

CHAPTER II LITERATURE REVIEW



2.1 Vegetable Oils

Vegetable oils are esters of glycerol called glycerides or acylglycerols. Mono-, di-, triglycerides are possible configurations since glycerol has three hydroxyl groups. Generally, vegetable oils are triglycerides (or triacylglycerols), and are generally formed as follows (Swern, 1979):

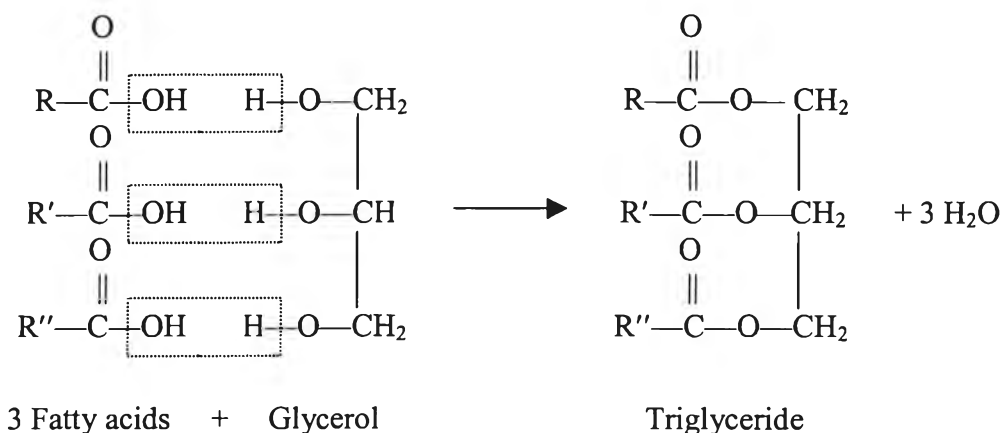


Figure 2.1 Formation of triglyceride (Swern, 1979).

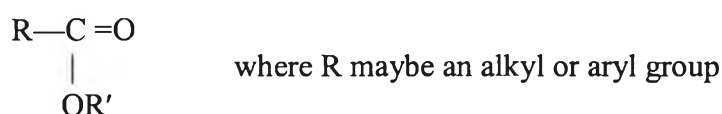
Differences in vegetable oils result from differences in fatty acids with which glycerol may be combined. The most common fatty acids in nature are those with 12, 14, 16, and 18 carbon atoms, and these are listed in Table 2.1.

Table 2.1 Common fatty acids in nature (Weiss, 1970)

Acids	Common Name	Structure
C ₁₂	Lauric	CH ₃ (CH ₂) ₁₀ COOH
C ₁₄	Myristic	CH ₃ (CH ₂) ₁₂ COOH
C ₁₆	Palmitic	CH ₃ (CH ₂) ₁₄ COOH
	Palmitoleic	CH ₃ (CH ₂) ₅ CH=CH-CH ₂ (CH ₂) ₆ COOH
C ₁₈	Stearic	CH ₃ (CH ₂) ₁₆ COOH
	Oleic	CH ₃ (CH ₂) ₇ CH=CH-CH ₂ (CH ₂) ₆ COOH
	Linoleic	CH ₃ (CH ₂) ₄ (CH=CH-CH ₂) ₂ (CH ₂) ₆ COOH
	Linolenic	CH ₃ CH ₂ (CH=CH-CH ₂) ₂ (CH ₂) ₆ COOH
	Ricinoleic	CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH=CH(CH ₂) ₇ COOH

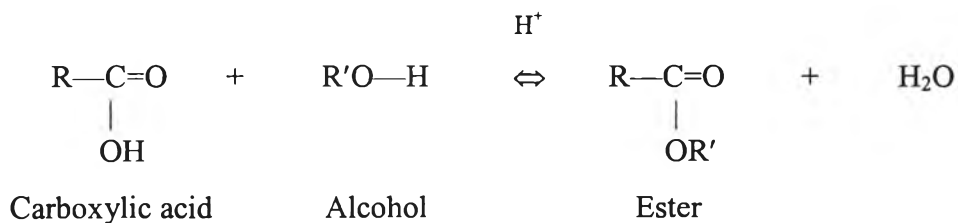
2.2 Synthesis of Esters

Esters are one class of the functional derivatives of carboxylic acids. These esters are compounds in which the -OH of a carboxyl group has been replaced by -OR':



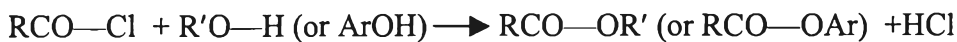
Esters are usually prepared by the most common methods outlined by Morrison and Boyd (1992) below:

- From acids.

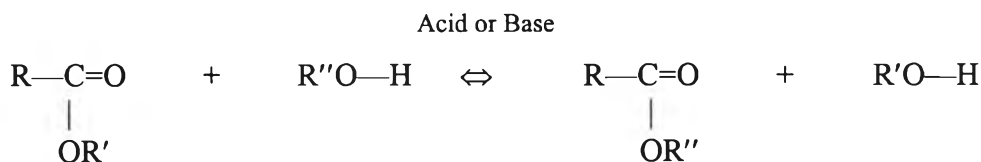


R may be alkyl or aryl R' is usually alkyl

- From acid chlorides or anhydrides.



- From esters.



2.3 Transesterification of Vegetable Oil

Since triacylglycerols (triglycerides) of vegetable oils are also esters, the production of esters directly from fats and oil can be accomplished by transesterification or alcoholysis. The overall transesterification reaction is given in Figure 2.2. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the right (Fangrui, 1999).

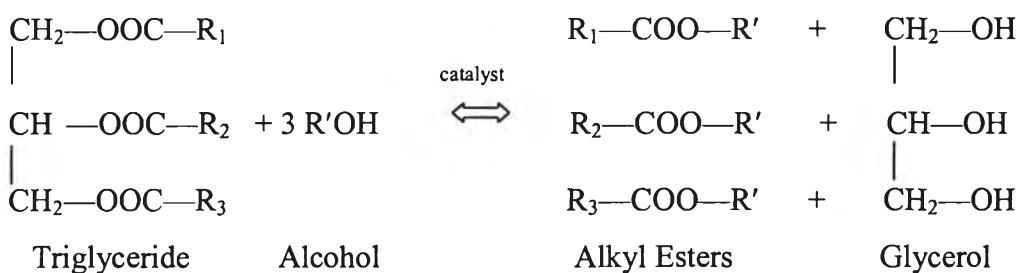


Figure 2.2 Transesterification reaction of triglycerides with alcohol (Fangrui, 1999).

Methanol is the preferred alcohol due to quick reaction with triglycerides thereby establishing higher ester conversion. It is also relatively cheap as compared to other alcohols.

However, three consecutive and reversible reactions are believed to occur in the transesterification of vegetable oils. The step reactions are shown in Figure 2.3. The first step is the conversion of triglycerides to diglycerides, followed by the

conversion of diglycerides to monoglycerides, and then monoglycerides to glycerol. For each step, one molecule of methyl ester is liberated (Srivastava, 2000).

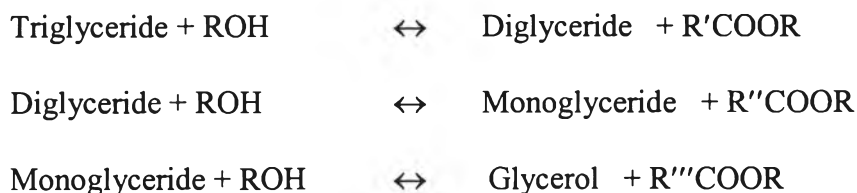


Figure 2.3 Transesterification reaction of vegetable oil (Srivastava, 2000).

The transesterification reaction can be catalyzed by an acid or an alkali. The acids used are Bronsted acids like sulfuric acid and sulfonic acid. These catalysts give very high yield in alkyl esters, but the reaction is slow, requiring temperatures above 100°C and more than 3 hr to reach complete conversion. Freedman *et al.* (1984) showed that the methanolysis of soybean oil, in the presence of 1 mole % H₂SO₄, with an alcohol/oil molar ratio of 30:1 at 65°C, takes 50 hr to reach complete conversion while the butanolysis (at 117°C) and ethanolysis (at 78°C), using the same quantities of catalyst and alcohol, take 3 and 18 hr, respectively (Schuchardt, 1998).

The mechanism of the acid-catalyzed transesterification of vegetable oil is shown in Figure 2.4.

Base-catalyzed transesterification is much faster than acid-catalyzed transesterification. The basic catalyst includes sodium methoxide, sodium propoxide, sodium butoxide, sodium hydroxide and potassium hydroxide. The mechanism of the base-catalyzed transesterification of vegetable oils was mentioned by Schuchardt *et al.* (1998) and is shown in Figure 2.5. The first 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, 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.

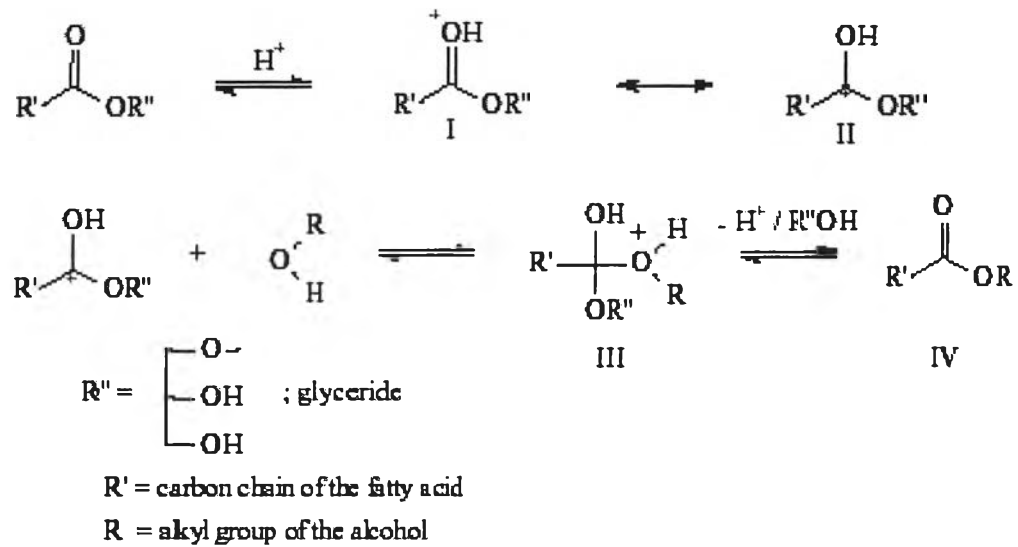


Figure 2.4 Mechanism of the acid-catalyzed transesterification of vegetable oil (Schuchardt, 1998).

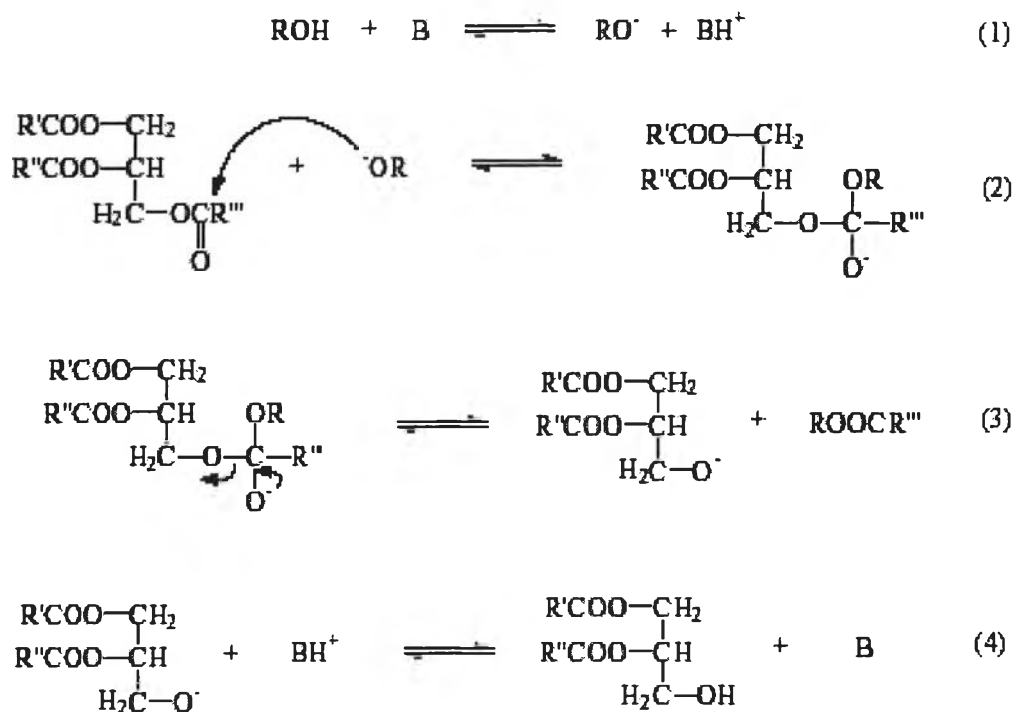


Figure 2.5 Mechanism of the base-catalyzed transesterification of vegetable oil (Schuchardt, 1998).

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

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 values ranging from 8-20 kcal/mol.

In addition, Nouredini *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. Their kinetic data appeared to be a good fit for a second order kinetic mechanism. They also determined the reaction rate constants and activation energy for all forward and reverse reactions. The results obtained in their study are consistent with the experimental values reported by the Freedman's group.

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. 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.

All of the parametric and kinetic studies done in the transesterification of vegetable oil involve the use of homogeneous catalysts. Although the reaction proceeds nicely, major problems such as removal of soluble catalyst and formation of side products were encountered. These hurdle lead to the idea of investigating possible heterogeneous catalyst.

2.4 Transesterification using Heterogeneous Catalysts

Several attempts have been done using heterogeneous catalysts on the transesterification of vegetable oils. Peterson *et al.* (1984) led the first study. They 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 saponified products thereby rendering the effectiveness of this heterogeneous catalyst.

Gryglewicz (1999) found out that the basic alkaline earth metal compounds could catalyze the transesterification of rapeseed oil effectively. Though the results were not the same as sodium hydroxide, the activity increase in the order: $\text{CaO} < \text{Ca}(\text{CH}_3\text{O})_2 < \text{Ba}(\text{OH})_2$. In spite of the high activity of $\text{Ba}(\text{OH})_2$, it is much more soluble in methanol than the other alkaline earth metal compounds.

More recently, Leclerq *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. They also examined that calcination of barium hydroxide overnight at 473 K under reduced pressure increases the activity with 96% methyl ester fraction that are now close to the conversion obtained when using homogeneous catalysts.

Experiments conducted by Suppes *et al.* (2001) indicate that CaCO_3 may be suitable as a heterogeneous catalyst. The alcoholysis were conducted in a batch

reactor and flow-reactor studies using beef tallow or soybean oil as the triglyceride source and diethylene glycol as the alcohol. Reaction times of 18 min provided essentially complete conversion. Khan (2002) attempted to verify these results but as yet have failed to replicate those results. Their only difference was the source of the CaCO_3 , which was not sourced from Lancaster (Windham, NH).

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 his results were just only based on the peak height obtained from gas chromatography. Khan (2002) tried to use Valfor as a heterogeneous catalyst and he confirmed that it is still not considered as a possible candidate.

Siegfried *et al.* (2002) synthesized fatty acid esters by methanolysis of palm oil using metal salts of amino acids as catalysts. 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 insoluble in oil as well as in alcohol and are suitable for heterogeneously catalyzed transesterification.

Most patents dealing with the heterogeneous transesterification of vegetable oils are carried out in temperature between 200 and 250°C and a pressure that is less than 60 bar. Gheorghiu (1996) patented a process for the preparation of methyl fatty acid esters from natural oil in the presence of an organotitanate base catalyst specifically tetrabutyl organotitanate. While Stern *et al.* (1999) obtained their patent of making esters in the presence of a catalyst that is selected from zinc oxide, mixture of zinc oxide and aluminum oxide and zinc aluminate. Recently, Kaita *et al.* (2002) received their patent on their catalyst for transesterification that is a phosphate of a metal selected from the group consisting of aluminum, gallium and iron.

2.5 Analysis of Methyl Esters

Biodiesel can be significantly contaminated with glycerol, mono-, di-, and triglycerides due to incomplete transesterification and insufficient purification. A sensitive and reliable analytical method is needed to monitor the purity of the methyl

esters. Various chromatographic techniques such as GC, TLC and HPLC are now being employed.

Plank (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 derivatization such as trimethylsilylation before analysis is needed for the free hydroxyl groups in the mono-, di- and triglycerides. Furthermore, Holcapek *et al.* (1999) mentioned that the derivatization step is unessential when high temperature (approximately 350°C) and a short capillary column with good temperature stability is employed.

Meanwhile Marquardt (1998) improved the separation of saturated methyl esters ranging from C₁₂ to C₂₂ by utilizing the reversed-phase thin layer chromatography (TLC) which employs silver nitrate in a mobile phase containing acetonitrile/1,4-dioxane/acetic acid. Freedman *et al.* (1984), Karaosmanoglu *et al.* (1996) and Diasakou *et al.* (1998) also used TLC equipped with FID in the analysis of their ester product.

The High Performance Liquid Chromatography (HPLC) makes feasible direct analysis of all the transesterification products without derivatization. Holcapek *et al.* (1999) used the gradient elution reversed phase HPLC in the determination of the biodiesel product 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 in 0 min, 100% acetonitrile in 10 min, 50% acetonitrile +50% 2-propanol-hexane in 20 min and 5 min final hold-up. They also showed that the atmospheric pressure chemical ionization mass spectrometry (APCI-MS) to be the best suited detection mode in the analysis of transesterification products. In addition, Nouredini (1997) and Saka (2001) utilized the isocratic-mode HPLC in their analysis of transesterification products using a C₁₈ HPLC column.

Furthermore, De 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.