## UNIVERSITI MALAYSIA PAHANG

| BORANG PENGESAHAN STATUS TESIS<br>JUDUL: BIODIESEL FROM VARIOUS VEGETABLES AND TALLOW<br>OILS |   |  |  |
|---|---|--|--|
|   | I PENGAJIAN: <u>2011/2012</u>   |  |  |
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## BIODIESEL FROM VARIOUS VEGETABLES AND TALLOW OILS

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Report submitted in partial fulfilment of the requirement for the award of the degree of Bachelor in Mechanical Engineering with Automotive Engineering

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> > JUNE 2012

# UNIVERSITI MALAYSIA PAHANG FACULTY OF MECHANICAL ENGINEERING

I certify that the project entitled "*Biodiesel from various vegetables and tallow oils*" is written by *Atiqah binti Nafsun*. I have examined the final copy of this project and in my opinion; it is fully adequate in terms of scope and quality for the award of the degree of Bachelor of Engineering. I hereby recommend that it be accepted in partial fulfilment of the requirements for the degree of Bachelor of Mechanical Engineering with Automotive.

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I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Dedicated to my beloved parents, friends and family

#### ACKNOWLEDGEMENTS

This accomplishment was not done by me alone. There are a lot of good person who guided and motivated me along the way. I would like to take this opportunity to express my greatest gratitude to all of them.

Firstly I would like thank the almighty for blessing me with all the courage and strength that took to complete my final year project in time without much predicament.

I am grateful and would like to express my sincere gratitude to my supervisor Dr. Rizalman bin Mamat for his bright ideas, invaluable guidance, continuous encouragement and advices that constantly support me in making this research possible.

Next on the list is my friend, a student from chemical engineering department, Liyana Amer Shah who helped and guided me a lot in the lab and being my backbone in this final year project accomplishment.

My sincere thanks go to all my friend, lab mates and members of the staff of the Mechanical Engineering Department and Chemical Engineering Department UMP, who helped me in many ways and made my stay at UMP pleasant and unforgettable.

Next, thank you to my special friend, Mohd Fiesol bin Alias that continued giving me advises, support, and encouragement and never let me down.

I hope this research project will be helpful for those who need reference in the field of metal casting process. Finally I would like to express my gratefulness to all of them who involved directly or indirectly in the completion of my final year project and thesis. Thank you.

## ABSTRACT

This thesis deals with Biodiesel from various vegetables and tallow oils. The objective of this thesis is to produce the biodiesel from various feedstocks which are palm oil, corn oil, chicken fat oil, soybean oil, sunflower oil and waste cooking oil and also to analyze the physical properties each of biodiesel oil. The thesis describes the proper biodiesel extraction process, using proper catalyst and solvent in order to get the biodiesel physical properties standard of B100, ASTM6571. The studies of physical properties of biodiesel that are involved in this thesis consist of density, viscosity, cetane number, flash point, cloud and pour point and also acid value. As result, we observed that palm oil has a nearest physical properties standard, ASTM6571. We compared these six different feedstock physical properties with some literature. As for the recommendation, conduct engine testing operating with various biodiesel and also perform one-dimensional simulation of internal combustion engine which operating with simulation such as GT-Power.

## ABSTRAK

Tesis ini berkaitan dengan Biodiesel dari pelbagai sayur-sayuran dan minyak lemak haiwan. Objektif tesis ini adalah untuk menghasilkan biodiesel daripada pelbagai bahan mentah iaitu dari minyak sawit, minyak jagung, minyak, lemak ayam, minyak kacang soya, minyak bunga matahari dan sisa minyak masak dan juga untuk menganalisis sifat fizikal setiap minyak biodiesel. Tesis ini menerangkan pengekstrakan proses biodiesel yang betul, menggunakan pemangkin yang betul dan pelarut untuk mendapatkan sifat-sifat biodiesel mengikut sifat-sifat fizikal piawaian B100, ASTM6571. Kajian sifat fizikal biodiesel yang terlibat di dalam tesis ini terdiri daripada ketumpatan, kelikatan, nombor cetana, takat kilat, awan dan takat tuang dan juga nilai asid. Hasilnya, kami memerhatikan bahawa minyak sawit mempunyai sifat-sifat fizikal yang terdekat dengan sifat-sifat fizikal standard, ASTM6571. Kita membandingkan sifat fizikal yang berbeza untuk setiap bahan mentah yang berbeza. Bagi syor itu, menjalankan operasi pengujian enjin dengan pelbagai jenis biodiesel dan juga melaksanakan satu dimensi simulasi enjin pembakaran dalaman yang beroperasi dengan simulasi seperti GT-Power.

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## LIST OF ABBREVIATIONS

| American Society for Testing and Material |
|---|
| Higher Heating Value                      |
| 5 % Biodiesel, 95 % Diesel                |
| 20 % Biodiesel, 80 % Diesel               |
| 100 % Biodiesel                           |
| Free Fatty Acid                           |
| Waste cooking oil                         |
| Small-angle neutron scattering            |
| Freeze-fracture electron microscopy       |
| Potassium Hydroxide                       |
| Sodium Hydroxide                          |
| Hydrocarbons                              |
| Polycyclic aromatic hydrocarbons          |
| Carbon Monoxide                           |
| Carbon Dioxide                            |
| Nitrogen Oxide                            |
| Exhaust-gas recirculation                 |
| Cold Filter Plugging Point                |
| European Environmental Bureau             |
| Brake specific fuel consumption           |
| Brake specific energy consumption         |
| Sulfur dioxide                            |
|   |

#### **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 BACKGROUND OF STUDY**

In this recent year, the world was hit by energy crisis. Nowadays, the increasing demand for energy and the diminishing of crude petroleum oil resources has lead to the research for a new alternative energy. The global concern about the petroleum resources was limited reserves and only concentrated in certain region in the world. Many researchers suggest that the sources reserve is only last for the next few decades. As we know that most of the transportation vehicles used fossil fuel such gasoline, liquid petroleum oil and diesel fuel. About 98 % of carbon emissions result from fossil fuel combustion. Alternatives energy such as hybrid technology requires extra modification to the vehicles engine. Beside the higher cost were needed, the time to develop is much longer, and inappropriate in short term replacement to fossil fuel.

Every sector across the globe needed energy, an energy that can be renewed and more important is a climate friendly that won't affect our green earth and human health as well. Transportation is one of the sectors that contribute to the energy application. Nowadays, the awareness about the energy losses and energy production are being considerate. There are some energy production developed from biomass, biogas, bioethanol, biohydrogen and biodiesel. The word bio significantly shows that the energy is safe for all of us. Among of them, biodiesel is a huge energy competitor that can go far. In term of production and application, biodiesel win a heart of researchers and leaders all over the world. Biodiesel is safely produced and handle, safely for our earth and easy to produce. The production of biodiesel will help the economic growth and help the development of the agriculture sector. It will help in increasing the exchange money rate and enhance the living standard particularly.

Biodiesel found out to be the best substitute for crude petroleum oil because it is renewable and sustainable. Moreover it is an environmental friendly fuel. The energy demand was fulfilled by conventional energy sources such as coal and fossil. Thus, renewable biodiesel replace the utilization of non renewable fossil fuels and coal that were limited.

Biodiesel is an alternative fuel for diesel engines that is produced by chemical reaction between a vegetable oils and fat oils with an alcohol. The reaction require a catalyst, whether acidic, alkaline catalyst or enzyme catalyst. Usually a strong alkali base, such as sodium or potassium hydroxide used in biodiesel production and produced a new compounds called methyl esters or ethyl esters. These fatty acid esters are also known as biodiesel. The combustion resulted by using biodiesel shown no decreasing in performance, instead its produce more clean exhaust emission. Three advantages that biodiesel has been recognize as major renewable energy resources are because its renewable resources that could be sustainable developed in the future, environmental friendly and give significant economic potential that can be developed in the near futures. With these advantages, biodiesel promises a bright future in the fuel industry.

In Malaysia, the biodiesel was accepted and known widely. The National Biofuel Policy was launched by government in 2006. The policy aimed to reduce country import bill and also promoting the further demand for palm oil for biodiesel production. The demand for biofuel in Europe is projected to increase from 3 million tonne in 2005 to 10 million tonne in 2010 (The National Biofuel Policy, 2006). Malaysia has aims to become a global leader in biodiesel production because Malaysia has a large palm oil plantation and the second exporter for palm oil worldwide behind Indonesia. In June 2010, Malaysia

considers cutting a diesel subsidy to make the biodiesel industry more attractive after production of the alternative fuel virtually ground to a halt. Because of the subsidy on diesel, it has somewhat distorted the price for biodiesel to be utilized.

Palm oil is one of the seventeen major oil traded in the global edible oil and fats market. Palm oil is consumed worldwide in more than 100 countries in the world (MPOC, 2007). Malaysia is a larger producer of palm oil worldwide and contributes 29% of biodiesel production from the palm oil. Government planned to provide a fund to palm oil producer across the country. One of them is Petronas Dagangan Berhad. This fund will growth the interest for palm oil company to set up new facilities in term of production and research. The rising cost for palm oil producing will increase the biofuels manufacturing process. Yet, the government should take a concern to give the subsidy to those who were involved.

### **1.2 PROBLEM STATEMENT**

Malaysia is known as the second exporter for palm oil worldwide behind Indonesia. Thus, Malaysia has the potential to lead the way in biofuel production capitalizing on its vast production of agricultural products and by-products. This will contribute in utilizing local resources for biofuel, exploiting local technology to generate energy for the transportation and industrial sectors, and paving the way for exports of biofuel. The price of biodiesel is much higher compare to conventional diesel makes it is less chosen by the customer. Thus the aim of this project is to produce biodiesel as diesel substitute with minimum cost with potential to be commercialized. The sensitivity of oil palm price resulted in instability of oil palm price. The higher prices of crude petroleum oil will shift the market trend favorable towards the palm oil. Thus, the high market demand of palm oil makes the prices more volatile. Even though the price of palm oil is much cheaper than crude petroleum oil, Malaysia government gives subsidized to petroleum oil in transportation sector resulted in lower prices compare to biodiesel. The main reason of high prices in production of biodiesel is because of its raw material. Thus, using waste cooking oil as raw material will make the biodiesel price more comparable than subsidized petroleum diesel. The availability, cost and the continuity are the main criteria for good raw material. The easy availability of waste cooking oil and continuity of supply make it as a good choice of raw material. Single steps transesterification process will be used in synthesizing waste cooking oil to methyl ester. Single steps transesterification process provide less time in reaction, lower temperature and pressure, gives a better yield and hence will result in less cost of production. The high content of free fatty acid in waste cooking oil need to be synthesize using homogenous catalyst. Even though the use of homogenous catalyst resulted in higher formation of soap, homogenous catalyst provides shorter reaction time compare to heterogeneous catalysts. Powdered sodium methoxide is used as homogenous catalyst in this experiment and methyl alcohol will use as alcohol solvent because of its price is cheaper among other alcohol solvent.

#### **1.3 PROJECT OBJECTIVES**

The objective of this project is to produce biodiesel from various vegetable oil such as palm oil, coconut oil, corn oil, olive oil, sunflower oil, peanut oil and from animal fats such as chicken, goat and cow fat.

#### **1.4 SCOPE OF THE STUDY**

This research is an experimental analysis study in a production of biodiesel from palm oil, corn oil, soybean oil, sunflower oil, waste cooking oil and animal fats from chicken as the feedstock. In order to achieve the project objective, three scopes have been identified to be studied. These three scopes are:

- i. Produces biodiesel with a various feedstock
- ii. Measure physical properties of biodiesel produced
- iii. Analysis and report writing

#### **CHAPTER 2**

## LITERATURE REVIEW

#### 2.1 OVERVIEW

Biodiesel is an alternative fuel for diesel engines. It chemically produced by reacting vegetable oil or fat oil with alcohol as a solvent. The most frequently alcohol used is acyl receptor particularly methanol and lesser extent which is an ethanol. The concept of using biodiesel in diesel engines originated by diesel engine inventor, Rudolf Diesel at the World Exhibition at Paris in 1900 as he used peanut oil as a fuel (Agarwal, 2001) However, due to the then-abundant supply of petroleum crude oil, research and development activities were not seriously pursued. Recently after the world having a energy crisis, the dramatic increase price of crude petroleum oil, the increasing concern regarding environment issues that is related to the greenhouse gas effect emission, the new health and safety consideration are forcing the search for energy sources and alternative ways in order to prevent all of these problems.

Biodiesel production is very modern and technological area for researchers due to the relevance that is winning every day. The commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure the high product quality and user confidence. The commonly standard use for biodiesel production is American Society for Testing and Materials, ASTM6751 and European standard EN14214, which was developed from previously existing standards in European countries (Knothe, 2005)

The American Society for Testing and Material (ASTM) defined biodiesel fuel as monoalkyl esters of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats. Biodiesel fuels are characterized by their cetane number, density, viscosity, cloud and pour points, flash point, copper corrosion, ash content, distillation range, sulfur content, carbon residue, acid value, free glycerine content, total glycerine content and higher heating value (HHV). The viscosity values of vegetable oils decreases sharply after transesterification reaction (Sharma, 2008). Biodiesel is the only alternative fuel that can be used in diesel engine directly without any modification of engine. Biodiesel fuel attracting more attention worldwide while introducing a blending component or direct replacement for diesel fuel in diesel vehicle engines (Demirbas, 2009). When blended with diesel fuel the designation indicates the amount of B100 in the blend, e.g. B20 is 20 % of B100 and 80 % diesel fuel and B5 is 5 % B100 in diesel fuel. Usually B20 is used because it is nearly all the diesel equipment are compatible to used with. These lower blends do not require any diesel engine modification compare to B100 that sometimes need a little modification. Table 2.1 shows the ASTM standard specification for neat biodiesel, B100 to be used in diesel engine.

 Table 2.1 : ASTM standard specification for neat biodiesel B100

| Property            | Test Method | ASTM D975                  | ATSM6751                   |
|---------------------|-------------|----------------------------|----------------------------|
|                     |             | (petroleum diesel)         | (biodiesel B100)           |
| Flash point         | D93         | 325K min                   | 403K                       |
| Water and sediment  | D2709       | 0.05 max vol.%             | 0.05 max vol.%             |
| Kinematic viscosity | D445        | 1.3-4.1 mm <sup>2</sup> /s | 1.9-6.0 mm <sup>2</sup> /s |
| (at 313K)           |             |                            |                            |
| Sulfated ash        | D874        | -                          | 0.02 max wt.%              |
| Ash                 | D482        | 0.01 max wt.%              | -                          |
| Sulfur              | D5453       | 0.05 max wt.%              | -                          |

Source : (Yusuf et al., 2011)

| Sulfur                 | D2622/129 | -              | 0.05 max wt.%  |  |
|------------------------|-----------|----------------|----------------|--|
| Copper-strip corrosion | D130      | No.3 max       | No.3 max       |  |
|                        |           |                |                |  |
| Cetane number          | D613      | 40 min         | 47 min         |  |
| Aromaticity            | D1319     | 35 max vol.%   | -              |  |
| Carbon residue         | D4530     | -              | 0.05 max mass% |  |
| Carbon residue         | D524      | 0.35 max mass% | -              |  |
| Distillation temp.     | D1160     | 555K min-611K  | -              |  |
| (90% volume recycle)   |           | max            |                |  |
|                        |           |                |                |  |

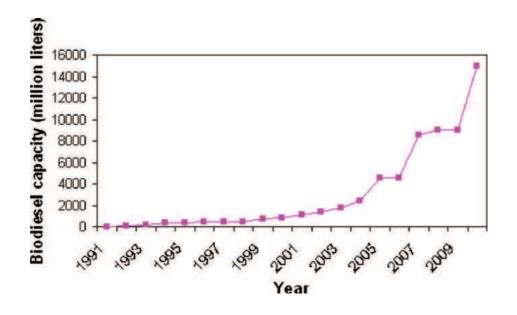


Figure 2.1 : World biodiesel capacity, 1991–2010

Source : (International Energy Agency).

### 2.1 RENEWABLE SOURCES FOR BIODIESEL PRODUCTION

#### 2.1.1 Animal fats

Another group of feedstock for biodiesel production is fats derived from animals. Animal fats used to produce biodiesel include tallow (Oner, 2009), white grease or lard (Lu, 2007), and chicken fat (Guru, 2010). Compared to plant crops, these fats frequently offer an economic advantage because they are often priced favorably for conversion into biodiesel (Wen, 2009). Moreover, it has some advantages such as high cetane number, non-corrosive, clean and renewable properties (Guru, 2009). Animal fats has a low free fatty acid (FFA) and water, but there is a limited amount of these oils available, meaning these would never be able to meet the fuel needs of the world (Sheedlo, 2008).

## 2.1.2 Edible oil

Biodiesel has been mainly produced from edible vegetable oils all over the world. Currently, more than 95 % of the world biodiesel is produced from edible oils which are easily available on large scale agricultural industry country (Gui, 2008). However, continuous and large scale production of biodiesel from edible oils has recently arise a concern because they are competing with food materials. There are concerns that biodiesel feedstock may compete with food supply in the long term (Refaat, 2010). Figure 2.2 shows the biodiesel production by vegetable oil globally.

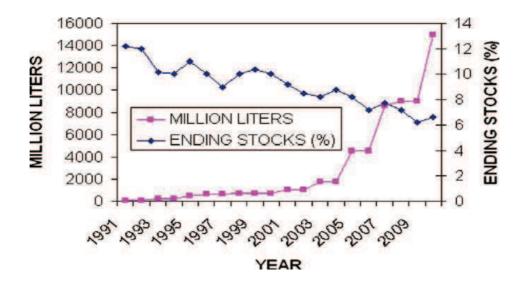


Figure 2.2 : Global vegetable-oil blending stock and biodiesel production

Source : Gui, M.M. et al., (2008).

Currently, biodiesel is prepared from conventionally grown edible oils such as rapeseed, soybean, sunflower and palm oils thus leading to the alleviate food versus fuel issues (Anwar, 2010). About 7 % of global edible vegetable oil supplies were used for biodiesel production in 2007 (Mitchell, 2008). The rapidly growing world population needs a food and the raise consumption of biodiesel cause a major problem.

### 2.1.3 Non-edible oil

Non edible plant oils have been found out to be promising crude oils for biodiesel production. The used of non-edible oils compared to edible oils is very significant in developing countries because of the tremendous demand for edible oils as a food. Edible oil are far too expensive to be used as a fuel (Pramanik, 2003). The production of biodiesel using non-edible oil has been investigated and carried out for the last few years. Some of these non-edible oilseed crops include jatropha tree (Jatropha curcas) (Tiwari, 2007),

karanja (Pongamia pinnata) (Naik, 2008), tobacco seed (Nicotiana tabacum L) (Veljkovic, 2006), ricebran (Sinha,2008),mahua (Madhuca indica) (Raheman, 2007), neem (Azadirachta indica) (Rao, 2008), rubber plant (Hevea brasiliensis) (Ramadhas, 2005), castor (Sousa, 2010), linseed, and micro-algae (Demirbas, 2009).

### 2.1.4 Waste cooking oil

The biodiesel production from waste cooking oil (WCO) has substitute the depletion of petroleum diesel. It is one of the measures for solving the problems of environment pollution and energy shortage. Waste cooking oil is more cheaper compared to other biodiesel feedstock. Moreover, the raw material is easy to get and the price is 2-3 times cheaper than virgin vegetable oils. Waste cooking oil is categorized based on its FFA. The amount of WCO generated in each country is different depending on overall country vegetable oil used. Management of WCO is a quite a challenge because of its disposal creates a huge problem and possible of contamination of the water and land resources.

#### 2.3 THE PRODUCTION OF BIODIESEL

There are many considerable efforts done to develop vegetable-oil derivatives that approximate the properties and performance of hydrocarbon based diesel fuels. The problem arise with substituting triglyceride mostly associated with (i) higher viscosity; (ii) low stability against oxidation(polymerization reactions); and (iii) low volatility which can be influence the forming of amount of ash due to incomplete combustion (Robles-Medina, 2005). Four ways are identified in order to overcome these problems in biodiesel production.

#### 2.3.1 Direct use and blending

Vegetable oil can be mixed with diesel fuel and can be used directly for running in the diesel engine. The successful experimental blending of vegetable oil with diesel fuel has been done by various researchers. A blend of 95 % filtered used cooking oil and 5 % diesel in 1982 used in a diesel fleet. In 1980, Caterpillar Brazil Company used pre-combustion chamber engines with a mixture of 10 % vegetable oil to maintain total power without any modification to the engine. Thus, a blend of 20 % oil and 80 % diesel was found to be successful and known as B20. Pramanik found that a 50 % blend of Jatropha oil can be used in diesel engines without any major operational difficulties but further study is required to determine the long-term durability of the engine. The direct use of vegetable oils or the use of oil blends have generally been considered to be unsatisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty-acid content, gum formation due to oxidation, polymerization during storage and combustion, carbon deposits and lubricating-oil thickening are the obvious problems.

The use of 100 % vegetable oil was also proven and it require a possible minor modification to the fuel system. There are some major problems that have been associated with the use of pure vegetable oils as fuels in compression ignition engines; it is mainly due to the increased viscosity. Micro-emulsification, pyrolysis and transesterification have been used as remedies to solve these problems encountered due to high fuel viscosity (Ramadhas, 2004).

#### 2.3.2 Microemulsion

Microemulsion is isotropic, clear or translucent, thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called a co surfactant. It is made of vegetable oils with an ester and dispersant (co solvent), or of vegetable oils, an alcohol and a surfactant, with or without diesel fuels. Because of their alcohol contents, microemulsions have lower volumetric heating values than diesel fuels, but these alcohols have high latent heats of vaporization and tend to cool the combustion chamber, which reduces nozzle coking. A microemulsion of methanol with vegetable oils can perform nearly as well as diesel fuels. The use of 2-octanol as an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil has been demonstrated,

the viscosity was reduced to 11.2 Cst at 25 °C. The reported engine tests on a microemulsion consisting of soybean oil: methanol: 2-octanol: cetane improver (52.7: 13.3: 33.3: 1) indicated the accumulation of carbon around the orifices of the injector nozzles and heavy deposits on exhaust valves (Srivasta, 2000)

Jesus et al. introduced a microemulsion used method for the determination of sodium and potassium in biodiesel using a water-in-oil emulsion process for biodiesel production from various and different sources such as soybeans, sunflower oil, animal fat and other vegetable oils. Wellert et al. studied the phase behavior of a microemulsion and a bi-continuous phase was identified using small-angle neutron scattering (SANS) and freeze-fracture electron microscopy (FFEM). The influence of choice of co-surfactant on the structural parameters was also studied.

## 2.3.3 Thermal cracking (Pyrolysis)

Pyrolysis is the conversion of an organic substance into another by means of heat or by no heat in the presence of a catalyst in the absence of air or oxygen. The material used for pyrolysis can be vegetable oils, animal fats, natural fatty acids and methyl ester of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engines. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadienes, aromatics and carboxylic acids (Pramanik, 2008)

## 2.3.4 Transesterification

Transesterification is a reaction process of triglyceride with an alcohol with the presence of catalyst usually acid and alkaline catalyst to produce fatty acid esters and glycerol. This process has been widely used to reduce the high viscosity of triglycerides. Methanol and ethanol widely used because of cheaper price easily dissolve and it can react

quickly compared to other alcohol solvent. A catalyst played along to improve the transesterification process in term of reaction rate and yield product. Normally, alkalinebase catalyst is used in transesterification process for large scale biodiesel production because alkaline metal such as potassium hydroxide, KOH and sodium hydroxide, NaOH are more effective than acid-base catalyzed transesterification process. Figure 2.3 shows the transesterification process of triglycerides with alcohol solvent.

| CH2-OOC-R1                          |   |         | Catalant | R <sub>1</sub> -COO-R' |   | CH2-OH   |
|-------------------------------------|---|---------|----------|------------------------|---|----------|
| CH-OOC-R2                           | + | 3R'OH   | Catalyst | R <sub>2</sub> -COO-R* | + | СН-ОН    |
| CH <sub>2</sub> -OOC-R <sub>3</sub> |   |         |          | R <sub>3</sub> -COO-R' |   | CH2-OH   |
| Glyceride                           |   | Alcohol |          | Esters                 |   | Glycerol |

Figure 2.3: Transesterification process of triglycerides with alcohol.

Source: Xu, G. et al., (2003)

From figure basically the transesterification is a reversible process. It can be either triglyceride convert to diglyceride or shifted diglyceride to triglyceride. Alcohol acts as a solvent and reacting with the vegetable oil and fat oil. As for catalyst it is help to improve reaction rate and yield process.

### 2.4 TRANSESTERIFICATION

### 2.4.1 Reaction and mechanism

In the transesterification process, triglycerides are firstly converted to diglycerides, then monoglycerides and lastly glycerol. Transesterification of triglycerides produce fatty

acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification is described in Figure 2.4, the reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In the presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by alkali.

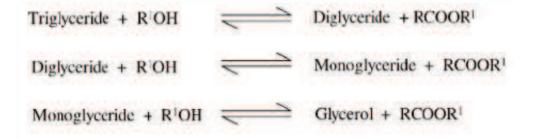


Figure 2.4: General equation for transesterification of triglycerides

Source: Kambiz, T.A. et al., (2011)

The mechanism of alkali catalyzed transesterification is described in Figure 2.5. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step, the rearrangement of the tetrahedral intermediate gives a result to an ester and alcohol.

Pre-step 
$$OH + ROH \iff RO^- + H_2O$$
  
or  $NaOR \iff RO^- + Na^+$ 

Step. 1.  

$$R' - C + RO^{-} \iff R' - C - OR$$

$$OR''$$
Step. 2.  

$$R' - C - OR + ROH \iff O^{-}$$

$$R' - C - OR + RO^{-}$$

$$R' - C - OR + ROH \iff R' - C - OR + RO^{-}$$

$$R' - C - OR + ROH$$
Step. 3.

$$\begin{array}{c} O \\ | \\ R'-C-OR \\ | \\ R"OH^{+} \end{array} R'COOR + R"OH$$

Where R" = 
$$CH_2$$
-  
 $CH_2$ -OCOR'  
 $CH_2$ -OCOR'  
R' = Carbon chain of fatty acid  
R = Alkyl group of alcohol

Figure 2.5: Mechanism of base catalyzed transesterification.

Source : Kambiz, T.A. et al., (2011)

### 2.4.2 Catalyst

There are three type of catalysts used in biodiesel production which are alkaline, acid, and enzyme. Nowadays, enzyme catalyst has become more attractive since it can avoid soap formation and the purification process is simple to accomplish. However, they are less often used commercially because of the reaction times is longer and due to the higher cost. In order to reduce the cost, some researchers developed new biocatalysts in this recent year. The alkaline and acid catalysts are more commonly used in biodiesel production compared to the enzyme catalyst. The alkaline and acid catalyst includes homogeneous and heterogeneous catalyst. Many researchers have been used homogeneous alkaline catalyst such as sodium hydroxide and potassium hydroxide to develop processes for the production of biodiesel from vegetable oils. Due to the low cost, both of these catalysts are most commonly used commercially (Leung, 2010). These materials are the most economic because the alkali-catalyzed transesterification process is carried out under a low temperature and pressure environment, and the conversion rate is high with no intermediate steps. However, the alkali homogeneous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affect the biodiesel yield. Therefore, they should be properly handled. On the other hand, some heterogeneous catalysts are solid and it could be rapidly separated from the product by filtration, which reduces the washing requirement. Besides that, solid heterogeneous catalysts can stimulatingly catalyze the transesterification and esterification reaction and pre-esterification step can be avoids. Thus, these catalysts are particularly useful for those feedstock with high free fatty acid content. However, using a solid catalyst, the reaction proceeds at a slower rate because the reaction mixture constitutes a three-phase system, which, due to diffusion reasons, inhibits the reaction.

#### 2.4.3 Solvent

The alcohol materials that can be used in the transesterification process include methanol, ethanol, propanol, butanol, and amyl alcohol. Among these alcohols, methanol

and ethanol are used most frequently. Methanol is especially used because of its lower cost and its physical and chemical advantages. Methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colorless and odorless. Both methanol and methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that no one exposed to these chemicals during biodiesel production.

#### 2.5 HIGH QUALITY OF BIODIESEL

The major point for biodiesel high quality is the compliance to biodiesel standard specifications. These standard specifications for biodiesel fuel could either be the American standards for testing materials (ASTM 6751) or the European Union (EN 14214). The technologies applied to refine the feedstock and convert it to fatty acid alkyl esters (biodiesel) determine whether the fuel produced will meet the designed specification standards. The quality of biodiesel fuel can be significantly influenced by factors such as : the quality of feedstock and fatty acid composition of the vegetable oils (virgin oils), animal fats and waste oils.

## 2.5.1 Feedstock quality

Raw materials contribute to a major cost of biodiesel production, and are classified into three: vegetable oils, waste cooking oils and animal fats. Vegetable oils can be edible such as cottonseed, groundnut, corn, rapeseed, soybean, palm oil, sunflower, peanut, coconut, etc. and nonedible such as jatropha, pongamia, neem, rubber seed, mahua, silk cotton tree, jojoba, and castor oil. While animal fats may of the following form; tallow, lard, and yellow grease. The degree of refining of the feedstock contributes a lot in the determination of the purity and high yield of biodiesel. Van Gerpen reported that analysis of crude and refined vegetable oils as feedstock in the production of biodiesel indicated yield reduction of methyl esters from 93 % to 98 % for refined oil to 67 % to 86 % for crude oil. This was attributed mostly to the presence of up to 6.66 % free fatty acids in the crude oil. Vegetable oils, animal fats, or greases naturally contains FFAs referred to as saturated or unsaturated mono carboxylic acids but are not attached to glycerol backbones (Sharma, 2009). Higher amount of free fatty acids leads to higher acid value. Vegetable oils should have free fatty acids within a desired limit for homogeneous alkaline catalyzed transesterification reaction to occur, beyond which either the reaction will not take place or the yield will be too low. Michael reported that vegetable oils suitable for use as a feedstock for biodiesel production should have water content lower than 0.06 %. Furthermore, the transesterified product obtained from such oils could be easily refined without much separation and purification difficulties.

### 2.5.2 Fatty acid composition of vegetable oil

Natural vegetable oils and animal fats are processed to obtain crude oil or fat oil. These oils or fats normally contain sterols, phospholipids, free fatty acid, and water, odorants and other contaminants. However, even refined oils and fats contain small of amount of free fatty acid and water. Free fatty acid and water content affect the transesterification reaction of triglycerides and also interfere with the separation and purification of fatty acid alkyl esters from other impurities. Thus, it will affect the quality and yield of the final biodiesel product.

#### 2.6 ADVANTAGES OF BIODIESEL

### 2.6.1 Availability and renewability of biodiesel

Biodiesel is one of the alternative fuels with the property that low concentration biofuel-petroleum fuel blends will run well in unmodified conventional engines. Biodiesel can be made from renewable crops such as palm, soybean, rapeseed and sunflower. Biodiesel is much safer in handling, transporting and storing because of its biodegradability and has a high flash point compared to petroleum diesel fuel. Beside, biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend is a mix of 20 % biodiesel with 80 % petroleum diesel, or B20 in recent scientific investigations; however, for future commercial applications in Europe the current regulation foresees a maximum of 5.75 % biodiesel (Demirbas, 2007).

#### 2.6.2 Lower emissions from biodiesel

The European Transportation Policy for 2010 created by the European White Paper Commission projects an increase in carbon dioxide emissions from vehicles of about 50% from the years 2000 to 2010. The White Paper states that the only way around this problem is to develop clean alternative fuels so that the greenhouse effects can be decreased (Kamaruddin, 2009). Biodiesel mainly emits carbon monoxide, carbon dioxide, and oxides of nitrogen, sulfur oxides and smoke. Combustion of biodiesel alone provides over a 90 % reduction in total unburned hydrocarbons (HC) and a 75 % - 90 % reduction in polycyclic aromatic hydrocarbons (PAHs). Biodiesel further provides significant reductions in particulates and carbon monoxide over petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on engine family and testing procedures (Demirbas, 2007). Currently, global warming caused by CO<sub>2</sub> is the main climatic problem in the world. Therefore, environmental protection is important for the future of the world. Because biodiesel is made from renewable sources, it presents a convenient way to provide fuel while protecting the environment from unwanted emissions. Biodiesel is an ecological and non-hazardous fuel with low emission values, and therefore it is environmentally useful. Using biodiesel as an alternative fuel is a way to minimize global air pollution and in particular reduce the emission levels of potential or probable carcinogens (Canakci, 2009)

Carraretto et al. investigated the emission of unburned hydrocarbons, carbon dioxide, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons and particulate matter from biodiesel; the net emission of  $CO_2$  was considerably lower than that of diesel oil. Kegl stressed the importance of fuel-injection

system to reduce engine emissions as well as fuel consumption. The author suggested that pressure squareness (ratio of mean to maximum injection pressure) should be at a maximum, and fuelling in the first part of the injection should be reduced to reduce NOx emission. Simultaneously, the fuelling in the last part of the injection should be lowered to reduce smoke emissions. Pradeep and Sharma studied the use of hot-exhaust-gas recirculation for the control oxides of nitrogen in a compression– ignition engine fuelled with biodiesel from Jatropha oil. Exhaust-gas recirculation (EGR) was shown to be an effective method for NOx control. The exhaust gases mainly consist of inert carbon dioxide and nitrogen and possess a high specific heat. When recirculated to the engine inlet, they reduce oxygen concentration and act as a heat sink. This process reduces oxygen concentration and peak combustion temperature, which results in reduced NOx. EGR also face a problem. It can significantly increase smoke and fuel consumption and reduce thermal efficiency unless suitably optimized.

#### 2.6.3 Biodegradability of biodiesel

The biodegradability of biodiesel has been proposed as a solution for the waste problem. Biodegradable fuels such as biodiesels have an expanding range of potential applications and are environmentally friendly. Therefore, there is growing interest in degradable diesel fuels that degrade more rapidly than conventional petroleum fuels. Biodiesel is non-toxic and degrades about four times faster than petroleum diesel. Its oxygen content improves the biodegradation process, leading to an increased level of quick biodegradation (Demirbas, 2008). Vegetable-oil methyl esters are reported to be non-toxic and easily biodegradable in an aquatic environment. It was determined that during a 21 days period, 98 % of pure rapeseed oil methyl ester (RME) was biologically decomposed, while only 60 % of pure fossil diesel fuel decomposed. This means that RME fully meets the main requirements of international standards for biological degradation (more than 90 % degraded within 21 days for biofuels) (Makareviciene, 2009). Pasqualino et al. reported more than 98 % degradation of pure biodiesel after 28 days in comparison to 50 % and 56 % for diesel fuel and gasoline respectively. Also, the time taken to reach 50 %

biodegradation was reduced from 28 to 22 days in 5 % biodiesel mixture and from 28 to 16 days in the case of a 20 % biodiesel mixture at room temperature. The biodegradability of the mixture was reported to increase with the addition of biodiesel.

#### 2.6.4 Higher lubricity

Biodiesel has good lubricant properties compared to petroleum diesel oil, in particular very-low-sulfur diesel. This is very important to reduce wear in the engine and the injection system (Carraretto, 2008). Demirbas stated that the oxygen content of biodiesel improves the combustion process and decreases its oxidation potential. The structural oxygen content of a fuel improves combustion efficiency due to the increase of the homogeneity of oxygen with the fuel during combustion. Due to this, the combustion efficiency of biodiesel is much higher than the petroleum diesel, and the combustion efficiency of methanol/ethanol is higher than that of gasoline. The overall injector coking is considerably low when biodiesel fuel used in engine. Biodiesel contains 11% of oxygen by weight and contains no sulfur. The life of diesel engines extended because biodiesel is more lubricated than petroleum diesel fuel. The HHVs of biodiesels 39-41 MJ/kg are slightly lower than that of gasoline at 46 MJ/kg, petroleum diesel at 43 MJ/kg or petroleum at 42 MJ/kg, but higher than coal 32-37 MJ/kg.

### 2.6.5 Engine-performance evaluation using biodiesel

Cetane number (CN) is widely used as a diesel-fuel quality parameter. It is related to the ignition-delay time and combustion quality; a higher CN indicates better ignition properties (Meher, 2006). CN is measured by the ISO 5156 test method. This test method is recommended for diesel and biodiesel and the passing limits are 46 and 51, respectively. However, there are reports of the theoretical estimation of cetane numbers without running extensive engine tests. The cetane number of biodiesel from various sources has been estimated to vary from 48 (grape biodiesel) to 61 (palm biodiesel) (Ramos, 2009). The CN of biodiesel is generally higher than for conventional diesel. The longer the fatty-acid carbon chains and the more saturated the molecules are, the higher the CN is. The CN of biodiesel from animal fats is higher than those of vegetable oils (Bala, 2005). Altin et al. studied a single-cylinder engine fueled with various types of vegetable oils. The results obtained gave a very good comparison of engine performance when various vegetable oils are used as fuel. The engine was operated at 1300 rpm and a torque of 35 Nm. Petroleum diesel fuel performance was used as a reference. The observed maximum torque differences between the reference value and peak values of the vegetable oil fuels were about 10 % with raw sunflower oil, raw soybean oil and opium poppy oil fuels. The maximum power differences between the reference value and peak values of the vegetable-oil fuels were about 18 % with raw cottonseed oil and raw soybean oil. The minimum torque and power difference was about 3 % between the reference value and the oils. These results may be due to the higher viscosity and lower heating values of vegetable oils.

The specific fuel consumption of petroleum diesel was very low in comparison with all vegetable oils and their esters. Specific fuel-consumption values of methyl esters were generally less than those of the raw oil fuels. The higher specific fuel-consumption values of vegetable oils are due to their lower energy contents. Relatively low CO emissions were obtained with the esters in comparison with raw vegetable oils. Maximum CO<sub>2</sub> emissions were about 10.5 % with petroleum diesel fuel and slightly lower with vegetable oil. This was due to the better spraying qualities and more uniform mixture preparation of these esters. NOx emissions with vegetable-oil fuels were lower than those with petroleum diesel fuel and the NOx values of the methyl esters were higher than those of the raw fuels. NOx formation is related to maximum combustion temperature. As the injected particle size of the vegetable oils was greater than with petroleum diesel fuel, the combustion efficiency and maximum combustion temperatures with each of the vegetable oils were lower and NOx emissions were reduced. Smoke-opacity percentages during each of the vegetable-oil operations were greater than that with petroleum diesel fuel. The opacity values of methyl esters were between those of diesel fuel and raw vegetable-oil fuels. The greater smokeopacity percentages of the vegetable-oil fuels were mainly due to the contents of heavier hydrocarbon molecules. Acceleration tests indicated that maximum engine-power output

depended on the biodiesel content in the fuel and decreased as the biodiesel concentration increased. It was observed that with pure biodiesel the acceleration time increased by approximately 8 % compared to the baseline petroleum diesel fuel, while B50 led to an increase of 4.1 %. These differences were expected due to the lower energy content of the blends. Poorer atomization may also explain reductions in maximum engine-power output (Fontaras, 2009).

## 2.7 DISADVANTAGES OF BIODIESEL

The main problem associated with the use of biodiesel, especially which prepared from palm oil, is its poor low-temperature flow properties, measured in terms of cloud point, pour point and CFPP. The low-temperature properties are very critical for the use of biofuels in aviation applications. The low-temperature properties can be improved by blending with biodiesel from unsaturated feedstocks (Sarin, 2007). Other disadvantages of biodiesel are its higher viscosity, lower energy content, higher nitrogen-oxides (NOx) emissions, lower engine speed and power, injector coking, engine compatibility, high price and higher engine wear. The important operating disadvantages of biodiesel while compared with petroleum diesel are includes cold-start problems, the lower energy content, higher copper-strip corrosion and fuel-pumping difficulty due to the higher viscosity. This increases fuel consumption when biodiesel is used, in comparison with pure petroleum diesel and in blends, in direct proportion to the share of the biodiesel content. Taking into account the higher production costs of biodiesel compared to petroleum diesel, this increase in fuel consumption compounds the overall increased cost of application of biodiesel as an alternative to petroleum diesel (West, 2008). As more than 95 % of biodiesel is made from edible oil, the concern about economic problems mostly in agriculture country arise. By converting edible oils into the biodiesel fuel, the food resources not only as a food but also used for automobiles. It is believed that large-scale production of biodiesel from edible oils may bring a global imbalance in the food supply and demand market for automobile fuels.

Recently, environmentalists have published the negative impact on the planet of biodiesel production, especially an impact of deforestation and the destruction of ecosystems. European Environmental Bureau (EEB), claimed that the expansion of oil crop plantations for biodiesel production on a large scale has caused deforestation in countries such as Malaysia, Indonesia and Brazil because more and more forest has been cleared for plantation purposes. Furthermore, the line between food and fuel economies is blurred as both of the fields are competing for the same oil resources. In other words, biodiesel is competing with the food industry for limited land availability for the plantation of oil crops. There has been significant expansion in the plantation of oil crops for biodiesel. Although there is continuous increase in the production of vegetable oil, the blending stocks of vegetable oils are continuously decreasing due to increasing production of biodiesel. Eventually, with the implementation of biodiesel as a substitute fuel for petroleum-derived diesel oil, this may lead to the depletion of edible oil supply worldwide.

#### 2.8 EFFECT ON BIODIESEL YIELD

#### 2.8.1 Alcohol quantity

The researchers recognized that one of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride (Zhang, 2003). Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. The yield of biodiesel is increased when the alcohol triglyceride ratio is raised beyond 3 and reaches a maximum. Further increasing the alcohol recovery (Leung, 2006). In addition, the molar ratio is associated with the type of catalyst used and the molar ratio of alcohol to triglycerides in most investigations is 6:1, with the use of an alkali catalyst (Freedman,

1986). When the percentage of free fatty acids in the oils or fats is high, such as in the case of waste cooking oil, a molar ratio as high as 15:1 is needed when using acid-catalyzed transesterification (Ali, 1995).

#### 2.8.2 Effect of molar ratio

Ramadhas et al. and Sahoo et al. reported 6:1 molar ratio during acid esterification and 9:1 molar ratio (alcohol:oil) during alkaline esterification to be the optimum amount for biodiesel production from high FFA rubber seed oil and polanga seed oil respectively. Sharma and Singh used similar two step transesterification and took 8:1 molar ratio for acid esterification and 9:1 molar ratio for alkaline esterification for optimum yield of biodiesel production from karanja oil. Veljkovic et al. used 18:1 molar ratio during acid esterification and 6:1 molar ratio during alkaline esterification. Meher et al. carried out investigation with 6:1 molar ratio during acid esterification and 12:1 molar ratio during alkaline esterification. Instead of taking molar ratio, Tiwary et al. used volume as a measure of ratio. Tiwary et al. used 0.28v/v (methanol/oil) during acid esterification and 0.16v/v (methanol/oil) during alkaline esterification. Karmee and Chadha used a single step transesterification and have achieved 92% conversion by taking 10:1 molar ratio. The presence of sufficient amount of methanol during the transesterification reaction is essential to break off the glycerine-fatty acid linkages. But excess of methanol should be avoided. Increasing the molar ratio of methanol/oil beyond 6:1 neither increases the product yield nor the ester content, but rather makes the ester recovery process complicated and raised its cost. Leung and Guo suggested that methanol has polar hydroxyl group which can act as an emulsifier causing emulsification. Thus separation of the ester layer from the water layer becomes difficult. Miao and Wu have reported that addition of large quantity of methanol, i.e. 70:1 and 84:1 molar ratio slowed down the separation of the ester and glycerol phases during the production of biodiesel. 56:1 molar ratio was reported to be optimum for transesterification of microalgae oil.

#### 2.8.3 Reaction time

Freedman et al. found that the conversion rate of fatty acid esters increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of < 90 min, and then remains relatively constant with a further increase in the reaction time (Alamu, 2007). Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps (Eevera, 2009).

#### 2.8.4 Reaction temperature

Temperature clearly influences the reaction and yield of the biodiesel product. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. However, Leung and Guo found that when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides. The reaction temperature must be less than the boiling point of alcohol in order to ensure the alcohol will not leak out through vaporization during the process. Usually the optimal reaction temperature for the process carried out of ranges from 50  $^{\circ}$ C to 60  $^{\circ}$ C.

## 2.8.5 Catalyst concentration

Catalyst concentrations affect the yield of the biodiesel product. The most commonly used catalyst for the transesterification process is sodium hydroxide. However, Freedman et al. found that sodium methoxide was more effective than sodium hydroxide because upon mixing sodium hydroxide with methanol a small amount of water will be produced, which will affect the product yield because of the hydrolysis reaction (Guo, 2008). This is the reason why the catalyst should be added into the methanol first and then mixed with the oil. As the catalyst concentration increases the conversion of triglyceride, the yield of biodiesel also will increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters (Leung, 2006). Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt % and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap (Eevera, 2009).

#### 2.9 **BIODIESEL AS AN ENGINE FUEL**

Biodiesel is an important alternative vehicular fuel. It has excellent properties as diesel engine fuel, so it can be used in compression-ignition diesel engines (Maria, 2008). Biodiesel can be derived from several different vegetable oils or animal fats feedstock. Vegetable oil and animal fat direct use as fuel in diesel engines is limited due to two main factors, low volatility and high viscosity (Boey, 2009). Traditional processing involves an alkali-catalyzed process, but this process is difficult for lower cost high free fatty acid feedstock due to soap formation. Pretreatment of the feedstock with high free fatty acid using strong homogeneous acid catalysts such as sulfuric acid have been shown to provide reasonable conversion rate, higher yields and high quality biodiesel final products. These technologies have played a vital role in ensuring the production of biodiesel from feedstock like soap-stock that are normally regarded as waste. Biodiesel is now mainly being produced from rapeseed, cottonseed, soybean, canola and palm oils (Peigang, 2008). Demirbas stated that the HHV of biodiesels are relatively high. The values of HHVs of biodiesels ranged from 39 to 41 MJ/kg. Ejaz and Younis reviewed biodiesel as vehicular fuel. The authors concluded that almost all types of vegetable oils can be used to replace the diesel oil; however the rapeseed oil and palm oil can be the most suitable vegetable oils which can be used as diesel fuel, additive or diesel fuel extender.

Biodiesel termed as clean fuel and its sulfur content level is also lower than its content in petro-diesel. The ability of biodegradable and its superb lubricating property when used in compression ignition engines makes it to be an excellent fuel. Also its renewability and similarities in physicochemical properties to petro-diesel, revealed its potentials and practical usability as fuel for the replacement of petro-diesel in the nearest future. Kegl reported that few other physical and chemical properties of biodiesel fuel are of great concern and require to be enhanced to make it fit for use in clean form (i.e. 100 % biodiesel). These properties include among others; engine power, increase in calorific value, reduced emission of nitrogen oxides (NOx), and low temperature properties improvement. Demirbas reported that methyl esters improve the lubrication properties of the diesel fuel blend. Biodiesel decrease long term engine wear in compression ignition engines. Biodiesel is a good lubricant and is about 66 % better than petro-diesel. Its oxidation stability improvement is also important to prevent it from deteriorating when stored over time. Currently biodiesel is compatible in blended form with petro-diesel in the ratio 20 (biodiesel): 80 (mineral diesel). Biodiesel has also being in use in many countries such as United States of America, Malaysia, Indonesia, Brazil, Germany, France, Italy and other European nations (Fangrui, 1998). Biodiesel could only be successfully used in compression-ignition diesel engines, if its physical and chemical properties meet the standard of international standard specifications of biodiesel. These standards (ASTM 6571, EN 14214) describe the minimum requirement that must be met before biodiesel is used as a pure fuel or blended with petroleum based diesel fuel.

Biodiesel fuels are characterized by their cetane number, density, viscosity, cloud and pour points, flash point, copper corrosion, ash content, distillation range, sulfur content, carbon residue, acid value, free glycerine content, total glycerine content and higher heating value (HHV), etc. The viscosity values of vegetable oils decreases sharply after transesterification reaction (Sharma, 2008). Demirbas stated that the flash point values of fatty acid methyl esters are significantly lower than those of vegetable oils. The author reported high regression between the density and viscosity values of vegetable oil methyl esters and a considerable regular relationship between viscosity and flash point of vegetable oil methyl esters. The relatively higher flash point of biodiesel to petro-diesel makes it a safer fuel to use, handle and store. Dube et al. stated that biodiesel is an ideal fuel for use in sensitive environments, such as marine areas, national parks and forests, and heavily polluted cities for its relatively low emission profile.

## 2.9.1 Physicochemical properties of biodiesel fuels

The physicochemical properties of biodiesel are similar to those of petro-diesel fuels. Viscosity is on of the important property of biodiesel fuels since it has tremendous effects on the operation of fuel injection equipment, particularly at lower temperatures where an increase in viscosity affects the fluidity of the fuel. Higher viscosity leads to poorer atomization of the fuel spray an affects the accuracy of the operation of fuel injectors. However, the lower the viscosity of the biodiesel, the easier it is to pump, atomizes and achieves finer droplets (Islam, 2004). Saka and Isayama revealed kinematic viscosity to be an index which measures fuel stickiness, better viscosity values inhibit nebulization of fuel in the ignition chamber, poor values hamper the engine lubrication effects, hence, the viscosity values of the biodiesel must be kept within the stipulation range of international standard specification. Transesterification reaction converts triglycerides into methyl or ethyl esters and reduces the molecular weight to one third that of the triglyceride and decreases the viscosity of vegetable oils by a factor of about eight (Demirbas, 2009). Virgin and waste vegetable oils can be used as fuel for compression ignition engines, but their viscosity is much higher than that of common diesel fuels and this requires major diesel engines modifications. Gunvachai et al. reported the burning of vegetable oils in diesel engines is not clean resulting to the formation of wanted materials such as acrolein and organic acid. These materials effect on the performance and longitudinal engine durability. However vegetable oils can be converted into their fatty acid methyl esters by transesterification reaction and can be convertibly used as fuels for diesel engine applications without major modifications (Demirbas, 2009).

## 2.9.2 Biodegradability of biodiesel

Biodegradability of biodiesel has been considered to be a solution for waste accumulation leading to environmental pollution. Demirbas stated that biodegradable fuels such as biodiesels have a wide range of potential applications and they are environmentally friendly. The author revealed that there is growing interest in degradable diesel fuels that degrade faster than the traditional disposable fuels. Biodiesel is nontoxic and degrades about four times faster than petro-diesel. Also the oxygen content in biodiesel improves the biodegradation process. Ferella et al. reported that biodiesel highly biodegradable in soil and also in fresh water. It stated that under either aerobic or anaerobic prevailing conditions the most important part of biodiesel is degraded within 21-28 days. Tian et al. reported that biodiesel biodegradability provides numerous positive contributions to the environment. Prafulla and Shuguang reported biodiesel to be better than petro-diesel in terms biodegradability, free sulfur content, viscosity, density, flash point and aromatic content.

#### 2.9.3 Higher lubricity

Lapuerta et al. reported that fatty acid alkyl esters (biodiesel) have improved lubrication characteristics, but they can contribute to the formation of deposits, plugging of filters, depending mainly on degradability, glycerol (and other impurities) content, cold flow properties, etc. The lubrication property help in improving the fuel injectors and fuel pumps lubrication capacity. Using biodiesel in diesel engine will reduced long term engine wear in test diesel engines to less than half of what was observed in engines running on current low sulfur diesel fuels. Demirbas stated that biodiesel provides significant lubricity improvement over petro-diesel fuel. Lubricity results of biodiesel and petro-diesel using the industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. It is reported that even biodiesel levels below 1 % can provide up to a 30 % increase in the lubricity.

## 2.9.4 Stability of biodiesel

The oxidation and polymerization of biodiesel fuel during combustion and storage is a major concern in terms of the quality of biodiesel. These problems lead biodiesel fuel to become acidic, form undissolvable gum and sediments that can plug the fuel filters. However, oxidation and polymerization occurs due to the presence of unsaturated fatty acid chains and the double bond in the parent molecule, which immediately react with the oxygen as soon as it is being exposed to air. Kapilan et al. reported that oxidation of fatty acid chains is a complex process that is followed by a variety of mechanisms. This oxidation process of biodiesel is influenced by several factors including; light, temperature, extraneous materials, peroxides, size of the surface area between biodiesel and air. The authors stated that one of the methods of improving biodiesel oxidative stability includes the deliberate addition of antioxidants or modification of the fatty ester profile.

#### 2.9.5 Lower emissions of biodiesel

The use of millions of vehicles across the globe especially in big cities and towns contribute a lot in generating gaseous emissions, hence polluting the environment. These emissions referred to as green house gases are attributed to the cause of global warming. Green house gases such as carbon-dioxide, carbon monoxide, nitrogen oxide, and sulfur causes climatic distraction resulting in drought and environmental adversities on both fauna and flora. Demirbas stated that commercial biodiesel fuel has significantly reduced exhaust emissions 75 % - 83 % compared to petrodiesel based fuels. Helwani et al. reviewed the technologies for production of biodiesel focusing on green catalytic techniques. The authors reported that combustion of neat biodiesel decreases CO emissions by 46.7 %, particulate matter emissions by 66.7 % and unburned hydrocarbons by 45.2 %. In addition, biodiesel is non-toxic, making it useful for transportation applications in highly sensitive environments, such as marine ecosystems and mining enclosures. Syed et al. reviewed the emission characteristics of biodiesel fuels. The authors revealed the works of many researchers and

scientists to agree with the emission reduction from the used of biodiesel compared to petrodiesel fuels.

## 2.9.6 Performance of biodiesel

Demirbas reviewed some performance parameter such as brake thermal efficiencies, torque, fuel consumption and power output of biodiesel fuels. Biodiesel are mono-alkyl esters containing approximately 10 % oxygen by weight. The author reported that oxygen improves the efficiency of combustion, but it cover up space in the blend and consequencely increases the apparent fuel consumption rate observed while operating an engine with biodiesel. The brake thermal efficiency was found to be better in the dual fuel operation and with the methyl ester of Jatropha oil as compared to the blend. It is increased from 27.4 % with neat Jatropha oil to a maximum of 29 % with the methyl ester and 28.7 % in the dual fuel operation. Michael et al. showed 18 % increases when pure biodiesel from soap-stock and soybean oil were used. These increases are presumably more than the loss of heating value, unless the ester content of biodiesel was unusually low. Various engine performance parameters such as thermal efficiency, brake specific fuel consumption (BSFC), and brake specific energy consumption (BSEC) can be calculated from the acquired data. The torque, brake power and fuel consumption values associated with CIE fuels were determined under certain operating conditions (Demirbas, 2009).

Bettis et al. studied the use of sunflower, safflower and rapeseed oils as liquid fuels. It is revealed that the compression engine power output of the fuels is similar to that of diesel fuel, but envisaged long-term durability severe problems due to effects of carbonization. The comparison between sunflower-oil biodiesel and diesel fuels at full and partial loads and at different engine speeds in a 2.5153 kW engine were conducted by Kapilan. It stated that the used of biodiesel in diesel engine results in a slight reduction in brake power and a slight increase in fuel consumption. However, the lubricant properties of the biodiesel are better than diesel, which can help to increase the engine life. Also, the exhaust emission of the biodiesel is lower than the neat diesel operation due to the presence

of oxygen in the molecular structure of the biodiesel. Moreover, the biodiesel fuel is environmentally friendly, because biodiesel does not produce SOx and also there is no increase in  $CO_2$  emission at global level. Usta et al. used biodiesel from tobacco seed oil to show an increase in torque and power (with a lower heating value of 39.8 MJ/kg). The author conducted several experimental blends with diesel fuel in an indirect injection diesel engine at 1500 and 3000 rpm. Maximum values of torque and power were recorded with a 17.5 % blend, inspite of reduced heating value of biodiesel.

While, Lapuerta et al. reported a test of 4.5 liter engine with different oxidized soybean oil biodiesel fuels. The increase in brake specific fuel consumption (BSFC) with pure biodiesel was 15.1 % in the case of oxidized biodiesel (with a peroxide index of 340 meq/kg) and 13.8 % in the case of non-oxidized biodiesel. They attributed this difference to the different heating value of both biodiesel fuels. Agarwal and Das conducted different blends on linseed-oil biodiesel with high sulfur diesel fuel in single cylinder 4 kW portable diesel engines generally used in the agricultural sector and thermal efficiency increases were recorded, especially at low load. On the other hand, Lin et al. recorded a decrease in efficiency when palm-oil biodiesel, pure and in 20 % blends, were used in a 2.8 liter indirect injection engine, although the small differences (< 2.3% in all cases) might be significant to be considered. The authors also reported increases in energy consumption. Kaplan et al. revealed the loss of torque and power ranged between 5 % and 10 %, and particularly at full load, the loss of power was closer to 5 % at low speed and to 10 % at high speed.

## 2.9.7 Biodiesel higher combustion efficiency

The oxygen content of biodiesel improves and facilitates the combustion process and decreases its oxidation potential. Demirbas reported that the structural oxygen content of a fuel enhances its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Beside, the combustion efficiency of biodiesel is higher than that of petro-diesel, and the combustion efficiency of methanol/ethanol is higher than that of gasoline and the overall injector coking is considerably low. The author also stated that visual inspection of the injector types would indicate no difference between biodiesel fuels and petro-diesel in testing. Charles and Todd concluded that complete combustion converts hydrocarbon fuels to carbon-dioxide and water. Diesel fuel represented by  $C_{16}H_{34}$  releases 3.11 kg of  $CO_2$  per kilogram of fuel used in combustion. Biodiesel represented by  $C_{22}H_{43}O_2$  releases 2.86 kg of  $CO_2$  per kilogram of fuel used in combustion. Incomplete combustion can result in small amounts of other compounds such as carbon monoxide and aldehydes which eventually also degrade into carbon-dioxide. Peterson et al. reported that carbon-dioxide ( $CO_2$ ) emissions are significantly lower with biodiesel fuels compared to non-renewable diesel fuels. While, Syed et al. reviewed different combustion characteristics such as ignition delay, ignition temperature, and spray penetration of different biodiesel fuels.

# **CHAPTER 3**

# METHODOLOGY

# 3.1 INTRODUCTION

There are several methods in producing biodiesel. The most common and preferred method is transesterification process with aid of catalyst. In this experiment, single step transesterification was conducted with aid of Sodium Methoxide as a catalyst. Figure 3.1 shows the diagram of experiment methodology. The experiment methodology consists of five basic steps which are:

- i. Raw material preparation
- ii. Equipment selection
- iii. Design of experiment
- iv. Experimental procedure
  - a. Pre-treatment
  - b. Transesterification process
  - c. Settling
  - d. Washing and methanol recovery
- v. Sample analysis

# **3.2 FLOW CHART OF EXPERIMENT METHODOLOGY**

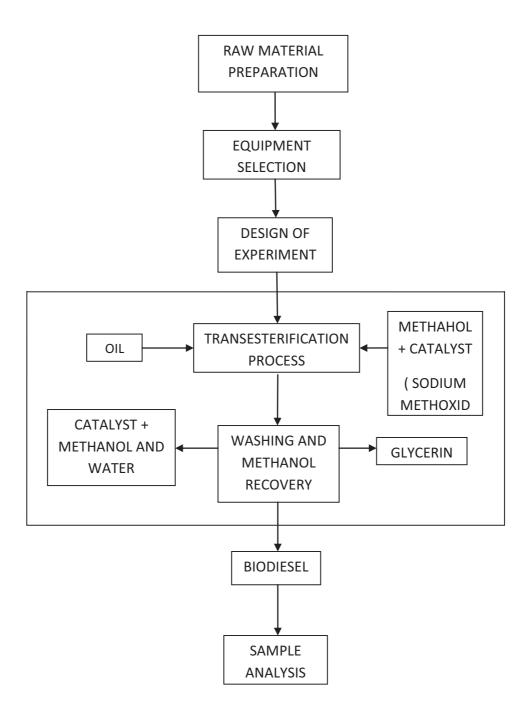


Figure 3.1: Flow chart of experiment methodology.

# 3.3 RAW MATERIAL PREPARATION

## 3.3.1 Material

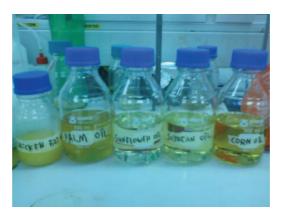


Figure 3.2: Feedstocks

Figure 3.2 shows different feedstock for biodiesel extraction process. From the left are chicken fat oil, palm oil, sunflower oil, soybean oil and corn oil. Chicken fat oil does not available in a store. The extraction process from chicken fat itself is needed in order to get the chicken fat oil. While for the palm oil, sunflower oil, soybean oil and corn oil, they are available in a market. Waste cooking oil can be found in the cafeteria kitchen, waste palm oil that been used atleast three times were used for the biodiesel extraction. In this experiment, 1 liter each of oil is prepared for the transesterification process. As can be seen in figure 3.2, the chicken fat has unclear yellow in color and has some contaminants. Sunflower oil has the clearest light yellow, while soybean has light yellow but darker compared to sunflower. Palm oil and corn oil has the darker yellow color but more clear compared to chicken fat oil.

## 3.3.2 Chemical



Figure 3.3: Fisher Scientific methanol solvent and Sigma-Aldrich sodium methoxide catalyst.

Figure 3.3 shows the methanol solvent, CH<sub>3</sub>OH and sodium methoxide catalyst, CH<sub>3</sub>NaO that were used in this experiment. Methanol and ethanol are used most frequently as a solvent for transesterification process. Methanol is used because of its lower cost and its physical and chemical advantages. Methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colorless and odorless. Both methanol and sodium methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that one is not exposed to these chemicals during transesterification of biodiesel. Usually potassium hydroxide, KOH and sodium hydroxide, NaOH is used as a catalyst for alkali catalyzed transesterification. It is due to the low cost of KOH and NaOH. Sodium methoxide is another choice for catalyst. The CH<sub>3</sub>NaO react faster that KOH and NaOH. It is extremely hazardous material that should be handled carefully. Futhermore, CH<sub>3</sub>NaO give a better yield and react faster than other alkaline catalyst.

# **3.4 EQUIPMENT AND APPARATUS SELECTION.**

There are many equipment involve in a process of making a biodiesel. These are includes:

- i. Beaker
- ii. Thermometer
- iii. Hot plate
- iv. Weighting scale
- v. Seperator funnel

#### **3.5 DESIGN OF EXPERIMENT**

The experiment was conducted in a room temperature. There are six differents feedstock which are palm oil, corn oil, sunflower oil, soybean oil, waste cooking oil and chicken fat oil. The type of extraction process is alkali base catalyzed transesterification, using 3:1 methanol to oil ratio, the catalyst is 1.5 wt. %. The reaction time is about 30 minutes and the settling time is up to 1 hour. The solvent used is methyl alcohol and the catalyst used is sodium methoxide,  $CH_3NaO$ .

## **3.6 EXPERIMENT PROCEDURE**

## 3.6.1 Feedstock preparation

In this step, the pure virgin oils were prepared. The palm oil, corn oil, sunflower oil and soybean oil can be found in a store. While for waste cooking oil, the palm oil that been used for 3 times were used in this transesterification process. For getting chicken fat oil, the extraction process from chicken fat itself has been done.

## **3.6.2 Transesterification Process**

In this step, the transesterification process was carried out in a room with temperature 27 °C. Firstly, the virgin oil was heated up to 70 °C on the hot plate. While, 1.5 wt% sodium methoxide mixed with methanol and heated up to 70 °C. The methanol to oil ratio used is 3: 1. After that, mixed up the two solutions and keep the heat up to 70 °C. Use a magnetic stirrer to ensure the solution mix up well. The thermometer attached to ensure the temperature is not above 70 °C. Aluminium foil used as a beaker wrapper so that the methanol is not vaporized outside. Then, left the solution up to 30 minutes and do not let the guard off.

## **3.6.3 Settling Process**



Figure 3.4: Settling process

Figure 3.4 shows the solution separated in a separator funnel. After the transesterification process, the mixture is transferred into a separator funnel for settling and separation and left for 8hours for settling to form a two layer or three layer separation. The glycerin is much dense compare to biodiesel phase and it can be separated by gravity

settling. If the mixture contains two layers formation, the upper layer is a FAME (Fatty Acid Methyl Esters) or crude biodiesel with lighter yellow colors while the lower layer is a glycerin with darker yellow colors. If there are three layers, the middle of two layers is emulsion which is in liquid phase and white in colors. The bottom layer which is glycerin was taken out because it is soap while the upper layer is crude biodiesel transferred out into another beaker for further process. It is recommended that the settling process is conduct in a place with temperature 25 °C to 30 °C to avoid the glycerin become jelly under the temperature 20 °C.

#### **3.6.4 Washing and Methanol Recovery**



Figure 3.5: Rotary evaporator

Figure 3.5 shows the rotary evaporator that used to remove the excess methanol in the biodiesel. After settling process is finished, the crude biodiesel will be transferred into a rotary evaporator for methanol recovery process. Here, the excess methanol during the transesterification process will be recovered in a vacuum at the temperature 70 °C. Then, the crude biodiesel was washed with water at 80 °C by slowly pouring hot water into crude biodiesel solution to remove remaining methanol, catalyst and glycerin. This washing step repeat for three times to ensure the crude biodiesel is freed from contaminant. After that,

the solution was heated at 100 °C to remove excess water and florisil was added to solution in order to get the clear crude biodiesel. Then, the crude biodiesel was filtered using filter paper to remove remaining solid, impurities and contaminant in the solution. The crude biodiesel was ready to next step, which is physical properties analysis.

## 3.7 ANALYSIS

There are six physical properties of crude biodiesel that needed to be analyzed which are the density, the viscosity, cetane number, flash point, cloud point and pour point. All of six of crude biodiesel extracted oil were undergoing these analyses.

# 3.7.1 Density

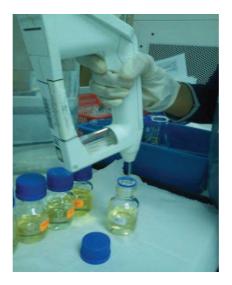


Figure 3.6: Mettler Toledo portable density meter

Figure 3.6 shows the density meter to measure the density each of biodiesel oil. The density meter used is Mettler Toledo. Biodiesel is sucked into the portable density meter by pressing the suction button. It is necessarily to ensure there is no bubble in the tube. After that, the measurement value of density appeared on the screen.

## 3.7.2 Viscosity



Figure 3.7: Cole-Parmer Viscometer

Figure 3.7 shows the viscometer to measure the viscosity of biodiesel oil. The viscometer used is Cole-Parmer Viscometer, Polystat® economical constant temperature bath, 120 VAC. Viscometer functioned to measure kinematic viscosity and viscosity of solution. There are two bulbs at capillary tube. The liquid sucked into the top bulb by suction pump. Both of bulbs have measurement mark level. When the liquid drop from top bulb, point 1 and reach the bottom bulb at the marked level point 2, the time was taken as can be seen in figure 3.8.

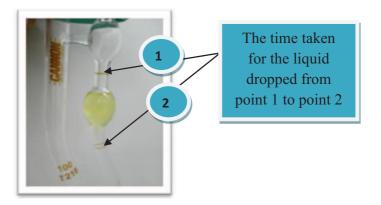


Figure 3.8: Mark level for time to drop from point 1 to 2

## 3.7.3 Cetane Number



Figure 3.9: SHATOX octane/cetane analyzer

Figure 3.9 shows the octane/cetane analyzer to measure the cetane number of biodiesel oil. The octane meter used is SHATOX octane/cetane analyzer. This analyzer can measure octane or cetane number by pouring the fuel into the cylinder metal detector about 5-20 millilitres. The function key can be choosed whether to measure cetane or octane number. The value of octane/cetane will be displayed on the screen.

## 3.7.4 Flash Point



Figure 3.10: Petrotest Flash Point & Auto ignition tester

Figure 3.10 shows the flash point tester to measure the flash point of biodiesel oil. The flash point tester used is Petrotest Flash Point & Auto ignition tester. The flash point tester used either open or closed cup. In this experiment, the closed cup is used. The test cup is filled with a fuel and the cover is fitted. The fuel was heated until the spark is flashed, and the spark appeared indicate the flash point of the fuel. The temperature at which the spark ignites was recorded.

## **3.7.5 Cloud Point and Pour Point**



Figure 3.11: Koehler K46100 Cloud Point & Pour Point Bath Apparatus

Figure 3.11 shows the cloud and pour point tester to. Koehler K46100 Cloud Point & Pour Point Bath Apparatus is used in this experiment. The fuel sample was put into the chamber. Three set point temperatures were used. The formation of crystallization in the sample fuel is observed. After the cloud point recorded, pour point process took place. If the sample is no longer crystallized in first point temperature, the process moved to second set point until fully crystallization of sample formed.

# 3.7.6 Acid Value



Figure 3.12: Mettler Toledo Titrator

Figure 3.12 shows the acid value tester. It is to measured the acid contain in biodiesel oil. The Mettler Toledo Titrator is used in this experiment. The potentiometer titrated is on for the dilution of mixtures fuel with an ethanol. After the mixture is diluted, the start button is pressed to get the result of acid number.

# **CHAPTER 4**

# **RESULT AND DISCUSSION**

# 4.1 INTRODUCTION

Table below shows the result of six biodiesel fuel properties that collected during experiment. There are seven physical properties that have been analyzed which are density, viscosity, cetane number, flash point, cloud point, pour point and acid value.

| Property   | Unit    | Palm   | Corn  | Chicken fat | Soybean | Sunflower | WCO    |
|------------|---------|--------|-------|-------------|---------|-----------|--------|
|            |         |        |       |             | •       |           | WCO    |
| Density    | kg/L    | 0.874  | 0.884 | 0.877       | 0.886   | 0.887     | 0.878  |
| Kinematic  |         |        |       |             |         |           |        |
| Viscosity  | Cst     | 3.9192 | 3.796 | 4.1445      | 4.031   | 4.046     | 4.4727 |
| Cetane     |         |        |       |             |         |           |        |
| Number     |         | 60     | 39    | 54          | 42      | 36        | 46     |
| Flash      |         |        |       |             |         |           |        |
| Point      | °C      | 150    | 260   | 165         | 238     | 160       | 178    |
| Cloud      |         |        |       |             |         |           |        |
| Point      | °C      | 14     | -2    | 10          | -1      | 2         | -4     |
| Pour Point | °C      | 10     | -12   | 7           | -3      | -3        | -9     |
| Acid       |         |        |       |             |         |           |        |
| Value      | mgKOH/g | 0.05   | 0.15  | 0.3         | 0.21    | 0.18      | 0.27   |

| Table 4.1: Result of | different feedstocl | k fuel properties |
|----------------------|---------------------|-------------------|
|----------------------|---------------------|-------------------|

## 4.2 DENSITY

Density is defined as mass per unit volume. The less dense fluids float on denser fluids. In these cases, the denser oil contains more energy. For comparison, petrol and diesel give comparable energy by weight but diesel is denser and hence gives more energy per liter than petrol. Higher density of biodiesel could affect the volatilization and atomization processes, and further deteriorate combustion in chamber. This viewpoint was applied to the explanation of the increased PM emissions for B100 fuels in (Aydin, 2010)

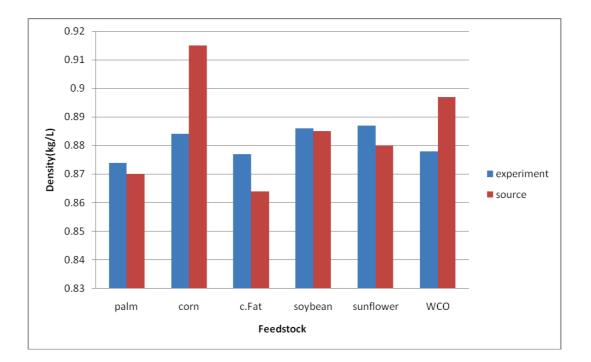


Figure 4.1: Graph of biodiesel density for different feedstock

Sources: Palm,(Demirbas, 2005), Corn, (Leung, 2010), Chicken fat,(Krones et al., 2008), Soybean, (Demirbas, 2005), Sunflower, (Demirbas, 2005), WCO, (Demirbas, 2009) Figure 4.1 shows the result of density for six different biodiesel. Palm has the lowest density compare to others biodiesel feedstock. While sunflower has highest density of 0.887 kg/L. Each of feedstock density was compared with other density from various literature reviews. Corn with 0.884kg/L density has greater difference with literature may be because of the experiment taken in a different place. Density is an important key fuel property that directly affects the performance of engine. The performance characteristics such as cetane number are related to density (Van Gerpen, 2000). Besides that, diesel fuel injection systems measure the fuel by volume. So the changes in the fuel density will influence engine output due to the different mass of fuel injected (Bahadur, 1995).

#### 4.3 VISCOSITY

Viscosity is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another. It will affect the atomization of a fuel while injection onto combustion chamber inside engine whereby affects the formation of engine deposits on the engine wall (Knothe, 2005). High viscosity leads to poorer atomization of fuel spray injection and consequently affects the accuracy of fuel injector. The poorer atomization of fuel gives the poor mixing of fuel and air inside the engine chamber result the longer ignition delay. Thus, the combustion of air-fuel mixing will be slower. The slower combustion will lead to low injection pressure of engine operation and produces higher brake specific fuel consumption (BSFC) due to power losses and fuel impingement (Montgomery, 2001). However, some author found that higher viscosity of biodiesel enhances the fuel spray penetration, and thus improves air-fuel mixing, is used to explain the recovery in torque and power (Lin, 2009). The lower the viscosity, the easier it is to pump, atomizes and achieves the finer droplets (Islam, 2004). The transesterification process that convert the triglyceride bond into methyl esters reduces the molecular weight of biodiesel to the one third of triglyceride and reduces the viscosity by factor about eight (Demirbas, 2008). Ozsezen et al. stated that advance of start of injection of biodiesel due to the higher density and viscosity and the lower compressibility prolong the residence time of soot particle in the high temperature environment, and thus further promote the oxidation in the presence of oxygen (Cardone, 2002).

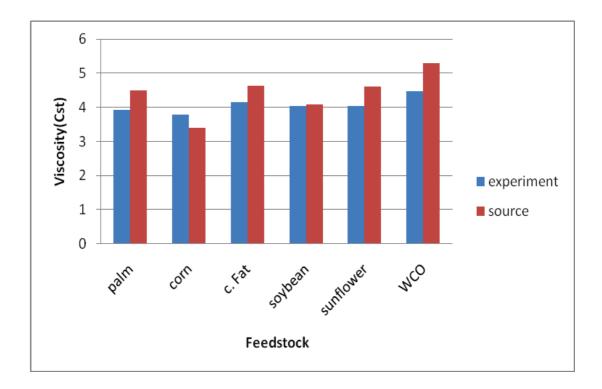


Figure 4.2: Graph of biodiesel viscosity for different feedstock

Sources: Palm, (Masjuki et al., 2009), Corn, (Leung, 2010), Chicken fat,(Krones et al., 2008), Soybean, (Demirbas, 2005), Sunflower, (Acaroglu et al., 2005), WCO, (Demirbas, 2009)

From figure 4.2, it shows that corn has the lowest viscosity. Palm is second lower in viscosity while waste cooking oil has the highest viscosity. It can be concluded that corn is the most suitable as a biodiesel fuel to run the engine vehicle in term of viscosity parameter. But, as long as the viscosity of the biodiesel is in the range of standard viscosity for neat biodiesel B100, that considered as quite good.

# 4.4 CETANE NUMBER

Cetane number is widely used as a diesel-fuel quality parameter. It is related to the ignition-delay time and combustion quality. The higher cetane number indicates the better ignition properties (Meher, 2006). Cetane number is measured by the ISO 5156 test method. This test method is recommended for diesel and biodiesel and the passing limits are 46 and 51, respectively (Ramos, 2009). The cetane number of biodiesel is generally higher than for conventional diesel. The longer the fatty-acid carbon chains and the more saturated the molecules are, the higher the cetane number. The cetane number of biodiesel from animal fats is higher than those of vegetable oils (Bala, 2005). The higher the cetane numbers, the better the fuel property. Inversely for low cetane number, the ignition properties would be poorer. Fuels with low cetane number can cause difficulty in initial starting of engines in cold weather. Advance in combustion for biodiesel, as a result of the higher cetane number. As for the effect of cetane number of biodiesel, Yoshiyuki showed that reducing cetane number would result in the decrease of particulate at high load. It was reported by Kidoguchi et al. that fuels with longer ignition delay by keeping the aromatic content constant, exhibited lower particulate emissions and higher NOx at high loads. However, it is believed that this effect is small.

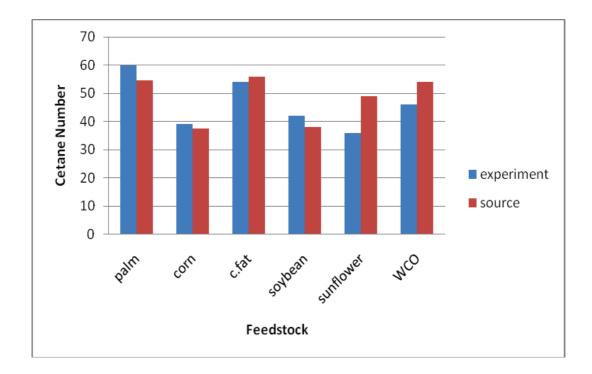


Figure 4.3: Graph of biodiesel cetane number for different feedstock

Sources: Palm, (Masjuki et al., 2009), Corn, (Demirbas, 2005), Chicken fat,(Krones et al., 2008), Soybean, (Demirbas, 2005), Sunflower, (Acaroglu et al., 2005), WCO, (Demirbas, 2009)

Figure 4.3 above shows the result of cetane number for different feedstock. Palm has higher cetane number which is 60. It is because the fatty acid carbon chain of palm is longer than other feedstock. Following by chicken fat oil with 54, waste cooking oil 46, soybean oil 42 and corn oil with 39. Sunflower oil has the lowest cetane number which is 36.

# 4.5 FLASH POINT

Flash point is a property that determines the flammability of a fuel. The flash point is the lowest temperature at which the applied ignition will cause the vapor of sample to ignite. Therefore, it is a measure of the tendency of a sample to form a flammable mixture with air. The value of the flash point is used for the classification of flammable and combustible material needed for safety and shipping regulation. The standard for measuring the flash point for diesel and biodiesel fuel is ASTM D93. B100's typical flash point is 200°C, classifying it as non-flammable. Dube et al. stated that biodiesel is an ideal fuel for use in sensitive environments, such as marine areas, national parks and forests, and heavily polluted cities for its relatively low emission profile.

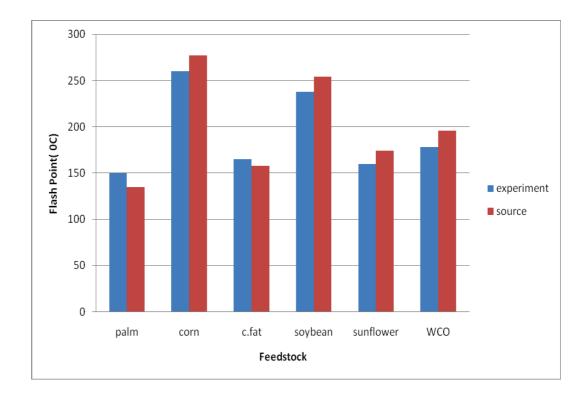
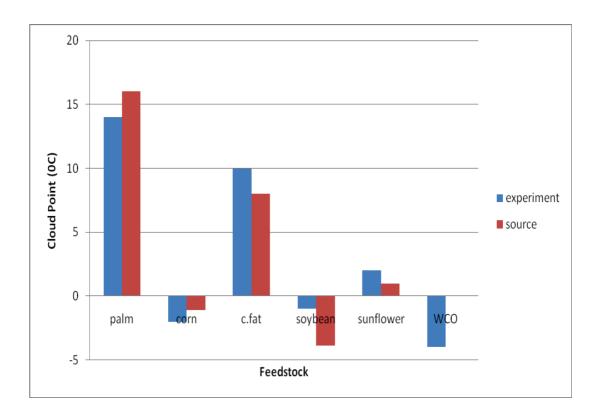


Figure 4.4: Graph of biodiesel flash point for different feedstock

# Sources: Palm, (Masjuki et al., 2009), Corn, (Demirbas, 2005), Chicken fat,(Cramer et al., 2009), Soybean, (Demirbas, 2005), Sunflower, (Demirbas, 2005), WCO, (Demirbas, 2009)

Figure 4.4 shows the result of flash point for each feedstock in this experiment. Corn oil has the highest flash point compare to other biodiesel oil. It is indicated that corn oil has the highest safety handling compared to others. While palm oil has the lowest flash point, it is easier to burn and needed more safety in handling.



#### 4.6 CLOUD POINT

Figure 4.5: Graph of biodiesel cloud point for different feedstock

Sources: Palm, (Masjuki et al., 2009), Corn, (Goering et al., 1982), Chicken fat, (Kambiz, T.A. et al., 2011) et al., 2011), Soybean, (Goering et al., 1982), Sunflower, (Antolin et al., 2001)

Figure 4.5 shows the result of cloud point in this experiment and compared with some from literature. Cloud point is a fuel property that is important for the operability of diesel fuel in a low temperature. It is critical factor in cold weather performance. Cloud point is the temperature at which a cloud of wax crystals first appear when the fuel is cooled. Thus, cloud point is an index of lowest temperature of the fuel's utility under certain application. Operating at temperatures below the cloud point can result in the fuel filter clogging due to the wax crystals. Biodiesel fuel typically has higher cloud point, means that the crystals begin to form at higher temperature compared to standard diesel fuel. This feature has implication for biodiesel in cold weather performance. From figure above, palm has the highest cloud point while waste cooking oil has the lowest cloud point. Corn oil and soybean has minus degree Celsius in temperature. It can be concluded that palm oil is not suitable to use in cold weather country, while corn oil, soybean oil and waste cooking oil can be used as commercial fuel in cold weather country.

# 4.7 POUR POINT

Pour point is a second measurement of low temperature performance after the cloud point. The pour point is the lowest temperature at which the fuel sample will flow. It is temperature at which the amount of wax from a solution is sufficient to gel the fuel. Pour point also influenced the fuel in cold weather performance. The standard procedure for measuring the pour point of fuel is ASTM D97.

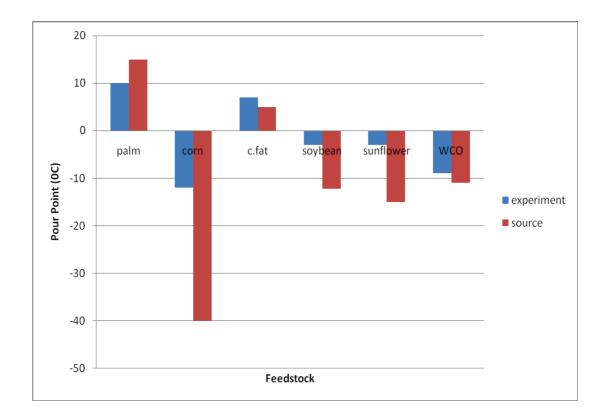


Figure 4.6: Graph of biodiesel pour point for different feedstock

Sources: Palm, (Gui et al., 2008), Corn, (Goering et al., 1982), Chicken fat, (Kambiz, T.A. et al., 2011), Soybean, (Goering et al., 1982), Sunflower, (Goering et al., 1982), WCO, (Demirbas, 2009)

Figure 4.6 show that the palm oil has the highest pour point which is 10°C. Palm oil and chicken fat oil has temperature above 0°C. Corn oil, soybean oil, sunflower oil and waste cooking oil have minus degree celsius in temperature. Thus, corn oil, soybean oil, sunflower oil and waste cooking oil give a better performance in weather performance because their ability to gel the fuel at lowers temperature.

## 4.8 ACID VALUE

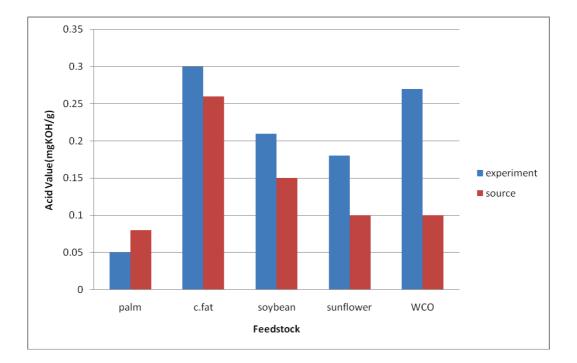


Figure 4.7: Graph of biodiesel acid value for different feedstock

Sources: Palm, (Gui et al., 2008), Corn, (Cramer et al., 2009), Soybean, (Leung, 2010), Sunflower, (Anderson, 2010), WCO, (Demirbas, 2009)

Figure 4.7 shows the acid number for different biodiesel oil. For a neat biodiesel, B100, the acid number is a measure of free fatty acid in a fuel. Acid value is the number of milligrams potassium hydroxide required to neutralize one gram of fat in free fatty acid. Acid number is one of most critical quality parameter of biodiesel. The free fatty acid can cause the corrosion inside engine vehicle and are symptom of water in the fuel. Chicken fat oil has highest acid number following by waste cooking oil. It is indicates that these two biodiesel oil is not suitable for engine performance. Palm oil has the lowest acid value number, which means good for engine vehicle.

# **CHAPTER 5**

#### **CONCLUSION AND RECOMMENDATION**

## 5.1 CONCLUSION

The biodiesel from various vegetables oil and tallow oil has been produced. The process used to extract the biodiesel is alkali base catalyst transesterification. Each of these biodiesel undergoes seven different analyses which are density, viscosity, cetane number, flash point, cloud and pour point and acid value. The result of these physical properties has been compared to some literature from other author.

Single step transesterification found to be the simplest yet give a good result in producing biodiesel. Powdered sodium methoxide give a better yield for even produce biodiesel from waste cooking oil. Palm oil, as far has the nearest standard of neat biodiesel B100 from biodiesel standard specification, ASTM6571.

Density is one of the most common physical properties that should be known for the fuel properties. From this research, palm has the lowest density which is 0.874kg/L. Sunflower has highest density which is 0.887kg/L followed by soybean with 0.886kg/L, corn oil with 0.884kg/L, waste cooking oil with 0.878kg/L and chicken fat oil with 0.877kg/L. Density affect the volatilization and atomization process of fuel inside the injector and inside the engine chamber. Higher density will give poor engine performance because it will cause the slower combustion process.

The second property is viscosity. Corn oil has the lowest viscosity with 3.796 Cst. While waste cooking oil has the greatest viscosity 4.4727 Cst. Followed by chicken fat oil with 4.1445 Cst, sunflower oil 4.046 Cst, soybean oil 4.031 Cst and palm oil 3.9192 Cst. Viscosity is the fuel key performance that affect the atomization in injector and mostly caused the injector coking in engine chamber. The higher the viscosity, the greater the ignition delays of air-fuel mixing.

Cetane number is used as a diesel-fuel quality parameter that related to the ignitiondelay time and combustion quality. The higher cetane number indicates the better ignition properties. Palm oil has the highest cetane number, which is 60. Followed by chicken fat oil 54, waste cooking oil 46, soybean oil 42, corn oil 39 and the lowest is 36 for sunflower oil. Palm oil give better performance compared to other biodiesel oil in term of cetane number property.

Flash point is a key property that would determine the flammability of a fuel. It is the lowest temperature at which the applied ignition will cause the vapor of sample to ignite. From the experiment, corn oil has temperature of 260 °C which is the greatest. Palm oil has the lowest temperature compared to other biodiesel oil which is 150 °C. Soybean oil also has great temperature for flash point which is 238 °C, followed by waste cooking oil, chicken fat oil and lastly sunflower with 160 °C. Corn oil gives the greater safety in handling, stored and used the fuel compared to other biodiesel.

Cloud point is a fuel property that is important for the operability of fuel in a low temperature. It is the temperature at which a cloud of wax crystals first appear when the fuel is cooled. Palm has highest cloud point with 14 °C. While, waste cooking oil has the lowest temperature which is -4 °C. Chicken fat oil also has great temperature with 10 °C, followed by sunflower oil with 2 °C. Soybean oil and corn oil has temperature -1 °C and -2 °C respectively. Palm oil is not suitable to use in cold weather. Instead, waste cooking oil biodiesel can be used and performed well in cold weather because of the lowest cloud point property.

Pour point is another key measurement of low temperature performance after the cloud point. The pour point is the lowest temperature at which the fuel sample will flow, at which the amount of wax from a solution is sufficient to gel the fuel. Palm oil has the pour point 10 °C which is greatest compared to other feedstock followed by chicken fat oil with 7 °C. Corn oil has the lowest pour point which is -12 °C, followed by second lower waste cooking oil -9 °C. While soybean oil and sunflower oil shared the same pour point which is -3 °C. Corn oil is the most suitable used in cold weather performances; palm oil is not suitable because at temperature 10 °C, it will turn into gel.

Acid number is one of most critical quality parameter of biodiesel fuel. It is the number of milligrams potassium hydroxide required to neutralize one gram of fat in free fatty acid. From the experiment, palm oil has the lowest acid number which is 0.05mgKOH/g. While chicken fat oil has the highest acid number with 0.3 mgKOH/g. Waste cooking oil has 0.27 mgKOH/g, followed by soybean oil with 0.21 mgKOH/g acid number, sunflower oil 0.18 mgKOH/g and corn oil with 0.15 mgKOH/g acid number. The free fatty acid can cause the corrosion of engine vehicle and are symptom of water in the fuel.

## 5.2 **RECOMMENDATION**

For the next future research, this experiment analysis project scope should be minimized for just two or three kind of feedstock. Beside, the biodiesel produced and already analyzed should be tested in the real engine, to see the performance of engine itself. Also, one-dimensional simulation of internal combustion engine should be performed which operating with simulation such as GT-Power using different biodiesel.

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