



**Table 2.1** Chemical structure of common fatty acids (Srivastava and Prasad, 2000)

Fatty acid	Systematic name	Structure <sup>a</sup>	Formula
Lauric	Dodecanoic	12:0	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>
Myristic	Tetradecanoic	14:0	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>
Palmitic	Hexadecanoic	16:0	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>
Stearic	Octadecanoic	18:0	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>
Arachidic	Eicosanoic	20:0	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>
Behenic	Docosanoic	22:0	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>
Lignoceric	Tetracosanoic	24:0	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>
Oleic	<i>Cis</i> -9-Octadecenoic	18:1	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>
Linoleic	<i>Cis</i> -9, <i>cis</i> -12-Octadecadienoic	18:2	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>
Linolenic	<i>Cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-Octadecatrienoic	18:3	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>
Erucic	<i>Cis</i> -13- Docosenoic	22:1	C <sub>22</sub> H <sub>42</sub> O <sub>2</sub>

<sup>a</sup> xx:y indicates x carbons in fatty acid chain with y double bonds.

**Table 2.2** Chemical composition of vegetable oils<sup>a</sup>(Srivastava and Prasad, 2000)

Vegetable oil	Fatty acids 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
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
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

<sup>a</sup> Tr = traces.

## 2.2 Derivatives of Triglycerides from Vegetable Oils as Diesel Fuels

There are four major ways to make vegetable oil derivatives that have the properties and performance similar to the petroleum-based diesel fuels.

### 2.2.1 Pyrolysis

Pyrolysis is defined as the decomposition of a macromolecule by heat under the absence of O<sub>2</sub> atmosphere. It involves heating in the absence of air or oxygen and cleavage of chemical bond to form small molecules (Fangrui, 1999).

The thermal decomposition of triglycerides from vegetable oils produces the compounds of classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids (Srivastava and Prasad, 2000).

### 2.2.2 Dilution or Blending

Dilution of vegetable oils can be accomplished with such materials as diesel fuel, a solvent or ethanol (Srivastava and Prasad, 2000). Several studies have shown that the diluted vegetable oils could be used for short term performance. However, their long term use is not recommended since they can lead to several problems, such as injector nozzle coking and thickening of lubricant (Fangrui, 1999; and Srivastava and Prasad, 2000).

Vegetable oils contain no petroleum, but it can also be blended with petroleum-based diesel fuel. The fuel blend can be used for short term. However, it can cause several difficulties to diesel engine. Those are high viscosity, acid composition, free fatty acid content, gum formation, carbon deposit, and lubricating oil thickening (Fangrui, 1999).

### 2.2.3 Microemulsification

Microemulsions are transparent dispersions containing two immiscible liquids that are dispersed one into another. The droplet size is in the range of 10 to 100 nm in diameter (Rosen, 1989). The microemulsification is used to solve the problem of high viscosity of vegetable oils.

#### 2.2.4 Transesterification

Transesterification is the general term used to describe the organic reactions when an ester is transformed into another (Schuchardt, 1998). Transesterification, often called alcoholysis, is the displacement of alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water (Fukuda *et al.*, 2001). This reaction is commonly used to produce biodiesel, which becomes more attractive recently because of its properties.

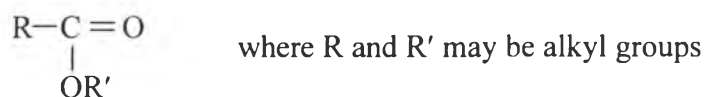
### 2.3 Biodiesel

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. Biodiesel is typically composed of fatty acid methyl esters which are derived from the triglycerides of the vegetable oils by transesterification with alcohol, usually methanol (Srivastava and Prasad, 2000).

The main advantages of using biodiesel are its low sulfur, hydrocarbon and particulate emission, biodegradability, good lubrication properties, renewability and availability. Biodiesel can be blended at any level with petroleum-based diesel fuel to create a biodiesel blend, although it contains no petroleum.

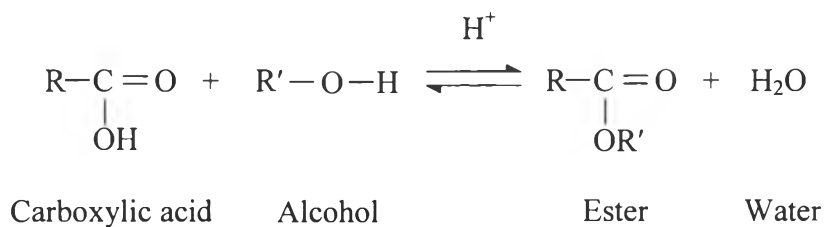
### 2.4 Synthesis of Esters

Esters can be considered as functional derivatives of carboxylic acids. The esters can be viewed as the –OH of a carboxyl group is replaced by –OR':



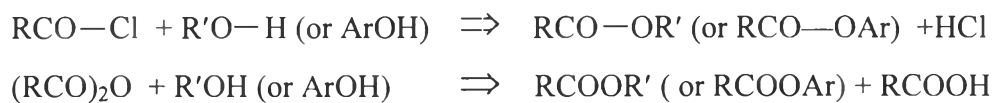
Esters are usually prepared by the most common methods outlined by Morrison and Boyd (1992) as following:

- From acids.

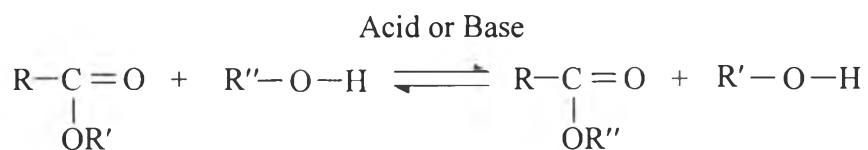


R may be alkyl or aryl R' is usually alkyl

- From acid chlorides or anhydrides.

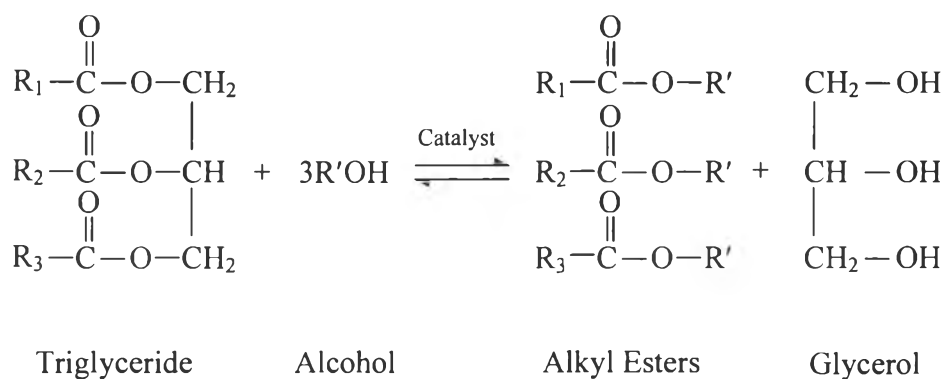


- From esters.



## 2.5 Transesterification of Vegetable Oils

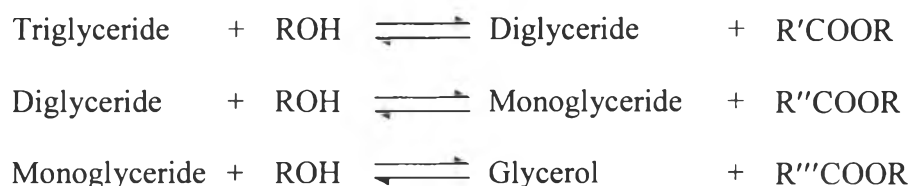
The overall transesterification reaction is illustrated in Figure 2.2. Stoichiometrically, the transesterification of triglyceride requires 3 moles of alcohol per mol of triglyceride and forms 3 moles of fatty acid esters and 1 moles of glycerol. Because the reaction is reversible, excess alcohol is usually used to shift the equilibrium to the products side (Fangrui, 1999).



**Figure 2.2** Transesterification reaction of triglycerides with alcohol (Fangrui, 1999).

Many short chain alcohols can be used in transesterification reaction, such as methanol, ethanol, propanol, and butanol (Fukuda *et al.*, 2001). Among these alcohols, methanol is the most prefer alcohol because it can quickly react with triglycerides resulting in higher conversion of esters. Furthermore, it is relatively cheap when compare to other alcohols. If methanol is used in this reaction, often the transesterification is referred as methanolysis.

The overall transesterification of triglyceride can be viewed as three consecutive reactions as shown in Figure 2.3. The triglycerides are first converted to diglycerides and then to monoglycerides and glycerol respectively. For each step, one molecule of methyl ester is liberated (Srivastava and Prasad, 2000).



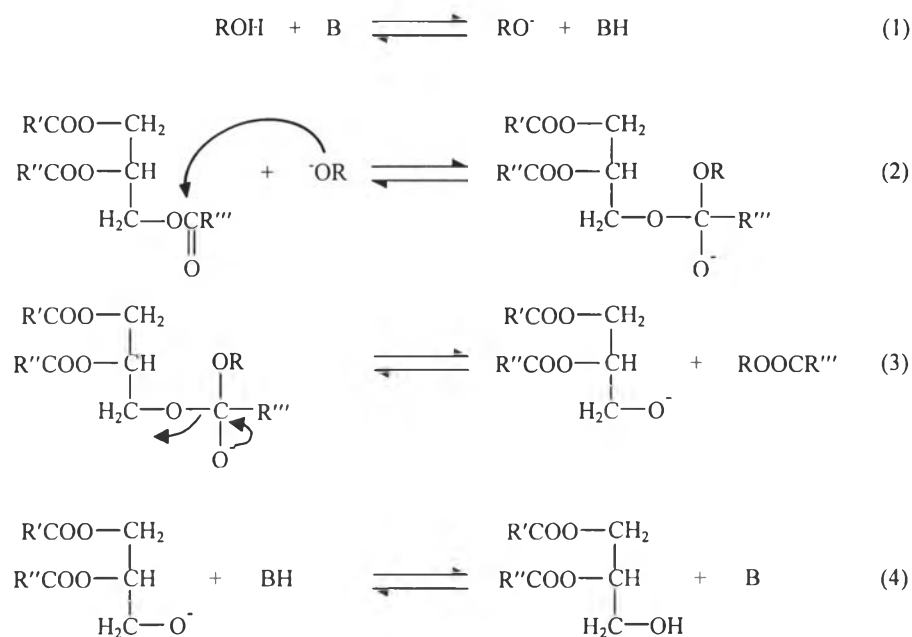
**Figure 2.3** Transesterification reaction of vegetable oil (Srivastava and Prasad, 2000).

The transesterification reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis can be NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acids and hydrochloric acid are usually used as acid catalysts.

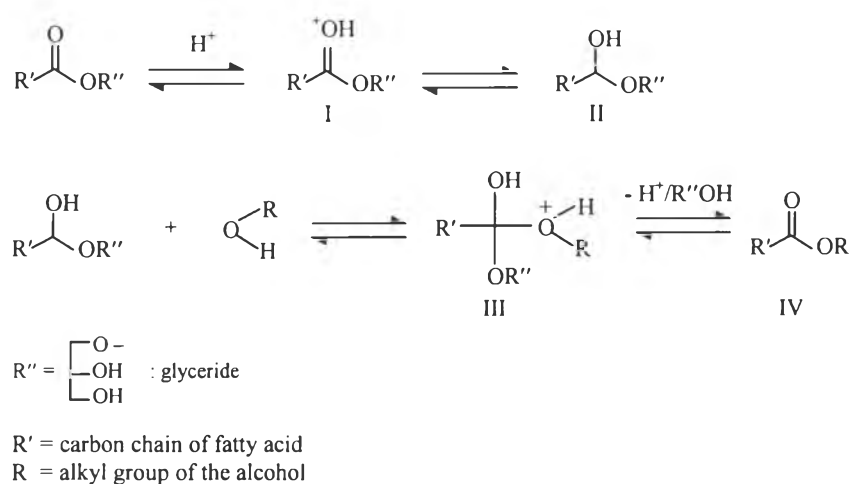
Base-catalyzed transesterification is much faster than acid-catalyzed transesterification. Examples of basic catalysts are sodium methoxide, sodium propoxide, sodium butoxide, sodium hydroxide and potassium hydroxide. The mechanism of the base-catalyzed transesterification of vegetable oils was proposed by Schuchardt *et al.* (1998) and is shown in Figure 2.4. First, the base reacts with alcohol and then results in generating an alkoxide 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.

Comparing with the base-catalyzed transesterification, acid-catalyzed transesterification is more suitable for glycerides that have relatively high amount of free fatty acid and water because, in alkali-catalyzed transesterification, water can cause soap formation, which consumes catalyst and reduces catalyst efficiency (Fukuda *et al.*, 2001). The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.5. The first step, the protonation of the carbonyl group of the ester leads to carbocation. After a nucleophilic attack, the carbocation produces the tetrahedral intermediate, which eliminates glycerol to form new ester IV, and to regenerate the catalyst  $H^+$  (Schuchardt, 1998).

Lipases can also be used as biocatalyst to catalyze transesterification of vegetable oils in either aqueous or nonaqueous systems (Fukuda *et al.*, 2001).



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



**Figure 2.5** Mechanism of the acid-catalyzed transesterification of vegetable oil (Schuchardt, 1998).

A review done by Srivastava and Prasad (2000) summarizes the important variables that influence transesterification and ester conversion. These variables are



reaction temperature, ratio of alcohol to oil, catalyst type and concentration, mixing intensity and purity of reactants. The maximum yield of alkyl esters occurs at temperatures close to boiling point of the alcohol used at a molar ratio (alcohol to oil) of 6:1. They also pointed out that the basic homogeneous catalysts like sodium alkoxide are the most effective for transesterification. However, the presence of free fatty acids and water can cause some side reactions thereby affecting the ester conversion.

Freedman *et al.* (1986) investigated both acid- and alkaline- catalyzed transesterification of soybean oil with methanol and butanol. They found that the alkaline-catalysts 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. They also estimated the activation energy for all forward and reverse reactions which are ranging from 8-20 kcal/mol.

Noureddini *et al.* (1997) focused on the effect of mixing intensity and temperature on the rate of reaction. They observed that the effect of mixing were in parallel with the temperature. They concluded that in the transesterification, the reactants initially form a two-phase liquid system, which is diffusion-controlled resulting in a slower rate. As the methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system is formed.

More recently, 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 6:1 methanol: oil molar ratio.

Numerous studies are reported in the transesterification of vegetable oil using homogeneous catalysts. Although the reaction proceeds nicely, major problems such as removal of soluble catalyst and formation of by-products were encountered. These hurdles lead to the idea of using heterogeneous catalysts for transesterification of vegetable oil.

## 2.6 Transesterification using Heterogeneous Catalysts

Several attempts have been carried out using heterogeneous catalysts on the transesterification of vegetable oils. Peterson and Scarrah (1984) discovered the CaO·MgO catalyst to have activity comparable to sodium methoxide-catalyzed transesterification with 95% methyl ester yield. However, the catalyst produces substantial amount of soaps thereby rendering this catalyst unsuitable for commercial application.

It was found that basic alkaline earth metal compounds could effectively catalyze the transesterification of rapeseed oil (Gryglewicz, 1999). The activity of 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 use since it is much more soluble in methanol than other alkaline earth metal compounds. Moreover, the soluble  $\text{Ba}(\text{OH})_2$  compounds are highly toxic.

Recently, Leclercq *et al.* (2001) investigated basic zeolites and solid catalysts in the transesterification of rapeseed oil. They found that magnesium oxide with a high surface area over  $300 \text{ m}^2/\text{g}$  is far more active than cesium-exchanged NaX faujasites and hydrotalcites.

Suppes *et al.* (2001) used  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{ZnCO}_3$ ,  $\text{MgCO}_3$  to catalyze alcoholysis of fats and oils. The results show that  $\text{CaCO}_3$  is of the greatest interest because of its low solubility and low cost. They also used  $\text{CaCO}_3$  to catalyze soybean oil ethanolysis. It was found that at high temperature, high conversion of soybean oil could be obtained when  $\text{CaCO}_3$  is used as a catalyst.

In addition, Zajdlewicz (2001) reported that there are five commercially available catalysts that are active for transesterification of soybean oil. The most active of these catalysts was Valfor (alumina silicate) followed by ZSM5, Beta zeolite, MCM-41, and then zeolite Y. This information needs further verification since the results were just only based on the peak height obtained from gas chromatography.

Bancquart *et al.* (2001) investigated the relationship between activity and basicity of four basic catalysts ( $\text{MgO}$ ,  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$  and  $\text{ZnO}$ ) in the glycerol

transesterification with methyl stearate. They found that the reaction rate of the transesterification directly depends on the basicity of the basic site.

Siegfried *et al.* (2002) used metal salts of amino acids as catalysts to synthesize fatty acid esters by methanolysis of palm oil. They found that salts containing a quaternary amino or a highly basic group e.g. zinc salts of arginine, carnitine or histidine have catalytic activity in alcoholysis. These salts are not soluble in neither oil nor alcohols, therefore, these salts are suitable for heterogeneous catalytic transesterification. Investigation of the effect of the reaction temperature and methanol concentration on the rate of reaction was also done. They found that the reaction rate increases strongly with increasing temperature.

## 2.7 Analysis of Methyl Esters

Biodiesel, obtained from transesterification of vegetable oil with alcohol, can be significantly contaminated with glycerol, mono-, di-, and triglycerides due to incomplete transesterification reaction and insufficient product purification. Consequently, a sensitive and reliable analytical method is needed to monitor the purity of the methyl esters. Various chromatographic techniques such as gas chromatography (GC), thin layer chromatography (TLC) and High Performance Liquid Chromatography (HPLC) have been employed (Freedman *et al.*, 1984, Plank and Lorbeer, 1995, Nouredini, 1997, and Holčapek *et al.*, 1999).

Plank and Lorbeer (1995) applied capillary gas chromatography (GC) equipped with flame ionization detector (FID) in determining the glycerol, mono-, di- and triglycerides in methyl esters in a single run. However, this method is less convenient because of derivatization before analysis is needed for the free hydroxyl groups in the mono-, di- and triglycerides. Furthermore, Holčapek *et al.* (1999) mentioned that the derivatization step is not necessary when high temperature (approximately 350°C) and a short capillary column with good temperature stability are used.

Freedman *et al.* (1984) used thin layer chromatography and flame ionization detector in their ester products analysis. Furthermore, Karasmanoğlu *et al.* (1996)

used the combined system of thin layer chromatography and flame ionization detector (TLC/FID) to determine the composition of their ester products.

The HPLC offers directly analysis of the transesterification products without derivatization (El-hamdy and Perkins, 1981, Nouredini, 1997, and Holčapek *et al.* 1999). El-hamdy and Perkins (1981) used HPLC equipped with differential refractometer detector to determine the composition of natural triglyceride mixtures. Mixtures of analytical grade acetone and glass-distilled acetonitrile (63.6:36.4 volume ratio) were used as the mobile phase.

Holčapek *et al.* (1999) used the gradient elution technique in reversed phase high pressure liquid chromatography (RP-HPLC) to determine the biodiesel products from rapeseed oil. The products were separated in 25 min using a combined linear gradient with aqueous-organic and non-aqueous mobile phase steps: 70 % acetonitrile+30% water at 0 min, 100% acetonitrile in 10 min, 50% acetonitrile +50% 2-propanol-hexane in 20 min and 5 min final hold-up. They also compared the sensitivity and linearity of various detection mode (UV detection at 205 nm, evaporative light scattering detection, and mass spectrometric detection) and found that the atmospheric pressure chemical ionization mass spectrometry (APCI-MS) to be the best suited detection mode in the transesterification products analysis. In addition, Nouredini (1997) utilized the isocratic-mode HPLC in their analysis of transesterification products using a C<sub>18</sub> HPLC column.

Exconde (2002) used HPLC equipped with refractive index detector to analyze the biodiesel products. A Zorbax Eclipse XDB- C18 column (4.6 mm x 250 mm x 5µm) was used and the mobile phase was acetone/ acetonitrile mixture (50:50 vol/ vol).

Furthermore, Filippis *et al.* (1995) had developed a simple and quick analytical method for the evaluation of methyl esters in the transesterification products. A correlation with viscosity is applied in a defined range of weight fractions. This correlation was tested on a wide range of samples with various methyl ester content and the results were in agreement with the values measured by GC analysis