CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Diesel fuels

There are three basic types of diesel fuels:

High-speed diesel is normally used as a fuel for high-speed diesel engines operating above 1,000 rpm such as trucks, cars, buses, locomotives, and pumping sets *etc*. Gas turbine requiring distillate fuels normally make use of high-speed diesel as fuel.

Medium-speed diesel is used for a wide range of purpose including generation of electricity, stationary power generators, railroads, and pipeline pumps. It operates range of 450 to 1,000 rpm.

Low–speed diesel or marine diesel is commonly used on ships. Fishing boats, and for generation of electricity. Low-speed diesel can operate below 300 rpm. Typical ranges of diesel engines are listed at Table 2.1

Table 2.1 Typical ranges of diesel engines

Type	Speed Range	Conditions	Typing application
Low Speed	<300 rpm	Heavy load, constant speed Fairy high load	Marine main propulsion; electric power generation
Medium Speed	300-1000 rpm	Relatively constant speed	Marine auxiliaries; Stationary power
High Speed	>1000 rpm	Frequent and wide variation in load and speed	Generators; pumping units Road transport vehicles; diesel locomotives

2.2 Biodiesel

Biodiesel produced from vegetable oil or animal fat including waste cooking oil. Biodiesel is used in diesel engine without modification because it has properties similar to petroleum diesel fuel. In comparison to diesel it has higher cetane number and lubricity, low particulate emission including reduction of sulfur emission, non-toxic and biodegradable. It can be used in a blend or in pure form in conventional diesel engines [8].

Some properties of palm oil methyl ester and diesel fuel are shown in Table 2.2.

Table 2.2 Some properties of palm oil methyl ester and diesel fuel

	Diesel fuel	Palm oil methyl ester
API Gravity@60°F	35.4	31.2
Specific Gravity @ 60/60 °F	0.8478	0.8697
Cetane Index	50.5	55.4
Kinematic viscosity @ 40°C, cSt	3.748	4.860
Pour point, °C	+3.0	+6.0
Flash point, (P.M.) °C	68	167
Distillation(C): IBP	145	213
10 % recovery	220	249
50% recovery	279	300
90% recovery	343	339

From Table 2.2, it can be seen that palm oil methyl ester has slightly higher density than diesel fuel. The cetane index of the ester fuel is higher than diesel fuel. The pour point of the ester fuel is higher than diesel. The ester fuel gave a flash point 167 degree, well above that of diesel fuel. The distillation point of ester fuel is higher than that of diesel fuel.

2.3 Catalysts

Biodiesel can be produced using either homogeneous catalyst or heterogeneous catalyst.

2.3.1 Homogeneous catalysts

Alkaline metal alkoxides are the most active active catalysts, since they give very high yield (> 98%) in short reaction time (30 min) even if they are applied at to low concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. However, even if a water-free alcohol/oil mixture is used, some water is produced in the reaction of the produced ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably disturbs the recovery of the glycerol due to the formation of emulsions. Potassium carbonate, used in concentration of 2 or 3 mol%, give high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water, which does not hydrolyse ester.

2.3.2 Heterogeneous catalysts

Heterogeneous solid base catalysts can be easily separated from the reaction mixture without any solvent, and show easy regeneration and have a less corrosive character, leading to safer, cheaper and more environment-friendly operation. Because of the presence of heterogeneous catalysts, the reaction mixture constitutes a three-phase system, oil/methanol/catalyst, which for diffusion reasons inhibits the reaction. Nevertheless, heterogeneous catalysts could improve the synthesis methods for the development of an environmentally benign process and the reduction of production cost.

2.4 Hydrotalcite

The hydrotalcite (HT) structure closely resembles that of brucite, in which magnesium cations are octahedrally coordinated by hydroxyl ions, giving rise to edge-shared layers of octahedra. In HT, part of the Mg^{2+} ions is replaced by Al^{3+} ions resulting in positively charged cation layers. The compensating negative charge is provided by anions, situated in the interlayer, which is the space between the brucite-like layers. Figure 2.1 depicts a schematical representation of the stacked HT structure [9].
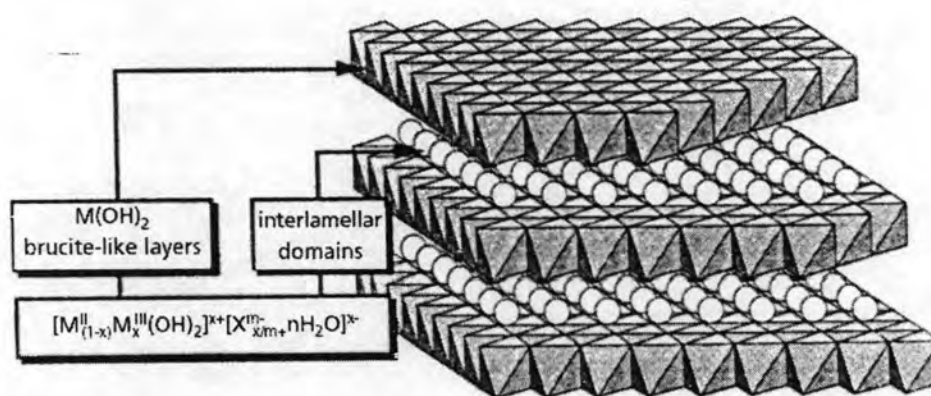
Figure 2.1 Schematic representation of the hydrotalcite anionic clay structure [9].

Mixed oxides are obtained after calcination performed in the temperature range of 450-500°C. In HT, physisorbed and interstitial water are removed at temperatures above ~100°C and ~187°C, respectively. At more elevated temperatures (above 250°C) the HT undergoes dehydroxylation and decarboxylation via H_2O and CO_2 evolution, giving rise to an increased surface area and formation of micropores [10].

2.5 Glycerol

Glycerin or 1, 2, 3,-propanetriol propantriol, $CH_2OHCHOHCH_2OH$, is colorless, odorless, sweet-tasting, syrupy trihydric alcohol. It melts at 17.8°C; boils with decomposition at 290°C. It is miscible with water and ethanol. It is hygroscopic; this property makes it valuable as moistener in cosmetics. It is present in the form of its ester (glycerides) in all animal and vegetable fats and oils and obtained

commercially as byproduct when fats and oils are hydrolyzed to yield fatty acids or their metal salts (soaps). In addition, it is widely used as a solvent; as a sweetener; in the manufacture of dynamite, cosmetics, liquid soaps, candy, liqueurs, inks, and lubricants; to keep fabrics pliable; as a component of antifreeze mixture; as a source of nutrients for fermentation cultures in the production of antibiotics; and in medicine.

2.6 Palm oil

Palm oil is derived from the flesh of the fruit of the oil palm species E. Guineensis. In its virgin form, the oil is bright orange-red due to the high content of carotene. Palm oil is semi-solid at room temperature; a characteristic brought about by its approx. 50 percent saturation level. Palm oil (and its products) has good resistance to oxidation and heat at prolonged elevated temperatures; hence, making palm oil an ideal ingredient in frying oil blends.

Palm olein is the liquid fraction obtained by fractionation of palm oil after crystallization at controlled temperatures. The physical characteristics of palm olein differ from those of palm oil. It is fully liquid in warm climate and has a narrow range of glycerides. Palm olein is widely used as a cooking oil.
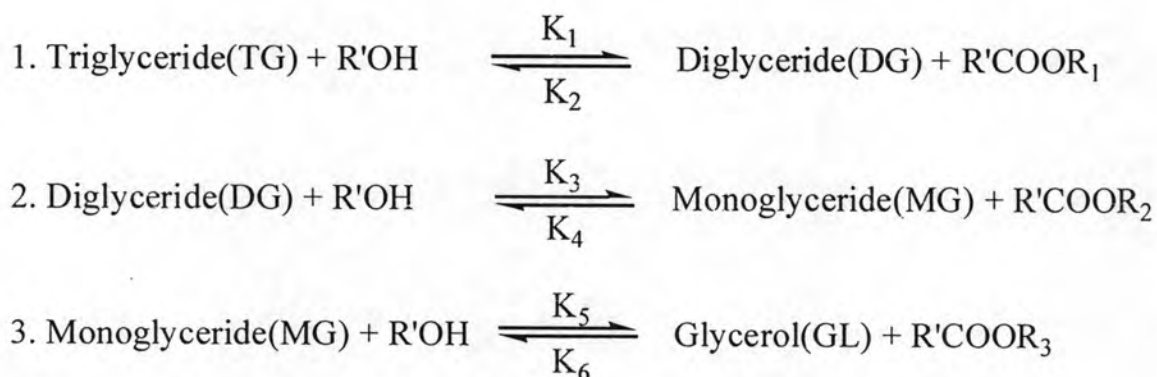
Palm stearin is the more solid fraction obtained by fractionation of palm oil after crystallization at controlled temperatures. It is thus a co product of palm olein. It is always traded at a discount to palm oil and palm olein; making it a cost effective ingredient in several applications.

Palm stearin is the more solid fraction obtained by fractionation of palm oil after crystallization at controlled temperatures. It is thus a co product of palm olein. It is always traded at a discount to palm oil and palm olein; making it an cost effective ingredient in several applications. Palm kernel oil is obtained from the kernel of the oil palm fruit. The oil composition is very different from that of the palm oil. Palm kernel olein is the liquid component of palm kernel oil obtained from fractionation. Palm kernel stearin is the more solid fraction of palm kernel oil obtained from fractionation.
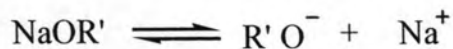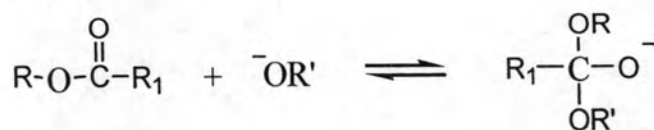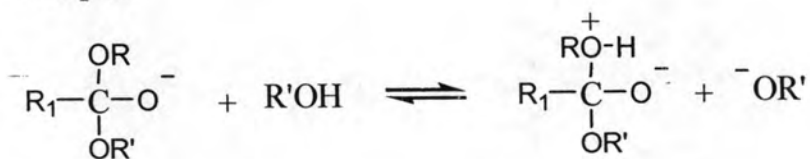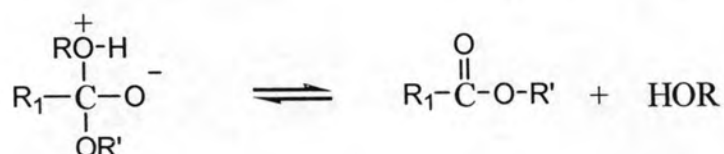
2.7 Transesterification

Transesterifications consist of a number of consecutive, reversible reactions [11]. The triglyceride is converted stepwise to diglyceride, monogylceride and finally glycerol (Fig.2.2). A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol.

The reaction mechanism for alkali-catalyzed tranesterification was formulated as three steps. The first step is an attack on the carbonyl carbon atom of triglyceride molecule by the anion of the alcohol (methoxide ion) to from a tetrahedral intermediate react with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate result in the formation of a fatty acid ester and digylceride. A small amount of water, generated in the reaction, may cause soap formation during transesterification.

1. Triglyceride(TG) + R'OH $\underset{K_2}{\overset{K_1}{\rightleftharpoons}}$ Diglyceride(DG) + R'COOR$_1$

2. Diglyceride(DG) + R'OH $\underset{K_4}{\overset{K_3}{\rightleftharpoons}}$ Monoglyceride(MG) + R'COOR$_2$

3. Monoglyceride(MG) + R'OH $\underset{K_6}{\overset{K_5}{\rightleftharpoons}}$ Glycerol(GL) + R'COOR$_3$

Figure 2.2 The transesterification reactions of vegetable oil with alcohol to esters and glycerol [12].

Pre-step:

$$OH^- + R'OH \rightleftharpoons R'O^- + H_2O \quad \text{or}$$

$$NaOR' \rightleftharpoons R'O^- + Na^+$$

Step 1.

$$\underset{\underset{R-O-\overset{\displaystyle O}{\overset{\|}{C}}-R_1}{}}{} + {}^-OR' \rightleftharpoons R_1-\underset{\underset{OR'}{|}}{\overset{\overset{OR}{|}}{C}}-O^-$$

Step 2.

$$R_1-\underset{\underset{OR'}{|}}{\overset{\overset{OR}{|}}{C}}-O^- + R'OH \rightleftharpoons R_1-\underset{\underset{OR'}{|}}{\overset{\overset{R\overset{+}{O}-H}{|}}{C}}-O^- + {}^-OR'$$

Step 3.

$$R_1-\underset{\underset{OR'}{|}}{\overset{\overset{R\overset{+}{O}-H}{|}}{C}}-O^- \rightleftharpoons R_1-\overset{\displaystyle O}{\overset{\|}{C}}-O-R' + HOR$$

Fig. 2.3 The mechanism of alkali-catalyzed transesterification of triglyceride with alcohol [12].

Parameters influencing the transesterification have been studied, and can be concluded as follows:

2.7.1 Effect of moisture and free fatty acid

The glycerides should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soap caused and increase in viscosity, formation of gels and made the separation of glycerol difficult [13].

2.7.2 Effect of alcohol/oil molar ratio

The stoichiometric ratio for transesterification requires three moles of alcohol and one mol of glyceride to yield three moles of fatty acids ester and one mole of glycerol. An acid catalyzed reaction needed a 30:1 alcohol/ oil ratio, while an alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time [11].

2.7.3 Effect of reaction time

The conversion rate increases with reaction time [11]. The reaction was initially very slow due to the mixing and dispersion of methanol into oil. Later on, the reaction proceeded very fast and reached the maximum value.

2.7.4 Effect of reaction temperature

Transesterification can occur at different temperatures, depending on the oil used. It can be room temperature or high temperature.

2.8 Literature reviews

Homogeneous catalysts

In 2001 Kuadiana *et al.* [14] prepared methyl esters from rapeseed oil by supercritical method. Effects of reaction temperature, reaction pressure and molar ratio of methanol to triglycerides were investigated. The results revealed that the supercritical treatment of 350°C, 30 MPa and 240 sec with molar ratio of 42 is the best condition for transesterification.

In 2003 Tomasevic *et al.* [15] performed transesterification reaction of refined sunflower oil and used frying oils at 25°C with homogeneous catalysts: potassium hydroxide or sodium hydroxide. Reaction parameters studied included oil quality, molar ratio of methanol to oil, type and catalyst concentration, temperature and reaction time. With 1% potassium hydroxide, temperature at 25°C, molar ratio of methanol to oil = 6:1 and reaction time of 30 min, all oils were sufficiently transesterified and could be used as fuel in diesel engines.

In 2005, Felizardo *et al.* [4] studied transesterification of waste frying oils with methanol using sodium hydroxide as catalyst. Methanol/oil molar ratios and catalyst/oil weight ratios were varied. For oils with an acid value of 0.42 mg KOH/g, the results showed that a methanol/oil ratio of 4.8 and a catalyst/oil ratio of 0.6 wt.% gave the highest yield of methyl esters in 1 h reaction time. Furthermore, an increase in the amount of methanol or catalyst quantity seems to simplify the separation/purification of the methyl esters phase, as shown by a viscosity reduction and an increasing purity to values higher than 98% for methyl esters phase.

Heterogeneous catalysts

In 2000, Choundary *et al.* [16] studied transesterification of normal and ß-ketoesters with primary, secondary, unsaturated, allylic, cyclic, hindered alcohols and amines using Mg–Al–O–*t*-Bu hydrotalcite catalyst. The catalyst showed 98% yield for the transesterification of methyl acetoacetate and 1-hexanol at 90°C for 2 h, using 10 ml toluene as a solvent. This catalyst can be reused 6 times without loss of activity

In 2004, Suppes *et al.* [7] studied transesterification of soybean oil with methanol. The reaction was carried out at 60, 120, and 150°C in the presence of a series of NaX faujasite zeolite, ETS-10 zeolite, and metal catalysts. The stock zeolites were exchanged with potassium and cesium; NaX containing occluded sodium oxide (NaOx/NaX) and occluded sodium azide (NaOx/NaX.). It was found that the ETS-10 catalysts provided higher conversions than the Zeolite-X type catalysts. The increased conversions were attributed to the higher basicity of ETS-10 zeolites and larger pore structures that improved intra-particle diffusion. Methyl ester yield increased with an

increase in temperature from 60 to 150°C. The metal catalysts increased conversion by one to over two orders of magnitude over the homogeneous reaction. The catalyst can be reused without observed loss of activity.

In 2004, Kim et al. [17] studied transesterification of vegetable oils using Na/NaOH/γ-Al$_2$O$_3$ heterogeneous catalyst which was prepared by loading 20 wt.% of sodium hydroxide and 20 wt.% sodium metal onto the alumina support in nitrogen atmosphere. The reaction conditions were optimized and found to be 1 h reaction time, the stirring speed of 300 rpm, n-hexane was used as cosolvent, the methanol to oil molar ratio = 9:1. The maximum yield reached 94%, which was close to the conventional homogeneous NaOH catalyst system.

In 2005, Dossin et al. [18] studied kinetics of heterogeneously MgO-catalyzed transesterification of ethyl acetate with methanol. Intrinsic kinetic data were obtained in a perfectly mixed slurry batch reactor. The influence of the temperature (10–50 °C) and the initial methanol to ethyl acetate molar ratio (M/E: from 0.1 to 10) was investigated over a broad ethyl acetate conversion range (1–95%). Transesterification reaction occurs between methanol adsorbed on a magnesium oxide free basic site and ethyl acetate from the liquid phase. Methanol adsorption is assumed to be rate-determining step.

In 2005, Corma et al. [19] studied transesterification of methyl oleate with glycerol using rehydrated and calcined hydrotalcite catalysts. The experiments were carried out under stirring speed at 500 rpm and reaction time of 8 h, glycerol and methyl oleate ratio of 6:1 and 4 wt% of catalyst at reaction temperature of 200°C. The rehydrated hydrotalcite catalyst showed higher activity than the calcined hydrotalcite. Calcined Li–Al hydrotalcite gave higher activity than MgO or calcined Al–Mg hydrotalcite because of the stronger Lewis basicity of the former. All of the solid Lewis basic catalysts have the same selectivity to monoglyceride regardless of the base strength.

In 2005 , Cantrell *et al.* [20] synthesized a series of $[Mg_{(1-x)}$ $Al_x(OH)_2]^{x+}(CO_3)_{x/n}{}^{2-}$ hydrotalcite materials with compositions over the range x = 0.25–0.55 using an alkali-free coprecipitation route. All materials exhibit XRD patterns characteristic of the hydrotalcite phase with a steady lattice expansion observed with increasing Mg content. All materials are effective catalysts for the liquid-phase transesterification of glyceryl tributyrate with methanol for biodiesel production. The rate increases steadily with Mg content. This catalyst is more active than MgO.

In 2005, Ebiura *et al.*, [21] studied selective transesterification of triolein (trioleoyl glycerol) with methanol to methyl oleate and glycerol. The reaction could be achieved at 60°C using alumina loaded with alkali metal salts as a catalyst. Alkali metal salts such as K_2CO_3 were loaded onto alumina by an impregnation method from aqueous solution followed by drying in air at 120°C for 12 h. The catalysts were evacuated at 550°C before use in the transesterification. A K_2CO_3-loaded alumina catalyst gave methyl oleate in the highest yield (94%) at 60°C in 1 h.