

CHAPTER II

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. Biodiesel is composed of fatty acid methyl esters that can be prepared from triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel, especially, its main characteristics, therefore, it is considered as a possible substitute of conventional diesel fuel.

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, the former is a strong candidate to replace diesel if the need arises.

There are many advantages for using biodiesel such as renewable resource, biodegradability and limitation on greenhouse gas emission because of the closed CO₂ cycle. Moreover, its composition has lower sulfur and toxicity. For usage, biodiesel can use without engine modification and makes good engine performance. It has good lubrication properties and ability to be blended in any proportion with regular petroleum-based diesel fuel.

The vegetable oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these, the oil cannot be used as fuel directly. To overcome these problems, the oil requires slight chemical modification mainly pyrolysis, dilution, microemulsion and transesterification as previously described. Among these, the transesterification is the key and important step to produce the cleaner and environmentally safe fuel from vegetable oils (Meher *et al.*, 2006).

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

Vegetable oil methyl ester	Kinematic viscosity (mm ² /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 (37.0°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 Chemistry of Transesterification Process

In a transesterification or alcoholysis reaction, one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of the respective fatty acid alkyl esters. The process is a sequence of three reversible reactions, in which the triglyceride molecule is converted step by step into diglyceride, monoglyceride and glycerol. In each step one mole of alcohol is consumed and one mole of ester is liberated, as can be seen in Figure 2.1, depicting the reaction scheme for the transesterification with methanol (methanolysis). In order to shift the equilibrium to the right, methanol is added in an excess over the stoichiometric amount in most commercial biodiesel production plants. Another advantage of methanolysis 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 phases—an upper ester phase and a lower glycerol phase. This process removes glycerol from the reaction mixture and enables high conversion. Ester yields can even be increased—while at the same time minimizing the excess amount of methanol—by conducting methanolysis in two or three steps. Here only a portion of the total alcohol volume required is added in each step, and the glycerol phase produced is separated after each process stage. Finally, regardless of the type of alcohol used, some form of catalyst has to be present to achieve high ester yields under comparatively mild reaction conditions (Mittelbach and Remschmidt, 2004).

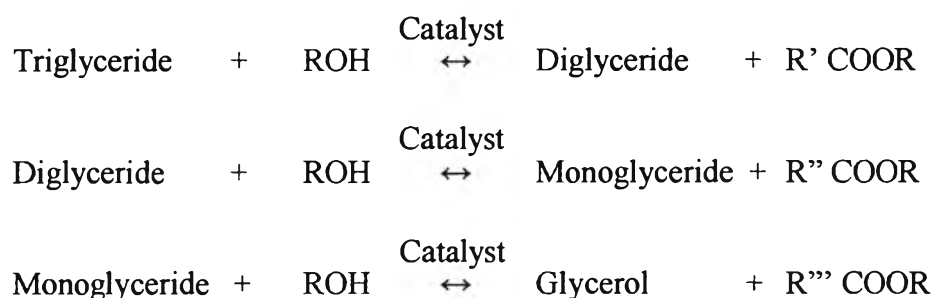


Figure 2.1 Reaction scheme for the transesterification of triglycerides with alcohol (Srivastava and Prasad, 2000).

The transesterification reaction can be catalyzed by alkaline (basic), acid or enzymes in order to increase the rate of reaction and yield of alkyl esters. Sodium hydroxide and potassium hydroxide are used most frequently as alkaline catalysts. Sulfuric acid, hydrochloric acid are usually used as acid catalysts. Moreover, the transesterification reaction can be reacted without catalyst by supercritical method.

2.3 Starting Materials for Biodiesel Production

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 diglycerides. 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.

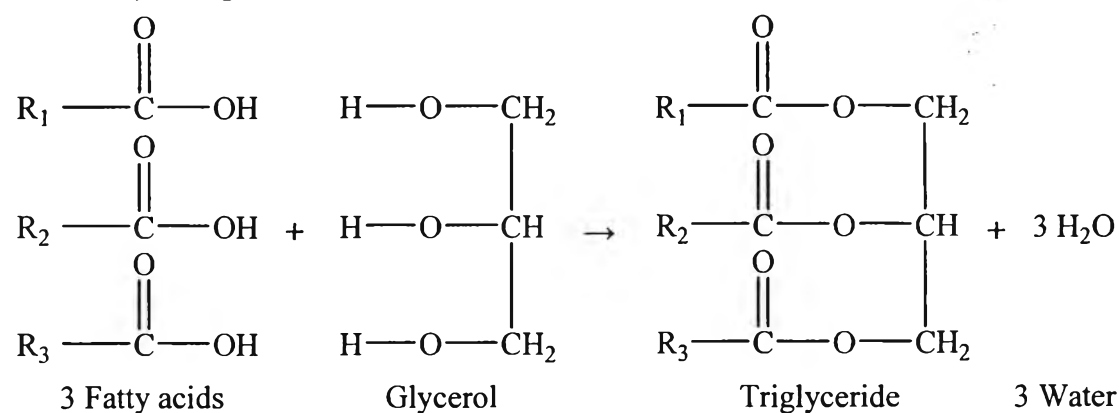


Figure 2.2 Formation of triglyceride (Noiroj, 2007).

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. The compositions of fatty acid in vegetable oils

are summarized in Table 2.3 (Srivastava and Prasad, 2000). Some properties of the vegetable oils are shown in Table 2.4 (Marchetti *et al.*, 2007).

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

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

Table 2.3 Chemical composition of vegetable oils (Srivastava and Prasad, 2000)

Vegetable oil	Fatty acid composition, wt%									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
H.O. Safflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0

^aTr = traces.**Table 2.4** Properties of the vegetable oils (Marchetti *et al.*, 2007)

Vegetable oil	Kinematic viscosity (mm ² /s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4.9	54	5	-	176	0.883	33.6
Soya bean	4.5	45	1	-7	178	0.885	33.5
Babassu	3.6	63	4	-	127	0.875	31.8
Palm	5.7	62	13	-	164	0.880	33.5
Sunflower	4.6	49	1	-	183	0.860	33.5
Tallow	-	-	12	9	96	-	-
Diesel	3.06	50	-	-16	76	0.855	43.8
20% bio-diesel blend	3.2	51	-	-16	128	0.859	43.2

Vegetable oils, such as palm, soy bean, sunflower, peanut, and olive oils, as alternative fuels for diesel engines dates back almost nine decades. Due to the rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is again promoted in many countries. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soy bean oil in the United States, rapeseed and sunflower oils in Europe, coconut oil in the Philippines, and palm oil in Southeast Asia (mainly Malaysia and Indonesia) and are being considered as substitutes for diesel fuels (Srivastava and Prasad, 2000).

In Thailand, several economic oilseeds can be used as a raw material but oil from palm fruits is the highest potential source. The government has planned to produce biodiesel of 8.5 Ml/d in 2012. Success of biodiesel commercialization is an important factor for Thailand's sustainable development from which the positive economic effects and an increase of energy security would be achieved. Consequently, production technologies are urgently required and being developed in Thailand (Leevijit *et al.*, 2008).

Palm oil is one of four oil crops clearly dominate the feedstock sources used, for world-wide biodiesel production. Various parts of the palm fruits can be utilized for oil production for human consumption and industrial applications. The mesocarp of the fruit yields palm oil, which is characterized by high amounts of medium-chain saturated (palmitic acid) and monounsaturated (oleic acid) fatty acids. Palm oil contains tocopherol in concentrations of 600 to 1000 ppm and carotenoid levels of 500 to 700 ppm. The latter give the oil its typical red color. As these minor components serve various industrial purposes (e.g. as food additives), recovery strategies from palm oil used for biodiesel production are very promising. Palm oil can be separated into two fractions—solid palm stearin and liquid palm olein—for which fatty acid compositions are listed in Table 2.5. So far palm oil itself and the palm stearin fraction have mainly attracted attention as raw materials for biodiesel production.

The main advantages of palm oil are outstandingly high hectare yields and moderate world-market prices compared to other edible vegetable oils. If biodiesel fuels are to be economically competitive with fossil diesel, even in the absence of tax concession programs, production costs have to be kept low. This poses consider-

able difficulty with most other highly refined vegetable oils, which could also be utilized for food purposes. The oil palm, however, is a low-value commodity crop, so that the production of biodiesel from palm oil makes sense from an economic point of view. Nevertheless, its high contents of saturated fatty acids, leading to unacceptably high values for cold filter plugging point (+11°C) and cloud point (+13°C), prevent winter operation on neat palm oil methyl esters in temperature climates. Moreover, high contents of free fatty acids in the feedstock cause problems in traditional alkali-catalyzed biodiesel production and thus necessitate deacidification or acid-catalyzed pre-esterification steps (Mittelbach and Remschmidt, 2004).

Table 2.5 Fatty acid composition of the palm oil used for biodiesel production (Mittelbach and Remschmidt, 2004)

	12:0 (wt%)	14:0 (wt%)	16:0 (wt%)	16:1 (wt%)	18:0 (wt%)	18:1 (wt%)	18:2 (wt%)	18:3 (wt%)	Other fatty acids (wt%)	Iodine value (g I ₂ /100g)
Palm oil	0.5	1–2	40–48	-	4–5	37–46	9–11	0.3	C20:0: 0.3	53–57
Palm olein	0.5	1	31.5	-	3	49	14	0.3	C20:0: 0.4	-
Palm stearin	0.3	1.5	62	-	5	24.5	6	0.3	C20:0: 0.4	-

2.3.2 Alcohols

An alcohol is a molecule in which any carbon atoms have the maximum number of hydrogen atoms attached, except for one atom which has an OH group attached. The simplest alcohol, and the one used often in biodiesel production, is methanol. Methanol consists of only one carbon atom, with three hydrogen atom attached, and one oxygen atom attached. The oxygen atom also has a hydrogen atom attached. Thus, methanol is often written as CH₃OH. Use methanol in transesterification can improve the property of biodiesel such as viscosity. Moreover, methanol has low price. The next simplest alcohol is ethanol, which has one more carbon atom,

with two hydrogen atom attached, in between the CH_3 group and the OH group. Ethanol is written as either $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{C}_2\text{H}_5\text{OH}$. The former method is often used to give more of a description of structure. The use of higher alcohol can improve the property of biodiesel such as cold point and pour point because it produces longer and branch of ester but it provides higher energy input and cannot be synthesized with alkaline catalyst (Iangthanarat, 2008).

2.3.3 Catalysts

There are many types of catalysts for transesterification reaction such as, acid- and alkali- catalyst using homogeneous or heterogeneous catalytic process. Moreover, the study of enzymatic catalyst is the most studied in last few years. However, transesterification reaction can conduct without a catalyst.

2.3.3.1 *Homogeneous Catalytic Process*

At the moment, nearly all commercial biodiesel production plants are utilizing homogeneous catalyst that has the same phase as the reactants. The reaction can occur easily because it is good for mixing between reactant and catalyst. This catalytic process can be divided into two types, acid catalysts, and alkaline catalysts.

2.3.3.1.1 *Homogeneous Acid Catalysts*

The acid-catalyzed transesterification is suitable for starting vegetable oil, which has high level of water and free fatty acid but the rate of reaction is slower than the base-catalyzed transesterification and also needs more extreme temperature and pressure condition. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.3. The first step is 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^+ .

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 (Schuchardt *et al.*, 1998).

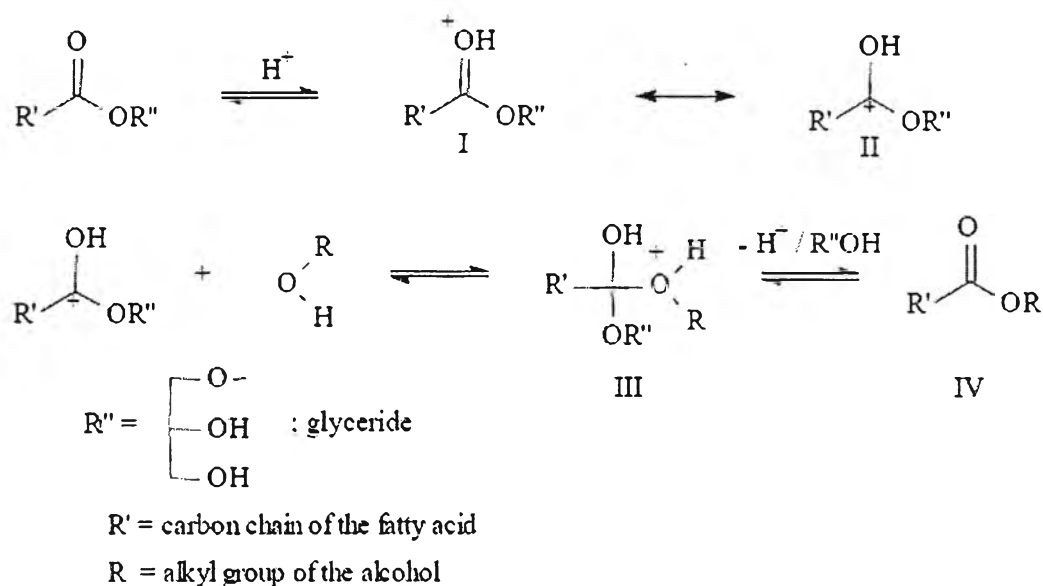


Figure 2.3 Mechanism of the acid-catalyzed transesterification of vegetable oils (Schuchardt *et al.*, 1998).

The acid-catalyzed process often uses sulfonic and sulfuric acid as homogeneous catalysts. Harrington and D'Arcy-Evans (1985) studied the transesterification of sunflower seed oil in the presence of sulfuric acid catalyst. The reaction is occurred under reflux for 3–4 hours. They found that it has produced methyl and ethyl esters in yield greater than 40% of the dry seed weight. This similar experiment is studied by Siler-Marinkovic and Tomasevic (1998). They found that the good results were obtained in mild reaction conditions (30°C) with a strong acidic catalyst (sulfuric acid) and high molar ratio. All of their results were obtained at least 90% of ester in oil basis. Moreover, Schwab *et al.* (1987) studied the methanolysis of soybean oil by using H₂SO₄ as a catalyst. They discovered that in the presence of 1 wt% of H₂SO₄ with a methanol/oil molar ratio of 30:1 at 65°C, it took 69 hours to reach complete conversion. Furthermore, Marchetti *et al.*, (2008) studied the use of sulfuric acid for biodiesel production by direct esterification of spent oil with high amounts of FFA. The results showed that the amount of FFA was reduced from 10.68% to values around 0.54% w/w. The amount of soap that might be produced by these FFA is reduced.

2.3.3.1.2 Homogeneous Alkaline Catalysts

Typically, the base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually prefer basic catalysts, such as sodium hydroxide, potassium hydroxide, and corresponding sodium and potassium alkoxide such as sodium methoxide and potassium methoxide. The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 2.4 (Schuchardt *et al.*, 1998). The first step is the reaction of the base with the alcohol, producing an alkoxide (type of alkoxide depend on type of catalyst used in reaction) and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst, thus regenerating the active species, 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.



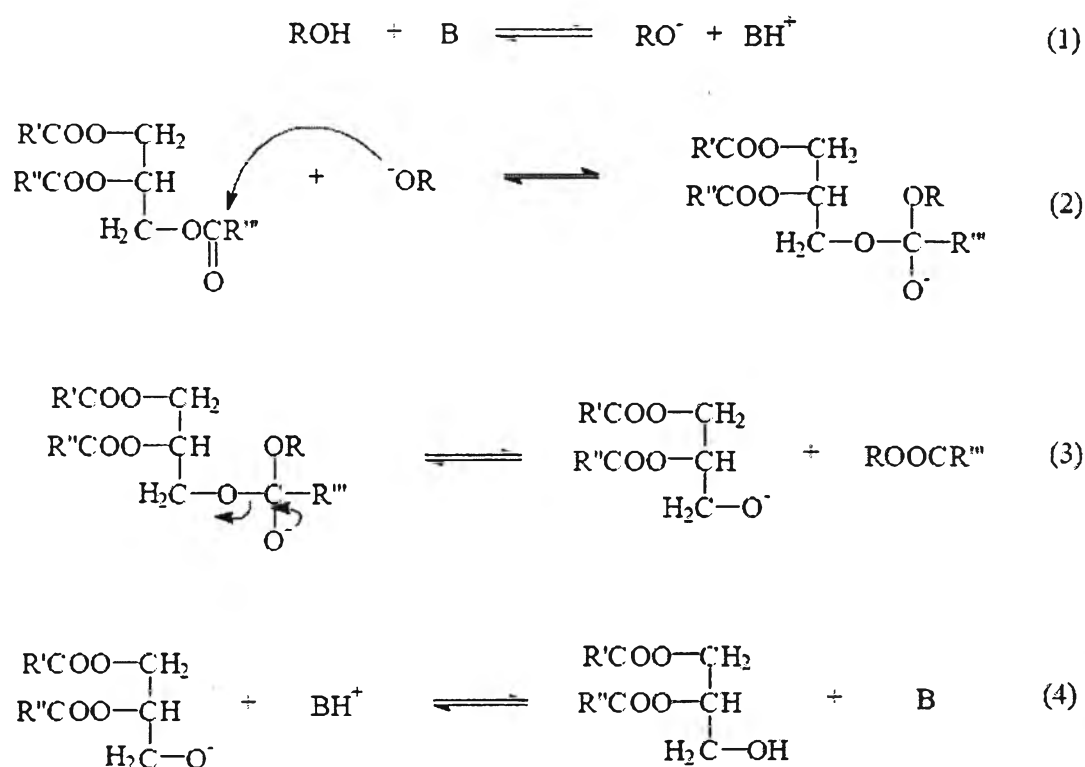


Figure 2.4 Mechanism of the base-catalyzed transesterification of vegetable oils (Schuchardt *et al.*, 1998).

Although the base-catalyzed transesterification is preferred but it has many limited conditions. For example, base catalysts are very sensitive to water and free fatty acid in the vegetable oil. The presence of water and free fatty acid lead to the hydrolysis of the ester and then soap is formed via saponification. The formation of soap reduces the biodiesel yield, consumes catalyst and causes significant difficulty in product separation. To solve this problem, starting vegetable oils must be dried (moisture level less than 0.06%) and free fatty acid content is less than 0.05 (Zullaikah *et al.*, 2005).

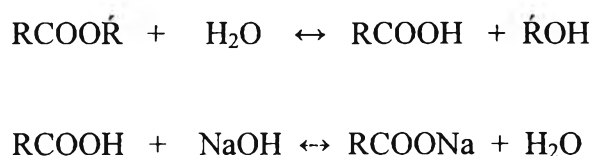


Figure 2.5 Saponification of fatty acid alkyl ester (Zullaikah *et al.*, 2005).

The alkaline processes are generally catalyzed by sodium alkoxides, sodium or potassium hydroxides as well as sodium or potassium carbonates (Pinto *et al.*, 2005). At this time, there are a number of reviews in the literature on alcoholysis of triglycerides using homogeneous alkaline catalysts. For example, Foidl *et al.* (1996) prepared biodiesel from *Jatropha curcas* L. oil. They used the 2 step transesterification process in the presence of KOH catalyst. The result showed that it reached 85–90% biodiesel yield in the first step and over 99% in the second step. Moreover, Karmee *et al.* (2005) prepared biodiesel from the non-edible oil of *Pongamia pinnata* by transesterification of the crude oil with methanol in the presence of KOH as a catalyst. They found that the maximum conversion of 92% (oil to ester) was achieved using a 1:10 molar ratio of oil to methanol at 60°C. And when tetrahydrofuran (THF) was used as a co-solvent, the conversion was increased to 95%. Furthermore, Encinar *et al.* (2002) studied the transesterification of *Cynara Cardunculus* L. oil by using sodium hydroxide and potassium hydroxide as catalysts. The biodiesel with the best properties of their research was obtained using an ethanol/oil molar ratio of 12:1, sodium hydroxide as a catalyst (1%) and 75°C. In addition, Dmytryshyn *et al.* (2004) studied transesterification from four types of vegetable oil; canola oil, greenseed canola oil, processed waste fryer grease, and unprocessed waste fryer grease by using KOH as a catalyst. They found that the best ester yield came from the canola methyl ester. Vicente *et al.* (2004) also studied about biodiesel production using different homogeneous basic catalysts; sodium methoxide, potassium methoxide, sodium hydroxide, and potassium hydroxide for methanolysis of sunflower oil. They found that almost 100 wt% biodiesel yields were only obtained with the methoxide catalysts and the reactions using sodium hydroxide turned out the fastest.

2.3.3.2 Heterogeneous Catalytic Process

Whereas traditional homogeneous catalysis offers a series of advantages, its major disadvantage is the fact that homogeneous catalysts cannot be reused. Moreover, catalyst residues have to be removed from the ester product, usually necessitating several washing steps, which increases production costs. Thus there have been various attempts at simplifying product purification by applying heterogeneous catalysts, which can be recovered by decantation or filtration or are alter-

natively used in a fixed bed catalyst arrangement. A large number of heterogeneous catalysts have been reported in literature, including zeolites, clays, guanidines heterogenized on organic polymers, ion-exchange resins, alkaline earth metal oxides, metal compounds loading on support, etc.

2.3.3.2.1 Bulk Catalysts

Some solid chemical compound can be bulk catalyst by itself. There are many researchers used bulk catalysts as heterogeneous catalysis of biodiesel production. Liu *et al.* (2007) studied the transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. The results showed that the yield of biodiesel production was in excess of 95% at temperatures below 70°C within 30 min. It was found that SrO had a long catalyst lifetime and could maintain sustained activity even after being repeatedly used for 10 cycles. Moreover, Gryglewicz (1999) found that the basic alkaline-earth metal compounds can be used as a catalyst in the transesterification of rapeseed oil by methyl alcohol. The reaction increases in the order of $\text{CaO} < \text{Ca}(\text{CH}_3\text{O})_2 < \text{Ba}(\text{OH})_2$. In spite of its high activity, $\text{Ba}(\text{OH})_2$ is not recommended to be used because it is much more soluble in methanol than other alkaline earth metal compound. Calcium catalysts are much cheaper and lead to a decrease in the number of technological stages and the amount of unwanted waste products. Furthermore, Suppes *et al.* (2001) studied the transesterification of soybean oil using calcium carbonate as a catalyst. Conversions above 95% are achieved at 260°C for ethyl esters, using flow reactors and 18 min as residence time.

2.3.3.2.2 Compound Catalysts

Compound catalyst is other types of catalysts that come from combining of different chemical substances. For example, Di Serio *et al.* (2006) discovered that MgO (type 3) gave 93 % yield of FAME because of high basicity. But calcined hydrotalcite (CHT), which have low basicity, gave high yield of FAME. They suggested that because CHT had large pore radius (20 Angstrom) that favored the reaction by rendering the active sites more accessible to bulky triglyceride molecules. In addition, Peterson and Scarrah (1984) discovered that CaO.MgO catalyst had activity comparable to sodium methoxide and catalyzed transesterification with 95% methyl ester yield. However, this catalyst produces substantial amount of soap product thereby rendering the effectiveness of this heterogeneous catalyst.

Xie *et al.* (2006) also investigated the calcined Mg-Al hydrotalcites as a solid base catalyst for methanolysis of soybean oil. They found that at a 15:1 molar ratio of methanol to oil, 9 hours and 7.5% amount of catalyst, soybean oil can be converted to biodiesel in 67% conversion.

2.3.3.2.3 Loading Catalysts

Some definition of loading catalyst is the use of metal load on the supported material. There are many literature review showed about the transesterification using loading catalyst. Xie *et al.* (2007) studied the transesterification of soybean oil using NaX zeolites loaded with KOH as heterogeneous basic catalysts. The best result was obtained with NaX zeolite loaded with 10% KOH and the conversion of soybean oil was 85.6%. Moreover, Furuta *et al.* (2005) studied biodiesel fuel production with amorphous zirconia catalysts, titanium-, aluminum-, and potassium-doped zirconias, were prepared and evaluated in the transesterification of soybean oil with methanol and the esterification of n-octanoic acid with methanol. They concluded that titanium- and aluminum-doped zirconias are promising solid catalysts because of their high performance, with over 95% conversion in both of the esterifications. Xie *et al.* (2006) also studied the transesterification of soybean oil to methyl esters using alumina loaded with potassium as a solid base catalyst. The catalyst with 35 wt% KNO₃ loaded on Al₂O₃ was found to be the optimum catalyst, which can give the highest basicity, the best catalytic activity, and the highest conversion reached 87%. Furthermore, Yang *et al.* (2007) used alkalined earth metal-doped zinc oxide as a catalyst for transesterification of soybean oil. The highest catalytic activity was obtained with ZnO loaded with 2.5 mmol Sr(NO₃)₂/g. The conversion of soybean oil was 94.7%. They found that when THF was used as co-solvent, the maximum conversion was 96.8%. Another example comes from Jitputti *et al.* (2006). They investigated several acid and base solids, such as ZrO₂, ZnO, SO₄²⁻/SnO₂, SO₄²⁻/ZrO₂, KNO₃/KL zeolite and KNO₃/ZrO₂ as heterogeneous catalysts for transesterification of crude palm kernel oil (PKO) and crude coconut oil (CCO) with methanol. They found that ZnO and SO₄²⁻/ZrO₂ exhibited the highest activity for both PKO and CCO transesterification. In the case of SO₄²⁻/ZrO₂, only 1 wt% of this acid solid catalyst was needed to catalyze the reaction, and resulted in fatty acid methyl esters content higher than 90%.

2.3.3.2.4 Other Types of Catalysts

There are other types of material that can be used as a heterogeneous catalyst of transesterification process. For example, Suppes *et al.* (2003) used zeolite which is porous material. The NaX zeolite was exchanged to potassium and cesium. They found that cesium gave the conversion of methyl ester (24.2 wt%) lower than potassium (31.5 wt%) because the large size of cesium cation limited the exchanged capacity lower than smaller potassium, which affect to the basicity. Moreover, they impregnated 1 M of sodium azide on the porous material. They found that the conversion of methyl ester (79.1 wt%) increase more than the parent zeolite (23.9 wt%). When the concentration of sodium azide was increased to 3 and 4 M, the conversion of methyl ester were 94 and 96.5 wt%, respectively.

The ion-exchange resin is one type of catalyst. Lopez *et al.* (2005) investigated the kinetics and selectivities of different solid catalysts for the transesterification of triacetin with methanol. They found that the homogeneous catalysts (NaOH and H₂SO₄) were compared with Amberlyst-15, Nafion NR50, sulfated zirconia, and ETS-10 (Na, K) as heterogeneous catalysts. The reactivity of acid catalysts are in the order of H₂SO₄ > Amberlyst-15 > SZ > Nafion NR50 > WZ > SPA > Zeolite Hb > ETS-10 (H) and the reactivity of basic catalyst, in the order of NaOH > ETS-10 (H) > MgO.

Some organic compounds can be used for transesterification process. Schuchardt *et al.* (1996) studied the comparison of activity of guanidine-containing polymers and their homogeneous analogues as catalysts in the transesterification of soybean oil with methanol. The heterogeneous catalysts were used at 5 mol% in contrast to the 3 mol% used with the homogeneous catalyst. They were nearly as active as their homogeneous analogues and reached the same high conversions (>90%) after prolonged reaction time.

2.3.3.3 Enzymatic Catalysts

Biocatalytic routes permit one to carry out the transesterification of a wide variety of oil feedstock in the presence of acidic impurities, such as free fatty acids. The enzymatic processes are very promising because of their high selectivity and mild operative conditions. Lipase is one type of enzymes that can be used in transesterification process. The advantage of using biocatalyst as a catalyst is

the separation and purification of the biodiesel fuels because of the absence of soap by-products. Biocatalysts are more expensive than traditional chemical catalysts; however, their recycle is compulsory to overcome economical costs (Iangthanarat, 2008). Up to now, there are many studies of using enzymatic catalyst for transesterification process. For example, Fernandes *et al.* (2007) obtained 94% of conversion of biodiesel by using the *Burkholderia capacis* as a catalyst. Although they obtained high conversion, the reaction time was very long (18 hours) and it required high molar ratio of alcohol (5:1). Moreover, Salis *et al.* (2005) investigated the activity of *Candida antarctica* B, *Rizhomicoccus miehei*, and *Pseudomonas cepacia* lipase in transesterification of pure triolein. They found that *Pseudomonas cepacia* lipase seemed to be the most active enzyme that can reach 100% of conversion after 6 hours.

2.3.3.4 No Catalyst

With the aim of developing a novel methanolysis process for oil without using any catalyst, the study of biodiesel production in supercritical methanol becomes more interesting. Supercritical transesterification is the process that uses high temperatures and high pressures to convert oil to biodiesel. It has 2 major steps, which are transesterification of triglyceride and esterification of free fatty acid. These two reactions occur at the same time. Supercritical transesterification has many advantages such as short reaction time, high yield of biodiesel, easy to separate the biodiesel from glycerol, and no effect with water and free fatty acid in starting vegetable oil. Although this process has many advantages, but it is not commercialized now because it is very expensive in operating cost due to this process requires high pressure and temperature (Fukuda *et al.*, 2001). Many groups of researchers are interested in transesterification using supercritical method such as Rathore and Madras (2007) who have tried to combine the enzymatic system with supercritical alcohol. They used Novdzym 435 lipase as enzyme and found that edible and non edible oil can be converted to biodiesel more than 80% within 10 minutes. When they compared between combine system with enzymatic system and supercritical system, they found that at the same conversion, supercritical system can be achieved in 40 minutes. For the enzymatic system, the conversion of 60–70% can be obtained within 8 hours. Other study comes from Kusdiana *et al.* (2001), they studied the condition of biodiesel production from rapeseed oil by supercritical methanol. They found that the

optimum condition was 300°C, 30 MPa in 240 seconds with a molar ratio of 42:1 and the maximum conversion of 98.5% was achieved. Furthermore, Wang *et al.* (2007) added Ethylenediamine (EDA), Diethylamine (DEA) or Triethylamine (TEA), to speed up the production of methyl ester from crude rapeseed oil in supercritical method. They found that the order of catalytic activity was EDA > DEA > TEA, respectively, in 10 minutes. They used the molar ratio of methanol to oil 24:1 at 290°C. But the yield of methyl ester could reach 89.5%, which is much lower than Kusdiana *et al.* work.

2.4 Process Variables in Biodiesel Production

The most important variables that influence transesterification reaction time and conversion are:

- Reaction temperature
- Reaction pressure
- Molar ratio of alcohol to oil
- Catalyst type and concentration
- Mixing intensity
- Purity of reactants

2.4.1 Reaction Temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, 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 feedstock is 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 temperatures ranging from 60 to 80°C at a molar ratio (alcohol to oil) of 6:1. Further increase in temperature is reported to have a negative effect on the con-

version. 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 given enough time, transesterification can proceed satisfactorily at ambient temperatures in the case of the alkaline catalyst (Srivastava and Prasad, 2000).

2.4.2 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. Trans-

methylation 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 and it adds to extra costs because it is necessary to remove it from the reaction medium at the end.

It has been shown that lipases are able to catalyze the alcoholysis of triglycerides in both aqueous and nonaqueous systems. The reaction follows Michaelis-Menten kinetics and enzymatic kinetics that agree with a Ping-pong Bi-Bi mechanism (Srivastava and Prasad 2000).

2.4.5 Mixing Intensity

In the transesterification reaction, the reactants initially form a two-phase liquid system. The reaction is diffusion-controlled and poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system is formed. The mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant. The understanding of the mixing effects on the kinetics of the transesterification process is a valuable tool in the process scale-up and design (Srivastava and Prasad, 2000).

2.4.6 Purity of Reactants

Impurities present in the oil also affect conversion levels. Under the same conditions, 67 to 84% conversion into esters using crude vegetable oils can be obtained, compared with 94 to 97% when using refined oils. The free fatty acids in the original oils interfered with the catalyst. However, under conditions of high temperature and pressure, this problem can be overcome (Srivastava and Prasad, 2000).

2.5 Biodiesel Production with Fixed Bed Reactor

The most commonly used technology for biodiesel production is based on the use of batch plants. However, a continuous process would be a good opportunity for reducing the production costs and is more suitable for industrial scale than a batch process. The continuous process of transesterification comprises bringing a stream of triglycerides into contact with a stream of alcohol in the presence of a catalyst. The suitable reactor for this process is the fixed-bed reactor that has solid catalyst contained inside it. For the product, it passes through reactor and separates into two phases of biodiesel and glycerol. The continuous process is the new biodiesel production. Up to now, many researchers are studying this method. For example: Park *et al.* (2008) studied the production of biodiesel from used vegetable oils using a continuous process. They found that the pellet-type WO_3/ZrO_2 catalyst showed highly active and durable catalytic activities in the continuous flow process. The steady state conversion of 70% was obtained in a 140 hours durability test. The acidic property and catalytic activity of WO_3/ZrO_2 were attributed to the oxidation state of tungsten.

Moreover, Kitakawa *et al.* (2007) studied the transesterification reaction of triolein with ethanol using various ion-exchange resin catalysts. The appropriate condition of their study was 50°C using a fixed-bed reactor that has water-jacketed column and the triolein was fed from bottom. From the result, the bed height and resin weight had linear dependence relationship and the anion exchange resin gave a high reaction rate as well as high conversion.

Furthermore, Furuta *et al.* (2004) studied the transesterification of soybean oil and the esterification of n-octanoic acid with methanol. Solid superacid catalysts of sulfated tin and zirconium oxides and tungstated zirconia were prepared as solid catalysts in a fixed-bed reactor under atmospheric pressure. They found that tungstated zirconia-alumina has high performance with the conversion over 90%. Moreover, in 2006, they also studied the synthesis of fatty acid methyl ester from soybean oil and methanol. Amorphous zirconia catalysts, titanium-, aluminum-, and potassium-doped zirconias, were prepared as the solid catalysts. The process was carried out in a fixed-bed continuous flow reactor. From the result, titanium- and aluminum-

doped zirconias are promising solid catalysts because of their high performance, with over 95% conversion.

In addition, Leevijit *et al.*, 2007 studied the performance test of a 6-stage continuous reactor for palm methyl ester production. They concluded that higher stirrer speed increased the reaction rate but excessive stirrer speed decreased the reaction rate. Higher NaOH catalyst concentration significantly increased reaction rate and production capacity of the reactor.

He *et al.*, 2007 also studied the continuous transesterification of vegetable oil using supercritical methanol in a tube reactor. The side reaction of unsaturated fatty acid methyl esters (FAME) occurred at high temperatures, which lead too much loss of material and the maximum production yield only 77% was achieved. However, they proposed a new technology to solve this problem, which is the gradual heating and the methyl esters yield more than 96% can be obtained.

Royon *et al.*, 2007 studied the production of biodiesel by methanolysis of cottonseed oil using immobilized *Candida Antarctica* lipase as a catalyst in *t*-butanol solvent. They found that a methanolysis yield of 97% was observed after 24 hours at 500°C when using a batch system. However, using a one step fixed bed continuous reactor, the ester yield of 95% was obtained.

2.6 Methods of Analysis for Characterization of Biodiesel

There are many researches that reported the methods employed for the quantification of the fatty acid composition of biodiesel. Most of them used Gas Chromatography (GC) and High-Performance Liquid Chromatography (HPLC).

2.6.1 Comparison between GC and HPLC

There is a large variety of analytical techniques for the detection, characterization and quantification of fatty acids in biodiesel. The two most common analytical methods for studying fatty acids and triglycerides are GC and HPLC. The comparison of these two methods should focus not only the chromatographic analysis but also the sample preparation.

Although the application of HPLC to fatty acid analysis has increased over the last decade, GC is still the most widely used technique. This well-established procedure coupled with flame ionization detection (GC–FID) is very efficient and rapid when complex mixtures with a broad molecular range are analyzed.

Fatty acids are suitable for separation, quantification, and analysis by GC without any derivatization. However, derivatization of fatty acids for GC analysis is performed to increase the volatility of the substances, to improve separation, and to reduce tailing. Recent developments in the technology of columns with bonded phases offer spectacular separation and little phase bleeding. Nevertheless, if a higher sensitivity is demanded, then derivatization is used. In recent times, GC has been used for the separation and analysis of geometric and positional isomers. Meanwhile, MS detection is a powerful technique for diagnostic fragmentation of saturated and unsaturated fatty acids and analysis of branching positions in fatty acids.

The major advantages of HPLC over GC are lower temperatures during analysis, which reduces the risk of isomerization of double bonds, and the possibility of collecting fractions for further investigation. The speed of analysis, selectivity, and sensitivity, are important parameters in HPLC that may be improved with derivatization.

Regarding the elution order of fatty acids, both methods are based on chain length and degree of unsaturation. Fatty acid retention times increase with carbon number. Regarding the required analysis time, sample preparation is much more time consuming in HPLC than in the GC method. Nevertheless, this disadvantage is largely compensated by the run time.

The HPLC method is sensitive and precise and may be considered a good optional tool for the routine determination of 18:1, 18:2 and 18:3 in any oil. However, when a more complete study of fatty acid profile is required, GC is the method of choice, since HPLC may present co-eluting peaks (Pinto *et al.*, 2005).

2.6.2 Parameters of GC and HPLC Analyses for Quantifying Biodiesel Conversion

Following the searches on the types of analysis employed for biodiesel characterization, some parameters were detached, which are usually used in GC and HPLC. These parameters are presented in Table 2.6 for GC and Table 2.7 for HPLC (Pinto *et al.*, 2005).

Table 2.6 Summary of some parameters for analyzing biodiesel by GC (Pinto *et al.*, 2005)

Column: l x id x fi (phase)	Injector Temp. (°C)	Oven Temperature
30 m x 0.25 mm x 0.25 μ m (polyethyleneglycol)	250	165-180 °C (4 °C min ⁻¹) 180-200 °C (5 °C min ⁻¹) 200-260 °C (15 °C min ⁻¹) 260 °C (2 min)
25 m x 0.53 mm x 1 μ m (acidified polyethylene glycol)	-	180-200 °C (4 °C min ⁻¹)
25 m x 0.32 mm x 0.52 μ m (5% diphenyl and 95% dimethyl polysiloxane)	250	150-225 °C (5 °C min ⁻¹)
30 m x 0.32 mm x 1 μ m	300 ^a	190-215 °C (6 °C min ⁻¹) 215-300 °C (3 °C min ⁻¹)

^a Splitless. ^b FID 250 °C. ^c FID 280 °C. ^d FID 300 °C.

Table 2.7 Summary of some parameters for analyzing biodiesel by HPLC (Pinto *et al.*, 2005)

Column: - l x id (TM)	Mobile phase	Temp (°C)
250 mm x 4.6 mm (STRODS-II)	methanol	40
250 mm x 4 mm (LiChro CART RP-C18)	hexane:isopropanol:methanol	-
300 mm x 7.8 mm (GPC-Styragel)	toluene	-
300 mm x 7.5 mm (GPC-Styragel 0.5)	tetrahydrofuran	35-40

^a 1.00 mL min⁻¹. ^b Injection loop of 10 μ L. ^c Injection loop of 500 μ L.

2.6.3 Parameters of ¹H NMR and TLC Analysis

The final product of the transesterification can possess some traces of triglycerides which can damage some components of the GC equipment, for example the column. To avoid this problem, it is important to be sure about the conversion achieved by the transesterification of the vegetable oil.

¹H NMR spectroscopy is a method used to quantify the conversion of vegetable oils in methyl esters by transesterification reaction. The relevant signals

chosen for integration are those of methoxy groups in the methyl esters at 3.7 ppm (singlet) and of the α -carbonyl methylene groups present in all fatty ester derivatives at 2.3 ppm. The latter appears as a triplet, so accurate measurements require good separation of this triplet from the multiplet at 2.1 ppm, which is related to allylic protons.

TLC is commonly used for qualitative analysis. It is fast and effective, and also can be used to verify the conversion of the oil during the reaction. After this previous analysis, the product can be quantified by GC. Some solvent systems and detecting reagents commonly used for evaluation of starting material conversion during the reaction are shown in Table 2.8 (Pinto *et al.*, 2005).

Table 2.8 Solvent systems and detecting reagents parameters by TLC (Pinto *et al.*, 2005)

Solvent system (v/v/v)	Detecting reagents
Hexane:ethyl acetate:acetic acid (90:10:1)	iodine vapour
Isohexane:diethyl ether:acetic acid (80:20:1)	ultraviolet light
Chloroform:petroleum ether (1:3)	-
Petroleum ether:diethyl ether:acetic acid (85:15:1)	iodine vapour
Hexane:ethyl acetate:acetic acid (90:10:1)	sulphuric acid: methanol 1:1