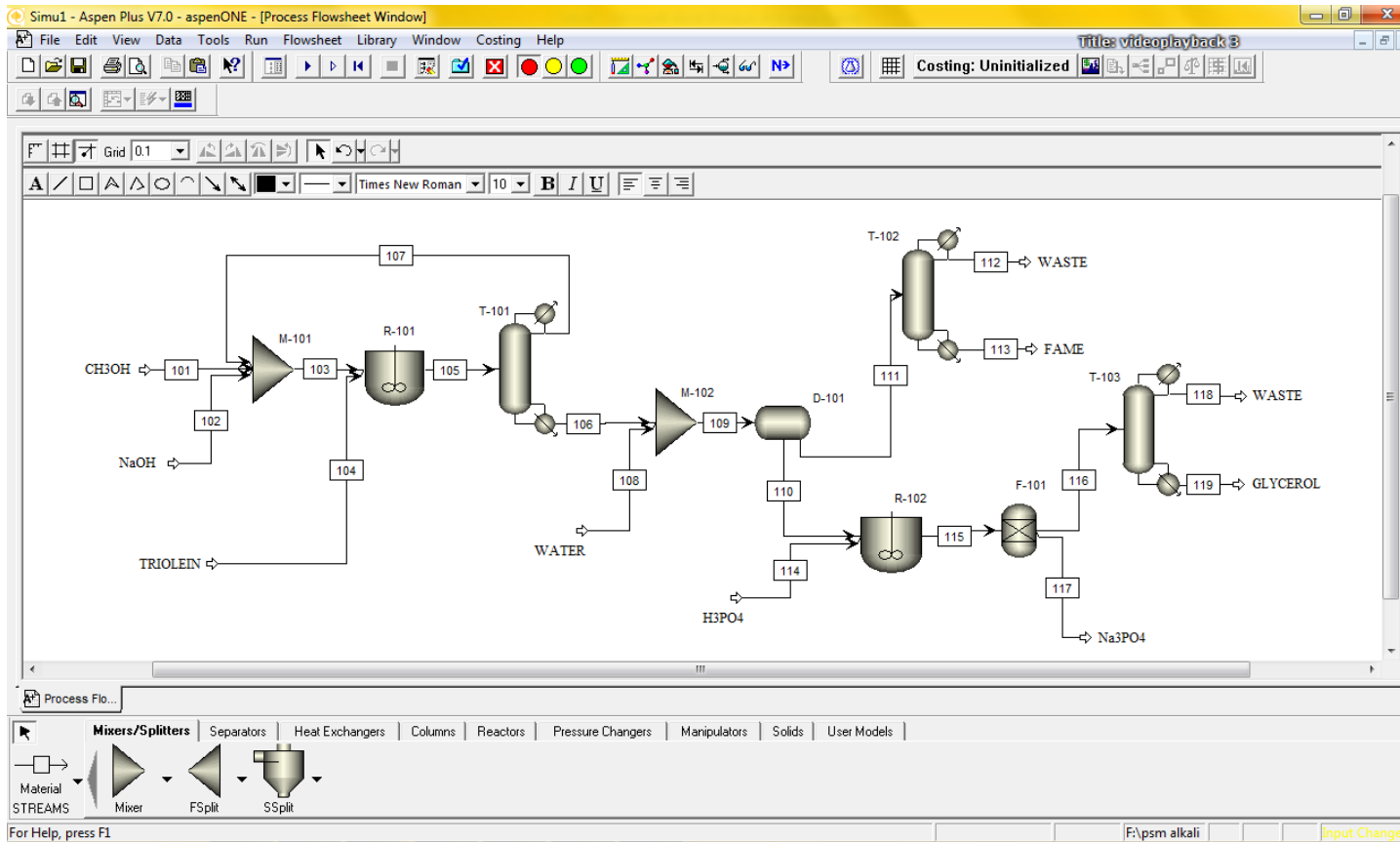
**APPENDIX B** shows the summary table for simulation process of homogenous alkali-catalysed biodiesel from virgin vegetable oil

| | | alkali transesterification of waste cooking oil | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Stream ID | | 101 | 102 | 103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 119 |
| Temperature | C | 30.0 | 30.0 | 31.3 | 30.0 | 60.0 | 126.9 | 32.9 | 30.0 | 125.2 | 30.0 | 30.0 | 45.2 | 280.1 | 30.0 | 30.0 | 30.0 | 30.0 | 73.9 | 280.1 |
| Pressure | bar | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 0.30 | 0.25 | 1.00 | 1.00 | 1.00 | 1.00 | 0.15 | 0.20 | 1.00 | 1.00 | 1.00 | 1.00 | 0.40 | 0.50 |
| Vapor Frac | | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 |
| Mole Flow | kmol/hr | 7.115 | 0.555 | 7.670 | 1.186 | 8.856 | 5.282 | 3.574 | 0.555 | 5.837 | 2.168 | 3.669 | 0.118 | 3.551 | 0.112 | 2.280 | 2.168 | 0.112 | 0.984 | 1.186 |
| Mass Flow | kg/hr | 227.982 | 10.000 | 237.982 | 1050.000 | 1287.982 | 1173.991 | 113.991 | 10.000 | 1183.991 | 1267.68 | 1057.222 | 4.269 | 1052.953 | 11.000 | 137.768 | 1267.68 | 11.000 | 17.978 | 1087.90 |
| Volume Flow | cum/hr | 0.290 | 0.010 | 0.301 | 1.199 | 1.514 | 1.466 | 0.145 | 0.010 | 1.477 | 0.101 | 1.221 | 0.005 | 1.558 | 0.018 | 0.106 | 0.101 | 28.29 | 0.019 | 0.102 |
| Enthalpy | MMBtu/hr | -1.605 | -0.150 | -1.756 | -2.094 | -4.065 | -3.115 | -0.807 | -0.150 | -3.265 | -1.011 | -2.471 | -0.036 | -1.852 | -0.135 | -1.162 | -1.011 | -0.151 | -0.265 | -0.687 |
| **Mass Flow** | **kg/hr** | | | | | | | | | | | | | | | | | | | |
| C3H8O-01 | | | | | | 1092.09 | 1092.09 | trace | | 1092.09 | 1087.91 | 0.418 | 0.418 | trace | | 1087.91 | 1087.91 | | 0.054 | 1087.37 |
| C4H-O | | 227.982 | | 227.982 | | 113.991 | 0.673 | 113.319 | | 0.673 | 0.395 | 0.278 | 0.278 | trace | | 0.395 | 0.395 | | 0.395 | trace |
| C19H36-01 | | | | | | 1054.781 | 1054.781 | trace | | 1054.781 | 0.033 | 1054.748 | 1.795 | 1052.953 | | 0.033 | 0.033 | | 0.033 | < 0.001 |
| H2O | | | | | | | | | 10.000 | 10.000 | 9.080 | 0.920 | 0.920 | trace | | 15.147 | 15.147 | | 15.101 | 0.046 |
| C57H-01 | | | | | 1050.000 | | | | | | | | | | | | | | | |
| H3PO4 | | | | | | | | | | | | | | | 11.000 | | | | | |
| Na3PO4-01 | | | | | | | | | | | | | | | | 11.000 | | 11.000 | | |
| NaOH | | | 10.000 | 10.000 | | 10.000 | 9.327 | 0.673 | | 9.327 | 8.469 | 0.858 | 0.858 | trace | | 2.403 | 2.403 | | 2.395 | 0.007 |
| **Mass Frac** | | | | | | | | | | | | | | | | | | | | |
| C3H8O-01 | | | | | | 0.085 | 0.093 | trace | | 0.092 | 0.858 | 396 PPM | 0.098 | trace | | 0.790 | 0.858 | | | 1.00 |
| C4H-O | | 1.000 | | 0.958 | | 0.089 | 573 PPM | 0.994 | | 568 PPM | 0.000 | 263 PPM | 0.065 | | | 0.003 | 0.003 | | 0.022 | 1.0 PPB |
| C19H36-01 | | | | | | 0.819 | 0.898 | trace | | 0.891 | 2.9 PPM | 0.998 | 0.421 | 1.000 | | 2.39 PPM | 2.9 PPM | | 0.002 | 268 PPB |
| H2O | | | | | | | | | 1.000 | 0.008 | 0.072 | 870 PPM | 0.215 | trace | | 0.110 | 0.119 | | 0.840 | 42.2 PPM |
| C57H-01 | | | | | 1.000 | | | | | | | | | | | | | | | |
| H3PO4 | | | | | | | | | | | | | | | 1.000 | | | | | |
| Na3PO4-01 | | | | | | | | | | | | | | | | 0.080 | | 1.000 | | |
| NaOH | | | 1.000 | 0.042 | | 0.008 | 0.008 | 0.006 | | 0.008 | 0.067 | 811 PPM | 0.201 | trace | | 0.017 | 0.019 | | 0.133 | 67 PPB |
| **Mole Flow** | **kmol/hr** | | | | | | | | | | | | | | | | | | | |
| C3H8O-01 | | | | | | 1.186 | 1.186 | trace | | 1.186 | 1.181 | 0.005 | 0.005 | trace | | 1.181 | 1.181 | | 0.001 | 1.181 |
| C4H-O | | 7.115 | | 7.115 | | 3.558 | 0.021 | 3.537 | | 0.021 | 0.012 | 0.009 | 0.009 | trace | | 0.012 | 0.012 | | 0.012 | trace |
| C19H36-01 | | | | | | 3.558 | 3.558 | trace | | 3.558 | < 0.001 | 3.557 | 0.006 | 3.551 | | < 0.001 | < 0.001 | | < 0.001 | trace |
| H2O | | | | | | | | | 0.555 | 0.555 | 0.504 | 0.051 | 0.051 | trace | | 0.841 | 0.841 | | 0.838 | 0.006 |
| C57H-01 | | | | | 1.186 | | | | | | | | | | | | | | | |
| H3PO4 | | | | | | | | | | | | | | | 0.112 | | | | | |
| Na3PO4-01 | | | | | | | | | | | | | | | | 0.112 | | 0.112 | | |
| NaOH | | | 0.555 | 0.555 | | 0.555 | 0.518 | 0.037 | | 0.518 | 0.470 | 0.048 | 0.048 | trace | | 0.133 | 0.133 | | 0.133 | < 0.001 |
| **Mole Frac** | | | | | | | | | | | | | | | | | | | | |
| C3H8O-01 | | | | | | 0.134 | 0.225 | trace | | 0.203 | 0.545 | 0.001 | 0.039 | trace | | 0.518 | 0.545 | | 396 PPM | 0.996 |
| C4H-O | | 1.000 | | 0.928 | | 0.402 | 0.004 | 0.990 | | 0.004 | 0.006 | 0.002 | 0.074 | trace | | 0.006 | 0.006 | | 0.013 | 2.9 PPB |
| C19H36-01 | | | | | | 0.402 | 0.674 | trace | | 0.609 | 5.1 PPM | 0.970 | 0.051 | 1.000 | | 4.9 PPM | 5.1 PPM | | 11.3 PPM | 8.3 PPB |
| H2O | | | | | | | | | 1.000 | 0.095 | 0.233 | 0.014 | 0.433 | trace | | 0.369 | 0.388 | | 0.852 | 0.004 |
| C57H-01 | | | | | 1.000 | | | | | | | | | | | | | | | |
| H3PO4 | | | | | | | | | | | | | | | 1.000 | | | | | |
| Na3PO4-01 | | | | | | | | | | | | | | | | 0.049 | | 1.000 | | |
| NaOH | | | 1.000 | 0.072 | | 0.063 | 0.098 | 0.010 | | 0.089 | 0.217 | 0.013 | 0.404 | trace | | 0.058 | 0.062 | | 0.135 | 34.3 PPB |

**APPENDIX C** shows the input of stream inventory table for WAR algorithm

**APPENDIX D** shows the input product stream which are FAME and glycerol in WAR Algorithm

**APPENDIX E** shows the input non-product or waste stream (except FAME and glycerol) in WAR Algorithm