

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Biodiesel

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from renewable feedstocks, such as vegetable oils or animal fats, for use in compression-ignition (diesel) engines. It is usually produced by transesterification and esterification reactions of vegetable or waste oil, respectively, with low molecular weight alcohol, such as ethanol and methanol. During this process, the triglyceride molecule from vegetable oil is removed in the form of glycerin. Once the glycerin is removed from the oil that is a liquid fuel similar to petroleum diesel in combustion properties. While the petroleum and other fossil fuels contain a lot of sulfurs, ring molecules and aromatics; but biodiesel molecules are very simple hydrocarbon chains and free of sulfurs, making it a cleaner burning fuel than petroleum diesel. Biodiesel has viscosity close to diesel fuels. These esters contain 10 to 11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels in an engine.

The advantage of biodiesel when use in diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. The use of biodiesel decreases the solid carbon fraction of particulate matter, which the oxygen in biodiesel enables more complete combustion to CO₂ and reduces the sulfate fraction, while the soluble, or hydrocarbon fraction stays the same or increases. Therefore, biodiesel works well with emission control technologies such as diesel oxidation catalysts. Emissions of nitrogen oxides increase with the concentration of biodiesel in the fuel. Table 2.1 shows the general property of biodiesel.

Table 2.1 General property of biodiesel

Property	Biodiesel
Specific gravity (kg/L)	0.87-0.89
Cetane number	46-70
Cloud point (K)	262-289
Pour point (K)	258-286
Flash point (K)	408-423
Sulfur (wt%)	0.0000-0.0024
Ash (wt%)	0.002-0.01
Iodine number	60-135
Kinematic viscosity, 313 K	3.7-5.8
Higher heating value, MJ/kg	39.3-39.8

2.2 Vegetable Oils

Vegetable oils are substances derived from plants, that are composed of triglycerides. Normally, oils are liquid at room temperature, and fats are solid; a dense brittle fat is called a wax. Although many different parts of plants may yield oil, in actual commercial practice oil is extracted primarily from the seeds of oilseed plants. Vegetable oil comes in very many shapes and sizes, with varying properties. The most important consideration is melting point. The actual vegetable oil molecule is composed of three long carbon chains on a glycerol 'backbone' and the properties are determined by the individual 'fatty acid' chains. Vegetable oils comprise of 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). Vegetable oils, also known as triglycerides, have the chemical structure as given in Figure. 2.1. There are four major techniques (dilution, microemulsion, pyrolysis, and transesterification modification techniques) as well as the direct use of the oil are used for viscosity reduction (Vyas *et al.*, 2010). Microemulsions with alcohols have been prepared to overcome the problem of high viscosity of vegetable oils. Pyrolysis or cracking, defined as the cleavage of longer to smaller molecules by thermal energy, of vegetable oils over catalysts has been investigated. Transesterification process has been widely used to reduce the high viscosity of triglycerides while esterification is the sub category of transesterification.

Some advantages of vegetable oils are following: available in almost every part of the world, renewable since the vegetables from oil seeds can be planted and harvested continuously throughout the year, appear to be a potentially “greener” fuel because the fuel derived from the oils contains no or the least sulfurs element, and help in CO₂ fixation during photosynthesis (Helwani *et al.*, 2009). But there are some disadvantages of vegetable oils which occupy a prominent position in the development of alternative fuels although. There have been many problems associated with using it directly in diesel engines especially in direct injection engine. These problems are associated with large triglyceride molecule and its higher molecular mass can be solved, if the vegetable oils are chemically modified to biodiesel, which is similar in characteristics to diesel (Enweremadu and Mbarawa, 2009). Other disadvantages to the use of vegetable oils and especially animal fats are the high viscosity (about 11–17 times higher than diesel fuel) and lower volatilities that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics (Meher *et al.*, 2006).

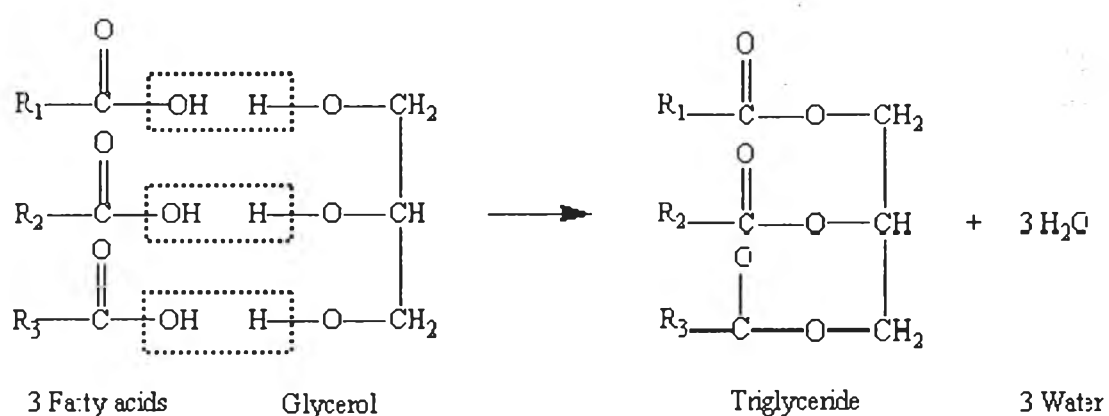


Figure 2.1 Formation of triglyceride (Srivastava and Prasad, 2000).

From Figure 2.1, R₁, R₂ and R₃ represent a chain of carbon atoms with hydrogen atoms attached. The differences of R₁, R₂, and R₃ 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. This reason leads to make different characteristics of vegetable oil. The common fatty acids found in vegetable

oils are stearic, palmitic, oleic, linoleic, and linolenic. Name and chemical structure of common fatty acids are shown in Table 2.2.

Table 2.2 Chemical composition of vegetable oils (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

^axx:y indicates x carbons in fatty acid chain with y double bonds

2.3 Transesterification

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield because the reaction is reversible. Excess alcohol is used to shift the equilibrium to the products side. This process has been widely used to reduce the high viscosity of triglycerides (Meher *et al.*, 2006). The transesterification reaction is represented by the general equation, as shown in Figure 2.2. Alcohols used in transesterification process are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain

alcohol). Moreover, methanol can quickly react with triglycerides and NaOH, which is easily dissolved in it.

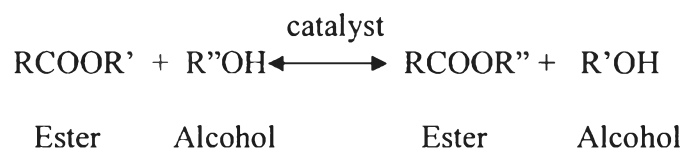


Figure 2.2 General equation for transesterification reaction.

In the transesterification of vegetable oils, triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol, as shown in Figure 2.3 (Fangrui and Hanna, 1999). The overall process is a sequence of three consecutive and reversible reactions, in which di- and mono-glycerides are formed as intermediates. The stoichiometric reaction requires 1 mole of triglyceride and 3 mole of alcohol. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield (Fangrui and Hanna, 1999). Moreover, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several aspects, including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the product yield of the transesterification and will be discussed below, based on the type of catalyst used.

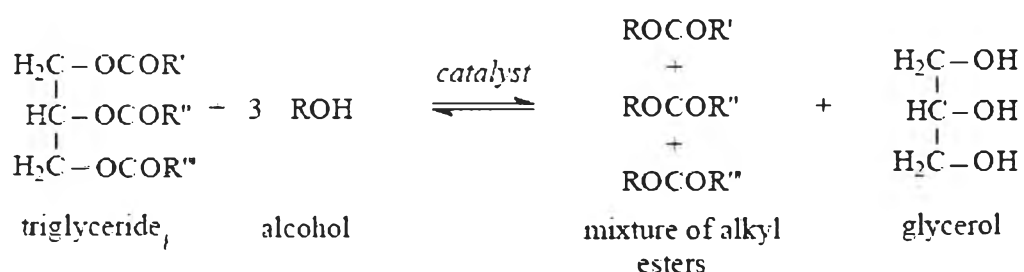


Figure 2.3 Transesterification reaction of triglyceride with alcohol.

2.4 Catalyst in Transesterification

In general, transesterification 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 (Helwani *et al.*, 2009). 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) (Helwani *et al.*, 2009). Table 2.3 summarizes reaction conditions used in acid catalyzed process of waste cooking oil using sulfuric acid as a catalyst (Helwani *et al.*, 2009).

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 ₂ SO 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.*, 1997). The protonation of the carbonyl group of the ester leads to the carbocation I 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⁺.

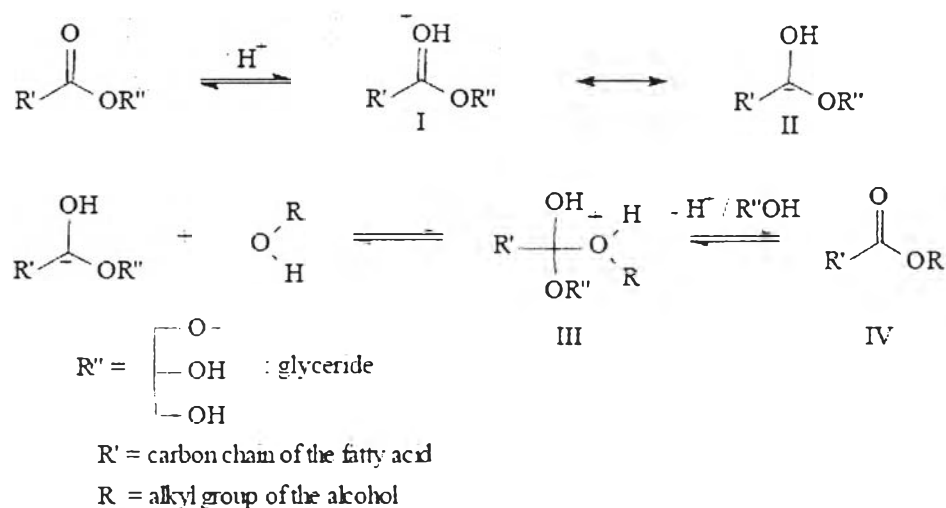


Figure 2.4 Mechanism of the acid-catalyzed transesterification of vegetable oils.

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.

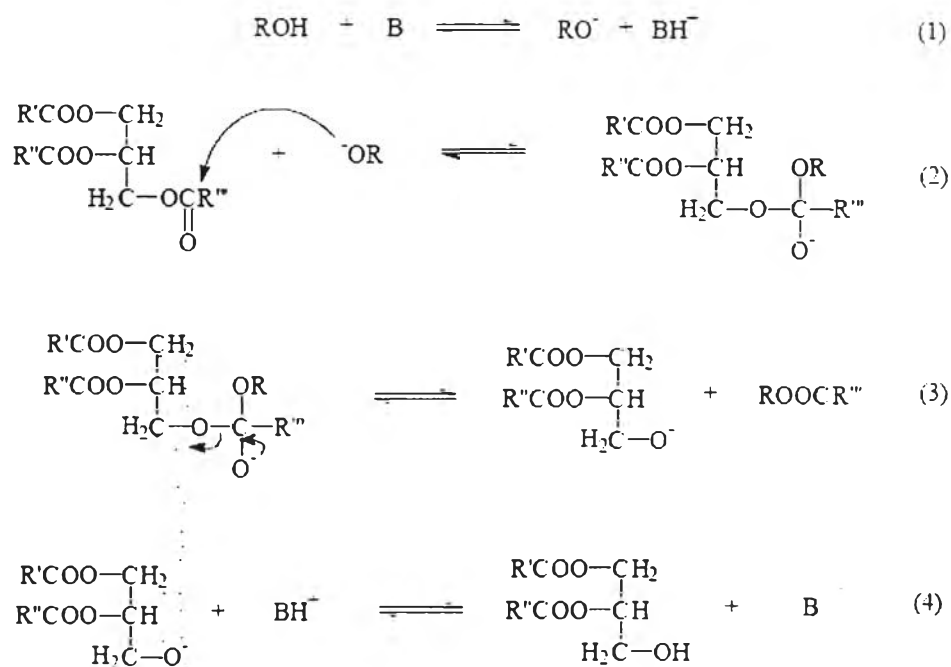


Figure 2.5 Mechanism of the base-catalyzed transesterification of vegetable oils.

Although the base-catalyzed are widely 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.



Figure 2.6 Saponification of fatty acid alkyl ester.

Darnoko *et al.* (2000) studied the kinetic transesterification 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 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.

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 (Wen *et al.*, 2010). 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 conversion 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 -Al₂O₃ 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 -Al₂O₃, 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/Al₂O₃ 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/Al₂O₃ 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_2CO_3 , KF, $LiNO_3$, and NaOH loaded on alumina support. They found that K_2CO_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 $60^\circ C$, 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_2CO_3 , KNO_3 , KOH on Al_2O_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.

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/Al₂O₃ 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 number 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 ZrO₂ is not active in their 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 has been reviewed. 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).