CHAPTER II
LITERATURE REVIEW

2.1 Biodiesel

More than hundred years old, the idea of using vegetable oils as fuels for diesel engines has been considered. In 1985, Rudolf Diesel discovered plant oils as possible for hydrocarbon-based fuels by developing new engine with the intention that it could be used with variety of fuels, including vegetable oils. At the World's Exhibition in Paris, he ran the engine with peanut oils on and that was so quite smoothly. Later on, several European countries considered this idea. However, the availability of petroleum in large quantities made the interest in plant oils diminished.

Moreover, plant oils typically have the viscosities ten to twenty times higher than the viscosity of the fossil diesel fuel. With this viscosity, encounter with poor fuel atomization and incomplete combustion. To solve these problems, it can either adapting the engine to be able to use fuels having high viscosity or improving the fuel properties that suitable for engine. The first strategy results in the development of engine for plant oils. The latter strategy focuses on modifying plant oil properties by using various technologies to produce fuels having properties and performance like fossil diesel fuel.

2.1.2 Biodiesel Production Technology

Generally, vegetable oils having high viscosity lead to atomization problem in engine. Thus, converting the vegetable oils or animal fats seems to biodiesel same to interesting. The three most widely used technologies to produce biodiesel are pyrolysis, microemulsification, and transesterification (Schwab *et al.*, 1987).

2.1.2.1 Pyrolysis

Pyrolysis refers to thermal decomposition reactions, usually taken place in the absence of oxygen. The mixture of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids produced from this treatment process is more similar to hydrocarbon based diesel fuels (Mittlebach and Remschmidt, 2004). Pyrolysis can be used to enchance the cetane number of plant oils and by–product concentrations of sulfur, water,

and sediment are acceptable (Mittlebach and Remschmidt, 2004). However, the viscosity of fuels is still high because of ash and carbon residues.

2.1.2.2 Microemulsification

Microemulsification is the thermodynamically stable dispersions of two immiscible liquid by usingone or more surfactants. The dispersed particles having a size in diameter of 100-1,000 A in microemulsions (Srivastava and Prassad, 2000). According to literature reviews, microemulsions of vegetable oils and alcohols (methanol, ethanol or 1-butanol) cannot be recommended for long-term use in diesel engines for similar reasons as apply to neat vegetable oils.

2.1.2.3 Transesterification

Transesterification or alcoholysis reaction is a reaction that one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of fatty acid alkyl esters. This process is a sequence of three reversible reactions, in which the triglyceride molecule is converted step by step into diglyceride and monoglyceride, respectively. In each step one mole of ester is replaced by one mole of alcohol, as shown in Figure 2.1 below.
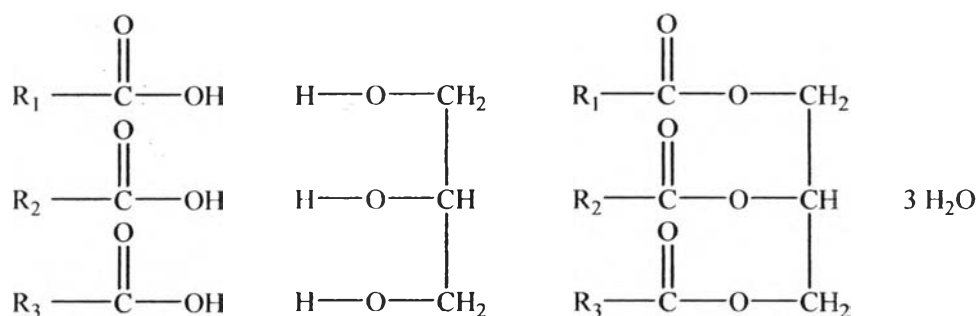
$$
\begin{array}{cccc}
R_1\!-\!\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!OH & H\!-\!O\!-\!CH_2 & & R_1\!-\!\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!O\!-\!CH_2 \\
R_2\!-\!\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!OH & H\!-\!O\!-\!CH & & R_2\!-\!\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!O\!-\!CH \quad 3\,H_2O \\
R_3\!-\!\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!OH & H\!-\!O\!-\!CH_2 & & R_3\!-\!\!\overset{\displaystyle O}{\overset{\|}{C}}\!-\!O\!-\!CH_2
\end{array}
$$

Figure 2.1 Reaction scheme for the transesterification of triglycerides with methanol

In order to shift equilibrium to the right, an excess methanol over the stoichiometric amount is required for commercial biodiesel production. An advantage of using methanol as compared to transesterification with higher alcohols is the fact that the two main products, glycerol and fatty acid methyl esters (FAME), are hardly miscible and thus form separate phase – an upper ester phase and a lower glycerol phases. Accordingly, the glycerol is easier to be removed for high conversion.

The properties of biodiesel and diesel fuels are compared in Table 2.1. Biodiesel fuels produced from various vegetable oils have viscosities close to those of diesel. Their volumetric heating values are a little lower, but they have high cetane numbers and flash points. Since the characteristics of biodiesel are generally similar to those of diesel; therefore, it is a strong candidate to replace diesel if the need arises.

Table 2.1 Fuel properties of biodiesel and diesel fuel (Fukuda *et al.*, 2001)

Vegetable oil methyl ester	Kinematic viscosity (mm²/s)	Cetane number	Lower heating value (MJ/l)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt%)
Peanut	4.9 (37.8°C)	54	33.6	5	176	0.883	-
Soybean	4.5 (37.8°C)	45	33.5	1	178	0.885	-
Babassu	3.6 (37.8°C)	63	31.8	4	127	0.879	-
Palm	5.7 (37.8°C)	62	33.5	13	164	0.880	-
Sunflower	4.6 (37.8°C)	49	33.5	1	183	0.860	-
Rapeseed	4.2 (40°C)	51–59.7	32.8	-	-	0.882	-
Used Rapeseed	9.48 (30°C)	53	36.7	-	192	0.895	0.002
Used corn oil	6.23 (370°C)	63.9	42.3	-	166	0.884	0.0013
Diesel fuel	12–3.5 (40°C)	51	35.5	-	-	0.830–0.840	-
JIS-2D (gas oil)	2.8 (30°C)	58	42.7	-	59	0.833	0.05

2.2 Starting Material for Biodiesel Production

The starting materials for biodiesel production depended on many purposes according to the price, availability, growing-land usage and etc. But any material contains fatty acids source can be used to produce biodiesel.

2.3.1 Vegetable Oils

Vegetable oils are triglycerides, which are esters of one glycerol with three long-chain acids (which can be different types), commonly called fatty acids. The major component of vegetable oils is triglycerides. Vegetable oils comprise 90 to 98% triglycerides and small amounts of mono- and di-glycerides. They contain free fatty acids (generally 1 to 5%) and traces of water (Srivastava and Prasad, 2000). The general formation of triglyceride is shown in Figure 2.2.
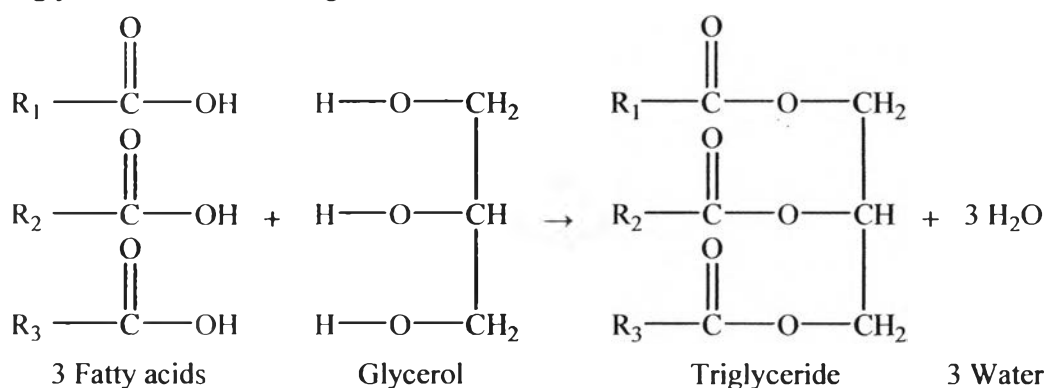

Figure 2.2 Formation of triglyceride (Noiroj, 2007).

From Figure 2.2, R_1, R_2, and R_3 represent a chain of carbon atoms with hydrogen atoms attached. The differences of R_1, R_2 and R_3 result in differences of fatty acids which glycerol backbone will be combined. Fatty acids vary in their carbon chain length and in the number of double bonds, leading to different characteristics of vegetable oil. The common fatty acids found in vegetable oils are stearic, palmitic, oleic, linoleic, and linolenic. The name and chemical structure of common fatty acids are shown in Table 2.2.

Table 2.2 Chemical structure of common fatty acids (Srivastava and Prasad, 2000)

Fatty acid	Systematic name	Structure[a]	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	cis-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucic	cis-13-Docosenoic	22:1	$C_{22}H_{42}O_2$

[a]xx:y indicates x carbons in fatty acid chain with y double bonds

2.2.3 Alcohol

Alcohol is one of the reactants that required for the transesterification. Due to the reversible reaction, the ratio of alcohol to triglyceride affects the direction of equilibrium or yield of ester. Methanol is the most commonly used alcohol for biodiesel production because of reaction mixture separation as well as its price and high activity (Lang et al., 2001). Although other alcohols can be used such as ethanol, isopopanol, and butyl alcohol, it was found that methanolysis using alkali-catalyst achieved esters yields more than 80% at room temperature even the reaction take placed in five minutes (Mittel-bach, 2004). According to stoichiometry, alcohol and vegetable oil molar ratio are required for three moles of alcohol per one mole of triglyceride. To shift the equilibrium to the right, an excess alcohol is required. But the optimal molar ratio of alcohol and vegetable oil still depends on the type of catalyst used, as shown in Figure 2.2.
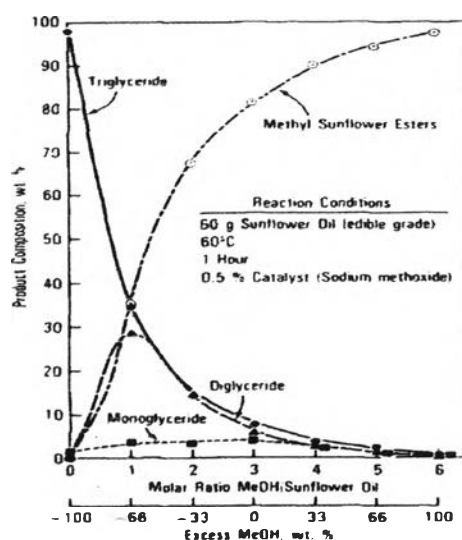
Figure 2.3 Effect of alcohol to vegetable oil ratio on product composition for transesterification of sunflower oil (Freedman *et al.*, 1984).

Figure 2.3 shows the influence of alcohol and vegetable oil molar ratio on product composition of transesterification of sunflower. It shows that the triglyceride composition in product stream continuously decrease with increasing methanol and sunflower molar ratio. At 6:1 methanol-to-oil ratio can drive the reaction complete. Mono-and di-glyceride also have the behavior like a triglyceride behavior when the ratio reached certain ratio. The reason why mono- and di-glyceride content increase at the beginning might because of the formation of mono- and di-glyceride. The desired product, methyl sunflower esters, is directly proportional to alcohol and vegetable oils ratio.

Beside the alcohol and vegetable type of oil ratio, water content in alcohol is also an important quality factor for selecting alcohol. Because water can participate undesired reaction that results in poor yields.

2.4 Catalyst in Transesterification

In general, transesreification of triglyceride with lower alcohol also proceed but it provides high energy input and long reaction time. To achieve satisfactory ester yield under the mild condition, biodiesel production is generally conducted in the presence of a catalyst. The catalyst can be divided into two types (homogeneous and heterogeneous catalyst).

Nowadays, in commercial biodiesel production used homogeneous catalyst in the process because homogeneous catalyst gives high conversion and short reaction time. The homogeneous catalyst can be divided into two types.

2.4.1 Homogeneous Acid Catalyst

In catalytic transesterification using homogeneous acid catalyst, the reaction is catalyzed by hydrochloric or sulphonic acids. In general, the acid catalyzed reactions are performed at high alcohol to oil molar ratios, low-to-moderate temperatures and pressures, and high acid catalyst concentrations. The acid-catalyzed reactions require the use of high alcohol to oil molar ratios in order to obtain good product yields within reasonable reaction time; however, ester yields do not proportionally increase with molar ratio. Freedman *et al.* (1984) studied the methanolysis of soybean oil by using H_2SO_4 as a catalyst. They discovered that in the presence of 1 mole % with the molar ratio of methanol to oil is of 30:1 at 65°C it take 50 h to reach complete conversion of the vegetable oil (> 99%) while the butanolysis (at 117°C) and ethanolysis (at 78°C), using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively. For instance, in soybean methanolysis using sulphuric acid, ester formation was sharply improved from 77% to 87.8% when increasing molar ratio of methanol to oil from 3.3:1 to 6:1. Higher molar ratio demonstrated only moderate improvement to a maximum of 98.4% (at 30:1). Table 2.3 summarizes reaction conditions used in acid catalyzed process of waste cooking oil using sulfuric acid as a catalyst.

Table 2.3 Reaction conditions in the acid-catalyzed synthesis of biodiesel from   waste cooking oil

	Acid-catalyzed biodiesel synthesis
Feedstock	Triglyceride mixtures with high free fatty acid contents (4%) e.g., waste cooking oil + methanol
Alcohol-to-oil molar ratio	50:1
Temperature	80°C
Pressure	4 bar
Catalyst	H_2SO_4
Catalyst load	1.3:1 molar ratio of sulfuric acid to waste oil
An oil conversion	97% is expected after 4 h of reaction

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.4 (Schuchardt *et al.*, 1998). The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+.
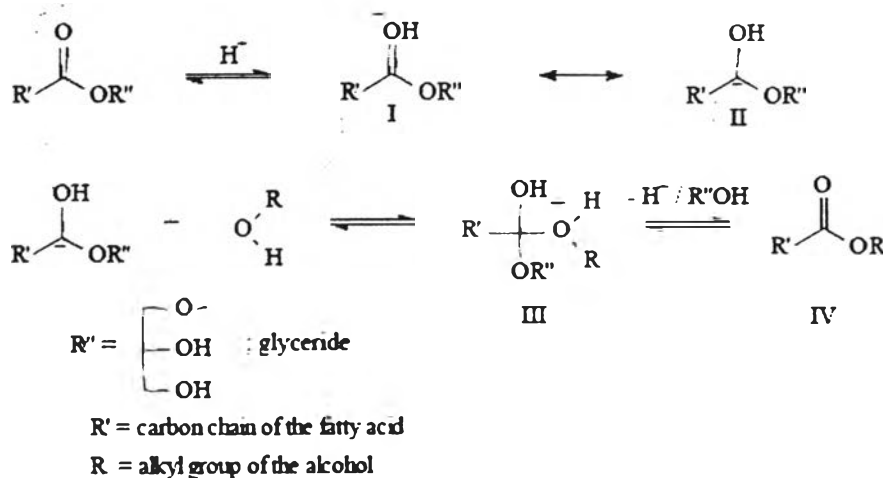

Figure 2.4 Mechanism of the acid-catalyzed transesterification of vegetable oils.

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to

avoid the competitive formation of carboxylic acids, which reduce the yields of alkyl esters.

The acid catalysts have many drawbacks such as long reaction time and high molar ratio of methanol to oil required. Besides, acid catalyst is more corrosive than base catalyst. Therefore, the most industrial process much prefer to use base catalyst instead of using acid catalyst.

2.4.2 Homogeneous Base Catalyst

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Moreover, the alkaline catalysts are less corrosive than acidic compounds. Thus the industrial processes usually favor base catalysts such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure. 2.5. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.
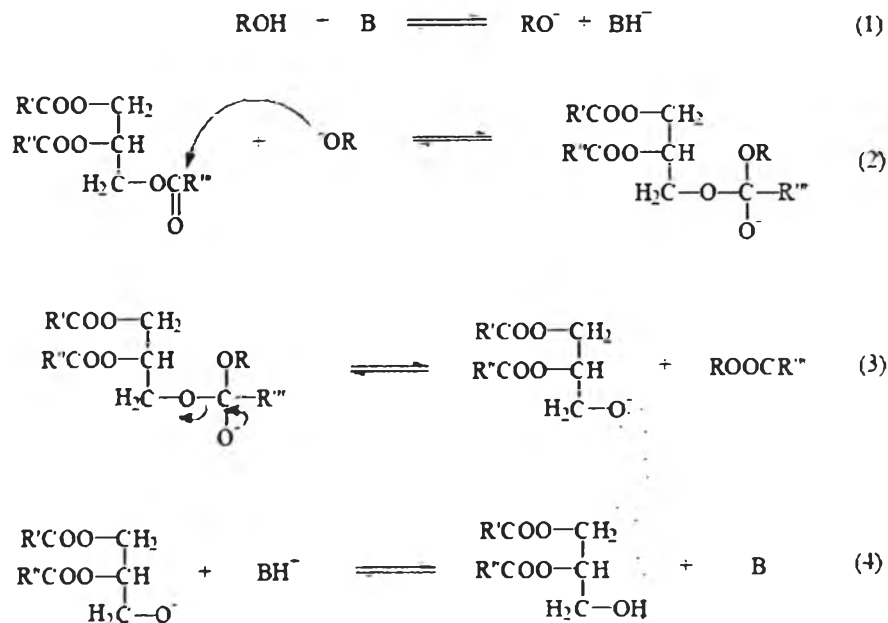
$$\text{ROH} \ - \ \text{B} \ \rightleftharpoons \ \text{RO}^- \ + \ \text{BH}^- \qquad (1)$$

R'COO—CH₂
R"COO—CH   +   ⁻OR   ⇌   R'COO—CH₂
H₂C—OCR"   R"COO—CH   OR   (2)
      ‖   H₂C—O—C—R"'
      O |
                                                     O⁻

R'COO—CH₂
R"COO—CH   OR   ⇌   R'COO—CH₂
H₂C—O—C—R"'   R"COO—CH   +   ROOCR"'   (3)
         O⁻   H₂C—O⁻

R'COO—CH₂
R"COO—CH   +   BH⁻   ⇌   R'COO—CH₂
H₂C—O⁻   R"COO—CH   +   B   (4)
                                   H₂C—OH

Figure 2.5 Mechanism of the base-catalyzed transesterification of vegetable oils.

Although the base-catalyzed are wildly used but they have many limit conditions such as it is very sensitive to water and free fatty acid. Some water reacts with alcohol lead to soap formation, as shown in Figure. 2.6 (Schuchardt *et al.*, 1997). This undesirable saponification reaction reduces the ester yields and considerably difficult to recover of the glycerol.

$$\text{RCOOR'} \ + \ \text{H}_2\text{O} \ \rightleftharpoons \ \text{RCOOH} \ + \ \text{R'OH}$$

$$\text{RCOOH} \ + \ \text{NaOH} \ \rightleftharpoons \ \text{RCOONa} \ + \ \text{H}_2\text{O}$$

Figure 2.6 Saponification of fatty acid alkyl ester.

Darnoko *et al.* (2000) studied the kinetic tranesterification of palm oil using potassium hydroxide as a catalyst. They found that the optimum amount of KOH should be 1% based on the weight of oil at the molar ratio of methanol to palm oil is 6:1. The conversion of glycerides to methyl esters fell out to be second order up to 30 min. Though

In addition, Vicente *et al.* (2003) compared the activity of different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide, and potassium hydroxide) for methanolysis of sunflower oil. They found that biodiesel purity was near 100 %wt for all catalysts. However, near 100 %wt biodiesel yields were only obtained with the methoxide catalysts. Although all the transesterification reactions were quite rapid and the biodiesel layers achieved nearly 100% methyl ester concentrations, the reactions using sodium hydroxide turned out the fastest.

Moreover, Karmee *et al.* (2005) used KOH as a catalyst for transesterification of the non-edible oil of Pongamia pinnata. They found that the maximum conversion of 92% (oil to ester) was achieved using a 1:10 molar ratio of methanol to oil at 60°C. The conversion was increased to 95% when tetrahydrofuran (THF) was used as a co-solvent.

However, in the homogeneous catalyst, the removal of the base catalysts after reaction is the major problem, since aqueous quenching resulting in the formation of stable emulsion and saponification, making separation of methyl ester difficult and a large amount of wastewater was produced to separate and clean the catalyst and product.

2.5 Heterogeneous Catalyst

Homogeneous catalysts showed greater performance toward transesterification; however, problems associated with the homogeneous catalysts are the high consumption of energy, form unwanted soap byproduct by reaction of the FFA, expensive separation of the homogeneous catalyst from the reaction mixture, and generation large amount of wastewater during separation and cleaning of the catalyst and the products. The use of heterogeneous catalysts could be an attractive solution since the catalysts can be separated more easily from reaction products. Biodiesel synthesis using solid catalysts could potentially lead to cheaper production costs because of reusability of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously.

Transesterification of soybean oil with methanol has been studied in a heterogeneous system on Li-doped MgO catalysts. It has been found that the addition of Li enhances the biodiesel yield of the parent MgO. It is confirmed that the beneficial of Li doping is attributed to the promotion on the formation of strong base sites. The biodiesel con-

version decreases with further increasing Li/Mg molar ratio above 0.08, which is most likely attributed to the excess Li ions forming separated lithium hydroxide and a concomitant decrease of BET surface area values. The results showed that the leaching from the catalyst and the agglomeration of crystallites give rise to the deactivation of the catalyst during the initial reaction cycles. More studies are needed to stabilize the catalysts for its application in the large-scale biodiesel production facilities.

Kim *et al.* (2004) used Na/NaOH/γ-Al$_2$O$_3$ heterogeneous base catalyst for the production of biodiesel from the soybean oil. They found that both the sodium aluminate formed by loading sodium hydroxide on γ-Al$_2$O$_3$, and the ionization of sodium, originated the strong basic sites of the catalysts. The activities of the heterogeneous base catalysts correlated with their basic strengths. The reaction conditions for the system were optimized to maximize the biodiesel production yield. A utilization of a co-solvent was found to be inevitable for the transesterification of vegetable oils to biodiesel. Among the co-solvent tested, *n*-hexane was the most effective with a loading amount of 5:1 vegetable oil to *n*-hexane molar ratio. The optimum methanol to oil loading ratio was found to be 9:1.

The KOH/Al$_2$O$_3$ and KOH/NaY can be used as solid base catalysts for biodiesel production via transesterification. By using the optimum conditions, about 51.26 and 3.18% of the K was leached from 25 wt% KOH/Al$_2$O$_3$ and 10 wt% KOH/NaY, respectively. The 10 wt% KOH/NaY should be proper for the transesterification reaction as a heterogeneous catalyst since the amount of K in the fresh catalyst is about the same as in the spent catalyst. It is reasonable to conclude that the type of support strongly affects the activity and leaching of the active species of the catalyst (Noiroj *et al.*, 2009).

Ebiura *et al.* (2005) used K$_2$CO$_3$, KF, LiNO$_3$, and NaOH loaded on alumina support. They found that K$_2$CO$_3$ loaded on alumina catalyst gave the highest yield of 94%. Alumina loaded with alkali metal salts was demonstrated as a solid-base catalyst for the transesterification of triolein with methanol. Transesterification over these catalysts proceed efficiently at 60°C, lower than the boiling point of methanol. This demonstration shows that it is possible to perform this reaction at atmospheric pressure using a heterogeneous catalyst. The effective transformation of triolein to methyl oleate over solid-base catalysts represents a convenient route for biodiesel and glycerol production.

On the other hand, Xie *et al.* (2006) varied the type of catalyst (KF, KCl, KBr, KI, K$_2$CO$_3$, KNO$_3$, KOH on Al$_2$O$_3$). They indicated that KI was the best catalyst, yielding

96% conversion of soybean oil. Besides, they varied the type of support (ZrO_2, ZnO, NaX zeolite, KL zeolite, and Al_2O_3) and found that the basic strength of the support affect to the conversion, the conversion increases when the basic strength was increased. Moreover, they suggested that the activity of catalyst was strongly affected not only by the strength of basic site but also by the amount of basis sites. Alumina loaded with potassium was demonstrated to be a strong solid-base catalyst for the transesterification of soybean oil with methanol. The catalytic activities of the heterogeneous base catalysts show a striking correlation with their corresponding basic properties. The decomposition products of the loaded KNO_3, forming either K_2O species or Al–O–K group in the composite, were probably the active basic sites (Xie *et al.*, 2006).

Furthermore, Xie *et al.* (2007) used NaX zeolites loaded with KOH as a solid base catalyst and discovered that loading of KOH on the NaX zeolite would increase the basic strength over the parent NaX zeolite. After being loaded with KOH, the pore structure of zeolites that necessary for catalysis could be retained. This approach was successfully used in an attempt to increase the catalytic activity of NaX zeolites towards the transesterification reaction.

Leclercq *et al.* (2001) used cesium-exchanged NaX faujasites for methanolysis of rapeseed oil. They found that among the different catalytic systems used in this work to perform the transesterification of rapeseed oil with methanol in the presence of solid basic catalysts, it is confirmed that strong basic properties are required to perform this reaction. Cation-exchanged zeolites are then not really appropriate, whereas systems in the form of a simple oxide with a high surface area show some interesting performances.

Verziu *et al.* (2009) used KF, LiF, and CsF/Al_2O_3 catalysts with different loadings from 1 to 20 wt%. They found that the deposition of alkaline fluorides on the alumina surface generates fluoroaluminates and aluminate species. The process starts at low temperatures and is definitivated at 400°C. Fluorine in these structures is less basic than in the parent fluorides, but the oxygen becomes more basic. Therefore, the active site is thought to be the consequence of the cooperation between the fluorine and oxygen. Using mesoporous MSU-aluminas provides large surface that allow the deposition of high loadings of alkaline fluorides. They are very active and efficient catalysts for transesterification of fatty esters with methanol at low temperatures using near stoichiometric amounts of methanol. Recycling experiments showed that these catalysts are very stable for a limited num-

ber of cycles and do not require any intermediate activation. Leaching of the active species depends on the reaction temperature.

In recent study, Hamad *et al.* (2010) prepared zirconia promoted with Cs by cationic exchange of zirconium hydroxide with Cs. They found that ZrOCs was obtained via cationic exchange between zirconium hydroxide with Cs^+ in basic conditions followed by calcination at high temperature. ZrOCs oxide has an excellent activity for vegetable oil transesterification with ethanol and methanol in mild conditions, while Cs-free ZrO_2 is not active in your standard conditions. Moreover, it is demonstrated that ZrOCs gives higher turnover rate than soluble NaOH. ZrOCs is believed to present a strong potential as a solid base catalyst due its basic features and thermal stability since this catalyst is formed via calcination at temperature of 550°C.

A summary of the advantages and disadvantages of each possibility technological, A solid heterogeneous catalyst integrated with continuous processing technologies is expected to gain wider acceptance in the future due to its potential effectiveness and efficiency. The use of solid catalysts and continuous flow reactors may complement the existing batch homogeneous catalyst production technology to reduce the cost of production. While there are potential benefits that the solid heterogeneous catalyst can offer, issues relating to the low catalytic activity, leachates, reusability and regeneration should be addressed and emphasized in the future research in order to ensure the sustainability of the process (Helwani *et al.*, 2009).

2.6 Process Variables in Biodiesel Production

The most important variables that affecting the rate of transesterification and reaction time are:

1. Reaction temperature
2. Reaction pressure
3. Molar ratio of alcohol to oil
4. Catalyst type and concentration

2.6.1 Reaction Temperature

The rate of reaction is strongly influenced by the reaction temperature; however, under the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60 to 70 °C) at atmospheric pressure. These mild reaction conditions, however, require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, the degummed and deacidified feedstocks are used at these conditions. The pretreatment is not required if the reaction is carried out under high pressure (9,000 kPa) and high temperature (240 °C). Under these conditions, simultaneous esterification and transesterification take place. The maximum yield of esters occurs at temperature ranging of 60 to 80 °C at a molar ratio (alcohol to oil) of 6:1. Further increasing temperature is reported to have a negative effect on the conversion. The butanolysis and methanolysis of soy bean oil were studied at different temperatures in the presence of acidic and alkaline catalysts. These studies indicated that transesterification can proceed at ambient temperatures in the case of the alkaline catalyst (Srivastava and Prasad, 2000).

2.6.2 Reaction Pressure

Basically, methyl esters can be produced by high-pressure or low-pressure methods. The former work at pressures of up to 100 bars and temperatures of about 250 °C with a 7–8 fold molar excess of methanol in the presence of alkaline or transient metal catalysts. These processes were long common in the detergent industry, followed by the conversion of the esters into fatty alcohols. The advantages of high-pressure transesterification are that raw materials, containing more than 20% free fatty acids can be used without pre-treatment and that high-purity glycerol can be sold as a by-product. Due to the high process costs, however, these methods are not suitable to biodiesel production (Mittlebach and Remschmidt, 2004).

2.4.3 Ratio of Alcohol to Oil

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3 moles of alcohol per mole of triglyceride to yield 3 moles of fatty esters and 1 mole of glycerol. To shift the transesterification reaction to the right, it is necessary to use either a

large excess of alcohol or to remove one of the products from the reaction mixture. The second option is preferred wherever feasible, since in this way, the reaction can be driven to completion. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight (Srivastava and Prasad, 2000).

2.4.4 Catalyst Type and Concentration

Alkali metal alkoxides are the most effective transesterification catalyst compared to the acidic catalyst. Sodium alkoxides are among the most efficient catalysts used for this purpose, although KOH and NaOH can also be used. Transmethylations occur approximately 4,000 times faster in the presence of an alkaline catalyst than those catalyzed by the same amount of acidic catalyst. Partly for this reason and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterifications are conducted with alkaline catalysts. The alkaline catalyst concentration in the range of 0.5 to 1% by weight yields 94 to 99% conversion of vegetable oil into esters. Furthermore, an increase in catalyst concentration does not increase the conversion but also it adds to extra costs because it is necessary to remove it from the reaction medium at the end.