



## OVERVIEW OF CATALYSTS IN BIODIESEL PRODUCTION

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### ABSTRACT

Transesterification is one of the methods for biodiesel production in which oil or fat is reacted with alcohol, such as methanol or ethanol, in the presence of a catalyst to form alkyl ester and glycerol. The cost of biodiesel production is mainly affected by the system used and cost of feedstock. Currently, waste oil or fat is used in the production of biodiesel as 70 to 90% of the production cost is attributed to raw materials. Alternatively, overall cost of production can also be reduced by optimizing the efficiency of catalyst used. Therefore, this review paper is aimed to give an overview on the recent trends of catalyzed transesterification and the advantages and disadvantages of heterogeneous acid/base, homogeneous acid/base, and enzymatic transesterification. Heterogeneous base catalyst is commonly used because of its reusability, easier to separate from product, higher reaction rate, lower cost, and require less energy as compared to acid-catalyzed transesterification. However, heterogeneous base catalyst still suffers with the limitations of diffusion, possibility of saponification to occur, sensitive to FFA content and produce more wastewater. With intense research focus and development, an ideal catalyst can indeed be developed for optimum production of biodiesel that economically feasible and environmentally benign for a better future.

**Keywords:** transesterification, biodiesel, homogeneous catalyst, heterogeneous catalyst, and enzyme catalyst.

### INTRODUCTION

The dwindling reserve of conventional energy resources and their associated environmental problems have increased the awareness to seek for alternative renewable and sustainable resources for fuel production. The production of biofuel is now escalating as a replacement of fossil fuel.

Biodiesel has become beguiling nowadays for its environmental benefits and it seems an apposite alternative fuels for future. It is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and also environmentally beneficial [1]. The name of Biodiesel was introduced in the United States in 1992 by the National Soy diesel Development Board (presently National bio Diesel Board) which has pioneered the commercialization of biodiesel in United States [2].

Biodiesel is registered with the US Environmental Protection Agency as a pure fuel or as a fuel additive and is a legal fuel for commerce. Biodiesel is an alternative fuel which can be used in neat form or blended with petroleum diesel for use in compression ignition (diesel) engines. The specification for biodiesel is approved by the American Standards for Testing and Materials (ASTM) under code 6751 [3].

### BIODIESEL PRODUCTION

Imperative efforts have been made to develop vegetable oil derivatives that have the properties and performance of hydrocarbons-based diesel fuel, thereabouts. Singh & Singh (2010) mentioned that substitutes of triglycerides for diesel fuel are often associated with the problem of high viscosity, low vitality and polyunsaturated characters. The problem of high

viscosity of vegetable oils has been approached in several ways such as preheating the oils, blending or dilution with other fuels, transesterification and thermal cracking/pyrolysis [4].

Demirbas (2009) agreed that transesterification method is the most viable process adopted known so far for the lowering of viscosity. Transesterification is defined as the reaction of a fat or oil with an alcohol in the presence of catalyst to form esters and glycerol. The byproduct, which is glycerol, has also commercial value. The physical characteristics of fatty acid methyl/ethyl ester are very close to those of petro-diesel fuel and the process is relatively simple.

### CATALYST

In general, there are three categories of catalysts used for biodiesel production known as alkalis, acids and enzymes [5]–[7]. As compared to enzyme catalysts, alkali and acid catalysts are more commonly used in biodiesel production [1]. They were then categorized into homogeneous and heterogeneous catalysts. However, enzyme catalysts have become more attractive recently since it can avoid soap formation and the purification process is simple to accomplish. Nonetheless, Leung *et al.* (2010) stated that they are not commercially used because of the longer reaction times and higher cost. To reduce the cost, some researchers developed new biocatalysts in recent years. An advantage is that no purification is necessary for using these biocatalysts [8]–[10].

#### Homogeneous base-catalyzed transesterification

Homogeneous alkaline catalysts are more preferable and commonly used since transesterification reaction using its acid counterpart has slower rate [11].



The most common basic catalysts are potassium hydroxide (KOH), potassium methoxide ( $\text{KOCH}_3$ ), sodium hydroxide (NaOH), sodium methoxide ( $\text{NaOCH}_3$ ), and sodium ethoxide ( $\text{NaOCH}_2\text{CH}_3$ ) [12] [13], [14]. These catalysts are commonly used because of several advantages such as able to catalyze reaction at low reaction temperature and atmospheric pressure, high conversion in shorter time, and economically available [12]. Sodium methoxide ( $\text{NaOCH}_3$ ) and potassium methoxide ( $\text{KOCH}_3$ ) are better catalyst than sodium hydroxide (NaOH) and potassium hydroxide (KOH) due to the ability to dissociate into  $\text{CH}_3\text{O}^-$  and  $\text{Na}^+$  and  $\text{CH}_3\text{O}^-$  and  $\text{K}^+$  respectively when comparing on biodiesel yield [14]. Alkaline catalyst is more commonly used in commercial biodiesel production because it does not form water during transesterification reaction [15].

NaOH and KOH are the most common homogeneous base catalyst in biodiesel production. Table 1 listed reports that used NaOH and KOH in their works. The highest biodiesel yield produced by *Calophyllum inophyllum* was reported by Silitonga *et al.* (2014) with 98.53% by using 1 wt% KOH and 9:1 methanol to oil ratio. Silva, Camargo, and Ferreira (2011) reported 95% of biodiesel yield from soybean oil by using NaOH with 1.3 wt% catalyst loading and ethanol to oil ratio of 9:1.

#### Homogeneous acid-catalyzed transesterification

Waste oils contain free fatty acids which cannot be converted to biodiesel using an alkaline catalyst. These FFAs will produce soap that inhibit the separation of the ester, glycerin, and wash water when react with an alkaline catalyst [5]. Hence, liquid acid-catalyzed transesterification is proposed in order to overcome lots of conundrum caused by liquid base catalysts. Sulfuric acid, sulfonic acid, hydrochloric acid, organic sulfonic acid, and ferric sulphate are most commonly acids used as catalysts in transesterification [14]. In the production of biodiesel, hydrochloric acid and sulfuric acid are favoured as catalyst [12]. Despite of its insensitivity to FFA in the feedstock and can catalyzes esterification and transesterification simultaneously, acid catalyst has been less popular in transesterification reaction because it has relatively slower reaction rate [16, 17, 18]. Thus, alcohol to oil molar ratio is the main factor influencing the reaction. Addition of excess alcohol can speeds up the reaction and favours the formation biodiesel product. The steps involve during acid-catalyzed transesterification are initial protonation of the acid to give an oxonium ion followed by the oxonium ion and an alcohol undergo exchange reaction to give the intermediate which later loses a proton to become an ester [14].

In a study of acid-catalyzed transesterification of sunflower oil using HCl as listed in Table 1, Sagioglu *et al.* (2011) reported 95.2% of biodiesel yield with 100°C reaction temperature and 1.85 wt% catalyst loading. Cao *et al.* (2013) used  $\text{H}_2\text{SO}_4$  in the acid-catalyzed transesterification with 0.5 wt% catalyst loading reported 92.5% biodiesel yield from *Chlorella pyrenoidosa*.

#### Heterogeneous base-catalyzed transesterification

Numbers of research have been conducted on heterogeneous catalysts to overcome the problems caused by homogeneous catalyst in biodiesel production. Most of the heterogeneous catalysts developed for production of biodiesel are either alkaline oxide or alkaline earth metal oxide supported over large surface area (Helwani, *et al.*, 2009). Heterogeneous basic catalysts are more active than heterogeneous acid catalyst, similar to their homogeneous counterparts [17]. In addition, solid alkaline catalysts, for instance, calcium oxide (CaO) provide many advantages such as higher activity, long catalyst life times, and could run in moderate reaction condition [18]. Nonetheless, CaO as catalyst can also slow down the reaction rate of biodiesel production [19]. Notwithstanding, reaction of CaO with glycerol can leach out calcium diglyceride during transesterification which result in necessity of an extra purification step such as ion exchange resin to remove the soluble content in the biodiesel (Gryglewicz, 1999; Kouzu *et al.*, 2008; Kouzu *et al.*, 2009). Table 1 lists some of the reaction conditions for various types of heterogeneous base catalysts in transesterification of lipid.

The highest biodiesel yield was reported by Nakatani *et al.* (2009) with 96.5% obtained from soybean oil by using oyster shells as catalyst. The transesterification was done in 65°C using methanol as alcohol with ratio of 6:1 and 25 wt% catalysts loading for 5 hours reaction. Viriya-empikul *et al.* (2012) and Wei *et al.* (2009) both reported transesterification by using eggshells as catalyst which is the closest comparison to this study. Viriya-empikul *et al.* (2012) obtained 94.1% biodiesel yield from palm olein oil when the transesterification was done in 60°C for 2 hours with methanol to oil ratio of 15:1 and 10 wt% catalysts loading. Whilst Wei *et al.* (2009) reported 95% biodiesel yield on soybean oil. The reaction was conducted in 65°C for 3 hours and the methanol to oil ratio was 9:1 with 3 wt% catalysts loading.

Most of the literature reported on heterogeneous base catalyst used lower reaction temperature (<65°C). As a matter of fact, temperature above 70°C will resulted in lower yield as methanol evaporates at 65°C [22]. Furthermore, base-catalyzed transesterification was proved to have higher reaction rate as compared to acid-catalyzed transesterification which need more vigorous reaction condition including higher temperature during transesterification [12].

#### Heterogeneous acid-catalyzed transesterification

Despite of the effectiveness of homogeneous acid catalyst, it can lead to absolute contamination problems which require good separation and product purification processes [11]. This will be resulted in higher production cost. It is believed that heterogeneous acid catalysts have the potential as alternative to homogeneous acid catalysts. Some of advantages of heterogeneous acid catalyst are insensitive to FFA content, can simultaneously conduct esterification and transesterification, eliminate the washing step of biodiesel, simpler separation process of catalyst



from product, regenerating and reusing the catalyst is possible and also reduce the corrosion problems [12], [23], [16], [24], [25]. In addition, solid acid catalysts are preferred over liquid acid catalysts due the fact that they contain a multiple sites with different strength of Bronsted or Lewis acidity [14], [26]. Bronsted acid catalysts have the advantage of promoting simultaneous esterification and transesterification with the use of cheaper feedstock containing high concentration of free fatty acids [27]. A Lewis acid site is more active as compared to Bronsted but is at risk to poisoning from water and/or free fatty acids. Generally said, the low activity of acid catalysts relative to the counterpart basic ones is due to different reaction mechanism. However, efforts to utilizing heterogeneous acid catalyst for transesterification of triglycerides are limited due to daunting point of view for its low reaction rates and possible adverse side reaction [26]. Consequently, the mechanisms and factors influence the reactivity of the solid acid catalysts have not fully understood.

Not many works were reported on heterogeneous acid catalyst as compared to heterogeneous base catalyst. Types of solid acid catalysts that were commonly used in esterification and transesterification reaction works include tungsten oxides, sulphonated zirconia (SZ), sulphonated saccharides, Nafionl resins, and organosulphoric functionalized mesoporous silicas [28]. Some of the reaction conditions using heterogeneous acid catalyzed transesterification are listed in Table 1. Muthu *et al.* (2010) reported 95% biodiesel yield from Neem oil by using sulphated zirconia as solid acid catalyst and methanol to oil ratio of 9:1. Comparing to Shu *et al.* (2010), biodiesel yield from waste vegetable oil was reported 94.8% by using carbon-based solid acid as catalyst and methanol for alcohol. Brucato *et al.* (2010) used titanium-doped amorphous zirconia as heterogeneous acid catalyst and obtained 65% biodiesel yield from rapeseed with higher methanol to oil ratio (40:1).

### Enzyme (Biocatalyst) catalyzed transesterification

Enzymatic transesterification has drawn researcher's attention due to the downstream processing problem posed by chemical transesterification. Huge amount of wastewater generation and difficulty in glycerol recovery are some of the problems that eventually increase the overall production cost of biodiesel and being not environmental benign. In contrast, enzyme catalysis occurs without the generation of by-products, easy recovery product, mild reaction condition, insensitive to high FFA oil and catalyst can be reuse [23]. Thus, enzyme catalyzed biodiesel production has proven to have high potential to be an eco-friendly process and a promising alternative to the chemical process. However, enzyme catalyzed biodiesel production has some limitations especially when implemented in industrial scale because of high cost of enzyme, slow reaction rate and enzyme deactivation [29].

Lipase is often used in enzymatic catalyzed transesterification. Table-1 listed some of works reported on lipase as biocatalyst in transesterification of biodiesel. Simões *et al.* (2015) reported the highest yield of biodiesel by using babassu oil with 96.0%. The transesterification reaction was done by immobilized lipase on SiO<sub>2</sub>. Lipase can also be immobilized on crystalline PVA as reported by Bergamasco *et al.* (2013). Bergamasco *et al.* (2013) reported 66.3% of biodiesel by using soybean oil and ethanol as alcohol with ratio 6:1. In comparison, work done by Chen *et al.* (2011) used methanol with the ratio to oil of 4:1 reported higher biodiesel yield compared to Bergamasco *et al.* (2013) with 83.31% FAME by using also soybean oil.

### Waste-derived heterogeneous catalyst

The use of heterogeneous catalyst is promising to reduce the present high production cost of biodiesel making it competitive with petro-diesel fuels. Therefore, research is being directed towards the development of environmental friendly and cost-effective heterogeneous catalyst for biodiesel production. In order to make the biodiesel production more sustainable, the utilization of waste heterogeneous catalysts has become recent interest.

The alkaline earth metal oxides such as MgO, CaO, and SrO have the high activity for using in the typical process which at low temperature and under atmospheric pressure condition. Among the alkaline earth metal oxides, CaO is close on the environmental material. Generally, Ca(NO<sub>3</sub>)<sub>2</sub>, CaCO<sub>3</sub>, or Ca(OH)<sub>2</sub> is the raw material to produce CaO catalysts (Cho *et al.*, 2009). As alternative way to synthesize CaO catalyst, there are several natural calcium sources from wastes, such as eggshell, mollusk shell, and bone. Not only eliminating a waste management cost, but also the catalysts with high cost effectiveness can be simultaneously achieved for biodiesel industry.

The shells of oysters and chicken eggs have been evaluated as effective catalysts to convert vegetable oil to methyl ester [31]. Nakatani *et al.* (2009) showed that by using 25 wt% of thermally activated (at 700°C) oyster shell at 6:1 methanol:oil molar ratio, the yield of biodiesel production is over 70% and purity of 98.4% was achieved in a 5h reaction time. The conversion at a moderate 6:1 (methanol:oil) ratio was achievable at the expense of a higher catalyst and longer reaction time. Soybean oil was transesterified with 3 wt% of calcined egg shell at 1000°C to obtain over 95% yield in 3h reaction time with the conditions of 9:1 methanol:oil molar ratio and a 65°C reaction temperature [33]. In addition, Wei *et al.* (2009) found that the waste catalyst is capable of being reused up to 13 times without much loss in the activity.

High active, reusable solid catalyst was obtained by calcining eggshell. Calcined eggshell exhibited high activity towards the transesterification of vegetable oil with methanol to produce biodiesel. The method of reusing eggshell waste to prepare catalyst could recycle the waste, minimizing contaminants, reducing the cost of



catalyst, and making the catalyst environmental friendly. In fact, this high efficient and low-cost eggshell catalyst could make the process of biodiesel production economic and fully ecologically friendly. The ecologically friendly and economic process could effectively reduce the processing cost of biodiesel, making it competitive with petroleum diesel [33]. Low-cost catalyst could be used in a large-scale industrial process of biodiesel, making the process cheap and ecologically benign. In addition to biodiesel production, such environmentally benign eggshell-derived catalysts should find application in a wide range of other base-catalyzed important organic reactions.

These catalysts have very high commercial prospects, especially in biodiesel industries, as they can be equipped at nominal cost from the waste materials reducing the biodiesel production cost and making it competitive with petroleum diesel. Sanjay (2013) mentioned that easy availability, biodegradability and environmental acceptability are three factors in favor of the catalysts as their large scale use will cause no disposal problem as of the fact they are reusable for several reaction cycles. These catalysts are considered as green-catalyst which is derived from renewable biomasses and the biodiesel production is also a promising green technology.

**Table-1.** Comparisons of reactions conditions for various types of catalysts.

Catalyst	Reaction conditions					Biodiesel yield	Remarks	Reference
	Temp, °C	Type of alcohol (alcohol to oil molar ratio)	Catalyst loading, wt %	Reaction time, h	Mixing, rpm			
Homogeneous base catalyst								
Sodium hydroxide (NaOH)	40	Ethanol (9:1)	1.3	1.33	-	Soybean oil, 95%	Batch reactor	[35]
Sodium hydroxide (NaOH)	55	Methanol (3:1)	0.5	2	250	Waste soybean cooking oil, 68.5%	Shake flask	[36]
Sodium hydroxide (NaOH)	60	Methanol (475:1)	0.1	1	-	Rapeseed, 88.8%	Soxhlet	[37]
Potassium hydroxide (KOH)	60	Methanol (4:1)	0.1	1	550	<i>Pongamia pinnata</i> seeds, 98.5%	-	[38]
Potassium hydroxide (KOH)	50	Methanol (6:1)	0.075	5	800	Jatropha seed, 87%	Three-necked round bottom flask equipped with reflux system	[39]
Potassium hydroxide (KOH)	55	Methanol (9:1)	1	1	-	<i>Calophyllum inophyllum</i> , 98.53%	-	[40]
Sodium methoxide (NaOCH <sub>3</sub> )	50	Methanol (6:1)	0.75	0.5	-	<i>Sesamum indicum</i> L. seed oil, 87.8%	Batch reactor	[41]
Heterogeneous base catalyst								
Bone	60	Methanol (20:1)	18	4	600	Rapeseed oil, 96% Peanut oil, 94%	Batch reactor	[29]
Rice Husk	65	Methanol (24:1)	4	3	300	Soybean oil, 99.5%	Shake flask	[42]
Snail shells	60	Methanol (6.03:1)	2	7	-	Waste frying oil, 99.58%	-	[43]
- Eggshells - Snail shells	60	Methanol (15:1)	10	2	-	Palm olein oil, 94.1% Palm olein oil,	-	[44]



- Venus shells						93.2% Palm olein oil, 92.3%		
Vegetable oil asphalt	220	Methanol (16.8:1)	0.2	4.5	-	Vegetable oil, 94.8%	-	[45]
Oyster shells	65	Methanol (6:1)	25	5	-	Soybean oil, 96.5%	Magnetic stirrer	[32]
Eggshells	65	Methanol (9:1)	3	3	-	Soybean oil, 95%	-	[46]
<b>Homogeneous acid catalyst</b>								
Hydrochloric acid (HCl)	100	Methanol	1.85	1	-	Sunflower oil, 95.2%	-	[47]
Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	120	Methanol (40:1)	0.5	3	-	<i>Chlorella pyrenoidosa</i> , 92.5%	-	[48]
Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	50	Methanol (6:1)	3	1	-	Vegetable oil by product, >90%	Reflux condenser reactor	[49]
<b>Heterogeneous acid catalyst</b>								
Titanium-doped amorphous zirconia	245	Methanol (40:1)	11	-	-	Rapeseed oil, 65%	-	[50]
Sulfated zirconia	65	Methanol (9:1)	1	2	-	Neem oil, 95%	-	[51]
Carbon-based solid acid catalyst	220	Methanol (16.8:1)	0.2	4.5	-	Waste vegetable oil, 94.8%	-	[45]
<b>Enzyme catalyst</b>								
Lipase	52.1	Methanol (4:1)	-	-	-	Soybean oil, 83.31%	Continuous packed bed reactor	[52]
Immobilized lipase on SiO <sub>2</sub>	50	Ethanol (12:1)	-	11	-	Babassu oil, 96.0%	Continuous packed bed reactor	[53]
Immobilized lipase on crystalline PVA	37	Ethanol (6:1)	4	72	-	Soybean oil, 66.3%	-	[54]

### ADVANTAGES AND DISADVANTAGES OF HOMOGENEOUS AND HETEROGENEOUS CATALYST

The advantages and disadvantages of homogeneous and heterogeneous catalyst are discussed in Table-2. In general, there are three types of catalyzed transesterification namely alkali-catalyzed, acid-catalyzed, and enzymatic transesterification. Enzyme catalysts are more attractive recently for its simpler purification process and it can avoid saponification. However, the drawbacks are high in cost and longer reaction time required.

On the other point, alkali and acid catalysts are more commonly used in transesterification because of their availability. Alkali and acid catalysts consist of homogeneous and heterogeneous types. Sodium hydroxide and potassium hydroxide are two most popular homogeneous base catalysts used in transesterification due to low cost and widely available [37-42]. Alkali-catalyzed

transesterification is considered as economical because the process can be carried out in low temperature and pressure environment with high yield. On the other hand, heterogeneous alkali catalysts are preferable for easier separation process. Nonetheless, acid catalysts are used because they can avoid saponification and their performance is insensitive to FFA content [11]. Homogeneous acid catalysts that are commonly used include hydrochloric acid and sulphuric acid [49-51]. Even though homogeneous acid catalysts transesterification is effective, it leads to serious contamination problems which require good separation and purification process of the product. To overcome the limitation, heterogeneous acid catalyst is used. The appropriate heterogeneous catalysts can be applied in the transesterification system to simplify the product separation and purification consequently reducing waste generation.



**Table-2.** Advantages and disadvantages of different types of catalyst used in transesterification.

Type of catalyst	Advantages	Disadvantages
Homogeneous base catalyst	<ul style="list-style-type: none"> <li>- Do not form water during transesterification reaction [14]</li> <li>- 4000 times faster reaction rate than acid-catalyzed transesterification [12], [14]</li> <li>- Two-step alkaline-catalyzed transesterification from used vegetable oil is an economic method for biodiesel production [13]</li> <li>- Reaction can occur at mild reaction condition and thus less energy required [12], [14]</li> <li>- NaOH and KOH are economically feasible and widely available [12]</li> </ul>	<ul style="list-style-type: none"> <li>- Sensitive to FFA content in the oil [12]</li> <li>- Saponification can occur if the FFA content in the oil is more than 2 wt.% [12]</li> <li>- Saponification will decrease the biodiesel yield and cause problem during product purification [12], [14]</li> <li>- Produce more wastewater from purification [55]</li> </ul>
Heterogeneous base catalyst	<ul style="list-style-type: none"> <li>- Reusable [47]</li> <li>- Easy to separate from product [47]</li> <li>- Relatively faster reaction rate than acid-catalyzed transesterification [12]</li> <li>- Reaction can occur at mild reaction condition and relatively lower energy [12]</li> <li>- Long catalyst life times [14]</li> </ul>	<ul style="list-style-type: none"> <li>- Poisoning of the catalyst when exposed to ambient air [12]</li> <li>- Sensitive to FFA content in the oil due to its basicity property [12]</li> <li>- Saponification can occur if the FFA content in the oil is more than 2 wt.% [12]</li> <li>- Saponification will decrease the biodiesel yield and cause problem during product purification [12], [14]</li> <li>- Higher molar ratio of alcohol to oil [55]</li> <li>- Produce more wastewater from purification [55]</li> <li>- Diffusion limitation [55]</li> </ul>
Homogeneous acid catalyst	<ul style="list-style-type: none"> <li>- Insensitive to FFA and water content in the oil [11]</li> <li>- Preferred-method if low-grade oil is used [12]</li> <li>- Esterification and transesterification occur simultaneously [12]</li> <li>- Saponification can be avoided [55]</li> <li>- Produce high yield of biodiesel [14]</li> </ul>	<ul style="list-style-type: none"> <li>- Low reaction rate [12], [14], [55]</li> <li>- Can lead to equipment corrosion [12], [55]</li> <li>- Harder separation of catalyst from product [12]</li> </ul>
Heterogeneous acid catalyst	<ul style="list-style-type: none"> <li>- Insensitive to FFA and water content in the oil [11]</li> <li>- Preferred-method if low-grade oil is used [12]</li> <li>- Esterification and transesterification occur simultaneously [12]</li> <li>- Easy separation of catalyst from product [12]</li> <li>- High possibility to reuse and regenerate the catalyst [12], [13]</li> <li>- Recyclable [55]</li> </ul>	<ul style="list-style-type: none"> <li>- Low reaction rates [12], [14], [55]</li> <li>- Unfavourable side reaction               <ul style="list-style-type: none"> <li>- Higher cost [55]</li> </ul> </li> <li>- High reaction conditions and longer reaction times [14], [55]               <ul style="list-style-type: none"> <li>- More energy requirement [12]</li> </ul> </li> <li>- Leaching of catalyst active sites may result to product contamination [12]</li> </ul>
Enzyme catalyst	<ul style="list-style-type: none"> <li>- Prevent saponification [55]</li> <li>- Only simple purification step is required [23], [55]</li> <li>- Environmental friendly and nonpolluting [14]</li> </ul>	<ul style="list-style-type: none"> <li>- Very slow reaction rate [12]               <ul style="list-style-type: none"> <li>- High cost [12], [55]</li> </ul> </li> <li>- Sensitive to alcohol, typically methanol that can deactivate the enzyme [29]</li> <li>- Inactivation and denaturation of enzyme can lead to decreasing yield of biodiesel [16], [55]</li> </ul>

## CONCLUSIONS

Biodiesel is a non-toxic, renewable, biodegradable, and more environmental friendly fuel which appears to be an alternative fuel to petro-diesel

counterpart [12], [56]. Biodiesel has become increasingly attractive for its environmental benefits and the fact that it is made from renewable sources. Currently, esterification and transesterification is the most commonly applied



method to synthesize biodiesel [12], [56]. Edible and non-edible vegetable oils or animal fats are generally used in transesterification to react with alcohols in the presence of catalyst. However, the prices of these oils and fats are high which make the overall production cost increased. As an alternative, many studies were done to develop low cost catalysts to reduce the production cost. Several catalysts such as homogeneous/heterogeneous acid catalysts, homogeneous/heterogeneous base catalysts and biocatalysts (enzymes) have been studied and applied in the synthesis of biodiesel. Base-catalyzed transesterification is commonly used in commercial production because of high FAME yield in short reaction time and the reaction can be done in mild conditions as compared to acid-catalyzed transesterification [12], [14], [56]. It was reported that acid-catalyzed transesterification needs higher alcohol to oil molar ratios despite of it is the preferable method when low-grade oil is used [12].

Transesterification using heterogeneous base catalysts are found to be cost effective because of its reusability, widely available, easy to separate from product and longer life time [12], [14], [47]. However, the use of solid alkaline catalysts needs to be thoroughly explored and developed to reduce saponification and overcome the diffusion limitations consequently produce better yield.

Development of enzyme catalysts is necessary to have a more environmental friendly process and fulfil the environmental needs. The process has potential to produce high quality product which can compete with petro-diesel fuel [14]. The concern of global warming inaugurated the demand of biodiesel over petro-diesel fuel. It is foreseeable that biodiesel usage would develop at a fast pace and thus trigger the need to find more sophisticated methods with both economical and environmental friendly to produce biodiesel.

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