CHAPTER II
LITERATURE REVIEWS

In this chapter, background information related to this work is described. First, introduction of the biodiesel, their properties, including the raw materials used for production the biodiesel-like hydrocarbons is presented. After that, the related works in deoxygenation reaction of oxygenated compound is summarized.

2.1 Definition of Biodiesel

Biodiesel is referred to a diesel equivalent produced from biological feedstock such as vegetable oil and animal fats. The idea to use bio-oils for diesel engines is more than a hundred years old. As Rudolf Diesel conducted and tested a prototype of diesel engine in World's Exhibition in Paris 1900 on peanut oil. However, as petroleum based fuels soon became available in large quantities at comparatively low cost, the use of in bio-oils was diminished. Except for some attempts at utilizing renewable sources of energy during the Second World War, it was only in the 1970s that the world-wide oil crises and growing environmental awareness led to rediscovery of bio-oils as possible alternatives to hydrocarbon-based fuels.

Biodiesel is defined as the mono-alkyl ester of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel is a light to dark yellow liquid. It is practically immiscible with water, has a high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of ~ 150 °C, making it rather non-flammable. Biodiesel has a density of ~ 0.88 g/cm³, less than that of water. For use as diesel engine fuel, biodiesel is conforming to international standard (ASTM D6751) specifications. It refers to the pure fuel before blending with conventional fossil diesel fuel. Biodiesel blends are denoted as "BXX" with "XX" representing the percentage of biodiesel contained in mixing process. For example, B5 is 5% biodiesel, 95% petroleum diesel.

2.1.1 Starting Material for Production of Biodiesel

Popular raw sources for biodiesel processing include rapeseed oil (Europe), soybean oil (USA), palm oil (South East Asia).

2.1.2.1 Rapeseed Oil

It was originally chosen for transesterification experiments by biodiesel pioneers because of its low price compared to other readily available vegetable oil (Mittebach, 1989). However, its components are high content of monounsaturated oleic aicd and the low levels of both saturated and polyunsaturated acids; the oil is practically the ideal raw material regarding combustion characteristic, oxidative, stability and cold temperature behavior. Presently, the prices of rapeseed oil are at very high levels due to increased demand on rapeseed oil for the production of biodiesel. Rapeseed oil is the preferred oil stock for biodiesel production in most of Europe, partly because rapeseed produces more oil per unit of land area as compared to other oil sources, such as soy beans. .·

2.1.2.2 Soybean Oil

It is the most popular biodiesel feedstock in the USA, and it is by far the most frequently produced vegetable oil worldwide, mainly due to the utilization of soybean meal as a protein fodder. The major unsaturated fatty acids in soybean oil are 7% linolenic acid (C18:3); 51% linoleic acid (C18:2); and 23% oleic acid (C18:1). It also contains the saturated fatty acids 4% stearic acid and 10% palmitic acid.

2.1.2.3 Palm Oil

It plays an important role for biodiesel production in South East Asia. Various part of the palm fruits can be utilized for oil production for human consumption and industrial applications. The major saturated fatty acids in palm oil are 44% palmitic acid (C16:0) and 5% stearic acid (C18:0). It also contains the unsaturated fatty acids 39% oleic acid (C18:1); and 11% linoleic acid (C18:2).

2.1.2 Production of Biodiesel

The biodiesel is mainly produced via a transesterification of triglyceride. However, it can also be produced by the deoxygenation of free fatty acid.

2.1.2.1 Transesterification of Triglyceride

Biodiesel is made through a chemical process called transesterification. Simply, triglyceride, the structure is shown in Figure 2.1, derived from vegetable and/or animal oils, fats or greases is combined with methanol in the presence sodium or potassium hydroxide (applied as a catalyst) to produce fatty acid methyl esters (FAME) and glycerol as shown in Figure 2.2 (Jon Van Gerpen et al., 2004). However, transesterification can be done with derivative of triglyceride (fatty acid).
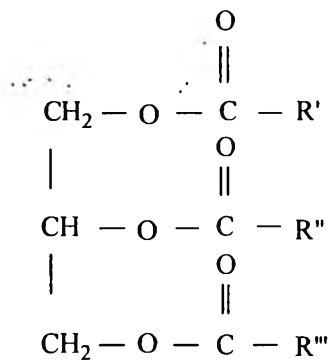
$$
\begin{array}{c}
\quad\quad\quad\quad\quad\quad O \\
\quad\quad\quad\quad\quad\quad \parallel \\
CH_2 - O - C - R' \\
| \quad\quad\quad\quad O \\
\quad\quad\quad\quad\quad \parallel \\
CH - O - C - R'' \\
| \quad\quad\quad\quad O \\
\quad\quad\quad\quad\quad \parallel \\
CH_2 - O - C - R'''
\end{array}
$$

Figure 2.1 Basic structure of triglyceride molecules.

In the Figure 2.1, R', R", and R'" represent the hydrocarbon chains of the fatty acid elements of the triglyceride. Triglyceride molecules contain mostly carbon and hydrogen atoms, with only six oxygen atoms per molecule. Moreover, R', R", and R'" indicate the fatty acid chains associated with the oil or fat which are largely palmitic, stearic, oleic, and linoleic acids for naturally occurring oils and fats.
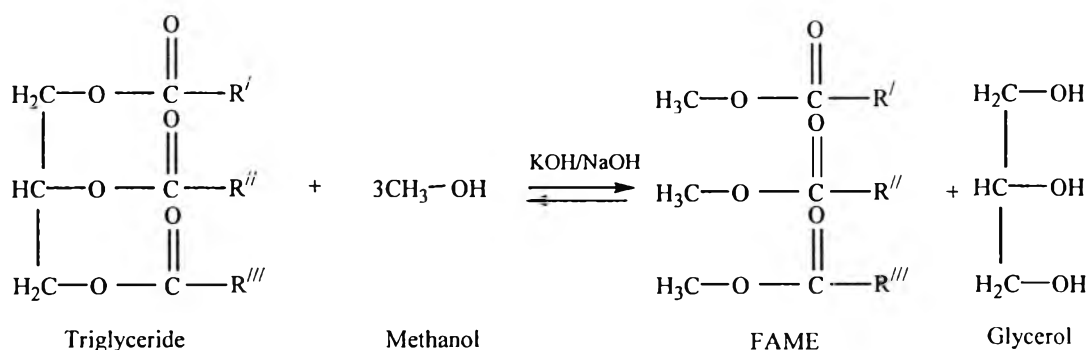
Figure 2.2 The production of biodiesel by transesterification of fatty acid.

The overall process is normally a sequence of three consecutive steps, which are reversible reactions as shown in Figure 2.2. In the first step, triglyceride is converted to dilglyceride and an alkyl ester molecule, then the diglyceride is converted to a monoglyceride and another alkyl ester molecule. In the last step, monoglyceride is converted to fatty acid methyl ester and glycerol. In all these reactions esters are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product.

The supercritical alcohol is concerned as an interesting process (Marchetti *et al.*, 2005). Under the term of biodiesel, different types of products, such as fatty esters (Ramadhas *et al.*, 2005) and hydrocarbons, are considered (Iva Kubičková *et al.*, 2005). Up to now, transesterification is the simplest process to produce fatty esters for biodiesel production. An example of a simple production flow chart with a short explanation of the general process is shown in Figure 2.3. The process variables are reaction temperature, ratio of alcohol to bio-oil, type of catalyst and amount of catalyst.
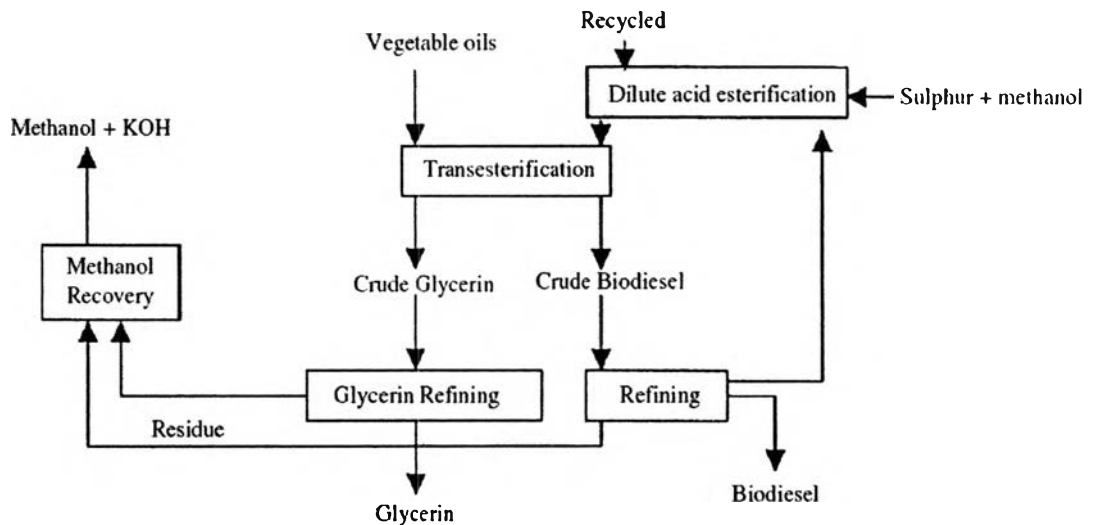
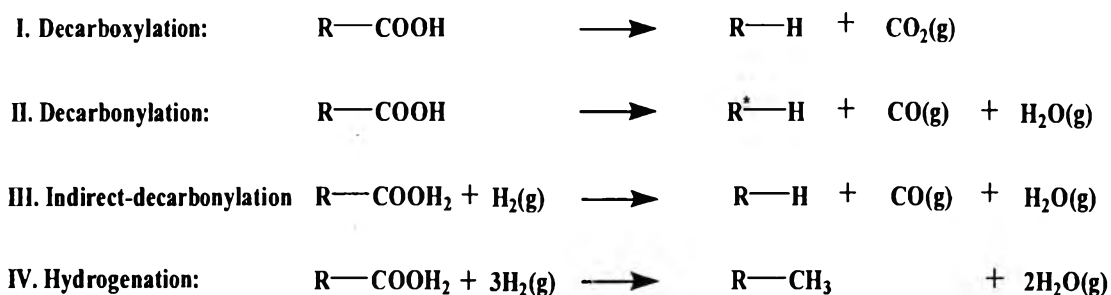**Figure 2.3** Basic scheme for biodiesel production.

2.1.2.2 Disadvantages of Fatty Acid Methyl Ester (FAME), Biodiesel

The disadvantages of biodiesel can be summarized as follows. Fatty Acid Methyl Ester (FAME) has a lower energy density than petro-diesel. Therefore, the energy content per gallon of biodiesel is approximately 11 percent lower than that of petroleum diesel. Vehicles running on biodiesel are therefore expected to achieve about 10% fewer miles per gallon of fuel than conventional diesel. For the low temperature application, FAME is less stable than petro-diesel. The cloud point is the temperature at which a sample of the fuel starts to appear cloudy, indicating that wax crystals have begun to form. At even lower temperatures, the fuel becomes a gel that cannot be pumped. The pour point is the temperature below which the fuel will not flow. As the cloud and pour points for biodiesel are higher than those for petroleum diesel, the performance of biodiesel in cold conditions is markedly worse than of petroleum diesel. At low temperatures, diesel fuel forms wax crystals, which can clog fuel lines and filters in a vehicle's fuel system. Vehicles running on biodiesel blends may therefore exhibit more drivability problem at less severe winter temperatures than do vehicles running on petroleum diesel (Koivusalmi and Jakkula, 2007). It also has a transporatation and storage problem. FAME requires special management. Some properties of biodiesel make it undesirable for use at high concentration. For example, pure biodiesel does not flow well at low tem-

peratures, which can cause problems for customers with outdoor storage tanks in colder climates. In case of solvent properties, biodiesel may dissolve any deposits in the filters and in the delivery system. Consequently, it needs for replacement of the filters. Petroleum diesel forms deposits in vehicle fuel systems, and because biodiesel can loosen those deposits, they can migrate and clog fuel lines and filter. The solvent property of biodiesel could also cause other fuel-system problems. Biodiesel maybe incompatible with the seals used in the fuel systems of older vehicles and machinery, necessitating the replacement of those parts it biodiesel blends are used. Additionally, the hydrophilic property of biodiesel caused the corrosion of the engine. Finally, FAME gives out more nitrogen oxide emission.

2.1.2.3 Deoxygenation of fatty acid

The production of alkane hydrocarbons can be done via the deoxygenation of fatty acids on homogeneous or heterogeneous catalysts. Typically, the deoxygenaion of fatty acids is related to pyrolysis (cracking), where the hydrocarbon chain is broken and the oxygen is removed. The selective production of diesel fuel hydrocarbons from renewable vegetable-based feeds was reported, where the deoxygenation was performed by selective removal of the carboxyl group. Plausible reaction paths for product of linear hydrocarbons from fatty acids are illustrated in Figure 2.4.

I. Decarboxylation: $R\text{---}COOH$ $\longrightarrow$ $R\text{---}H$ $+$ $CO_2(g)$

II. Decarbonylation: $R\text{---}COOH$ $\longrightarrow$ $R^*\text{---}H$ $+$ $CO(g)$ $+$ $H_2O(g)$

III. Indirect-decarbonylation $R\text{---}COOH_2 + H_2(g)$ $\longrightarrow$ $R\text{---}H$ $+$ $CO(g)$ $+$ $H_2O(g)$

IV. Hydrogenation: $R\text{---}COOH_2 + 3H_2(g)$ $\longrightarrow$ $R\text{---}CH_3$ $+$ $2H_2O(g)$

R = saturated alkyl group   *R* * = unsaturated alkyl group*

Figure 2.4 Liquid phase reactions (thermodynamic data for production of linear C17 hydrocarbons from stearic acid are provided from 300 °C).

There are several possible reaction paths for production of straight-chain hydrocarbons. Fatty acids can be directly decarboxylated or dearbonylated. Direct decarboxylation removes the carboxyl group by releasing carbon dioxide and producing a paraffinic hydrocarbon, while direct decarbonylation produces an olefinic hydrocarbon via removal of the carboxyl group by forming carbon monoxide and water, as illustrated by reactions I and II. Additionally, the fatty acid can be deoxygenated by adding hydrogen; in this case, the production of linear hydrocarbon can occur via direct hydrogenation or indirect decarbonylation, reactions III and IV, respectively.

Moreover to the liquid-phase reactions, the water gas shift and methanation reaction are occurred with a number of carbon monoxide, carbon dioxide, hydrogen, and water formed during decarbonylation/decarboxylation reaction (Figure 2.5).
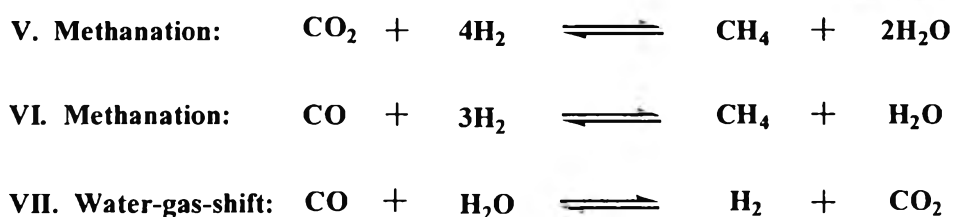
V. Methanation: $\quad CO_2 \; + \; 4H_2 \; \rightleftharpoons \; CH_4 \; + \; 2H_2O$

VI. Methanation: $\quad CO \; + \; 3H_2 \; \rightleftharpoons \; CH_4 \; + \; H_2O$

VII. Water-gas-shift: $CO \; + \; H_2O \; \rightleftharpoons \; H_2 \; + \; CO_2$

Figure 2.5 Gas phase reactions of CO or CO_2 with H_2 or H_2O (thermodynamic data for gas phase reaction are provided at 300 °C).

2.1.3 Advantages of Biodiesel

The benefits of biodiesel can be summarized as follows. Biodiesel is made from non-petroleum, renewable resources that can be produced domestically; therefore, it reduces the country's foreign-currency spending on imported oil and increasing energy security. It produces less noxious emissions than petro-diesel. It reduces tailpipe particular matter, hydrocarbon, and carbon monoxide emission from most modern four-stroke compression ignition engines. The reason is mainly associated with the presence of oxygen in the fuel which allows more complete combustion. Particulates are mainly carbon dust, commonly describes as soot,

and contain very fine particles that can be dangerous in the atmosphere since they can get into the lung by bypassing the body's natural filter mechanisms. Together with the unburned hydrocarbons, particulates are suspected of being carcinogens and can cause other serious toxic effects. Carbon monoxide is, of course, well known for its lethal action in the bloodstream. Fairly obviously, the higher the proportion of biodiesel in a mixture, the more these noxious exhausts is reduced. Moreover, biodiesel has a very low concentration of sulphur. The amount is very much less than traditional diesel oils and is comparable with the amount in Ultra Low Sulphur Diesel (ULSD). Therefore, the amount of sulfur dioxide emission is reduced. Biodiesel is nearly carbon-neutral, meaning it contributes almost zero emissions to global warming and biodegradable. The physical and chemical properties of biodiesel standard, ASTM D6751, compare to the conventional diesel standard, ASTM D975, is illustrated in Table 2.1.

Table 2.1 Selected properties of typical diesel and biodiesel

Fuel Property	Diesel	Biodiesel
Fuel Standard	ASTM D975	ASTM D6751
Lower Heating Value, Btu/gal	~129,050	~118,170
Kinematic Viscosity, @ 40°C	1.3-4.1	4.0-6.0
Specific Gravity kg/l @ 60°F	0.85	0.88
Density, lb/gal @ 15°C	7.079	7.328
Water and Sediment, vol%	0.05 max	0.05 max
Carbon, wt %	87	77
Hydrogen, wt %	13	12
Oxygen, by dif. Wt %	0	11
Sulfur, wt %	0.05 max	0.0 to 0.0024
Boiling Point, °C	180 to 340	315 to 350
Flash Point, °C	60 to 80	100 to 170
Cloud Point, °C	-15 to 5	-3 to 12
Pour Point, °C	-35 to -15	-15 to 10
Cetane Number	40-55	48-65
Lubricity SLBOCLE, grams	2000-5000	>7000
Lubricity HFRR, microns	300-600	<300

2.2 Literature Review

2.2.1 Deoxygenation Reaction

More than 80 years ago, a study of homogeneous catalyst reaction was investigated that, only 50% yield of paraffin over selenium catalyst was observed (Betram *et al.*, 1936).

The heterogeneous catalyzed deoxygenation of fatty acids (vegetable oil based) feeds has been studied barely in the past (in the conception of cracking). Decarboxylation of aliphatic and aromatic carboxylic acids was carried out in the gas phase over Pd/SiO_2 and Ni/Al_2O_3 (Maier *et al.*, 1982). The investigational results showed, that Pd/SiO_2, catalyst gave a higher yield in decarboxylating heptanoic and octanoic acid (98% and 97%, respectively) than that achieved over the Ni/Al_2O_3 catalyst (26% and 64% respectively). Later, the nickel based catalyst with either tin, germanium, or lead was a subject to U.S. patent for a production of straight-chain olefins from saturated fatty acid ester (Stern *et al.*, 1985).

In 2006, Murzin et al. studied deoxygenation of Lauric acid ($C_{12}H_{24}O_2$) in the continuous mode (Murzin et al., 2006). They found that lauric acid was completely converted to undecane having selectivity of 92 mol% by using 5wt% Pd/C as the catalyst at reaction temperature and pressure of 270°C and 0.8 MPa, respectively. This reaction was carried out via the decarboxylation path since the oxygen was removed in the form of CO_2 and the paraffinic hydrocarbon has one carbon atom less than the original fatty acid.

Influence of the hydrogen sulfide partial pressure and of a nitrogen compound on the hydrodeoxygenation activity of a CoMo/Carbon catalyst was conducted by Maria Ferrari *et al.* The experiments were carried out in the hydrogen sulfide atmosphere (as a partial pressure 10-150 kPa), under a total pressure of 7 MPa, at 200 and 270 °C in the fixed bed continuous flow tubular reactor. The transformation of a mixture of reactants, guaiacol, ethyldecanoate, and 4-methylacetophenone in *p*-xylene was likely three different active sites were responsible for hydrogenolysis, hydrogenation, and acid-catalyzed reactions. The activity of sulfided CoMo/C catalyst was rarely affected by additions of the hydrogen sulfide partial pressure. Hydrogen sulfide did not affect to the activity and conversion of guaiacol on the Co-

Mo/Carbon catalyst. For ethyldecanoate, the conversion was not influenced by hydrogen sulfide and the selectivity in hydrogenated and decarboxylated products was slightly changed. Methylacetophenone was the only reactant molecule whose conversion was inhibited by the H_2S (Maria Ferrari et al., 2001).

In 2005, Senol et al. studied on hydrodeoxygenation of methyl esters on sulphided NiMo/γ-Al$_2$O$_3$ and CoMo/γ-Al$_2$O$_3$ catalysts (Senol et al., 2005). The reaction was carried out in a tubular continuous flow reactor at various temperatures of 250, 275, and 300°C. The system pressure is 1.5 MPa with hydrogen. Methyl heptanoate and methyl hexanoate were used as model compounds. It was found that the sulphided NiMo/γ-Al$_2$O$_3$ catalyst is more active than CoMo/γ-Al$_2$O$_3$ catalyst. Moreover, the aliphatic methyl esters are converted to hydrocarbons via three paths as shown in Figure 2.6. The first path gave alcohols followed by dehydration to alkenes with the same number of carbon atoms as in the acyl group of the ester. Deesterification yielded and alcohol and a carboxylic acid in the second path. Carboxylic acid was further converted to hydrocarbons either directly or with an alcohol intermediate. Decarboxylation of the esters led to alkenes with on carbon atom less than in the acyl group in the third path. The hydrogenation of the formed alkenes takes place following this deoxygenation. The major formation of alkanes on the sulphided Ni-Mo catalyst is consistent with its higher hydrogenation activity. The most alkanes formed from methyl heptanoate is n-heptane and from methyl hexanoate is n-hexane under all conditions. Later on, they studied the effect of water on the hydrodeoxygenation of methyl heptanoate (Senol et al., 2006). They observed that water decreases the conversion on the esters and suppresses the oxygen removal reaction on both sulphided NiMo/γ-Al$_2$O$_3$ and CoMo/γ-Al$_2$O$_3$ catalysts. In addition, the results show that water mainly affects the decarboxylation reaction, suppressing the formation of C_6 hydrocarbons. The addition of H_2S effectively compensates the inhibition by water but also changes the product distribution. It shifts the main products towards the C6 hydrocarbon. This may be a drawback since the production of carbon oxides increases accordingly.
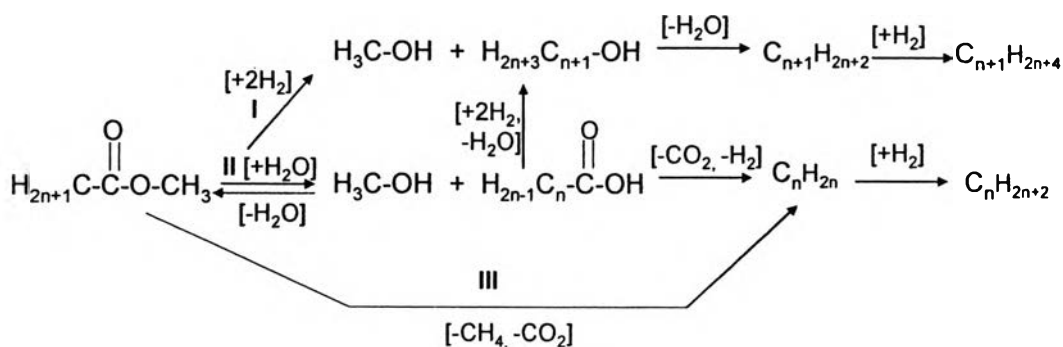
$$[+2H_2]$$
$$H_3C\text{-}OH + H_{2n+3}C_{n+1}\text{-}OH \xrightarrow{[-H_2O]} C_{n+1}H_{2n+2} \xrightarrow{[+H_2]} C_{n+1}H_{2n+4}$$

$$H_{2n+1}C\text{-}\overset{O}{\underset{\|}{C}}\text{-}O\text{-}CH_3 \underset{[-H_2O]}{\overset{II\ [+H_2O]}{\rightleftharpoons}} H_3C\text{-}OH + H_{2n-1}C_n\text{-}\overset{O}{\underset{\|}{C}}\text{-}OH \xrightarrow{[-CO_2,\ -H_2]} C_nH_{2n} \xrightarrow{[+H_2]} C_nH_{2n+2}$$

$$[+2H_2,\ -H_2O]$$

III

$$[-CH_4,\ -CO_2]$$

Figure 2.6 Hydrodeoxygenation reaction scheme of aliphatic methyl esters (n=6 for methyl heptanoate and n=5 for methyl hexanoate)

The pyrolysis reactions of soybean, palm and castor oils were studied. Pyrolysis experiments were done at temperature ranging from 350 to 400 °C using batch reactor. The vapor feed leaving the reactor was forced into the catalytic deoxygenating reactor which was placed between the pyrolysis reactor and the heat exchanger, before its condensation. The HZSM-5 was packed in the bottle of glass tube. The deoxygenation reactor was heated to maintain temperature feed at approximately 400 °C. The heavy fraction was analyzed by GC and compared with non deoxygenated analogue. The results clearly indicated that the deoxygenated vegetable oil pyrolysis product obtained is an enriched hydrocarbon diesel like fuel. (Daniela G. Lima *et al.*, 2004)

The fatty acid mixture can be converted to liquid hydrocarbon fuel and chemicals using catalytic technology. The HZSM-5 catalyst was applied in a study of catalytic conversion of palm oil-based fatty acid mixture to liquid fuel in fixed bed micro reactor at atmospheric pressure. The reaction temperature was 400-450 °C and space velocity around 2.5-4.5 h⁻¹. HZSM-5 produced an organic liquid product rich in gasoline fraction from the catalytic cracking of palm oil-based fatty acid mixture. The optimum yield of gasoline fraction was 44.4 wt% at weight hourly space velocity of 3.66 h⁻¹, reaction temperature of 440°C and fatty acid mixture to catalyst ratio of 9.64. The fatty acid mixture residue can be utilized to produce value added product such as liquid fuel using catalytic technology (Yean-Seng Ooi *et al.*, 2004).

Catalytic deoxygenation of heavy gas oil was researched. The extent of oxygen removal during catalytic hydrotreatment of heavy gas oils depends on the chemical composition of catalysts. Deoxygenation increases with the concentration of MoO_3 (6 wt %) on the alumina support. Further increase in the MoO_3 concentration do not appreciably increase the oxygen removal. The deoxygenation reaction is also improved by the addition of cobalt and nickel oxides to the molybdate catalysts. Independent acidity measurements on the liquid products suggest the presence of phenols (Edward Furimsky 1977).

Vegetable oils were hydrocracked with a $NiMo/Al_2O_3$ catalyst sulfided in situ with element sulfur under hydrogen pressure. The research was studied at hydrogen pressure 10-200 bar and temperature 623-673 K. Oxygen in the feed was liberated as CO_2, H_2O, and CO. the resulting product was a mixture of hydrocarbons, mainly alkanes, in the diesel fraction. Hydrogenolysis of palm oil over Ni/SiO_2 or over Co at 300 °C and 50 bars provided likely colorless oil, mainly C15-C17 alkane. However, the same process brought a solid liked with 80% C17 alkanes when applied to rapeseed oil. The octadecane model compound gave 50% conversion over Co/oil catalyst to C17 alkane as the main product (Gerhard Knote., 2004).

Iva Kubickova *et al.* (2005) had done a study as a suitable reaction for production of diesel-fuel-like hydrocarbons. The deoxygenated experiments were performed in a conventional Parr autoclave (300 ml) operating in a semi-batch mode at 300-360 °C and overall pressure 17-40 bar. Dodecane was employed as a solvent. Activated carbon supported palladium (5 wt. %), commercial grade, was used as catalyst. In order to determine the influence of hydrogen partial pressure on the conversion and products distribution, different reaction atmospheres, e.g. helium (He), hydrogen (H_2), hydrogen (5 vol.%)-argon (H_2-Ar) mixture, were applied. It was observed that the final products from all the three reactants, that are stearic acid, ethyl stearate, and tristearine representing as vegetable oils, were almost extremely converted to n-heptadecane with high selectivity. Isomer of heptadecanes and isomers of undecylbenzenes are observed as the by-products. Gas phase products in the ethyl stearate transformation reaction consisted of carbon dioxide, and carbon monoxide. Ethane and ethylene also was found from the decomposition of ethyl stearate. In case

of stearic acid had lower concentration of unsaturated C17 than the transformation of ethyl stearate.

Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel was done by Mathais Snåre and co-workers (2006). The deoxygenation reaction was carried out in a semi batch reactor under constant temperature and pressure, 300 °C and 6 bar, respectively. The solvent, dodecane was supplied in this reaction. A thorough catalyst screening was performed to obtain the most promising metal and support combination. The metals studied were Ni, Mo, Pd, Pt, Ir, Ru, Rh, and Os on Al_2O_3, Cr_2O_3, MgO, and SiO_2 as well as activated carbon. The catalytic deoxygenation of stearic acid over heterogeneous catalysts was profitably achieved with high activity and selectivity to n-heptadecane, desired product. Although the effectively reaction was performed over a palladium and platinum supported on activated carbon. Furthermore, Pd/C was more preferably for the decarboxylation reaction and also the decarbonylation was more evident over the Pt/C catalyst. The addition of hydrogen can also related in the indirect decarbonylation or direct hydrogenation reaction of fatty acids to produced the linear hydrocarbons.

Päivi Mäki et al. (2007) studied the catalytic deoxygenation of fatty acids and their derivatives. The reaction was investigated over palladium supported on activated carbon in a semi batch reactor. The investigated parameters are different of reactant types (nonanoic, stearic, behenic, and oleic acid, as well as ethyl stearate), initial feed concentration of stearic acid, catalyst amounts. Effects of support acidity and reaction atmosphere were also studied. The results demonstrate that the catalytic transformation of fatty acids proceeded mainly via decarboxylation, whereas decarbonyltion was the main route for esters. Over alkaline catalysts as well as under a hydrogen atmosphere, higher yields of desired product, n-heptadecane was obtained. The conversion level was the highest after 360 min for stearic acid. The decarboxylation (catalytic transformation) of unsaturated fatty acids leaded to hydrogenated products that reacted further to hydrocarbons.

The hydrogenation of C=O bond is commonly achieved using transition metal catalyst. The reaction can be significantly improved using the reducible oxide support for example TiO_2, WO_3, and MoO_3 (Kluson et al., 1995 and 1997). Recently, the hydrogenation reaction of oleic acid on ruthenium catalyst was investi-

gated (Mendes *et al.*, 2001). The reaction has taken place in a Parr semi batch reactor at 250 °C and 5 MPa in hydrogen atmosphere. The ruthenium supported on titanium catalyst was prepared by impregnation method. The result showed that Ru/TiO_2 is more active and selective than Ru/Al_2O_3. Moreover, the addition of promoters such as Sn (Coupe *et al.*, 2000), Fe (Candy *et al.*, 1991), and Ge (Lafaye *et al.*, 2002 and 2004) can also improve the hydrogenation activity.

Huber and coworker studied the feasibility to utilize the existing petroleum refineries for the production of biodiesel by hydrotreatment of vegetable oil (Huber et al., 2007). The reaction conditions for catalytic hydrotreating experiments were done at temperature in the range of 300-450°C, pressure of 50 bar, LHSV 4.97 hr^{-1}, and H_2 to feed ratio of 1600 ml H_2 gas/ml liquid feed. It was found that vegetable oils can be converted into liquid alkanes by hydrotreating with sulphided Ni-Mo/γ-Al_2O_3 catalyst by using existing petroleum refineries for biodiesel production without the need to purchase additional capital equipment. The reaction involves hydrogenation of the C=C bonds of the vegetable oils followed by alkane production by three different pathways which are decarbonylation, decarboxylation and hydrodeoxygenation as shown in Figure 2.7. Furthermore, it was observed that the selectivity of the decarbonylation plus decarboxylation products increases with increasing temperature. However, the acid organics produced in the hydrotreating process may catalyze the straight chain alkane and produce the isomerized or cracked products via isomerization and cracking, respectively. In addition, they proposed that the catalyst and reaction condition play an important role to determine the yield of the decarbonylation, decarboxylation and hydrodeoxygenation pathways.
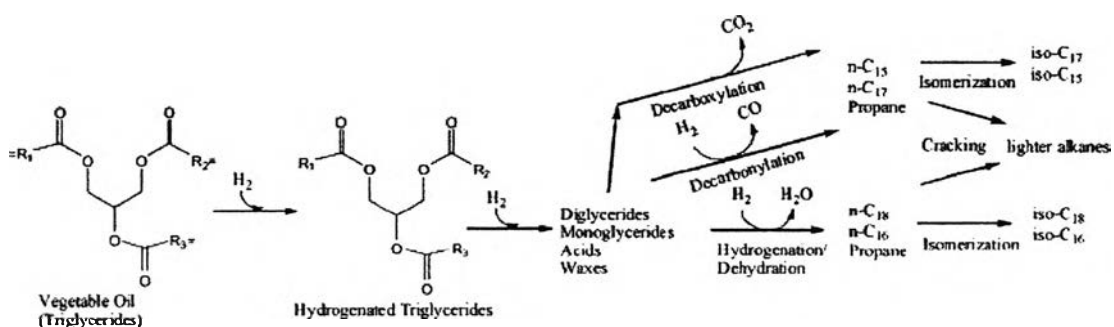

Figure 2.7 Reaction pathway for conversion of triglycerides to alkanes.

2.2.2 Catalyst for Deoxygenation Reaction

From the above literature reviews, the most active catalysts used for removing the oxygen atom from the oxygenate compounds are sulphided $NiMo/\gamma$-Al_2O_3, $CoMo/\gamma$-Al_2O_3, and 5wt% Pd/C. The former group is the common catalysts used in the hydroprocessing reaction, even though the most active metal sulfides are typically several orders of magnitude less active than the most active metals. But they are not poisoned by sulfur compounds and are therefore used as catalysts with feedstocks that contain sulfur. MoS_2 is the one of the most active among metal sulfides catalyze the hydroprocessing reactions. Since MoS_2 is expensive, it is used in a highly dispersed form, supported on a metal oxide, usually γ-Al_2O_3. There are other catalyst components, including cobalt or nickel, which is promoters, and sometimes Ni is used in combination with W rather than Mo, especially when hydrogenation is the principal goal. Usually, Mo and some fraction of the Co in the catalyst are converted into the sulfide form by treatment with H_2S in H_2 or with organosulfur compounds and H_2. The catalyst must be operated in the presence of H_2 and H_2S (or precursors that give H_2S, i.e., organosulfur compounds) to prevent their being reconverted into oxide form, which is less active. From the literature, it was observed that the sulphide $NiMo/\gamma$-Al_2O_3 was usually prepared by treating $NiMo/\gamma$-Al_2O_3 with 5 vol.% $H_2S,/H_2$ mixture at 400 °C under atmospheric pressure (Seno et al., 2005 and Huber et al., 2007).

The surface structures formed in the sulfiding step have been characterized by many spectroscopic methods and have been observed by electron microscopy. They resemble rafts of MoS_2 on the support surface, with a thickness of only a few layers. Bulk MoS_2 has a layer structure represented schematically in Figure 2.7. The planar surface of sulfur atoms is relatively unreactive, but the edges, with exposed Mo^{2+} ions, are reactive. The cobalt and nickel promoter ions are believed to be present at the edges, perhaps as shown schematically in Figure 2.8. This picture of the catalyst structure suggests that the catalytic activity is associated primarily with the promoter nickel more than the molybdenum sites at the MoS_2 crystallite edges; the model is simplified and the structure is complex but rather well understood (Gate, 1992).
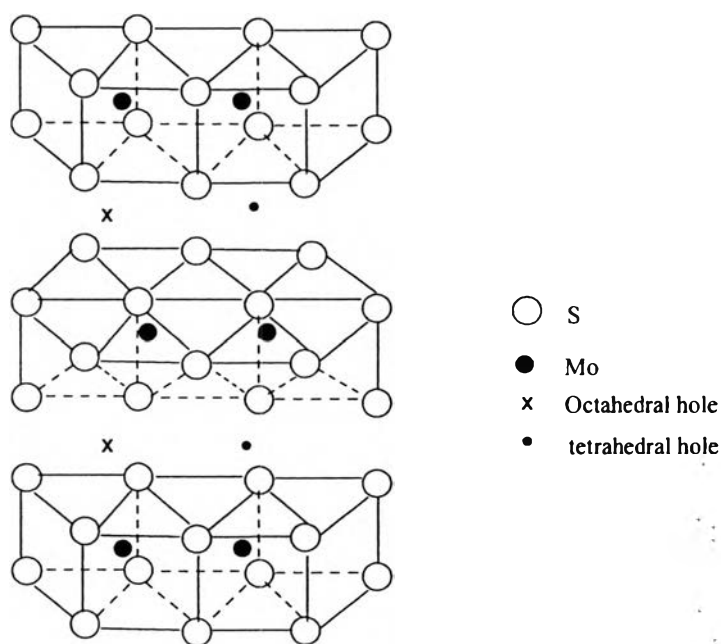
Figure 2.8 Layer structure of MoS_2. There are alternating layers of sulfur anions interspersed with layers of molybdenum cations, and there are empty layers between some of the sulfur layers
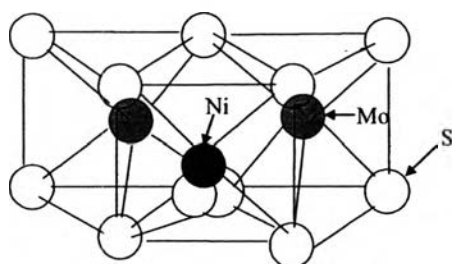

Figure 2.9 Schematic representation of nickel-containing sites at the edges of a MoS_2 layer on a carbon support (Bouwens et al., 1990)

In the case of Pd/C catalyst which is the heterogeneous catalyst frequently used in the hydrogenation reaction, it was observed that under the semi-batch or continuous mode, fatty acid was converted to long chain hydrocarbon with one atom less than the original fatty acid via decarboxylation reaction using Pd/C as the catalyst (Kubickova et al., 2005 and Murzin et al., 2006). Nevertheless, it was found

that when the starting material contains carbonyl compound in their structure, Pd catalyst can hydrogenate C=O group to methyl group via several mechanisms with out losing the carbon atom. First carbonyl group can be hydrogenated to alcohol, then dehydrated to form C=C bond, which is finally hydrogenated to the desired saturated hydrocarbon (C=O   C-OH   C=C   C-C). In the second mechanism, carbonyl compound is also at first hydrogenated to corresponding alcohol, which is followed by the hydrogenolytic splitting of the C-OH bond. The third mechanism involves direct hydrogenolysis of C=O bond of the reactant molecule. In 2005, Bejblova and coworker observed that in case of bezophenone transformation, the hydrogenation-dehydration mechanism with olefinic intermediate is excluded. However, benzophenone was converted to diphenylmetane via hydrodeoxygenation which proceed only according to pathway as shown in Figure 2.9 (Bejblova et al., 2005). There are two possible path ways considered that are hydrogenation-hydrogenolytic way (I ·. II → III) and the direct hydrogenolysis of the C=O bond of benzophenone (I → III). Therefore, it is so interesting that –COOH group might be hydrogenated to –CH_2OH and followed by the hydrogenolytic splitting of the bond C-O producing hydrocarbon by using Pd/C as the catalyst.
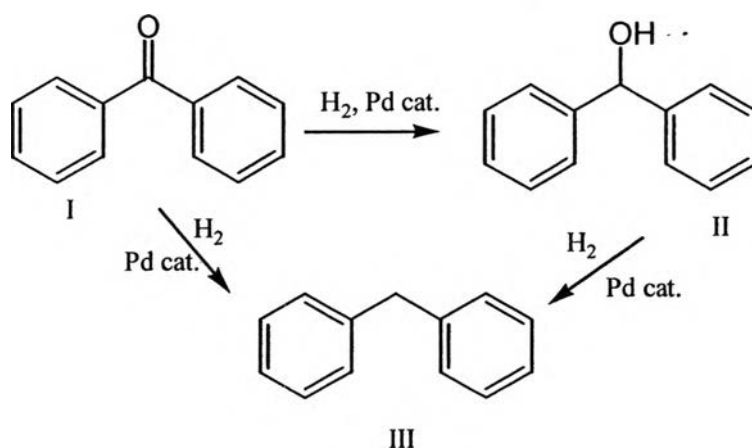

Figure 2.10 Reaction scheme of benzophenone (I) transformation to diphenyl-methane (III)

2.2.3 GC Derivatization

The products from the deoxygenation of fatty acid which are mostly composed of hydrocarbon and carboxylic compounds are analyzed by using gas chromatograph equipped with FID detector. The column used for separation the products is DB-5 column (non-polar column) which is suitable for analysis the non-polar compounds but it is not appropriate for detection of the carboxylic compound. Therefore, the carboxylic group (-COOH) in the structure is required to modify to the new functional group which exhibits non-polar properties by GC derivatization method.

Derivatization is the process of chemically modifying a compound to produce a new compound which has properties that are suitable for analysis using a GC. Derivatives are used for improve resolution and reduce tailing of polar compounds (-OH, -COOH, =NH, -NH₂, -SH, and other functional groups), analyze relatively nonvolatile compound, improve analytical efficiency and increase detectability, and improve stability of compounds.

There are many types of derivatization which are silylation, alkylation, acylation. Silylation produces derivatives which are more volatile, less stable, and more thermally stable. In this method, the active hydrogens are replaced by trimethylsilyl (TMS) group. In contrast, alkylation reduces molecular polarity by replacing active hydrogens with alkyl group. Acylation is commonly used to add fluorinated groups for enhances the sensitivity for ECD (Electron Capture Detection). By this method, the polarity of amino, hydroxyl, and thiol groups are replaced by halogenated group. The choice of a derivatizing reagent is based on the functional group requiring derivatization, the presence of other functional groups in the molecule, and the reason for performing the derivatization. The chemical structure and properties of the molecule influence the reagent choice. In this project, the carboxylic group is required to convert to non-polar group by using silylation or alkylation method.

2.2.3.1 Silylation Method

Silylation is the most widely used derivatization procedure for GC analysis. In silylation, an active hydrogen is replaced by an alkylsilyl group, most often trimethylsilyl (TMS). Compared to their parent compound, silyl derivatives generally are more volatile, less polar, and more thermally stable. Silyl deriva-

tives are formed by the displacement of the active proton in –OH,-COOH, =NH, -NH₂, and –SH groups. The general reaction for the formation of trialkylsilyl derivative is shown in Figure 2.10.
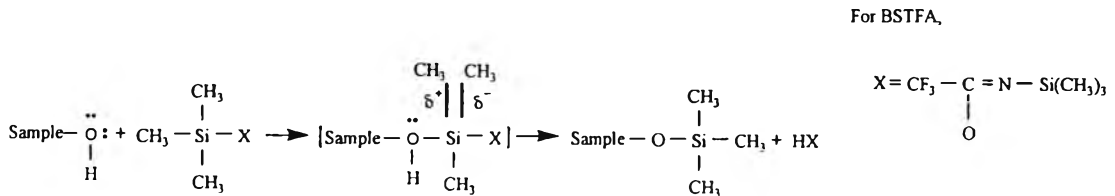

Figure 2.11 The general reaction of BSTFA for the formation of trialkylsilyl derivatives

       The silylation reagents used to achieve this process are HMDS (Hexamethyldisilzane), TMCS (Trimethylchlorosilane), TMSI (Trimethylsilylimidazole), BSA (N,O-Bis(trimethylsilyl)acetamide), BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide), MSTFA (N-methyl-trimethylsilyltrifluoroacetamide, TMSDEA (N-Trimethylsilyl-diethylamine), MTBSTFA (N-Methyl-N-t-butyldimethylsilyltrifluoroacetamide), DMCS (Di-methyldichlorosilane), MBDSTFA (N-Methyl-N-tert-butyldimethylsilyl-trifluoro-acetamide), TSIM (N-Trimethylsilyl-imidazole), and MSHFBA (N-Methyl-N-trimethylsilyl-heptafluorobutyramide). However, BSTFA and BSA are the two most popular reagents for silylation (Scott, 2003). Their structures are shown in Figure 2.11 (a) and (b)
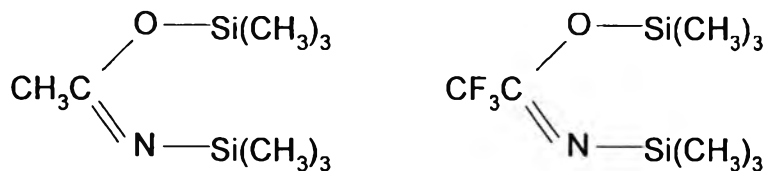

Figure 2.12 The structure of (a) BSA and (b) BSTFA

BSA is a strong silylation reagent which can be used to form very stable TMS derivatives of a wide variety of compounds such as alcohols, amines, carboxylic acids, phenols, steroids, biogenic amines and alkaloids. However, it is not recommended for use with hydrocarbons or very low molecular weight compounds. BSA is a good solvent for polar compounds, but frequently it is used in combination with a solvent (pyridine, DMF etc.) or together with other silylation reagents. When used with DMF, BSA is the reagent of choice for derivatizing phenols.

BSTFA is a powerful trimethylsilyl donor with approximately the same donor strength as the unfluorinated analog BSA. Reagents of BSTFA are similar to those of BSA. The major advantage of BSTFA over BSA is the greater volatility of its reaction products. BSTFA and its by-products (trimethylsilyltrifluoroacetamide and trifluoroacetamide) are more volatile than many other silylating reagents, causing less chromatographic interference.

In case of silylation of fatty acid, Snare and co-workers (Snare et al., 2006) used 30wt% pyridine and 100wt% excess of BSTFA for preparation the sample. This pretreated sample is heated up to 60°C for 30 minutes before injection into GC.

However, the silylating reagent is moisture sensitive. Water in the reaction mixture often can hinder the reaction and/or hydrolyze the derivative, reducing the yield of derivative for analysis. Tightly seal opened reagents during storage. If necessary, add sodium sulfate to the reaction mixture to trap water present in the sample.

2.2.3.2 Alkylation Method

Alkylation involves adding an alkyl group (aliphatic or aliphatic aromatic) to an active functional (H) group. Replacement of hydrogen with an alkyl group is important because the derivative has lower polarity, relative to the parent substance. Alkylation reagents are used to modify compounds containing acidic hydrogens, such as carboxylic acids and phenols. The resulting products are ethers, esters, thioethers, thioesters, n-alkylamines, andn-alkylamides. Alkylation of weakly acidic groups (e.g., alcohols) requires strongly basis catalysts (sodium or potassium

methoxide). More acidic OH groups (phenols, carboxylic acids) require less basic catalysts (hydrogen chloride, boron trifluoride).

Alkylation is generally used to convert organic acids into esters. As the acidity of the active hydrogen decreases, the strength of the alkylating reagent must be increased. The harsher the reaction conditions or reagents, the more limited the selectivity and applicability of this method. Alkyl esters have excellent stability and can be isolated and stored for long periods of time.

In this method, DMF (dialkylacetals), TBH (tetrabutylammonium hydroxide), BF_3 in methanol or butanol, and PFBBr (Pentafluorobenzyl bromide) were used as alkylating reagents. Among these alkylating reagent, BF_3 in methanol, boron trifluoride in the form of its coordination complex with methanol, is a powerful acidic catalyst for the esterification of fatty acid and it is convenient to use and inexpensive for forming esters. Boron trifluoride is supplied as a 14% solution in methanol. Boron trifluoride-catalyzed reactions are very fast and can be complete in a few minutes. 1 to 15 mg of the acid are placed in a vial fitted with a ground glass stopper and 1 ml of 14% boron trifluoride in methanol added. The mixture is heated on a water bath for 2 minutes and then cooled. The esters can be extracted with n-heptane with vigorous shaking. Care must be taken to extract all the derivative (Scott, 2003).