

CHAPTER II

LITERATURE REVIEW

2.1 Feedstocks in biodiesel production

The primary raw materials used in the production of biodiesel are vegetable oils, animal fats, and recycled greases. These materials contain triglycerides, free fatty acids, and other contaminants depending on the degree of pretreatment they have received prior to delivery. Most processes for making biodiesel use a catalyst to initiate the esterification reaction. The catalyst is required because the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. The most common catalysts used are strong mineral bases such as sodium hydroxide and potassium hydroxide.

Typical proportions for the chemicals used to make biodiesel are:

Reactants	•Fat or oil (e.g. palm oil) •Primary alcohol (e.g. methanol)
Catalysts	•Mineral base (e.g. KOH, NaOH)

Fats and Oils: Choice of the fats or oils to be used in producing biodiesel is both a process chemistry decision and an economic decision. With respect to process chemistry, the greatest difference among the choices of fats and oils is the amount of free fatty acids that are associated with the triglycerides. Most vegetable oils have a low percentage of associated free fatty acids. Crude vegetable oils contain some free fatty acids and phospholipids. The phospholipids are removed in a “degumming” step and the free fatty acids are removed in a “refining” step. Oil can be purchased as crude, degummed, or refined. The selection of the type of oil affects the production technology that is required.

The options for the triglyceride choice are many. Among the vegetable oils sources are soybean, canola, palm and rape. Animal fats are products of rendering operations. They include beef tallow, lard, poultry fat and fish oils. Yellow greases can be mixtures of vegetable and animal sources. There is other less desirable, but also less expensive triglyceride sources such as brown grease and soapstock. The free

fatty acid content affects the type of biodiesel process used, and yield of fuel from that process. The other contaminants present can affect the extent of feedstock preparation necessary to use a given reaction chemistry.

Alcohol: The most primary alcohol used in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol and butanol can be used. A key quality factor for the primary alcohol is the water content. Water interferes with transesterification reaction and can result in poor yields and high levels of soap, free fatty acids, and triglycerides in the final product. It takes three moles of alcohol to react completely with one mole of triglycerides. In addition, a basic catalyzed process typically uses an operating mole ratio of 6:1 mole of alcohol rather than 3:1 ratio required by the reaction stoichiometry. This means that the excess alcohol must be recovered to minimize operating costs and environmental impacts. The alcohol quality requirements are that it be un-denatured and anhydrous.

Catalyst: The options of catalyst can be classified into the following group

Basic catalysts such as NaOH, KOH and NaOCH₃

Acid catalysts such as H₂SO₄, H₃PO₄ and CaCO₃

Lipase enzymes

Non-catalyst options such as supercritical process and co-solvent

Basic catalysts are used for essentially all vegetable oil biodiesel production. The initial free fatty acid content is generally low and the water content is also generally low. If the initial free fatty acid content is greater than about 1%, it must be pretreated to either remove the free fatty acid or convert the free fatty acid to esters before beginning the basic catalyzed reaction. Otherwise, the basic catalyst will react with free fatty acids to form soap and water. The soap formation reaction is very fast goes to completion before any esterification begins. Basic catalyzed reactions are relatively fast, with residence times from about 5 minutes to about 1 hour, depending on temperature, concentration, mixing and alcohol: triglycerides ratio.

Acid catalyst systems are characterized by slow reaction rates and high alcohol: triglycerides requirements (20:1 and more). Generally, acid catalyzed reactions are used to convert free fatty acids to esters, or soaps to esters as a

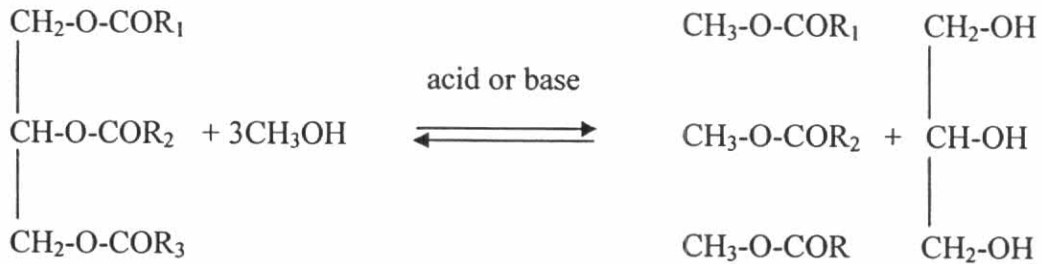
pretreatment step for high free fatty acids feedstocks. Residence times from 10 minutes to about 2 hours are reported.

Lipase catalyzed reactions have the advantage of producing only esters and pure glycerol. The enzyme reactions are highly specific and chemically clean. Because the alcohol can be inhibitory to the enzyme, a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each. The reactions are very slow, with a three step sequence requiring from 4 to 40 hours, or more. The reaction conditions are modest, from 35 to 45°C.

The non-catalyst options are designed to overcome the reaction initiation lag time caused by the extremely low solubility of the alcohol in the TG phase. One approach that is nearing commercialization is the use of a co-solvent, tetrahydrofuran, to solubilize the methanol. The result is a fast reaction, on the order of 5 to 10 minutes, and no catalyst residues in either the ester or the glycerol phase. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. This system requires a rather low operating temperature, 30°C. Another non-catalytic approach is the use of a high (42:1) alcohol to oil ratio. Under supercritical conditions are (350 to 400 °C and > 80 atm or 1200 psi). The reaction is complete in about 4 minutes.

2.2 Transesterification

Transesterification or alcoholysis is the reaction of alcohol and vegetable oil or animal fat to produce alkyl ester of fatty acid. This process has been widely used to reduce the high viscosity of triglycerides. If methanol is used in this process it is called methanolysis. Methanolysis of triglyceride is represented in equation 2.1, R_1 , R_2 , and R_3 of hydrocarbon constituting fatty acids which may be the same or different. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or basic) accelerates the conversion.



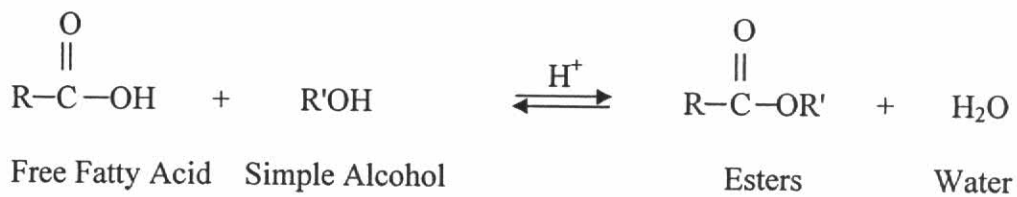
Equation 2.1 General equation for transesterification of triglycerides

The stoichiometry required three moles of alcohol and one mole of triglyceride to produce three moles of alky esters and one mole of glycerol. In practice this is usually increased to 6:1, because this reaction is reversible. Excess of 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, molar ratio of oil and alcohol, glycerol separation and quality of vegetable oil such as fatty acid composition.

2.3 Esterification

High free fatty acid feedstocks will react with the catalyst and form soaps if they are fed to a basic catalyzed system. The maximum amount of free fatty acids acceptable in a basic catalyzed system is 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 process. The caustic is added to the feedstock and the resulting soaps are stripped 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 FFA feedstock, such as tallow or yellow grease, are characteristically high in free fatty acids (FFA). The standard for tallow and yellow grease is ≤ 15 percent.

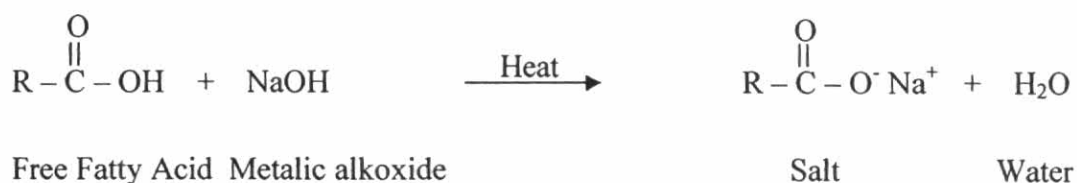
Direct acid esterification of a high free fatty acid feed requires water removal during the reaction, or the reaction will be quenched prematurely. Also, a high alcohol to free fatty acid ratio required, usually between 20:1 and 40:1. Direct esterification may also require rather large amounts of the acid catalyst depending on the process used. The esterification reaction of free fatty acids with methanol produces byproduct water that must be removed, but the resulting mixture of esters and triglyceride can be used directly in a conventional basic 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. The equation for esterification reaction is represented in Equation 2.2.



Equation 2.2 Esterification reaction of free fatty acid with alcohol

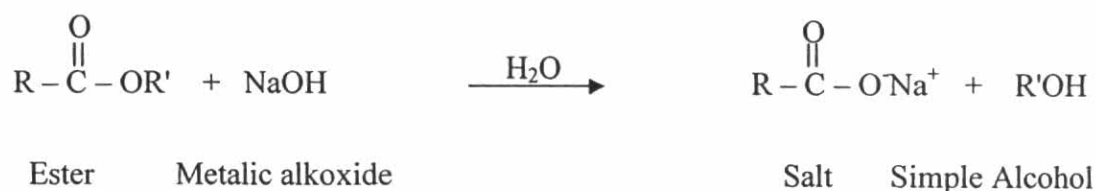
2.4 Saponification

The production of soap sometimes called alkaline hydrolysis, converts triglycerides to glycerol and a mixture of salts of long-chain carboxylic acids. As can be seen from Equation 2.3 and Equation 2.4, 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).



Equation 2.3 Saponification reaction from free fatty acid

Or



Equation 2.4 Saponification reaction from alkyl ester

2.5 Biodiesel production process

2.5.1 Basic catalyzed process

Basic catalyzed processes dominate current commercial production. These reactions are relatively fast but are sensitive to water content and free fatty acids. The typical alcohol used is methanol with a 6:1 molar ratio. Typical basic concentrations are 0.3 to 1.5% based on the weight of oil. When sodium methoxide was used, the concentration can be 0.5% or less. Essentially all of the current commercial operations use basic catalyzed reactions. Most use NaOH as the catalyst. There are some operations that use KOH, in spite of the higher cost, because the potassium can be precipitated as K_3PO_4 , a fertilizer, when the products are neutralized using phosphoric acid. This can make meeting water effluent standards a bit more difficult because of limits on phosphate emissions. The typical alcohol: triglyceride mole ratio for batch reactions and sequential batch reactions is 6:1. There have been reports that continuous flow systems operate better with a ratio of 8:1. Sodium methoxide, usually as a 25 % solution in methanol, is a more powerful catalyst on a weight basis than the mixture of NaOH and methanol. A block diagram of the system is shown in Figure 2.1.

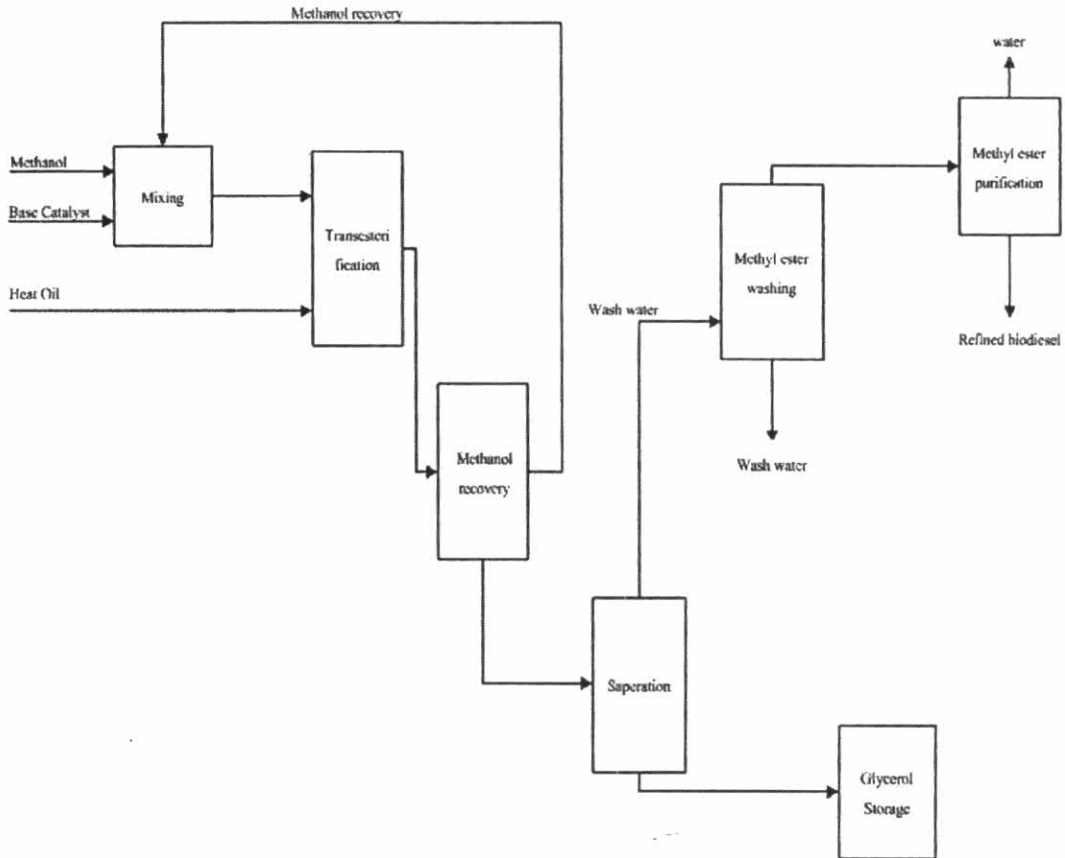


Figure 2.1 Simple block diagram of basic catalyzed process

Figure 2.1 shows a block diagram of a typical basic transesterification in batch system. The oil is first charged to the reactor, followed by the catalyst and methanol. The system is agitated during the reaction time. Then agitation is stopped. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other process the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge. Methanol can be removed from biodiesel and glycerol by distillation. After remove methanol biodiesel will carried out to washing steps for washed with hot water and purification.

2.5.2 Acid catalyzed process

Despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. Freedman et al. (1968) investigated the transesterification of soybean oil with methanol using 1 wt.% concentrated sulfuric acid based on weight of oil. They found that at 65°C and a molar ratio of 30:1 methanol to oil, it took 69 hours to

obtain more than 90% oil conversion to methyl esters. Canakci and Gerpen (1999) studied the effects of the molar ratio of alcohol to soybean oil, the reaction temperature, the amount of catalyst, and the reaction time on the ester conversion by acid-catalyzed transesterification. Each effect is studied independently of the other effects. They found that increased ester conversions could be obtained at increased molar ratios of alcohol to oil, increased reaction temperatures, increased concentrations of sulfuric acid, and longer reaction times. However, possible interaction of these variables was not investigated and optimal conditions for the acid-catalyzed reaction were not recommended. In this process the transesterification reactions of oil with an excess of methanol in the presence of sulfuric acid catalyst at 60°C. A minimum molar ratio of 6:1 methanol to oil and acid concentrations of 0.5–1% (based on the oil) were used. A block diagram of the system is shown in Figure 2.2.

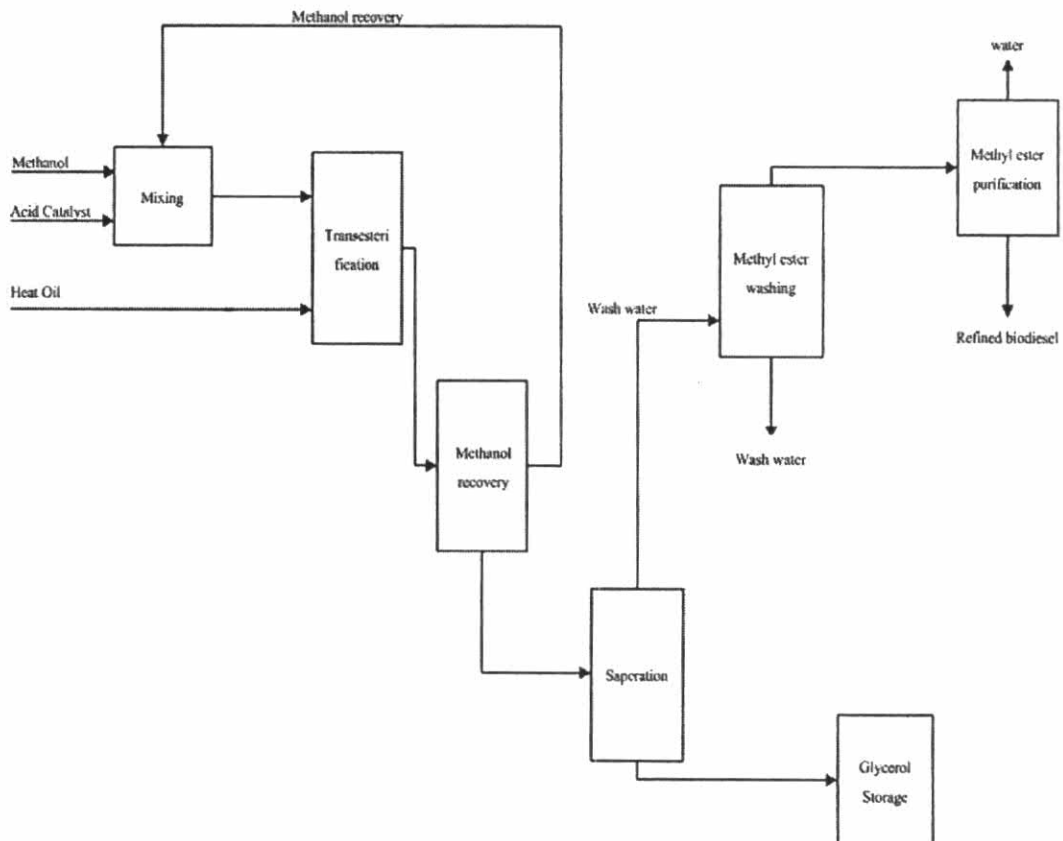


Figure 2.2 Simple block diagram of acid catalyzed process

Figure 2.2 shows a block diagram of a typical acid transesterification in batch system. The step of typical acid catalyzed process is same the process of basic catalyzed process.

2.6 Waste from transesterification process

In the typical of biodiesel production process, there are three or four steps in the process. The first step is transesterification step. The product output from this step is contained crude glycerol, crude biodiesel, remained catalyst, excess methanol and soap. After allowed the product mixture, they are separate into two phases. The upper phase is contained crude biodiesel, small amount of residue catalyst, methanol and soap. The bottom phase is contained crude glycerol, most of residue catalyst, soap, and methanol. The excess methanol in each phase is recovery back to direct use in process again or treated before used. In the commercial process crude glycerol by product is add to purification process and sell to the soap industry or pharmaceutical industry for use as raw material in the process. So glycerol is not estimate in the waste form. The upper phase after removed the excess of methanol, crude biodiesel is send to the purification process. In this process crude biodiesel is purified by washing with water or other techniques. The wash water is add into crude biodiesel for eliminate the residue catalyst and soap. After finished the purification step washed water is separate and drain to disposal. The output of washed water is estimate to the waste from process. Biodiesel is evaporated the small amount of wash water before use as diesel fuel. So the washed water is the waste from process, but the direct wastes are the dissolved of residue catalyst and soap in the washed water.

2.7 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 hours. At 32°C, vegetable oil 99% transesterification was obtained in 4 hours 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 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 ratios, 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 effects 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.

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.

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 within the range of 3:1- 40:1, the effect of amount of catalyst within the range of 1-5% H₂SO₄ (vol/wt%) and temperature reaction. The optimized variables, 40:1 methanol to oil (mol/mol) with 5% H₂SO₄ (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 oil to methanol, 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 to oil (mol/mol) with 5% H_2SO_4 (vol/wt) reacted at $95^\circ C$ for 9 hours. The result is show that condition gives a maximum ester yield about 97%.

Laoprasert (2002) studied the methyl ester synthesis from used cooking oils by transesterification reaction. The investigated variables were temperature about $15-60^\circ C$, catalyst type (sodium hydroxide and potassium hydroxide), catalyst concentration (0.5-1.0 wt%), methanol concentration (10-40 wt%), and reaction time (15-90 min). For NaOH as catalyst, the optimum conditions were 25% methanol, 1.0% NaOH, $30^\circ C$ and reaction time of 30 min gives the maximum yield was 94.95%. For KOH as catalyst, the optimum conditions were 25% of methanol, 1.0% KOH, $30^\circ C$ for reaction time of 30 min gives the maximum yield was 91.87%. The percentage of 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 ≈ 4) with methanol, using basic catalysts such as KOH and NaOH at three 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, type and amount of alkaline catalyst, 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 at $25^\circ C$; and reaction time for 30 min. It was observed that, under the optimal conditions of methanolysis, the quality of the used frying oil did not have an essential effect on the quantity of methyl esters produced. An increase in the quantity of catalyst and molar ratio of methanol to oil did not change the yield or quality of the esters. When compared 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. 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 focus on the transesterification of crude palm kernel oil and crude coconut oil with NaOH as catalyst. Results showed that the crude palm kernel oil and crude coconut oil could be used as a material having a methyl ester content of 95- 99% and a product yield of 75%. It was found that the optimum condition for the transesterification of crude crude palm kernel oil and crude coconut oil was 0.5-1% NaOH as catalyst at methanol to oil mole ratio 6:1 and temperature 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 to 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.

Udomsab (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 to 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 to 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.