CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Palm Fatty Acid

Palm fatty acid is separation of liquid mixture into their several components is one of the major process of the chemical industries. Fatty acid in palm oil has saturated and unsaturated fatty acids which palmitic acids and oleic acids are the main component acids.

Fatty acid, any of the organic carboxylic acids present in fats and oils as esters of glycerol. Molecular weights of fatty acids vary over a wide range. The carbon skeleton of any fatty acid is unbranched. Some fatty acids are saturated, i.e., each carbon atom is connected to its carbon atom neighbors by single bonds; and some fatty acids are unsaturated, i.e., contain at least one carbon-carbon double bond (see chemical bond). The characteristics of common fatty acids and their methyl ester can be see in Table 2.1.

Table 2.1 Characteristics of Common Fatty Acids and Their Methyl Esters

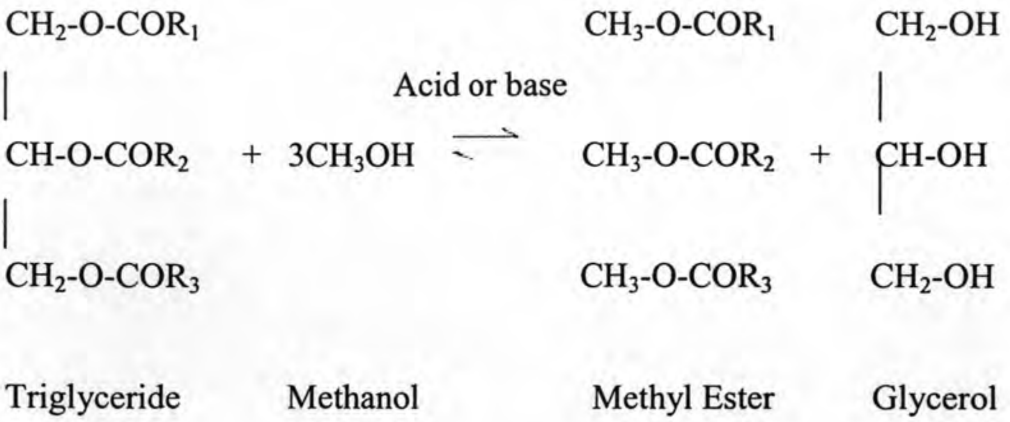
Fatty acid Methyl Ester	Formula	Molecular weight	Melting point (°C)
Palmitic acid	$C_{16}H_{32}O_2$	256.428	63-64
Methyl palmitate	$C_{17}H_{34}O_2$	270.457	30.5
Stearic acid	$C_{18}H_{36}O_2$	284.481	70
Methyl stearate	$C_{19}H_{38}O_2$	298.511	39
Oleic acid	$C_{18}H_{34}O_2$	282.465	16
Methyl oleate	$C_{19}H_{36}O_2$	296.495	-20
Linoleic acid	$C_{18}H_{32}O_2$	280.450	-5
Methyl linoleate	$C_{19}H_{34}O_2$	294.479	-35
Linolenic acid	$C_{18}H_{30}O_2$	278.434	-11
Methyl linolenate	$C_{19}H_{32}O_2$	292.463	-52 / -57

2.2 Palm stearin

Palm stearin are separated from process palm oil. This process is established mainly to add value to by byproducts from the refinery. Palm stearin is the more saturated and more solid fraction of palm oil. Palm stearin is the solid fraction obtained by fractionation of palm oil after crystallization at a controlled temperature. It is not used directly for edible purposes due to its high melting point ranging from 44 to 56°C (Pantzaris, 2000). At room temperature (25°C), palm stearin behaves as a solid and lacks the spreadability needed in products like margarine and shortening. The components of palm stearin are palmitic acids, oleic acids, linoleic acids, stearic acids, and others.

2.3 Transesterification

Transesterification (also called alcoholysis) is a reaction of vegetable oils such as palm oil, soy bean oil, sunflower oil, coconut oil, rapeseed oil, or animal fat (or known as triglycerides) to produce fatty acid esters, and glycerol as a co-product. A catalyst is usually used to speed up the reaction and may be basic, acid or enzymatic in nature (Ma, 1999). This reaction takes a long time to complete, and thus generally requires some base or acid catalyst to improve reaction rate and yield. Examples of these catalysts are sodium or potassium hydroxide, or sulfuric acid. General equation of this reaction is shown in Equation 2.1 R_1, R_2, and R_3 of hydrocarbon constituting fatty acids which may be the same or different.



$$\begin{array}{l} CH_2\text{-}O\text{-}COR_1 \\ | \\ CH\text{-}O\text{-}COR_2 \\ | \\ CH_2\text{-}O\text{-}COR_3 \end{array} + 3CH_3OH \xrightleftharpoons{\text{Acid or base}} \begin{array}{l} CH_3\text{-}O\text{-}COR_1 \\ \\ CH_3\text{-}O\text{-}COR_2 \\ \\ CH_3\text{-}O\text{-}COR_3 \end{array} + \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array} \qquad (1)$$

Equation 2.1 Transesterification reaction of triglycerides with alcohol (Fangrui, 1999).

The stoichiometry requires three moles of alcohol and one mole of triglyceride to produce three moles of fatty esters and one mol of glycerol. However in practice this is usually increased to 6:1 to increase product yield. However, this reaction is reversible, and therefore excess alcohol is used in reaction to shift the equilibrium to the right side (products). Typically, the variables affecting reaction rate and yield include: type and amount of catalyst, type of alcohol, reaction temperature, reaction time, molar ratio of oil and alcohol, glycerol separation and quality of vegetable oil such as fatty acid composition.

The transesterification reaction shown in Equation 2.1 is indeed the overall reaction for three stepwise reactions with intermediate formation of diglyceride and monoglyceride (Equation 2.2). In the first reaction, triglyceride (TG) react with alcohol to produce diglyceride (DG), then in the second reaction, diglyceride (MG) react with alcohol to form monoglyceride (MG). Finally, in the third reaction, monoglyceride (MG) react react with alcohol to give glycerol.

Stepwise Reaction:

1. Triglyceride + ROH $\rightleftharpoons$ Diglyceride + R'COOR
2. Diglyceride + ROH $\rightleftharpoons$ Monoglyceride + R''COOR
3. Monoglyceride + ROH $\rightleftharpoons$ Glycerol + R'''COOR

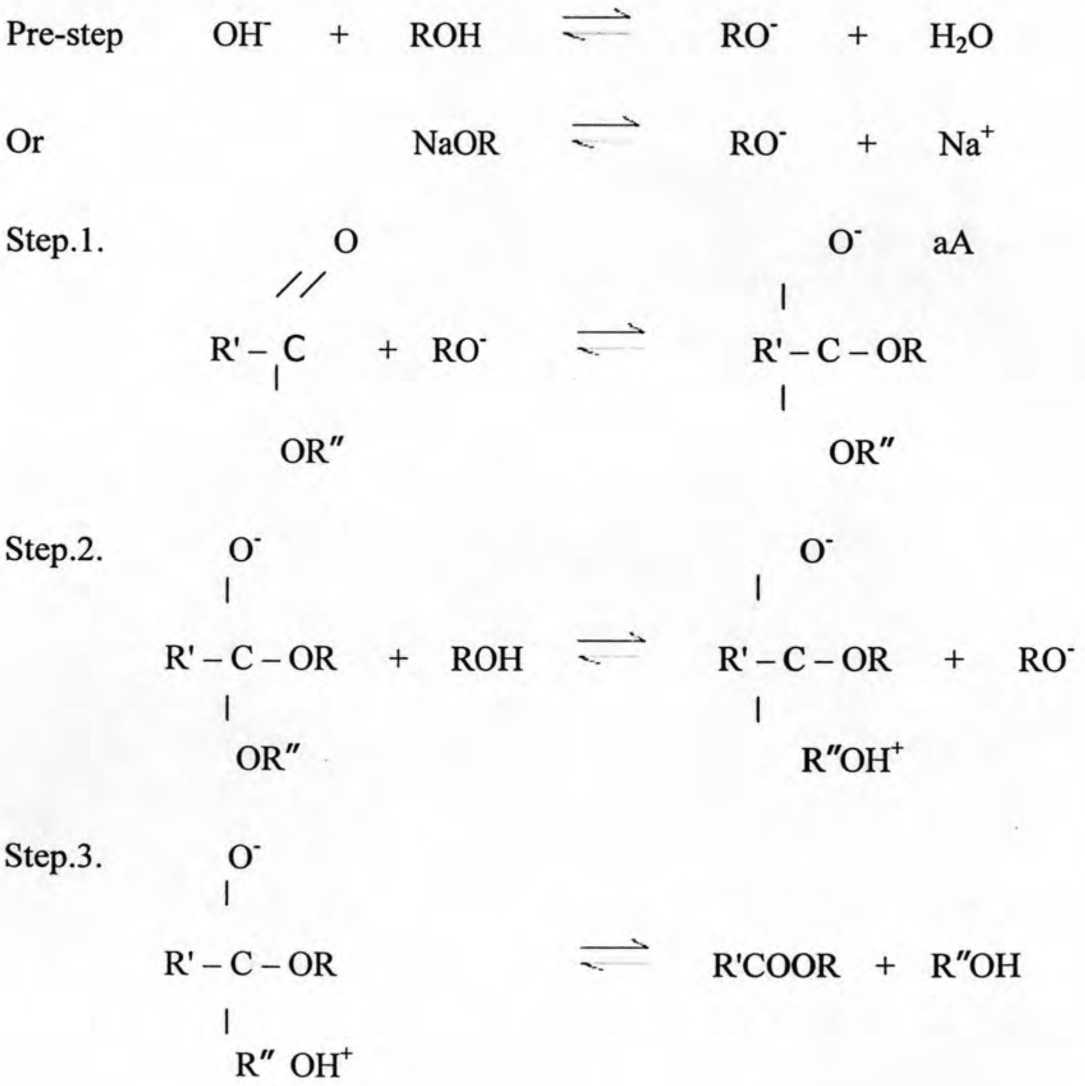
Equation 2.2 The transesterification reaction of vegetable oil with alcohol to esters and glycerol (Freedman et al., 1986)

2.3.1 Transesterification reaction with catalyst process

2.3.1.1 Alkali catalyzed process

All commercial methyl ester production today employs an alkali-catalyzed transesterification process. The alkalis that are generally used include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, ethoxide, propoxide and butoxide. Sodium hydroxide is the most common alkali catalyst that is used, due to economical reasons and availability. Alkali catalyst that is used, due to economical reasons and availability. Alkali catalysed reactions are used more often commercially than acid catalysts, as the reaction are faster. This process is accomplished by mixing methanol (alcohol) with potassium hydroxide or sodium hydroxide to make potassium methoxide and sodium methoxide. Then the sodium methoxide is added to vegetable oil in a reactor at molar ratio of oil and alcohol 6:1. The mixture was stirred and heat at 60-63°C. After complete reaction mixture is allowed to cool to room temperature, and the ester and glycerol in were separated. Glycerol is left on the bottom and methyl esters, or biodiesel, is left on top. The ratio of 6:1 was found to be the best condition because methanol/oil molar ratio less than 6:1 the reaction resulted in incomplete reaction, and that above 6:1 methanol/oil molar ratio makes the separation of glycerol difficult, since the excess methanol hindered the decantation by gravity so that the apparent yield of esters decreased because part of the glycerol remained in the methyl ester phase (Freedman et al.,1984).

The mechanisms of alkaline catalyzed transesterification are depicted in Figure 2.1. The first step is an attact on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride (Fangrui Ma et al., 1999)



Pre-step $OH^- + ROH \rightleftharpoons RO^- + H_2O$

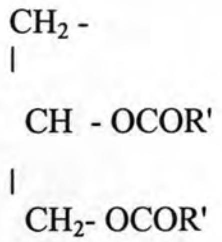
Or $NaOR \rightleftharpoons RO^- + Na^+$

Step.1. $R'-\overset{\overset{O}{/\!/}}{\underset{\underset{OR''}{|}}{C}} + RO^- \rightleftharpoons R'-\overset{\overset{O^-}{|}}{\underset{\underset{OR''}{|}}{C}}-OR$

Step.2. $R'-\overset{\overset{O^-}{|}}{\underset{\underset{OR''}{|}}{C}}-OR + ROH \rightleftharpoons R'-\overset{\overset{O^-}{|}}{\underset{\underset{R''OH^+}{|}}{C}}-OR + RO^-$

Step.3. $R'-\overset{\overset{O^-}{|}}{\underset{\underset{R''\ OH^+}{|}}{C}}-OR \rightleftharpoons R'COOR + R''OH$

Where R'' =

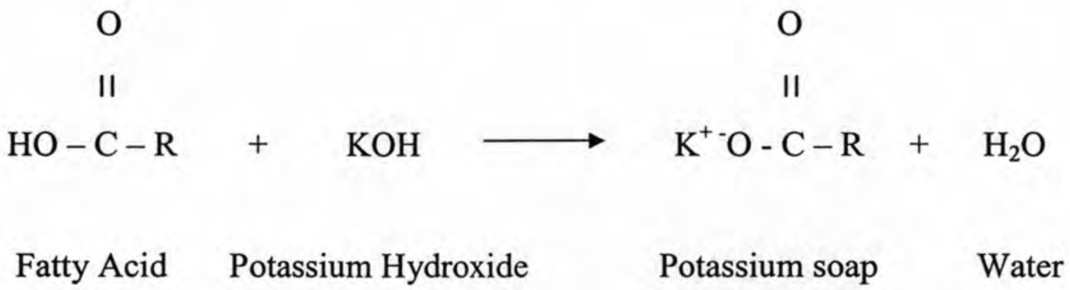


$$\begin{array}{l} CH_2- \\ | \\ CH-OCOR' \\ | \\ CH_2-OCOR' \end{array}$$

R' = Carbon chain of fatty acid

R = Alkyl group of alcohol

Figure 2.1 Mechanism of base catalyzed transesterification (Meher, 2004)



$$\underset{\text{Fatty Acid}}{HO-\overset{\overset{\displaystyle O}{\|}}{C}-R} \quad + \quad \underset{\text{Potassium Hydroxide}}{KOH} \quad \longrightarrow \quad \underset{\text{Potassium soap}}{K^{+}\,{}^{-}O-\overset{\overset{\displaystyle O}{\|}}{C}-R} \quad + \quad \underset{\text{Water}}{H_2O}$$

Equation 2.3 Reaction of fatty acid reacts with base catalyst

When the triglyceride contain high free fatty acid (about 5%), alkali-catalyst ineffective because reaction want more alkali-catalyst for neutralization and the excess catalyze can react with free fatty acid to form soap (Equation 2.3). The soap increases the viscosity or formation of gel or emulsion and interfered with separation of ester and glycerol (Freedman et al., 1984). Although the alkali catalyzed process has short reaction time and high conversion, the process has several problems such as difficult recovery of glycerol due to the soap production from free fatty acid and the catalyst. In addition, The alkaline catalyst has to be removed from the product by washing with water, thus alkaline waste water in generated. Thus, for oil with high content of free fatty acids, an acid catalyst, such as sulfuric acid, can be used to esterification the free fatty acids to methyl esters.

2.3.1.2 Acid catalyzed process

Most of the methyl ester is currently made from edible oils by using methanol and alkaline catalyst. However, if there are large amounts free fatty acids in the starting oil such as in waste oils and fats, this large amount of free fatty acids cannot be effectively converted to methyl ester using alkaline catalyst. Consequently, acid catalyst can be used for transesterification. Thus acid catalyzed process can reduce methyl ester production cost as low cost feedstock (waste frying oil) with high free fatty acid can be used as a raw material.

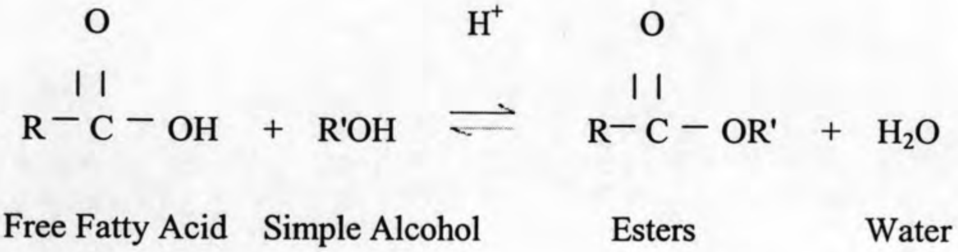
Although this process can be used with vegetable oils and fats that have more free fatty acids, it requires long reaction time, high temperature (above 100°C) and the acid catalyst has to be removed from product. In addition, the presence of water in the oil has negative effect on the yield methyl ester. With the acid catalyzed process, water has more negative effect on methyl ester formation than the alkali catalyzed process. Because the presence of polar compounds during acid catalyzed transesterification significantly reduce reaction rates. Considering the strong affinity acid has for water, it is likely that the acid will interact more strongly with water molecules than alcohol molecules. Thus, if water is present in the reactant or during the reaction, the acid catalyst will bind to the water, leading to a reversible type of catalyst deactivation.

For base or acid catalyzed processes, the most commonly used primary alcohol used in methyl ester production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. Furthermore, in these processes, neutralizers are generally used to remove the base or acid catalysts from the product methyl ester and glycerol. If a base catalyst is used, the neutralizer is typically an acid which can be added to the wash water. For example hydrochloric acid is a common choice to neutralize base catalysts. As many processes such as neutralization, washing and drying process are required in the acid or alkali processes, production is complicated and requires a long time, thus an alternative process such as enzymatic transesterification is considered.

Only simple alcohols can be used in transesterification such as, methanol, ethanol, propanol, butanol and amyl alcohol. Methanol is most often used for commercial and process reasons related to its physical and chemical nature (shortest chain alcohol and is polar). Methanol is the preferred alcohol due to quick reaction with triglycerides thereby establishing higher conversion. It is also relatively cheap as compared to other alcohols. However ethanol is becoming more popular as it is a renewable resource and does not raise the same toxicity concerns as methanol.

2.4 Esterification

The formation of esters occurs through a condensation reaction known as esterification. This requires two reactants, carboxylic acids (fatty acids) and alcohols. Esterification reactions are acid catalysed and proceed slowly in the absence of strong acids such as sulfuric acid, phosphoric acid, organic sulfonic acids and hydrochloric acid. The equation for and esterification reaction can be see in Equation 2.4.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'OH \overset{H^+}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + H_2O$$

Equation 2.4 Esterification reaction of free fatty acid with alcohol

When high free fatty acid feedstocks will react with the catalyst and form soaps if they are fed to a base catalyzed system. The maximum amount of free fatty acids acceptable in a base catalyzed system is less than 2 percent, and preferable less than 1 percent. Some approaches to using high free fatty acid feedstocks use this concept to "refine" the free fatty acids out of the feed for disposal or separate treatment in an acid esterification unit. The caustic is added to the feedstock and the resulting soaps arestipped out using a centrifuge. This is called caustic stripping. Some triglycerides are lost with the soaps during caustic stripping. The soap mixture can be acidulated to recover the fatty acids and lost oils in a separate reaction tank. The refined oils are dried and sent to the transesterification unit for further processing. Rather than waste the free fatty acids removed in this manner, they can be transformed into methyl esters using an acid esterification process. As described earlier, acid catalyzed processes can be used for the direct esterification of free fatty acids in a high free fatty acid feedstock.

Direct acid esterification of a high free fatty acid feed required water removal during the reaction, or the reaction will be quenched prematurely. Also, a high alcohol to FFA ratio required, usually between 20:1 and 40:1. Direct esterification may also require rather large amounts of the acid catalyst depending on the process used.

The esterification reaction of free fatty acid with methanol produces by product water that must be removed, but the resulting mixture of esters and triglyceride, can be used directly in a conventional base catalyzed system. The water can be removed by vaporization, settling, or centrifugation as a methanol-water mixture. Counter-current continuous-flow systems will wash out the water with the exiting stream of acidic methanol.

2.5 Saponification

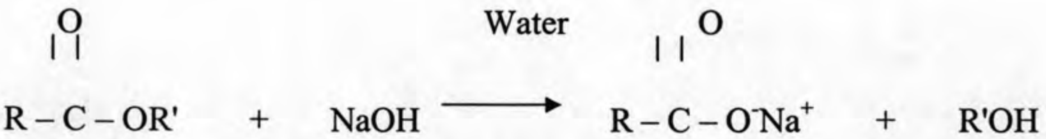
The production of soap sometimes called alkaline hydrolysis, converts triacyglycerols to glycerol and a mixture of salts of long-chain carboxylic acids. As can be seen from equation 2.5 and equation 2.6, the reaction can be carried out with an ester (i.e. triglycerides) or with carboxylic acids (i.e. free fatty acids). However, the production of fatty acids is an intermediate step when triglycerides are directly used for saponification. The commercial production of soap is usually conducted in two phases. The first phase is the conversion of lipids into free fatty acid by boiling with aqueous sodium hydroxide until hydrolysis is complete and then adding sodium chloride to precipitate the soap (Solomon, 1996).

$$R-\overset{\overset{O}{\|}}{C}-OH \quad + \quad NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^- Na^+ \quad + \quad H_2O$$

Free Fatty Acid Metalic alkoxide Salt Water

Equation 2.5 Saponification from free fatty acid

Or



$$R-\overset{\overset{O}{\|}}{C}-OR' \quad + \quad NaOH \xrightarrow{Water} R-\overset{\overset{O}{\|}}{C}-O^- Na^+ \quad + \quad R'OH$$

Ester Metalic alkoxide Salt Simple Alcohol

Equation 2.6 Saponification from ester

2.6 LITERATURE REVIEW

Freedman et al. (1984) studied the variables that affect yield and purity of alcohol ester product from crude and refined vegetable oil. These are such as molar ratio of methanol and oil, type of catalyst, and temperature. Their results showed that alkaline catalyzed reaction of fully refined oil at 60°C or higher, with the molar ratio of 6:1 could be complete and the conversion to esters resulted in 1 hr. At 32°C, vegetable oil 99% transesterification was obtained in 4 hr with alkali catalyst. The reason for low reaction rate at low temperature was that the miscibility of methanol and oil was low.

Freedman et al. (1986) investigated both acid- and alkaline- catalyzed transesterification of soybean oil with butanol and methanol. They found that the alkali could catalyze the reaction at a faster rate as compared to acid catalysts. They determined the reaction rate constants by varying the temperature, molar ratio of alcohol to soybean oil and catalyst type and concentration. Generally, a second order reaction for all three reversible reactions provided a satisfactory kinetic mechanism. However, the reaction of methanol to soybean oil ratio of 6:1 consists of a combination of second order consecutive and fourth order shunt reaction. They also estimated the activation energy for all forward and reverse reactions to have value sranging from 8-20 kcal/mol.

Canaki et al. (1999) studied how the reagent molar ratio affected reaction rates and product yield in the transmethylation of soybean oil by sulfuric acid. Five different molar ratio, from 3.3:1 to 30:1, were studied. Their results indicated that ester formation increased with increasing molar ratio, reaching its highest value, 98.4%, at the highest molar ratio used, 30:1 used. Beside oil and methanol molar ratio, the effect of temperatures were determined in the study by Freedman et al. (1986). However, the benefits from higher alcohol-to–triglycerides molar ratios became limited with increasing ratio, ester formation increase sharply from 77% at 3.3:1 to 87.8 % at 6:1 and ultimately reaching a plateau value of 94.8% at 30:1.

Srivastava et al. (2000) includes the important variables that influence transesterification and ester conversion. These are reaction temperature, ratio of alcohol to oil, catalyst type and concentration, mixing intensity and purity of reactants. The maximum yield of alkyl esters occurs at temperatures close to boiling point of the alcohol used at molar ratio (alcohol to oil) of 6:1. They also pointed that the basic homogeneous catalyst like sodium alkoxide are the most effective for transesterification. However, the presence of free fatty acids and water in the reactants interfere the basic catalyst thereby affecting the ester conversion.

Darnoko et al. (2000) studied the kinetic transesterification of palm oil using potassium hydroxide as a catalyst. They found that the optimum amount of potassium hydroxide should be 1% based on the weight of oil at 6:1 methanol: oil molar ratio. The conversion of glycerides to methyl esters fell out to be second order up to thirty minutes. Though the results were convincing, they reported the reaction rate constants based on the glyceride hydrolysis reaction, which is not the usual method applied in studying the kinetics.

David et al. (2000) studied the base-catalyzed methanolysis of vegetable oils. The results showed that it occurred much slower than butanolysis because of the two liquid phases initially present in the former reaction. In addition, the use of a co solvent such as tetrahydrofuran or methyl tertiary butyl ether speeds up methanolysis considerably. And the half-life of the hydroxide catalyst is too long to explain the sudden slowing of the reaction. Increasing the methanol/oil molar ratio to 27 in the one-phase system raises the polarity such that the methyl ester content of the ester product exceeds 99.4 wt% in 7 min.

Crabbe et al. (2001) investigated acid catalyzed (sulfuric acid) production of methyl ester (biodiesel) from crude palm oil. The reactions were carried out at 95°C .They determined the effect of molar ratio with in the range of 3:1- 40 :1, the effect of amount of catalyst with in the range of 1-5% H_2SO_4 (vol/wt%) and temperature reaction. The optimized variables, 40:1methanol/oil (mol/mol) with 5%H_2SO_4 (vol/wt%) reacted at 95 °C For 9 hour, gave a maximum ester yield of 97%.

Edward et al. (2001) studied three principal variables, molar ratio of methanol to oil, amount of catalyst, and reaction temperature, affecting the yield of acids-catalyzed production of methyl ester from crude palm oil were investigated. The optimized variables, 40:1 methanol/oil (mol/mol) with 5% H_2SO_4 (vol/wt) reacted at 95°C for 9 h, gave a maximum ester yield of 97%.

Widyan et al. (2002) studied a comparison of the catalytic activities of HCL and H_2SO_4 for the transesterification of waste palm oil. Compared to HCL, H_2SO_4 was as a better catalyst. The use of excess alcohol can reduce the longer reaction time that is required for the acid-catalyzed reaction. Thus, Bronsted acid catalyst transesterification requires high catalyst concentration and a higher molar ratio to reduce the reaction time. Lewis acids can also act as a catalyst for the transesterification of vegetable oil.

Laoprasert (2002) studied the methyl ester synthesis from used cooking oils by transesterification. The investigated variables were temperature (15-60°C), catalyst type (sodium hydroxide and potassium hydroxide), catalyst concentration (0-1.0 wt%), methanol concentration (10-40 wt%), and reaction time (15-90 min). For NaOH as catalyst, the optimum condition were 25%MeOH, 1.0%NaOH, 30 °C and reaction time of 30 min and the maximum yield was 94.95%. For KOH as catalyst, the optimum conditions were 25%MeOH, 1.0%KOH, 30 °C for reaction time of 30 min and the maximum yield was 91.87%. The %yield of the methyl ester by using NaOH was higher than KOH for all experiments.

Tomasevic et al. (2003) studied the transesterification of used sunflower oil (which has an acid value of ~ 4) with methanol, using alkaline catalysts such as KOH and NaOH and different molar ratios of methanol to oil (4.5:1, 6:1, 9:1). The effects of various parameters such as the variation in oil quality, the molar ratio of methanol to oil, the type and amount of alkaline catalyst, the time and temperature of reaction on the yield, and the properties of esters were studied. The optimum conditions developed for the production of good-quality biodiesel from used sunflower oil were as follows: molar ratio of methanol to oil, 6:1, with 1% of KOH; reaction temperature, 25°C; and reaction time, 30 min. It was observe that, under the optimal conditions of methanolysis, the quality of the used frying oil did not have an essential effect on the quanlity of methyl esters producted. An increase in the quantity of catalyst and molar ratio of methanol to oil did not change the yield or quality of the esters. Of the two catalysts NaOH and KOH, 1%KOH has given the best yields and viscosities of esters.

Abigail et al. (2003) studied fatty acid methyl ester prepared from transesterification of vegetable oil is believed to be a viable alternative for diesel fuel. Homogeneous basic catalysts such as NaOH and KOH are commonly used to obtain high methyl esters conversion from several vegetable oils such as refined palm, rapeseed and soybean oil. This research is focused on the transesterification of crude PKO and CCO with NaOH as catalyst. Results showed that the crude PKO and CCO could be used as a material having a methyl ester content of 95-99% and a product yield of 75%. It wasfound that the optimum condition for the transesterification of crude PKO and CCO was 0.5-1% NaOH as catalyst at methanol: oil mole ratio 6:1 and 60-65°C.

Encinar et al. (2005) studied a comparison of the catalytic activities of NaOH , KOH, sodium methoxide, and potassium methoxide for the transesterification of used frying oil with methanol. The effects of operation variables such as the molar ratio of alcohol to oil (3:1- 9:1), the catalyst concentration (0.1%-1.5%), the temperature 25-65°C, and the catalyst type on the ester yield were studied. The biodiesel with the best properties was obtained using a methanol/oil molar ratio of 6:1 potassium hydroxide as the catalyst (1%), and temperature of 65 °C. Two-stage transesterification with a separation of glycerol after the first stage was determined to be better than a one-stage process.

omsab (2005) studied the transesterification of crude palm oil and palm stearin with ethanol was carried out in a batch reactor by using sodium hydroxide as a catalyst. The major variables investigated were: molar ratio of ethanol/oil, amount of catalyst, reaction temperature and reaction time. The optimal condition to transesterify crude palm oil and palm stearin were similar as follows : 12:1 molar ratio of ethanol/oil, 75°C of reaction temperature, 1% weight of sodium hydroxide and 60 minute reaction time. At this condition, the ethyl ester conversion of crude palm oil and palm stearin were 87.79 and 94.42% weight respectively. The characteristics of ethyl esters from both crude palm oil and palm stearin were similar to low speed diesel.

Narumol et al. (2005) studied biodiesel was prepared from the non-edible seed oil of Brassica juncea by alkaline-catalyzed transesterification of the crude oil with methanol at molar ratios of oil:methanol (1.3 – 1.7) at 70°C. At molar ratio of 1:5 a maximum conversion 98%. A higher conversion level of oil to methyl ester was achieved using a 1:5 molar ratio of oil to methanol at 70°C. The properties of methyl esters of Brassica juncea were measured and compared with ASTM standards. The fatty acid composition of mustard seed oil is dominated by erucic acid (32.5%), eicosenoic acid (18.4), oleicacids (17.8%) and linoleic acid (8.3%).

Waeasae et al. (2005) studied ester from coconut oil or palm oil was prepared by reactions between fatty acid and alcohol using sulfuric acid as a catalyst. The experiment started from refluxing the oil with 7 M sodium hydroxide at the ratio of 5:6 v/v and the temperature of 75°C for 9 hours to form soap. Fatty acid was then prepared by adding 4 M hydrochloric acid to soap. It was futher reacted with either methanol, ethanol or isopropanol in the present of sulfuric acid for 8 hours to obtain esters with the percentage yield of more then 80% t-Butyl ester, however, was prepared by a different route. T-Butanol was reacted with fatty acid chloride to give t-butyl ester. T-Butyl ester prepared has the characteristics of having low ash and low viscosity. It has a boiling point in the range of 160-210°C which is lower than the other esters and a specific gravity of 0.8593 Kg/L which is comparable to that of methyl ester. It is expected that t-butyl ester prepared form palm oil is able to use for better diesel oil.

Lertsathapornsuk et al. (2005) studied the methods of continuous preparation of fatty acid ethyl esters (FAEE) from coconut, rice bran and used frying (palm) oils in a modified home made microwave oven (800 Watts) are described. Good yield FAEEs are obtained with 1.0% sodium hydroxide (in excess) as a catalyst. With the alcohol to oils molar ratio 9:1, 100% conversion is obtained within 30s for coconut oil, 94% conversion for rice bran oil and 83% conversion for used frying oil. Percent conversion is slightly increased for used frying oil but not for rice bran oil, when the reaction time is increased to 60s. The temperatures of the reaction mixtures are rapidly increased to the boiling point of alcohol within 30s and increased slightly above the boiling point of the alcohol, to 83.4 °C at 60s.

Goodwin et al. (2005) was to investigate the kinetics and selectivities of different solid catalysts for the transesterification of triacetin (a model compound for larger triglycerides as found in vegetable oil and fats) with methanol. Reaction was carried out at 60°C in a batch reactor with a variety of solid and liquid, acid and base catalysts. The homogeneous phase (i.e.,liquid) catalysts (NaOH and H_2SO_4) were studied for comparison. While on a wt.% basis (of reaction mixture) the homogeneous phase catalysts gave higher rates of reaction, on a rate-per-site basis the solid acids were similar to H_2SO_4. Sulfated zirconia and tungstated zirconia had comparable turnover frequencies as H_2SO_4. The deactivation characteristics of some of these catalysts were also studied.

Wenlei et al. (2006) studied transesterification of soybean oil with methanol to methyl esters was carried out using NaX zeolites loaded with KOH as a solid base catalyst. Best result was obtained with NaX zeolite loaded with 10% KOH, followed by heating at 393 K for 3 h. When the transesterification reaction was carried out at reflux of methanol (338K), with a 10:1 molar ratio of methanol to oil soybean oil, a reaction time of 8 h and a catalyst amount of 3 wt%, the conversion of soybean oil was 85.6%.

Kulkarni et al. (2006) were made as shown the transesterification of edible oil using strong acids (Bronsted acids) such as sulfuric and hydrochloric acid are available in literature reports. The acid-catalyzed transesterification of pure soybean oil was studied by Canakci and Gerpen. The optimal condition to transesterification were: 6:1 molar ratio of methanol/oil, 60°C of reaction temperature, 3% weight of sulfuric acid and 96 hours reaction time. The results obtained at high free fatty acid (33% FFA) are conversion 60%.

Goodwin Jr et al. (2006) was investigation into the impact of carboxylic acid chain length on the kinetics of liquid-phase acid-catalyzed esterification. Using sulfuric acid and a commercial Nafion/silica composite solid acid catalyst (SAC-13), initial kinetics were measured for the reactions with methanol at 60°C. It was found that reaction rate decreased as the number of carbons in the linear alkyl chain increased for both H_2SO_4 and SAC-13.