

**UTILIZATION OF MODIFIED WASTE  
*STAGHORN* CORAL AS A BASE CATALYST IN  
BIODIESEL PRODUCTION**

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*STAGHORN* CORAL AS A BASE CATALYST IN  
BIODIESEL PRODUCTION**

by

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## LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATR-FTIR	attenuated total reflectance-Fourier transforms infrared
AV	acid value
BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
CaO	calcium oxide
CN	cetane number
CO <sub>2</sub>	carbon dioxide
CSC	calcined staghorn coral
DTG	derivative thermogravimetric
FAME	fatty acid methyl ester
FFA	free fatty acid
GC-FID	gas chromatography-flame ionization detector
GHGs	greenhouse gases
GC-MS	gas chromatography-mass spectrometry
H <sub>2</sub> O	water
IUCN	International Union for Conservation of Nature
K-CSC	calcined KOH impregnated staghorn coral
KOH	potassium hydroxide
ME	methyl esters
RBD	refined, bleached and deodorized
SEM	scanning electron microscopy
SV	saponification value

TGA	thermal gravimetric analysis
USC	uncalcined staghorn coral
WBD	White Band Disease
WCO	waste cooking oil
XRD	x-ray diffraction
XRF	x-ray fluorescence

## LIST OF SYMBOLS

$^{\circ}\text{C}$	Celcius
K	Kelvin
B	volume of hydrochloric acid solution used for blank sample
V	volume of hydrochloric acid solution used for oil sample
V	volume of potassium hydroxide
M	molar concentration of hydrochloric acid
M	molar concentration of potassium hydroxide
W	weight of sample
H <sub>-</sub>	basic strength
wt.	weight
w/w	weight/weight
V <sub>tot</sub>	total pore volume
$\theta$	theta
$\Sigma^A$	total peak area of FAME
A <sup>ISTD</sup>	peak area of methyl heptadecanoate
C <sup>ISTD</sup>	concentration of methyl heptadecanoate
V <sup>ISTD</sup>	volume of methyl heptadecanoate
m	mass of sample
T	transmittence

**PENGUNAAN SISA BATU KARANG *STAGHORN* TERUBAH SUAI  
SEBAGAI MANGKIN BES DALAM PENGHASILAN BIODIESEL**

**ABSTRAK**

Kajian ini memfokuskan penghasilan pemangkin yang baharu bagi menghasilkan metil ester daripada trigliserida melalui tindak balas dengan metanol. Pertamanya, kalsium oksida daripada batu karang staghorn telah dicirikan dan diaplikasi dalam proses transesterifikasi minyak olein sawit yang ditapis, dilunturkan dan dinyahbaukan, (RBD). Tindak balas tersebut hanya menghasilkan  $62.1 \pm 4.3$  % metil ester. Oleh yang demikian, pengubahsuaian mangkin telah dilakukan dengan mengimpregnasi batu karang staghorn bersama kalium hidroksida, KOH sebagai usaha untuk meningkatkan lagi aktiviti pemangkinnya. Mangkin terubah suai (K-CSC) kemudiannya telah digunakan sebagai mangkin bes dalam metanolisis minyak olein sawit RBD dan sisa minyak masak. Bagi transesterifikasi minyak olein sawit RBD, keadaan tindak balas yang terbaik untuk mendapatkan  $94.8 \pm 0.5$  % kandungan metil ester dicapai dengan 4 wt.% pemangkin, 4 jam masa tindak balas dan 15:1 nisbah molar metanol kepada minyak. Selain itu, pemangkin K-CSC juga telah berjaya mentransesterifikasikan sisa minyak masak pada keadaan tindak balas 4 wt.% mangkin, 5 jam masa tindak balas dan 18:1 nisbah molar metanol kepada minyak dan menghasilkan  $89.5 \pm 4.8$  % biodiesel. Penggunaan semula mangkin K-CSC turut dikaji and malangnya, pemangkin tersebut mempunyai ciri-ciri penggunaan semula yang lemah. Kajian toleransi mangkin K-CSC terhadap asid lemak bebas (FFA) dan air mendedahkan keupayaannya yang lemah terhadap kehadiran asid lemak bebas dan air.

# UTILIZATION OF MODIFIED WASTE *STAGHORN* CORAL AS A BASE CATALYST IN BIODIESEL PRODUCTION

## ABSTRACT

This work focuses on producing a novel catalyst to synthesize methyl esters from triglycerides by the reaction with methanol. Firstly, calcium oxide derived from staghorn coral was characterized and applied in the transesterification process of refined, bleached and deodorized, (RBD) palm olein. The reaction only yielded about  $62.1 \pm 4.3$  % methyl esters. Therefore, a catalyst modification was carried out by impregnating the staghorn coral with potassium hydroxide, KOH as an effort to further enhance its catalytic effect. The modified catalyst (K-CSC) was then used as a base catalyst in the methanolysis of RBD palm olein and waste cooking oil. For RBD palm olein transesterification, the best reaction conditions to obtain methyl esters content of  $94.8 \pm 0.5$  % was found to be 4 wt.% catalyst, 4 h reaction time, and 15:1 methanol to oil molar ratio. Besides that, K-CSC catalyst also successfully transesterified waste cooking oil at the reaction conditions of 4 wt.% catalyst, 5 h reaction time and 18:1 methanol to oil molar ratio and produced  $89.5 \pm 4.8$  % biodiesel. The reusability of K-CSC catalyst was also studied and unfortunately, the catalyst has poor reusability characteristic. The free fatty acid (FFA) and water tolerance analyses of K-CSC catalyst has revealed its poor ability to tolerate with free fatty acid and water presence.



## **CHAPTER ONE**

### **INTRODUCTION**

#### **1.1 Background of the study**

Nowadays, fossil fuel utilization as the main energy resource is no longer recommended due to its high price and negative impacts on the environment and human health. This problem can be alleviated by emphasizing the use of biodiesel. Biodiesel is defined as fatty acid methyl ester (FAME) that is derived from the transesterification of vegetable oil/animal fat together with methanol and catalyst. Biodiesel has become current worldwide interest in the search for effective and promising energy, which is mainly associated with its advantages such as renewable, biodegradable and environmental friendly. Malaysia, the second largest palm oil producer and exporter, has manufactured biodiesel from palm oil since several years ago. The process of exporting biodiesel to the main exporters (U.S and EU) had begun since 2006 (Applanaidu et al., 2009; Applanaidu et al., 2014).

Apart from palm oil, biodiesel can also be synthesized from several other types of feedstocks such as edible oils, inedible oils, waste oils and animal fats. 70-95 % of the total biodiesel manufacturing costs arise from feedstock (Apostolakou et al., 2009). Waste oil and animal fat are the cheapest biodiesel feedstocks and their usage as feedstocks would lower the production cost. The cost of waste oil is approximately half the cost of virgin oil and it keeps gaining attention due to its renewability and availability. Meanwhile, for the selection of catalyst, heterogeneous

catalysts especially calcium oxide (CaO) is regarded as the most promising and practical catalyst. Interestingly, CaO can be easily derived from waste materials such as ostrich eggshell (Tan et al., 2015a), chicken eggshell (Tan et al., 2015a), shrimp shell (Yang et al., 2008) and others, where they consist of calcium carbonate as their main compound. Staghorn coral (*Acropora cervicornis*) is also a natural source of calcium. The major inorganic compound of coral is calcium carbonate (CaCO<sub>3</sub>) which degrades into CaO at very high temperature. Since Malaysia is surrounded by oceans, abundance of dead staghorn coral remnants can be easily found in the coastal areas. More importantly, the utilization of staghorn coral as catalyst not only helps in reducing the production cost but also promotes the environmental benign process. The catalyst can be prepared by several methods such as thermal activation and wet impregnation methods. The main purpose of employing wet impregnation method is to further enhance the catalytic ability of the catalyst. Many researchers have tested impregnated alkali metal ions (Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>) onto the catalyst surface (Boro et al., 2014; Kataria et al., 2017) and found out that all the catalysts performed excellently during the alcoholysis process.

## **1.2 Problem statement**

Due to the staggering growth of the world's population, the transportation sector as well as the industrial sector, the world is currently facing a very serious energy crisis where the energy usage has exceeded its production rate especially in developing countries. Besides food and water, energy is also one of the three most important basic needs for human survival (Zou et al., 2016). Currently, fossil fuels account for about 80 % of the world's energy needs (Huang et al., 2012). However, the use of fossil fuel has become a global issue as it emits greenhouse gases (GHGs)

especially carbon dioxide (CO<sub>2</sub>) into the air. This has led to global warming and air pollution, which in turn affect human health. Petroleum-based fuel vehicles are the main CO<sub>2</sub> emission contributors as they are responsible for approximately 23 % of world CO<sub>2</sub> emission (Saboori et al., 2014). Additionally, world's overall transport energy consumption and CO<sub>2</sub> release are expected to increase by 80 % in 2030 (Saboori et al., 2014). Due to this, biodiesel has been chosen as the replacement and extender of fossil fuel. Nevertheless, the biggest barrier in biodiesel commercialization is the high cost of production, which is mainly associated with the biodiesel feedstock and catalyst.

The utilization of edible oils such as sunflower oil, rapeseed oil, palm oil, cottonseed oil and others as the raw materials are the main contributors that lead to higher cost. Viable solution to this issue is to use waste cooking oils or animal fats as biodiesel feedstock. In addition, most of the waste oils are simply discarded into the drains, rivers and sinks without further utilization and consequently resulting in water pollution. Besides that, a lot of efforts have been made in search for catalyst with good catalytic activity and at the same time being cheap, environmentally benign and readily available. Interestingly, staghorn coral (*Acropora cervicornis*) has been seen to meet all the criteria, making it a perfect choice as catalyst. This coral species thrive in the biodiverse waters of Malaysia especially in the east coast areas. However, the corals are threatened by ocean acidification, high seawater temperature and human activities, causing slower coral growth rate, weakening of coral skeleton, coral bleaching and making them more susceptible to diseases. Due to that, dead staghorn corals are abundantly found along the seashores in many parts of Malaysia as they are washed ashore during strong tide. The dead corals might seem impotent

but they actually have a variety of uses. They are usually harvested for building materials, jewellery and aquarium but they also suitable to be used as catalyst in biodiesel production. In addition, the corals grow, die and endlessly repeat the cycle over time. This cycle of growth, death and regeneration ensure sufficient sources of dead corals.

### **1.3 Research objectives**

In this research study, the process of biodiesel production was carried out *via* the transesterification of two different types of feedstocks using staghorn coral and K-impregnated staghorn coral as catalysts. Therefore, the purposes of this study are:

- 1) To determine physicochemical properties of staghorn coral and K-impregnated staghorn coral.
- 2) To determine the effects of different reaction variables, FFA and water contents on the catalytic activity.
- 3) To study the reusability of K-impregnated staghorn coral.

### **1.4 Scope of study**

The target of this study was to synthesize a low cost and green catalyst derived from dead staghorn coral. The aspects looked into were the effectiveness of prepared catalyst in biodiesel production, its characteristics (reusability, FFA and water tolerance) and effect of reaction parameters on its activity. The research has reached its aims but there were some limitations faced in this study and they are:

- 1) Some testing were done in other places. For example:
  - Karl Fischer titration analysis was done by Biochem Laboratories Sdn Bhd.
  - XRF analysis was conducted at Centre for Global Archaeological Research, Universiti Sains Malaysia, Penang.
  - SEM analysis was carried out at Centre for Global Archaeological Research, Universiti Sains Malaysia, Penang.
  - XRD analysis was conducted at School of Physics, Universiti Sains Malaysia, Penang.
  
- 2) Lack of data
  - Other reaction parameters, leaching test, properties of biodiesel and used catalyst should be studied to improve the quality of the work. However, they can be proposed for the extension of this research.
  
- 3) Limited laboratory apparatus
  - The limited amount of laboratory apparatus has slower the work progress.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Biodiesel

Fossil fuel which took millions of years to form, plays a crucial role in the global energy systems. Sadly, fossil fuel supplies have started to diminish day by day, resulting in fossil fuel price increment. Efforts are being exerted to look out for the best substitute for fossil fuel and it was found that biodiesel is the most economically practicable option for solving this problem. According to the American Society for Testing and Materials (ASTM), biodiesel is described as monoalkyl esters of long chain fatty acids made from a renewable feedstock such as vegetable oil or animal fat by the reaction with alcohol and catalyst. “Bio” refers to its renewability and biological source, while “diesel” means its usage in a diesel engine (Zhang et al., 2003). Biodiesel is commonly named as B100 and it must meet the requirements of ASTM D6751 (Mofijur et al., 2012).

The concept of using biodiesel as fuel in a diesel engine is not something new as it was discovered more than 100 years ago by Dr. Rudolf Diesel. During the World Exhibition in Paris in the year 1900, he had successfully operated the diesel engine using 100 % pure peanut oil as fuel (Kapilan et al., 2009; Owolabi et al., 2012). Twelve years later, Diesel said, *“The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as the petroleum and coal tar products of the present time”* (Owolabi et

al., 2012). Interestingly, this statement has become a reality today. Biodiesel has no petroleum, but it can be used either in a neat form or blended with petroleum diesel in any proportions (Kapilan et al., 2009; Idusuyi et al., 2012). Biodiesel blends are denoted as BXX. The XX shows the quantity of biodiesel in the blend. For instance, B20 blend means 20 % biodiesel and 80 % petroleum diesel. The physical properties of biodiesel are listed in Table 2.1. Biodiesel is not only used as fuel in vehicles such as diesel engine-cars, lorries, trucks, boats and buses, but it is also being applied in generators, oil home heating units and constructional equipment (Bajpai and Tyagi, 2006).

Table 2.1: Physical properties of biodiesel (Demirbas, 2009a)

Properties	Biodiesel (bio-diesel)
Common Chemical name	Fatty Acid Methyl Ester (FAME)
Chemical Formula Range	C14–C24 methyl esters
Kinematic viscosity range ( $\text{mm}^2 \text{s}^{-1}$ , at 313 K)	3.3–5.2
Density Range ( $\text{kg}^{-1} \text{m}^3$ , at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600
Vapour pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical Appearance	Light to dark yellow, clear liquid
Odour	Light musty/soapy odour
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

In Malaysia, the production of biodiesel has been developing rapidly since many years ago. As an effort to encourage the use of “green” and renewable energy and at the same time minimize the dependency on fossil fuel, Malaysian government had introduced the National Biofuel Policy in 2006 (Mofijur et al., 2012; Wahab, 2016). The implementation of B5 blend was first introduced in mid-2011 in the

selected states and the full implementation was accomplished at the end of 2014. However, biodiesel production in Malaysia is still far below industry full capacity, which is probably due to several factors such as high feedstock transportation cost and utilization of feedstock to make other products like pharmaceutical grade sugar, soap noodle and fatty alcohol (Wahab, 2016).

## **2.2 Advantages of biodiesel**

Fossil fuel exerts a highly negative impact on the ecosystem and human health. With growing concerns over the fossil fuel, biodiesel has gained much attention and popularity as a “green” and excellent fuel since it offers numerous advantages. Biodiesel is well known as an environmentally benign fuel since its usage emits much lower CO<sub>2</sub> into the atmosphere compared to other fossil based fuels (Figure 2.1). Moreover, in comparison to diesel, biodiesel consists of about 10-11 % oxygen content, whilst diesel does not have oxygen (Canakci, 2007; Ge et al., 2017). The molecular structures of diesel and biodiesel are illustrated in Figure 2.2. As reported by Demirbas (2009a), the presence of oxygen in biodiesel leads to the rise in homogeneity of oxygen with the fuel. Due to the aforementioned reason, biodiesel exhibits better combustion efficiency compared to petroleum diesel and emits less exhaust emission such as carbon monoxide, unburnt hydrocarbon and particulate matter. These are the reasons which make biodiesel the most suitable fuel for transportation especially in sensitive areas like forests, national parks, mining enclosures, heavily polluted cities and coastal areas.



Carbon dioxide (CO<sub>2</sub>) produced per MJ of energy

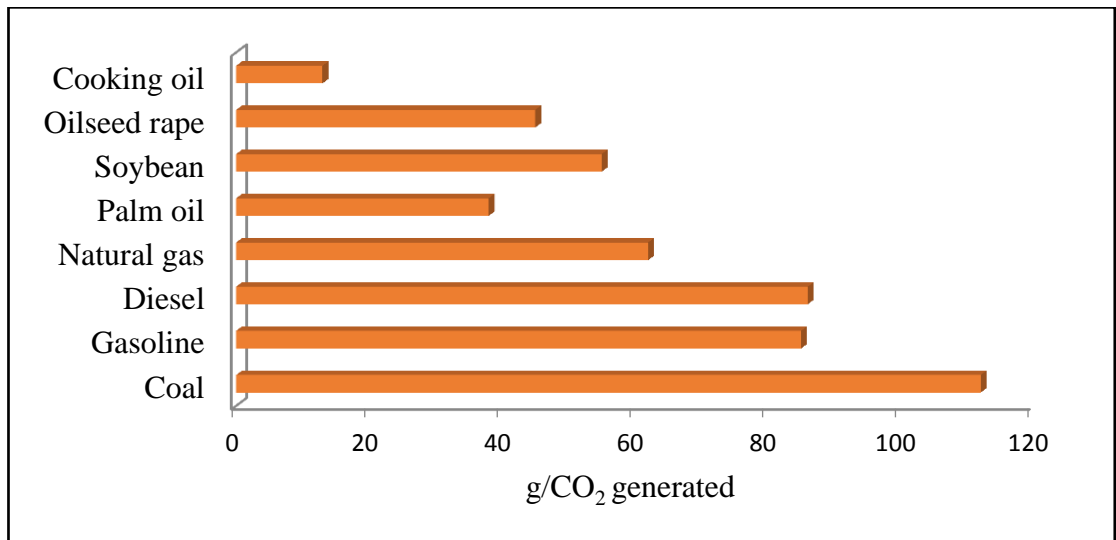


Figure 2.1: Comparison of the carbon intensity of biodiesels fuels against fossil fuels (UK Department for Transport, 2008).

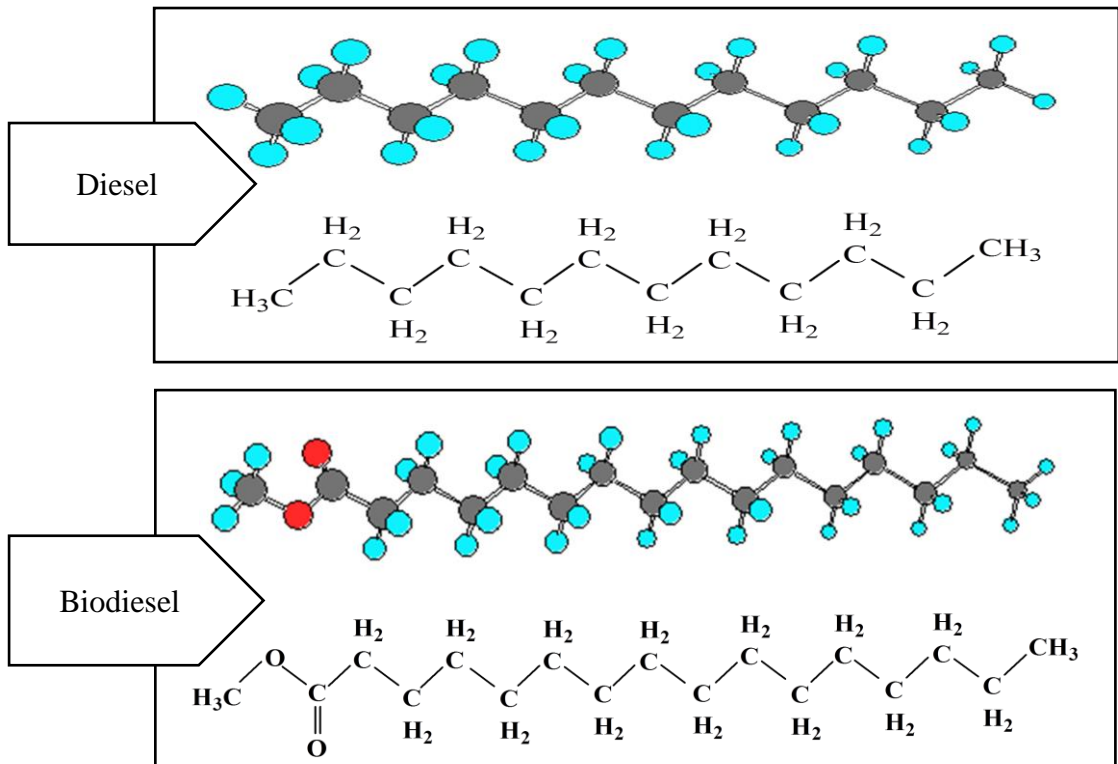


Figure 2.2: Molecular structure of diesel and biodiesel (Ge et al., 2017).

The use of biodiesel is beneficial to reduce the global warming effect and air pollution as well as the ability to improve human health. As an alternative fuel, biodiesel has lots of other unique characteristics. One of them is its excellent lubrication property which can help to lower down the friction loss and at the same time improves the efficiency of the brake (Xue et al., 2011). The use of high lubricity biodiesel would result in extending engine's lifespan. The presence of biodiesel contributes massively in solving insufficient energy supply issue. At the same time, the dependency on imported fuel would decline. One of the prolific aspects about biodiesel is that it is easy to use, as neither modification nor fueling equipment is required. In terms of performance, it displays a good performance and high-power generation (Firoz, 2017). Besides, biodiesel is known as a "safe" fuel in view of handling, storage and transport, which corresponds to its low toxicity and high flash point (Atadashi et al., 2010; Firoz, 2017). It commonly possesses a flash point higher than 150 °C whereby conventional diesel fuel has a much lower flash point, which is around 55-66 °C (Sanford et al., 2009).

Biodiesel has superior biodegradable and renewable characteristics that make it a promising fuel. Surprisingly, biodiesel degrades four times faster than petroleum diesel (Demirbas, 2008). It also has high biodegradability in fresh water as well as in soil (Ferella et al., 2010). In contrast to mineral diesel, biodiesel does not possess any carcinogens and has a much lower sulfur content which makes it the reason to be called as clean fuel (Sharma and Singh, 2009). Another advantage of biodiesel is its high cetane number (CN). Cetane number is an indicator to determine the ignition quality and it is highly controlled by the amount of saturated fatty acids and its chain length. According to Lapuerta et al. (2008) and Karmakar et al. (2010), higher the

CN, shorter the time between the ignition and the initiation of fuel injection into the combustion chamber. Therefore, fuel with high CN has better combustion efficiency compared to the fuel that has low CN. More importantly, biodiesel is the most suitable replacement for petroleum diesel due to their similarities in physicochemical properties (Atadashi et al., 2010).

### **2.3 Raw materials**

Biodiesel can be synthesized from a variety of feedstocks such as edible oil, inedible oil, waste oil, and animal fat. About 75 % of the overall cost for methyl ester production derives from feedstock (Figure 2.3). According to Ayetor et al. (2015), more than 100 raw materials have been utilized in biodiesel production. Biodiesel feedstock is controlled by climate and soil conditions (Huang et al., 2012). The suitability of vegetable oil as a feedstock is determined by the composition of the raw material itself which in turn measures the quality of the formulated biodiesel. Meanwhile, the selection of feedstock for each country is highly influenced by edibility, cost and availability (Ayetor et al., 2015). Therefore, different countries have different sources and types of feedstocks. For instance, France and Italy mainly utilize sunflower oil as the feedstock in biodiesel formulation process. Soybean oil is the main raw material in USA and Brazil, while China prefers oil from Guang Pi, an oil-bearing tree as the raw material because soybean has a very high demand in Chinese food preparation (Bajpai and Tyagi, 2006; Beckman and Junyang, 2009). As the largest and second largest palm oil producer and exporter respectively, Indonesia and Malaysia benefit from palm oil to produce biodiesel which is in abundance in both countries.

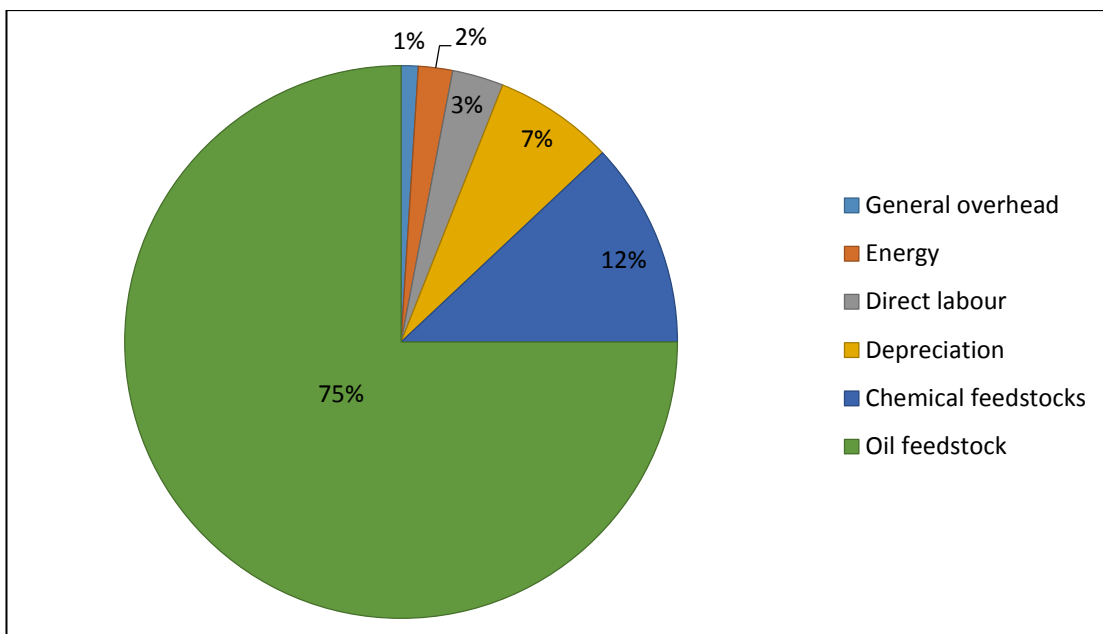


Figure 2.3: General cost breakdown for biodiesel production (Lim and Teong, 2010).

Currently, most of methyl esters are prepared from edible oils such as rapeseed (59 %), soybean (25 %), palm oil (10 %), sunflower oil (5 %) and other types of oil (1 %) (Pahl, 2008; Demirbas, 2015). However, the use of edible oil in producing large quantities of biodiesel negatively affects the global food supply and consequently cause an increase in edible oils' prices. Hence, one of the viable ways to overcome this hurdle is by replacing the edible oil with non-edible oil or used oil. Some examples of inedible oil sources are *Jatropha curcas* (Chhetri et al., 2008; Buasri et al., 2015; Reddy et al., 2016), *Pongamia edule* (Atabani et al., 2015), soapnut *Sapindus mukorossi* (Chhetri et al., 2008) and rubber seed (Zamberi and Ani, 2016). There are significant advantages with regards to the usage of non-edible oil over edible oil. For an example, inedible plants can be planted in wastelands that are unsuitable for food crops and they only need low cultivation cost since they can maintain high yield even without a thorough care (Fatah et al., 2012). Apart from those benefits, these plants can also cope with arid, semi-arid conditions and they

only need low fertility and moisture demand to grow (Atabani et al., 2013). Unfortunately, inedible oils have very high FFA content and contain several toxic compounds which make them unsuitable for human consumption.

Waste cooking oil is defined as used oil that is no longer safe for reuse due to its high content of FFA. When comparing to virgin vegetable oil, biodiesel formulated from waste oil has more complicated steps and has a poorer fuel characteristic, which is associated with high FFA content. Usually, to produce methyl esters, feedstocks that contain more than  $2 \text{ mg KOH g}^{-1}$  of acid value need to be pre-treated to lower the acid content (Knothe and Steidley, 2005). Therefore, most of the waste oils would be subjected to esterification process first before proceeding to the transesterification process. Due to its low price, waste oil is believed to be a suitable raw material in methyl esters production. Additionally, most of waste cooking oils from houses and restaurants are simply thrown away into sinks and drains. Practicing appropriate approaches to dispose waste oil may lead to reduction in environmental problems and vice versa. Besides being used as a feedstock in biodiesel formulation process, waste oil is also used as animal feed. However, this oil contains dangerous compounds and they could simply get into the food chain when they are being used as animal feed (Kulkarni and Dalai, 2006). Hence, the oils must undergo treatment to lower its effects on the ecosystem. One of the feasible methods to treat the oil is by converting it into methyl esters.

Currently, the number of studies on the use of animal fats in biodiesel preparation process is much lower in comparison to vegetable oils. The use of animal fats assists in reducing the disposal rate as well as ensuring the continuity of the

biodiesel supply. In 2011, Boey et al. successfully produced biodiesel using chicken fat as feedstock. It was reported that more than 98 % biodiesel conversion was obtained under the optimized reaction conditions. Moreover, catfish fat has also been tested in the transesterification reaction using catalysts prepared from marine barnacle and bivalve clam shells (Maniam et al., 2015). The catfish oil has an acid value of 3.85 mg KOH g<sup>-1</sup>, FFA content of 1.75 %, and a moisture content of 0.22 %. Although the acid value is relatively high, the conversion of catfish fat into biodiesel was a success achieving more than 96 % of methyl esters content upon 4 h of the transesterification reaction. However, since animal fat is in solid form, it is not suitable to be used as fuel in its original form. Not only that, the use of animal fats could also lead to various complications such as contamination of lubricating oil, incompatibility with existing engine, carbon deposits in the engine and reduction in engine durability. All these issues could probably be due to the presence of high amount of saturated fatty acids in animal fats.

## **2.4 Methods of biodiesel production**

There are several techniques that can be employed to produce methyl esters such as direct use and blending, microemulsion, thermal cracking (pyrolysis), and transesterification.

### **2.4.1 Direct use and blending**

The utilization of vegetable oils such as peanut oil, soybean oil, olive oil, palm oil and sunflower oil as fuels to replace non-renewable and non-biodegradable

diesel fuels has started flourish since last few decades. But, as the crude oil supply is getting diminished, utilization of vegetable oil as a replacement is being promoted again in most countries around the world. Vegetable oils have become the current interest in seeking for biodiesel substitute as they are safe to use, readily available, carbon neutral, renewable and biodegradable.

Although they have similar properties with reference to diesel fuel (Dunn and Bagby, 2000), the direct use of vegetable oils and animal fats as an engine fuel is not recommended. This is due to the negative impact imparted by vegetable oils and animal fats on engine performances and emission, causing contamination of lubricating oil, thickening and gelling of the lubricating oil and coking of injector nozzles due to their low CN, low heating value, low volatility and higher viscosity and freezing point than diesel fuel (Melo-Espinosa et al., 2016). Therefore, blending (dilution) technique was proposed as an effort to improve the oil's grade (Mendhe et al., 2015).

Blending, also called as dilution is a very easy and straightforward technique to lower the viscosity and density of vegetable oils (Demirbas, 2009b). In this method, vegetable oils are directly mixed with diesel fuel. Although it can enhance the fuel quality and lower the oil's viscosity, these fuels also face the same problems as vegetable oils (Mendhe et al., 2015).

## 2.4.2 Microemulsion

Microemulsion is a method where two or more immiscible fluids are mixed together to form emulsion. Emulsion consists of a mixture of oil and water and one of the phases present in droplet form and it dispersed within the other phase. It is known as dispersed phase (Figure 2.4). For instance, oil-in-water emulsion is made up of mixture of oil and water. In this case, oil is considered as the dispersed phase, while water is the dispersion medium (Tan et al., 2015b). Other than that, there are also multiple emulsion stages such as water-in-oil-in-water emulsion and oil-in-water-in-oil emulsion (Khan et al., 2006). The stabilization of the mixture is carried out using film of surfactants and/or co-surfactants (Dunn, 2004; Rosen, 2004).

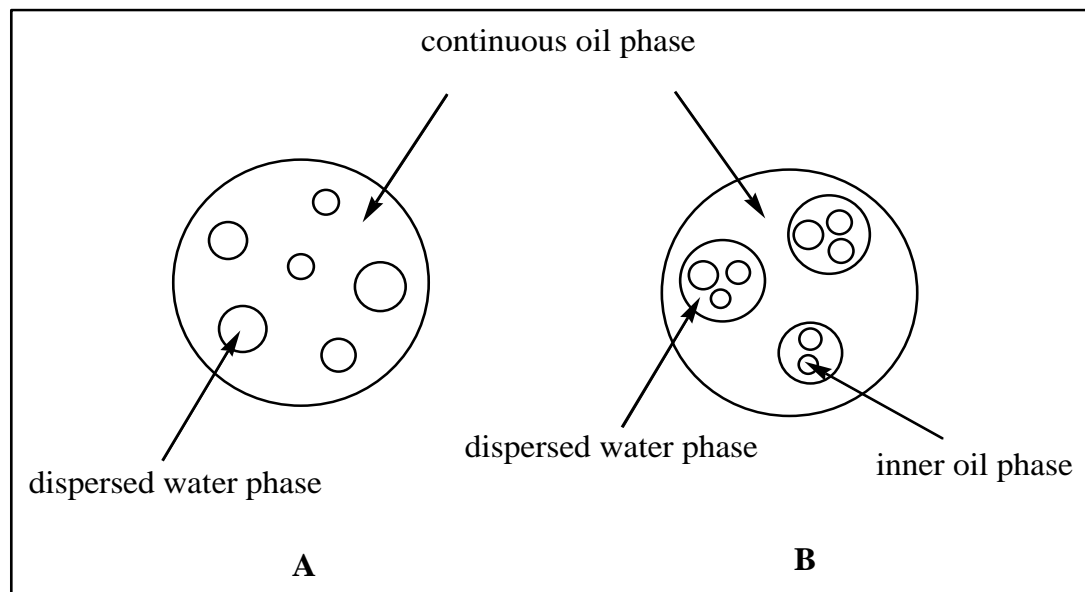


Figure 2.4: Schematic structures of (A) water/oil biodiesel emulsion and (B) oil/water/oil biodiesel emulsion (Lin and Lin, 2007).

The advantages of microemulsion technique such as no engine modification needed, straightforward, easy implementation, and low production cost, make it the choice of many researchers as an attempt to reduce oil's viscosity (Lif and



Holmberg, 2006). Microemulsion with solvents like methanol, ethanol, butanol, hexanol, octanol or other alcohols is a practical way to lower the vegetable oil's viscosity and minimize smoke emission. Some of the interesting facts about this method are its capability in minimizing the nitrogen oxide (NO<sub>x</sub>) production and enhancing the combustion efficiency of biodiesel. However, some researchers do not encourage the use of this microemulsified diesel due to its unacceptable properties that would lead to nozzle failure, incomplete combustion and carbon deposition (Koh and Gazi, 2011).

### **2.4.3 Thermal cracking (pyrolysis)**

Thermal cracking (Figure 2.5), also called as pyrolysis is defined as a process where deoxygenation of vegetable oils occurs because of the thermal degradation reaction where the final product acquired is the enriched diesel-like hydrocarbon (Bridgwater, 2004). During the first and second world wars, pyrolysis of oils from biomass was used to cover up the depleted fuel supply in areas that faced a shortage of petroleum supply. For instance, China applied pyrolysis batch system of tung oil. The bio-oil obtained acted as a raw material in the process of making diesel-like fuel and gasoline (Demirbas, 2003; Lima et al., 2004). Specialities of this method are the flexibility of the raw material, greater compatibility with fuel standards and engines and low operation cost (Tan et al., 2015a). This method is not only a promising method for lowering oil's viscosity and density, but it is also capable to transform triglycerides into fuels. It is advantageous to the hydroprocessing industry due to the technological similarities with conventional petroleum refining. In 2009, Wiggers et al. and Junming et al. reported on the success of pyrolysis of soybean oil in biofuel

production. The biofuel obtained was comparable with petroleum-based fuel.

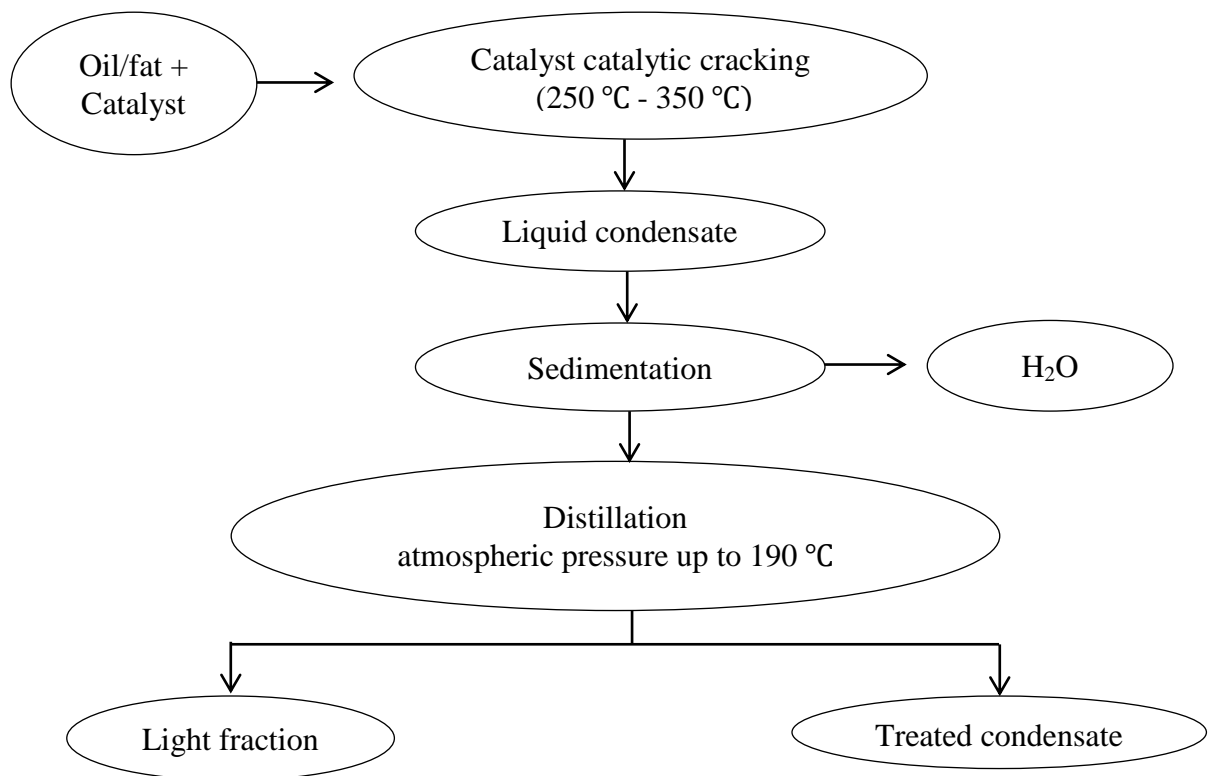
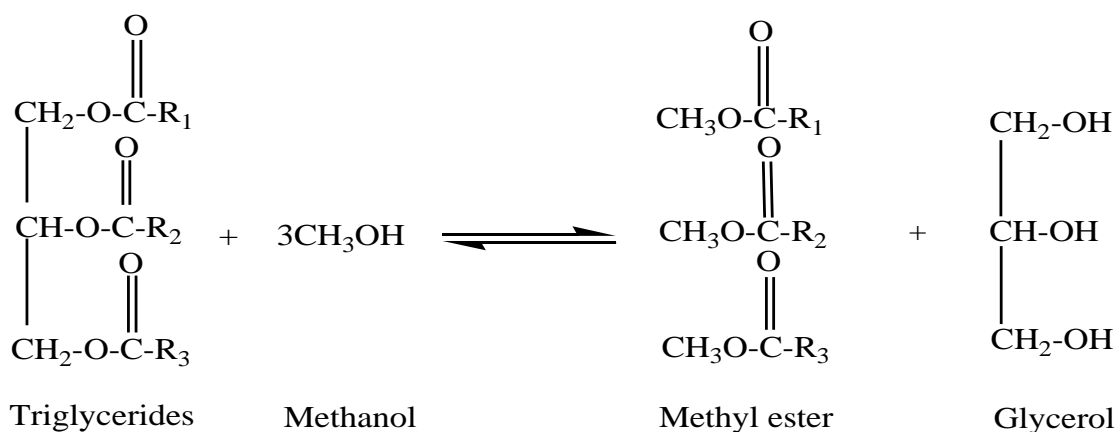


Figure 2.5: Thermal cracking process (Rajalingam et al., 2016)

Despite all the advantages, there are some challenges to overcome when using this method. One of the biggest concerns is the difficulty to control the quality of the product. The formation of unwanted products such as mono-, di- and triglycerides might occur due to the incomplete reaction (Lima et al., 2004). In addition, the fuel produced by this technique is unstable and corrosive, which is mainly associated with the high acid value (Wiggers et al., 2013). During vegetable oil cracking processes, there also exists the formation of a highly toxic compound of acrolein (Prado and Filho, 2009).

#### 2.4.4 Transesterification

Among biodiesel production methods, transesterification has been chosen as the most ideal and effective chemical process to produce biodiesel as it can deal with high viscosity problem. It is also known as a practical way to produce a greener and a safer fuel. Transesterification which is also called as alcoholysis, is simply described as taking a triglyceride molecule, neutralizing the FFA, eliminating the glycerol and forming an alkyl ester. A triglyceride consists of one molecule of glycerol and three molecules of long chain fatty acids that are usually found in vegetable oils or animal fats. This reversible process involves three sequence steps, which requires one mole of triglyceride and three moles of alcohol. During the reaction, triglycerides are broken down into diglycerides, monoglycerides and finally glycerol, producing one mole of ester in every step. The basic reaction for transesterification is shown in Scheme 2.1.



Scheme 2.1: The basic transesterification reaction.

The most frequently used alcohol during alcoholysis process is methanol. This is perhaps due to its various advantages such as low price, good physical and chemical properties. Transesterification is an equilibrium reaction. During the

reaction, the addition of alcohol would cause the shifting of the equilibrium towards the forward direction, thus increasing the amount of biodiesel produced. Biodiesel can be produced directly through the conversion of both FFA and oil using acid esterification process. Nevertheless, the reaction is too slow, and it gives low biodiesel yield. Interestingly, Melo-Espinosa et al. (2016) stated that most of the biodiesel produced through transesterification process have almost similar properties as compared to diesel fuel. There are several parameters that control the triglycerides' conversion into biodiesel namely; alcohol to oil molar ratio, reaction time, temperature, type and amount of catalyst.

There are several catalyst systems used in the production of methyl esters *via* transesterification. One of them is acid-catalyzed transesterification. Acid-catalyzed transesterification is a conversion process of triglycerides into methyl esters and glycerol in the presence of an acid catalyst such as sulfonic acid and sulfuric acid. This catalyst usage could yield a high biodiesel content up to 99 %. However, the reaction is too slow, and it requires elevated reaction conditions.

Another example for the catalyst system is base-catalyzed transesterification. Base-catalyzed transesterification is the process of biodiesel production using a base catalyst such as sodium hydroxide, sodium methoxide, sodium ethoxide and potassium hydroxide. To produce methyl esters through base-catalyzed process, the feedstock used should have low FFA value. The presence of a high acid value in the oil would increase the base catalyst usage to neutralize the FFA (Gashaw and Teshita, 2014). When using alkali catalysts, the alcohol and glycerides must be free of water because the presence of water would causes the formation of soap through

saponification. Soap formation must be avoided as it causes a drastic drop in the catalytic effect and accounts for the difficulty in biodiesel separation and purification processes. However, in comparison to acid-catalyzed process, the base-catalyzed process is employed more frequently since it has a shorter reaction time. For commercialization purpose, the use of alkaline catalysts is more favoured compared to acid catalyst due to its fewer corrosive properties. Triglycerides with low FFA content are usually being transesterified using alkali-catalyzed process, while triglycerides with a high content of FFA and water should undergo acid-catalyzed process.

Meanwhile, lipase-catalyzed transesterification process is more favourable as it requires a low reaction temperature, has high tolerance towards neutral pH environment and a low probability of soap formation (Semwal et al., 2011). Despite its advantages, this type of catalyst system is unfavourable compared to the alkaline-catalyzed transesterification especially in terms of the reaction time and yield (Ekijeme et al., 2010).

## **2.5 Catalyst**

Catalyst is defined as a substance that helps to escalate the reaction. The catalyst would provide a new route with lower activation energy (Clark, 2002). As illustrated in Figure 2.6, the reaction with catalyst possesses lower activation energy compared to the uncatalyzed reaction, leading to a better reaction rate. The general chemical reaction with catalyst's presence is depicted in Figure 2.7.

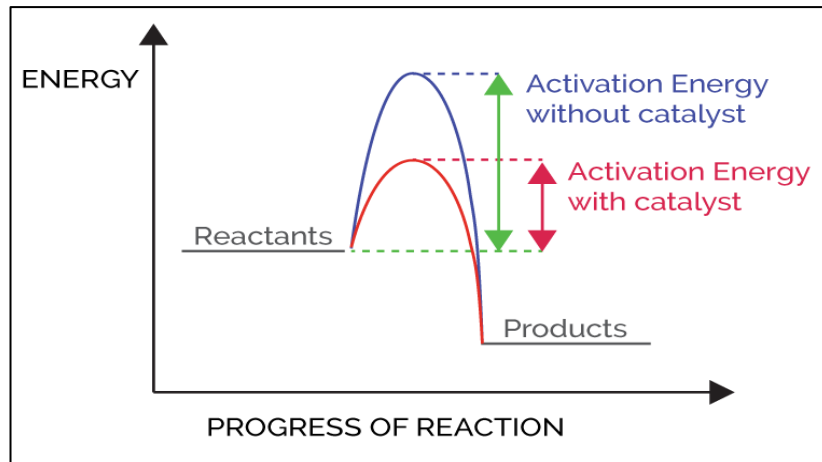


Figure 2.6: The difference between uncatalyzed and catalyzed reactions.

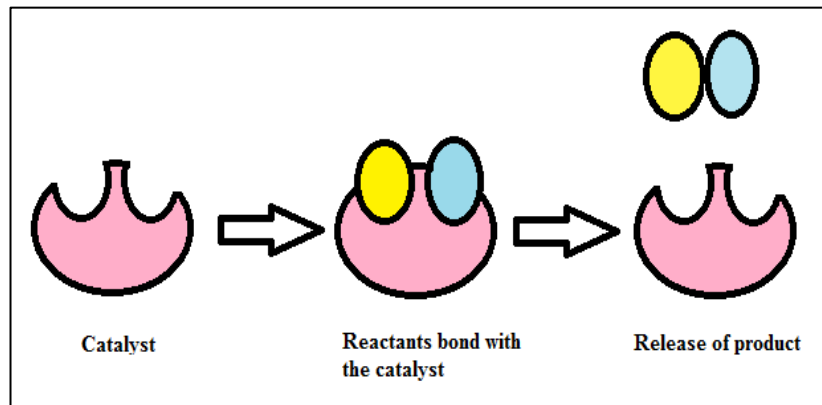


Figure 2.7: Illustration of general reaction in the presence of a catalyst.

Generally, there are three categories of catalysts that are commonly applied in biodiesel production, which are acid, base and enzyme catalysts. When compared to acid and base catalysts, enzyme catalyst is the least used catalyst. Acid and base catalysts can be divided into two classes, which are homogeneous and heterogeneous catalysts. It has been acknowledged that heterogeneous catalysts exhibit cleaner and recyclable catalyst systems with regards to homogeneous catalysts (Wen et al., 2010a).

### 2.5.1 Enzyme catalysts (Biocatalysts)

Talha and Sulaiman (2016) reported that enzyme catalysts have gained more attention since their usage does not cause the formation of soap and additionally, the purification process is very simple. Besides that, this environmental benign catalyst is also reusable and does not produce any by-products (Kulkarni and Dalai, 2006; Atadashi et al., 2013). They are also capable of catalyzing the reaction using milder reaction conditions compared to chemical catalysts. A few examples of enzyme catalysts are Novozyme 435 (Jeong and Park, 2008; Zheng et al., 2009) and *Rhizopus oryzae lipase* (Pizarro and Park, 2003).

In 2009, Novozym 435 lipase (also known as *Candida antarctica lipase*) was utilized as a catalyst to transesterify soybean oil in the production of biodiesel (Zheng et al., 2009). During the alcoholysis reaction, *tert*-amyl alcohol was mixed together with lipase, oil and methanol where *tert*-amyl alcohol functioned as the reaction medium. A very high biodiesel yield (97 %) was recorded under the optimized conditions where the catalytic activity remained stable even after being reemployed for 150 cycles. A year before, Jeong and Park (2008) conducted almost a similar research as Zheng et al. (2009). They used the same catalyst, which is Novozym 435 lipase but a different reaction medium (*tert*-butanol). A yield of about 76.1 % of biodiesel was obtained after 24 h of reaction time at 40 °C in the presence of 5 % (w/w) of Novozym 435, 1 % (w/w) of water content and 3:1 of methanol to oil molar ratio.

Nonetheless, according to Jeong and Park (2008), Zheng et al. (2009) and Leung et al. (2010), the usage of biocatalysts in biodiesel production keeps on decreasing due to the high price, slow reaction, short lifetime as well as the need for higher amounts of enzyme catalyts. In addition, enzyme catalyts have a very high sensitivity towards alcohol especially methanol as it can cause enzyme deactivation (Bajaj et al., 2010). Furthermore, the inactivation and denaturation of the enzyme exerts a highly negative impact on methyl esters yield.

### **2.5.2 Homogeneous acid catalyts**

Sulfuric acid, sulfonic acid, organic sulfonic acid, hydrochloric acid, and ferric sulphate are the most widely used homogeneous acid catalyts during transesterification reaction. Among those catalyts, sulfuric acid and hydrochloric acid are the most explored catalyts and they could tolerate with the FFA content in the oils/fats. Due to the long reaction time, the use of acid catalyts in the transesterification process has reduced even though they work effectively in the esterification and transesterification reactions. Some of the other drawbacks of this type of catalyts are the high probability of causing contamination problems and equipment corrosion and the difficulties in separating out from the product (Lam et al., 2010; Leung et al., 2010).

### **2.5.3 Homogeneous base catalyts**

Some of the examples of frequently used homogeneous base catalyts are sodium hydroxide, potassium hydroxide, sodium methoxide, sodium ethoxide and