CHAPTER II
LITERATURE REVIEW

Diesel fuel in general is any liquid fuel used in diesel engines. It refers to a specific fractional distillate of petroleum fuel oils, which is intended for compression ignition engines or diesel engines. Generally, diesel fuel is mainly referred to petroleum-based diesel. Nowadays, there have been many attempts to displace non-renewable petroleum-based resources with renewable biomass-based resources, such as biodiesel and renewable diesel, which are called bio-based diesel.

The search for alternatives to petroleum-based fuels has led to development of fuels from various sources, including renewable feedstocks, such as oils and fats. Several types of fuels can be derived from the triacylglycerol-containing feedstocks.

2.1 Bio-based Diesel

Bio-based diesel can be classified based on their production technologies into 4 types, as shown in Table 2.1 (Fatih, 2009).

Table 2.1 Classification of renewable biofuel based on their production technologies

Generation	Feedstock	Example
First generation biofuels	Sugar, starch, vegetable oils, or animal fats	Bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Second generation biofuels	Non-food crops, wood, wheat straw, corn, energy crop, solid waste	Bioalcohols, bio-oil, biohydrogen, wood diesel, bio-Fischer–Tropsch diesel, bio-DMF
Third generation biofuels	Algae	Vegetable oil, biodiesel
Fourth generation biofuels	Vegetable oil, biodiesel	Biogasoline

First generation biofuels (FGBs) refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. FGBs, which are produced from food crops, such as grains, sugar beet, and oil seeds, are limited in their ability to achieve targets for oil-product substitution, climate change mitigation, and economic growth. Second and third generation biofuels are also called advanced biofuels. Second generation biofuels are made from non-food crops, such as wheat straw, corn, wood, and energy crop, using advanced technology. Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae. The fourth generation is based on the conversion of vegoil and bio-diesel into biogasoline, which uses the most advanced technology (Demirbas, 2009).

2.1.1 Biodiesel

Biodiesel refers to any diesel-equivalent biofuel comprising mono-alkyl esters of long chain fatty acids derived from the transesterification of renewable lipid feedstock, such as fats and oils (vegetable oils, animal fats or even used cooking oils, and other biomass-derived oils) under mild conditions in the presence of a base catalyst. The major components of biodiesel are straight-chain fatty acids, and the most common ones contain 16 and 18 carbon atoms. However, some feedstocks contain significant amounts of fatty acids other than the typical C16 and C18 acids.

Biodiesel is a liquid varied in color, golden to dark brown, depending on type of feedstock. It is immiscible in water. Most of mono-alkyl esters have high boiling point (in the range of 620-630 K) and low vapor pressure (less than 1 mm Hg). Its density is in the range of 0.86 to 0.90 g/cm^3, less than the density of water, and its flash point is higher than 130 °C, significantly higher than that of the conventional diesel (64 °C). Flash point (ASTM D93) is the lowest temperature, at which a combustible mixture can be formed above the liquid fuel. It is dependent on both the lean flammability limit of the fuel, as well as the vapor pressure of the fuel constituents. The flash does not correspond to a sustained flame. The "fire point" is sometimes used to designate the fuel temperature that will produce sufficient vapor to maintain a continuous flame.

There are many advantages of using biodiesel. It is renewable, simple to use, and biodegradable. It produces less harmful gas emissions, such as sulfur

oxide, and it is essentially aromatic-free. Biodiesel reduces net carbon dioxide emissions by 78 % on a life-cycle basis when compared to conventional diesel fuel (Tyson, 2001). It has also been shown to have improvements on engine exhaust emissions. The combustion of neat biodiesel decreases carbon monoxide (CO) emissions by 46.7 %, particulate matter emissions by 66.7 %, and unburned hydrocarbons by 45.2 % (Shumaker, 2007). Additionally, biodiesel is non-toxic. Therefore, it is useful for transportation applications because it is highly sensitive to environments. Biodiesel can be used directly to run existing diesel engines without modifying. It can be used instead of diesel as a pure fuel (B100) because it has the similar properties to that of diesel produced from crude oil. Moreover, it can be blended with the petroleum-based diesel. Biodiesel blends are denoted as "BXX" with "XX" representing the percentage of biodiesel contained in mixing process. In Thailand, there is B5, which is the blending of 5 % biodiesel with 95 % conventional diesel.

2.1.2 Hydrogenated Biodiesel or Renewable Diesel

Hydrogenated biodiesel or renewable diesel is defined as diesel fuel produced from biological material. Normally, renewable diesel is referred to hydrocarbons that do not contain oxygen in their molecular structure. It derives long-chain polymers of hydrogen, oxygen, and carbon into short-chain hydrocarbons with a maximum length of around 18 carbon atoms.

Hydrogenated biodiesel is produced from the fat or oil by a deoxygenation reaction at controlled hydroprocessing conditions in the presence of homogeneous or heterogeneous catalyst (Knothe, 2010), known as hydrotreating or hydrocracking processes. In hydrodeoxygenation reaction, the hydrocarbon chain is broken, and undesired oxygen is removed, leading to a production of straight-chain hydrocarbons suitable for diesel fuel.

2.2 Feedstock

Biodiesel is produced from any triglyceride containing raw material. Vegetable oils and animal fats are considered as raw materials for biodiesel and

renewable diesel production because they are widely available from a variety of sources, and they are renewable. The example of vegetable oils used for production are soybean oil, palm oil, sunflower oil, corn oil, jatropha oil, olive oil, canola oil, castor oil, coconut oil, cottonseed oil, etc. As well as recycled cooking oil, animal fats, trap grease (from restaurant grease traps), and float grease (from waste water treatment plants), are also available as raw materials for biodiesel and renewable diesel production. These products, when compared to plant-derived oils, often offer an economical advantage as a feedstock. There is also some indication that these sources, which are high in saturated fats, produce less nitrous oxide compared to plant-derived oils.

Both oils and fats consist of molecules called triglycerides. Fat generally refers to the triglycerides in solid form at room temperature, whereas oils are liquid at room temperature. The molecule of triglyceride is composed of three long-chain fatty acids of 8 to 22 carbons attached to a glycerol backbone. Figure 2.1 shows the chemical structure of a triglyceride, where R1, R2, and R3, which may be the same or different, represent long chain fatty acids, which are mostly palmitic, stearic, oleic, linoleic, and linolenic acids. Vegetable oils contain free fatty acids (generally 1-5 %), carotenes, phosphatides, phospholipids, sulphur, tocopherols compounds, and traces of water.
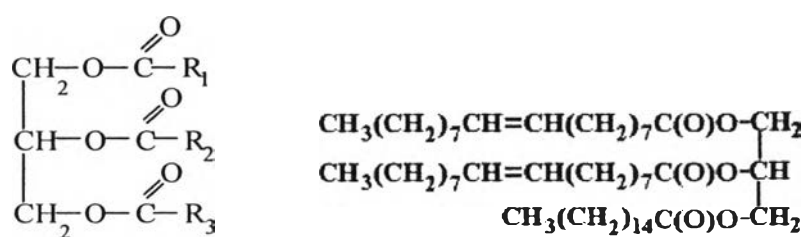
$$CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-R_1$$
$$CH-O-\overset{\displaystyle O}{\overset{\|}{C}}-R_2$$
$$CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-R_3$$

$$CH_3(CH_2)_7CH=CH(CH_2)_7C(O)O-CH_2$$
$$CH_3(CH_2)_7CH=CH(CH_2)_7C(O)O-CH$$
$$CH_3(CH_2)_{14}C(O)O-CH_2$$

Figure 2.1 A chemical structure of triglyceride.

The kinematic viscosity of vegetable oils varies in the range of 30-40 mm^2/s at 38 °C. High viscosity of these oils is due to large molecular mass and chemical structure. Vegetable oils have high molecular weights in the range of 600-900, which are three or more times higher than diesel fuels. The flash point of vegetable oils is very high (above 200 °C).

The volumetric heating values of these oils are in the range of 39-40 MJ/kg, which are low, compared to diesel fuels (about 45 MJ/kg). The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10 %. The iodine value ranges from 0-200 depending upon unsaturation.

The cloud and pour points of vegetable oils are higher than that of diesel fuels (Srivastava et al., 2000). The cloud point (ASTM D2500) is the temperature, at which a cloud of wax crystals first appears in a fuel sample that is cooled under conditions. For biodiesel derived from soybean oil, the CP is around 0 °C, and for biodiesel derived from rapeseed (canola) oil, it is only slightly lower. Biodiesel fuels derived from palm oil or animal exhibit significantly higher CP, around 15 °C, due to their content of saturated fatty esters. For the pour point, it is the lowest temperature, at which movement of the fuel sample can be determined when the sample container is tilted. The sample must be cooled following the procedure described in ASTM D97. That is to say, the cloud point is the highest temperature used for characterizing cold flow, and the pour point is the lowest. Another test related to cold flow properties is the cold filter plugging point (CFPP), which is a filterability test and linearly related to the CP.

The cetane numbers of vegetable oils are in the range of 32 to 40. The cetane number is an engine-based test that follows ASTM standard D613. It is based on a special engine produced by Waukesha Engine Company. The test is based on a careful adjustment of the fuel/air ratio and the compression ratio to produce a standard ignition delay (the period between the start of fuel injection and the start of combustion) of 13 degrees while operating on the test fuel. Then, the engine is switched to operate on a blend of two reference fuels. Different blends are tested until a formulation is found that restores the ignition delay to 13 degrees. The primary reference fuel is n-cetane (n-hexadecane), which has a cetane number of 100. The normal alkanes have a high cetane number (above 98), whereas typical diesel fuel has a cetane number around 45. The normal alkanes also have good cold flow properties (Helwani, 2009). The cetane number of fatty esters depends on chain length and degree of unsaturation. The presence of polyunsaturated fatty esters is the cause of oxidative stability problems with biodiesel, and the presence of higher amounts of saturated fatty esters is the cause of cold flow problems.

2.2.1 Animal Fat

The main constituent of animal fat (i.e. beef tallow, lard, poultry fat, and fish oils) is triglycerides. Triglyceride, also called triacylglycerol (TAG), is a chemical compound formed from one molecule of glycerol and three fatty acids. Fatty acid composition of some common edible fats and oils is shown in Table 2.2

Table 2.2 Fatty acid composition of some common edible fat and oil (Zamora, 2005)

Oil or Fat	Unsat. Sat. ratio	Saturated					Mono unsaturated	Poly unsaturated	
		Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid (ω6) C18:2	Alpha Linolenic Acid (ω3) C18:3
Almond Oil	9.7	-	-	-	7	2	69	17	-
Beef Fat	0.9	-	-	3	24	19	43	3	1
Canola Oil	15.7	-	-	-	4	2	62	22	10
Cocoa Butter	0.6	-	-	-	25	38	32	3	-
Cod Liver Oil	2.9	-	-	8	17	-	22	5	-
Coconut Oil	0.1	6	47	18	9	3	6	2	-
Corn Oil	6.7	-	-	-	11	2	28	58	1
Cottonseed Oil	2.8	-	-	1	22	3	19	54	1
Flaxseed Oil	9.0	-	-	-	3	7	21	16	53
Grape seed Oil	7.3	-	-	-	8	4	15	73	-
Lard (Pork fat)	1.2	-	-	2	26	14	44	10	-
Olive Oil	4.6	-	-	-	13	3	71	10	1
Palm Oil	1.0	-	-	1	45	4	40	10	-
Palm Olein	1.3	-	-	1	37	4	46	11	-
Palm Kernel Oil	0.2	4	48	16	8	3	15	2	-
Peanut Oil	4.0	-	-	-	11	2	48	32	-
Sesame Oil	6.6	-	-	-	9	4	41	45	-
Soybean Oil	5.7	-	-	-	11	4	24	54	7
Sunflower Oil	7.3	-	-	-	7	5	19	68	1
Walnut Oil	5.3	-	-	-	11	5	28	51	5

Note Percent by weight of total fatty acid

There are many research works studied on vegetable oil but a few for animal fat. Some studied the co-processing between petro-diesel and bio-diesel. There are also literatures about using the pure vegetable oil as the feed for the production of hydrogenated biodiesel, but the pure animal fat is rarely studied. The price of animal fat is lower than vegetable oil, and it can be used to produce hydrogenated biodiesel, which has more value. Thus, this research focuses on using the pure animal fat as feedstock for the production of hydrogenated biodiesel. In Thailand, animal fat is produced about 50 million liters/year.

In 2005, FUMPA (Farmers Union Marketing and Processing Association) began using animal fat feedstock. Minnesota's first commercial-scale biodiesel plant was beginning to blend animal fats into its virgin soy oil feedstock. FUMPA began production in early December 2004. The plant exceeded ASTM standards in testing and met the more strict European DIN standards.

In this research, beef fat was used as the model feedstocks for the production of hydrogenated biodiesel by deoxygenation process. As the fatty acid composition shown in Table 2.2, beef fat consists of C_{14}-C_{18}. Normally, it is solid in the room temperature. Thus, we needed to add dodecane as the additive in feedstock.

2.3 Biodiesel Production

2.3.1 Transesterification Process

Biodiesel is derived from the transesterification of fats and oils under mild conditions in the presence of a base catalyst, can yield high conversion (98 %) with minimal side reactions and reaction time, and are a direct conversion to biodiesel with no intermediate compounds. The major components of biodiesel are straight-chain fatty acids, and the most common ones contain 16 and 18 carbon atoms.

Biodiesel, which is referred to mono-alkyl ester, is normally produced via the transesterification of vegetable oils or animal fats (triglycerides). In this process, triglycerides react with alcohols, generally methanol or ethanol, in the presence of a catalyst to produce mono-alkyl esters and glycerol. The transesterification reaction can be catalyzed by bases, acids, or enzymes. The most

common catalysts used are strong bases, such as sodium hydroxide, potassium hydroxide, and sodium methoxide. The typical transesterification process is shown in Figure 2.2
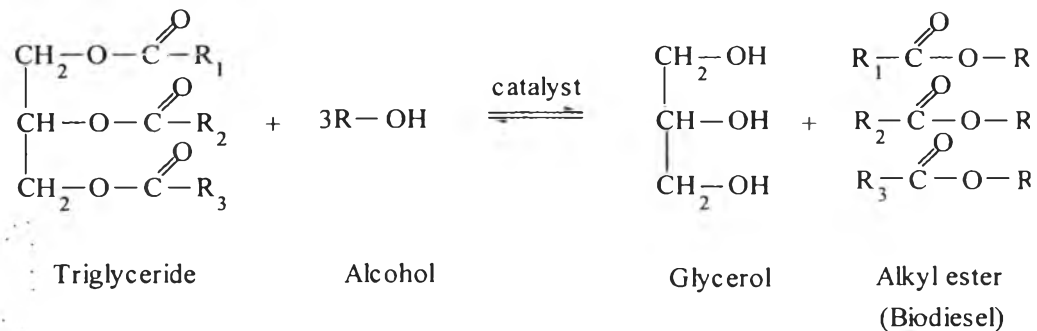

Figure 2.2 The production of biodiesel via transesterification of triglyceride.

The stoichiometric relation between triglyceride and alcohol is a one mole of triglyceride reacting with three moles of alcohol. However, for transesterification to occur, usually 6 moles of alcohol are used for every mole of triglyceride, which is more than the equation indicated. The reason is that the equilibrium of the reaction needs to be shifted toward the right side of the equation. To force the equilibrium in the direction of the desired products, one or more parameter(s) of the reaction may need to be changed, such as the molar ratio, temperature, pressure, and catalyst type.

The overall process of transesterification is shown in Figure 2.3. It is normally three consecutive steps, which are reversible reactions.
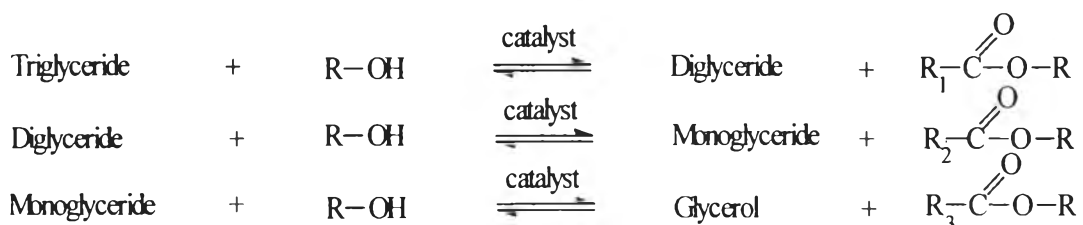

Figure 2.3 The transesterification reactions of triglyceride with alcohol to ester and glycerol (Srivastava and Prasad, 2000).

Figure 2.4 shows the simple reaction of triglyceride with methanol, resulting in the most popular mono-alkyl ester, which is methyl ester.
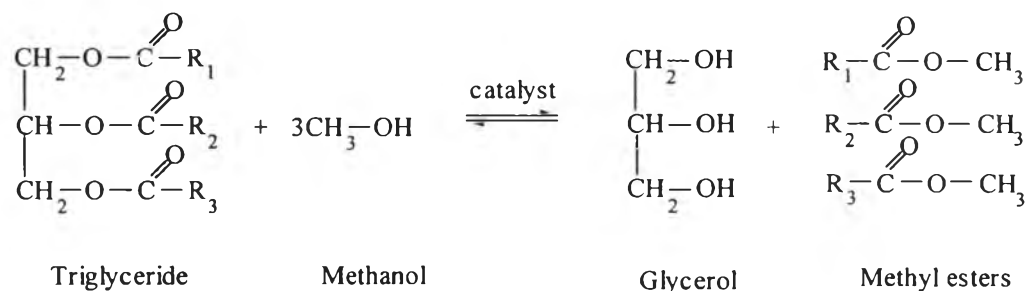

Figure 2.4 The transesterification reactions of triglyceride with methanol.

The carbon is lost via the conversion of triglycerides into mono-alkyl esters through the transesterification reaction, leading to the reduction of the molecular weight to one-third of the triglyceride and the slight increase in the volatility.

2.3.2 Hydrodeoxygenation Process

Hydrotreating is another route to produce of renewable diesel or renewable liquid alkane substitute from vegetable oils and fats, which contain the triglyceride, as shown in Figure 2.5. The standard hydrotreating conditions are 300-450 °C with conventional hydrotreating catalysts (i.e. $NiMo/\gamma-Al_2O_3$, sulfided $NiMo/\gamma-Al_2O_3$, Pd/C). In hydrotreating process, the hydrocarbons are produced by the three difference pathways: (i) hydrodeoxygenation (or dehydration/ hydrogenation), (ii) hydrodecarboxylation, and (iii) hydrodecarbonylation. In hydrodeoxygenation reaction, the hydrocarbon chain is broken, and undesired oxygen is removed, leading to a production of straight-chain hydrocarbons suitable for diesel fuel. The normal alkanes originating from HDO have the same carbon number as the original fatty acid chain, i.e. even carbon number, typically 16 or 18.

The hydrodeoxygenation of triglyceride becomes an alternative process of renewable diesel production because there are a lot of advantages of this process over transesterification, including compatibility with infrastructure, engines and fuel standards, and lower processing costs and raw materials flexibility.

Moreover, the obtained products from this process have high quality and have similar property to the conventional diesel fuel.
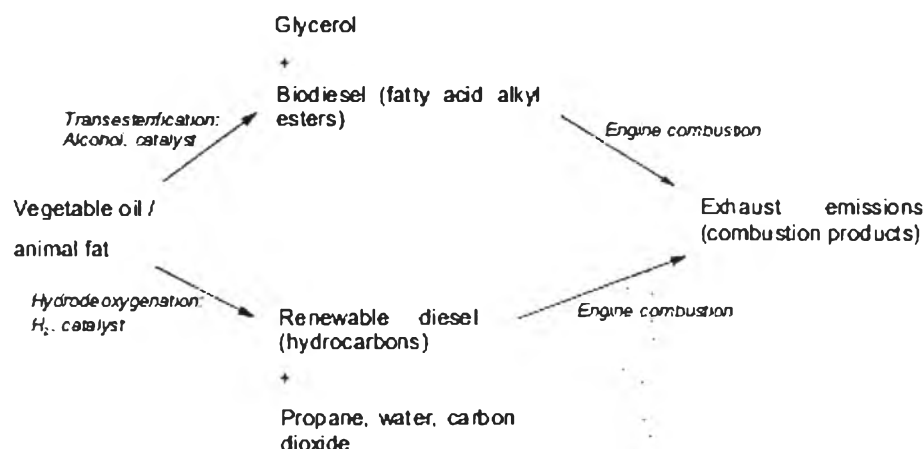
Glycerol
+
Biodiesel (fatty acid alkyl esters)

Transesterification:
Alcohol. catalyst

Engine combustion

Vegetable oil /
animal fat

Exhaust emissions
(combustion products)

Hydrodeoxygenation:
H₂. catalyst

Renewable diesel
(hydrocarbons)

Engine combustion

+

Propane, water, carbon dioxide

Figure 2.5 Flow chart for transformation of lipid materials (biodiesel and renewable diesel by hydrodeoxygenation) to products of engine combustion (Knothe, 2010).

The production of straight-chain hydrocarbons has several possible reaction pathways, as shown in Figure 2.6. Carboxylic acids have been used to represent feedstock. Fatty acids can be directly decarboxylated or decarbonylated. Direct decarboxylation of unactivated carboxylic acids removes the undesired oxygen by releasing carbon dioxide and producing aliphatic hydrocarbon chains with one carbon atom less than in the original feed. The direct decarbonylation removes the undesired oxygen by forming carbon monoxide and water, as explained by reactions I and II. Moreover, the fatty acid can be deoxygenated by adding hydrogen, leading to a production of straight-chain hydrocarbons, and undesired oxygen will be removed through formation of water, as explained by reaction III (Murzin *et al.*, 2006).
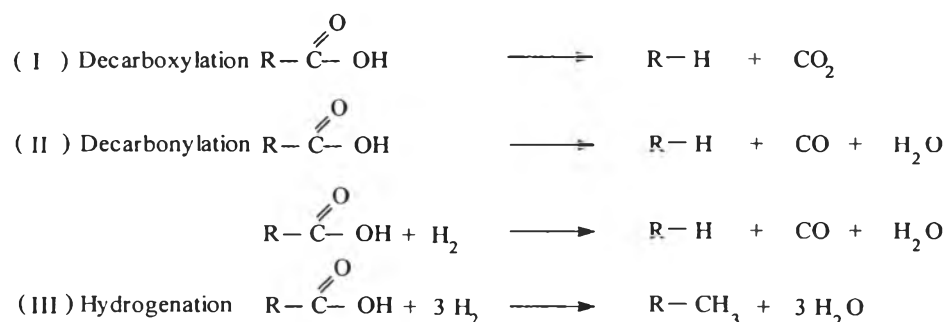
$$(I) \text{ Decarboxylation } R - \overset{O}{\overset{\|}{C}} - OH \longrightarrow R - H + CO_2$$

$$(II) \text{ Decarbonylation } R - \overset{O}{\overset{\|}{C}} - OH \longrightarrow R - H + CO + H_2O$$

$$R - \overset{O}{\overset{\|}{C}} - OH + H_2 \longrightarrow R - H + CO + H_2O$$

$$(III) \text{ Hydrogenation } R - \overset{O}{\overset{\|}{C}} - OH + 3\,H_2 \longrightarrow R - CH_3 + 3\,H_2O$$

Figure 2.6 The possible liquid-phase reaction pathways for production of straight-chain hydrocarbons from fatty acids.

In addition to the liquid-phase reactions, the water gas shift and methanation reactions occur with a number of carbon monoxide, carbon dioxide, hydrogen, and water formed during decarbonylation/decarboxylation reaction. The water-gas-shift reaction may balance the concentrations of CO and CO_2, while methanation reaction of fatty acids gives methane and water, as shown in Figure 2.7
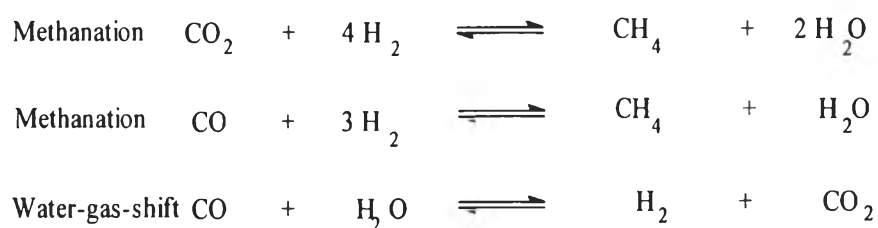
$$\text{Methanation} \quad CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O$$

$$\text{Methanation} \quad CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O$$

$$\text{Water-gas-shift} \quad CO + H_2O \rightleftharpoons H_2 + CO_2$$

Figure 2.7 Gas phase reactions of CO or CO_2 with H_2 or H_2O.

Hydrogenation involves bifunctional catalyst that contains sites for hydrogenation reactions (possibly NiMo sites) and for dehydration reactions (acid catalytic sites). It is possible that the free fatty acid intermediates are catalyzing the dehydration reaction. The hydrogen requirements decreases as hydrodeoxygenation pathway > decarbonylation pathway > decarboxylation pathway (Corma *et al.*, 2007).

In the decarboxylation and decarbonylation, the main reaction by-products are water and propane. On the other hand, HDC yields hydrocarbons with

an odd carbon number; they have one carbon atom less in the molecule than the original fatty acid chain. The dominant by-products are CO, CO_2 and propane (Huber, 2006).

Knothe (2010) described that in hydrodeoxygenation, the synthesis of heptadecane (molecular weight 240.475) requires hydrogen to saturate the double bond but with loss of a carbon from the original fatty acid chain through decarboxylation and without retention of the glycerol carbon. Thus, on a weight basis, hydrodeoxygenation yields approximately only 81 % of the yield from biodiesel production. This observation also relates to the energy content (kJ/kg). The issue of the energy balance is affected by the energy necessity for producing the alcohol and hydrogen, as well as the catalyst requirement for the production process. It is further complicated by the fact that alcohol and hydrogen amounts can depend on the feedstock (as shown by the fatty acid profile). In the case of renewable diesel, the amount of hydrogen used can depend on the eventual use of the desired product, which influences its composition and production.

2.3.3 Influence of Condition

For all reactions, the conditions are very important because they have the effect on the reaction, i.e. efficiency of reaction, quality of the product, quantity of the product, and activity of catalyst.

Filho et al. (1993) studied the reaction conditions and the composition of the feedstock, which can be used to control the nature of the product. More unsaturated feedstocks led to greater formation of cycloalkanes and alkylbenzenes with only comparatively small amounts of shorter-chain alkanes. More saturated feedstocks led to alkanes with the one less or the same number of carbons than in the original fatty acid chains.

In 2005, Kubickova et al. studied the influence of hydrogen partial pressure on the conversion and product distribution on the deoxygenation of stearic acid, ethyl stearate, and tristearine, over palladium supported on activated carbon to produce diesel fuel-like hydrocarbons. The experiments were done at temperature ranging from 300 to 360 °C and overall pressure 17-40 bar in a conventional Parr autoclave (300 ml) operating in a semi-batch mode. Different reaction atmospheres,

e.g. helium (He), hydrogen (H_2), hydrogen (5 vol.%)–argon (H_2-Ar) mixture, were applied. The results showed that all the three reactants were converted to the same final products, n-heptadecane, with high selectivity. The presence of hydrogen in the reaction atmosphere particularly diminished the undesired products such as unsaturated C17 and aromatic hydrocarbons.

In 2007, Maki-Arvela *et al.* studied the catalytic decarboxylation of fatty acids and their derivatives for production of linear hydrocarbons. The reaction has been investigated over Pd/C catalysts in a semibatch reactor under temperature and pressure range of 300-320 °C and 6-17.5 bars, respectively. The reaction atmosphere was helium, nitrogen, argon, hydrogen, and a mixture thereof. The results showed that there are different reaction pathways for the catalytic transformations of stearic acid and ethyl stearate. Decarboxylation is the main path for the catalytic transformations of stearic acid, whereas for ethyl stearate, the main reaction path under inert gas mixtures is decarbonylation over alkaline catalysts forming n-heptadecane as the main product, while over the acidic catalyst, decarboxylation is the main path and yieled mainly stearic acid. Moreover, the main reaction path of the catalytic transformations of ethyl stearate under hydrogen-rich conditions over acidic catalysts is decarbonylation, forming n-heptadecane as a main product. In the presence of gas mixture and hydrogen, decarboxylation proceeded faster, and there were higher conversions and yields of desired product, which n-heptadecane was obtained as the main product. The conversion level was the highest after 360 min for stearic acid. The decarboxylation (catalytic transformation) of unsaturated fatty acids led to hydrogenated products that reacted further to hydrocarbons.

The temperature also has the effect to the product. The yield of straight-chain alkanes decreases at temperatures higher than 350 °C because the alkanes undergo cracking and isomerization at higher temperatures (Huber, 2007). Accordingly, the recent experiments carried out at different temperatures showed that the heptadecane yield decreases as the temperature rises, whereas the yield of light hydrocarbons becomes higher (Yakovlev *et al.*, 2009). It is possible that at higher temperatures, along with hydrogenation and HDO processes, the hydrocracking occurs, leading to the formation of CH_4 and hydrocarbons with a lower molecular

weight. Besides, one should not ignore a possible occurrence of decarboxylation reaction with the CO_2 formation, although CO_2 and CO are absent in the gas products of the reaction.

2.4 Catalyst

2.4.1 Heterogeneous Catalyst

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen). The total surface area of solid has an important effect on the reaction rate. The smaller the catalyst particle size, the larger the surface area for a given mass of particles.

Normally, a solid heterogeneous catalyst with continuous processing technologies is expected to gain wider acceptance due to its potential effectiveness and efficiency, leading to reducing the cost of production. While there are potential benefits that the solid heterogeneous catalyst can offer, issues relating to the low catalytic activity, leachates, reusability and regeneration should be reported and emphasized in the future research in order to ensure the sustainability of the process.

Moreover, when carrying out over solid catalysts without the presence of dangerous solvents, it would become economically and environmentally attractive.

2.4.1.1 Kinetics Model of Heterogeneous Catalytic Reaction

The overall process of heterogeneous catalytic reaction can be classified into the sequence of individual steps, as shown in Table 2.3.

Table 2.3 Steps in a catalytic reaction (Fogler, 2006)

Step	Process
1	Mass transfer (diffusion) of the reactant(s) (e.g. species A) from the bulk fluid to the external surface of the catalyst pellet
2	Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3	Adsorption of reactant A onto the catalyst surface
4	Reaction on the surface of the catalyst (e.g., A → B)
5	Desorption of the products (e.g., B) from the surface
6	Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7	Mass transfer of the products from the external pellet surface to the bulk fluid

2.4.1.2 Catalyst Deactivation

The mechanisms of catalyst deactivation can be grouped into six mechanisms of catalyst decay (Bartholomew, 2001). The causes of deactivation are basically three-fold: chemical, mechanical, and thermal. Each of the six basic mechanisms is defined in Table 2.4, and mechanisms of catalyst deactivation are shown in Figure 2.8

Table 2.4 Mechanisms of catalyst deactivation

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores

Table 2.4 Mechanisms of catalyst deactivation (Cont.)

Mechanism	Type	Brief definition/description
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and solid–solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical-induced crushing of the catalyst particle

A supported metal catalyst can also deactivate due to the sintering of the support. When the support sinters, the supported metal particles come closer, making easier to sinter. Besides, when supports sinter, the nature of the surface can undergo modifications, resulting in weakened metal–support interactions. Sometimes, the sintering support may also trap metal particles inside their closed pores, preventing their accessibility to the reactants.

Supports can sinter through one or more of the following mechanisms:

(1) Surface diffusion,

(2) Solid-state diffusion,

(3) Evaporation/condensation of volatile atoms/molecules,

(4) Grain boundary diffusion, and

(5) Phase transformation.

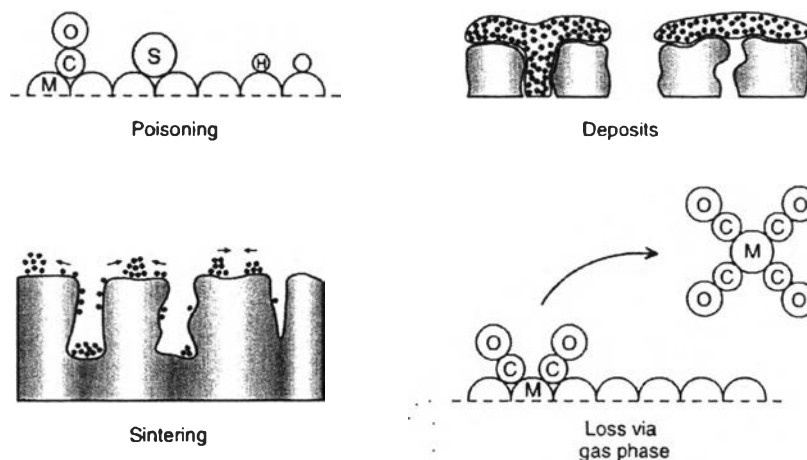**Figure 2.8** Mechanisms of catalyst deactivation (M = metal).

2.4.1.3 Preparation of Supported Metal Catalysts

Supported metal oxide comprises a large class of catalytic materials used in numerous industrial processes. There are conventional approaches to prepare these materials. The methods that have found wide use (including industrial use) are impregnation and co-precipitation.

In the last two decades, the greatest progress has been made in the sol–gel preparation of dispersed single component and multicomponent systems by the hydrolysis of solutions of metal alkoxides and in the synthesis of new, so-called mesophase mesoporous materials (Pakhomov and Buyanov, 2005).

2.4.1.3.1 Impregnation

Impregnation is a preparation technique, in which a solution of the precursor of the active phase is brought in contact with the support. Two methodologies exist. In dry impregnation, also referred to as "pore volume impregnation", just enough liquid (solution of the precursors) is used to fill the pore volume of the support. In wet impregnation, the support is dipped into an excess quantity of solution containing the precursor(s) of the impregnated phase. In dry impregnation, the solubility of the catalyst precursors and the pore volume of the support determine the maximum loading available each time of impregnation. If a high loading is needed, successive impregnations and heat treatments may be

necessary. When several precursors are present simultaneously in the impregnation solution, the impregnation is called "co-impregnation".

2.4.1.3.2 Co-precipitation

Co-precipitation differs from the other methods significantly. It is a method, by which a solid is precipitated from a solution containing soluble precursors of both the support and surface oxides. Nucleation of the solid phase is initiated by mixing the solution with precipitating agent that either (1) changes the solution pH and leads to precursor condensation to form oxide or hydroxides, or (2) introduces additional ions into the system, by which the solubility product for a certain precipitates is exceeded (Schuth and Unger, 1997). Filtration and washing of counterions from the precipitate yield the final solid. The resultant architecture of the coprecipitated binary framework is more spatially distributed than restrict supported metal oxide material prepared by the above methods. The distinct structure allows for better interaction between support and active species, but also results in partial exclusion of the active species from the surface, rendering it inaccessible for catalysis. Surface density calculations for resulting materials thus overestimate actual value.

Inverse co-precipitation offers an improved alternative to co-precipitation. A limitation for co-precipitation is that the support and metal oxide precursors are unlikely to share similar solubilities (i.e. solubility products). Consequently, dropwise addition of a precipitating agent generates solids dominated by the more insoluble precursor during early stages and rich in the latter precursor at late stages. This gives rise to temporal-spatially inhomogeneous compositions. In contrast, inverse co-precipitation adds the precursor mixture dropwise to an excess of precipitating agent, this approach ensures that a strict ratio of precursors is maintained throughout the course of batchwise addition and leads to better co-precipitate homogeneity.

2.4.2 Catalyst for Deoxygenation

In any reaction, the catalysts used depend on the exact nature or desired products. Several catalytic systems are applied to obtain petrodiesel-like fuels from triacylglycerol feedstocks. Cracking or pyrolysis is often promoted by zeolite

catalysts while hydrotreating (hydrodeoxygenation) is accomplished with catalysts, such as NiMo/γ-Al₂O₃ and CoMo/γ-Al₂O₃. Cracking will generally lead to shorter-chain hydrocarbon products while hydrodeoxygenation will generally lead to saturated longer-chain alkanes from which the ester moiety has been removed (for example, formation of C17 compounds, such as heptadecane, from C18 fatty esters). Cracking or pyrolysis is accomplished at elevated temperatures (300-400 °C) at normal pressure without the presence of hydrogen. Hydrodeoxygenation requires elevated temperatures and elevated pressure, as well as the presence of hydrogen.

Decarboxylation requires high transition state energies, which is reflected in reaction conditions, such as elevated temperature and pressure. The types of catalysts most commonly discussed in the many literatures are NiMo/Al₂O₃, CoMo/Al₂O₃, CoMo/C, CoMo/Si, Rh/Al₂O₃, Pd/SiO₂, reduced Ni/SiO₂, Pd/C, Pt/C, and others. The NiMo/Al₂O₃ or CoMo/Al₂O₃ catalysts refer to metal oxides (NiO, MoO₃, etc.) supported on alumina.

Noble metals (Pt, Pd, and Rh) are commonly used for the hydrogen activation. However, since the hydrodeoxygenation of bioliquids is expected to be a large-scale process, employment of the noble metal-based catalyst could significantly raise the cost of the processing. It seems more reasonable to use Ni–based catalysts for the process since these are also able to activate dihydrogen under the reaction conditions. A transition metal in its reduced state is required to activate dihydrogen. It must be taken into account that the catalyst is able to deactivate due to the coke formation; therefore the reaction temperature should not exceed 350-400 °C, and the dihydrogen pressure should be as high as 8.0– 10.0 MPa (Yakovlev et al., 2009).

Huber et al. (2007) studied the hydrotreating of pure sunflower oil with sulfided NiMo/γ-Al₂O₃ catalyst in a fixed bed reactor. The conditions were at temperature ranging from 300 to 450 °C, pressure of 50 bar, LHSV 4.97 h⁻¹ and H₂ feed ratio of 1600 ml H₂/ml liquid feed. The gas inlet was 91 % H₂ with the balance being Ar. The products were analyzed by GC. It was found that the fraction distillated from 250 to 350 °C was the major distillation fraction. This fraction is mostly n-C15, n-C16, n-C17, and n-C18. The maximum in this fraction occurred at reaction temperature at 350 °C. The reaction pathways involve hydrogenation of the

C=C bonds of the vegetable oils, followed by alkane production by three different pathways, as shown in Figure 2.9. Moreover, the straight chain alkanes can undergo isomerization and cracking to produce lighter and isomerized alkanes. In addition, they proposed that the catalyst and reaction condition play an important role to determine the yield of hydrodeoxygenation, decarbonylation, and decarboxylation pathways.
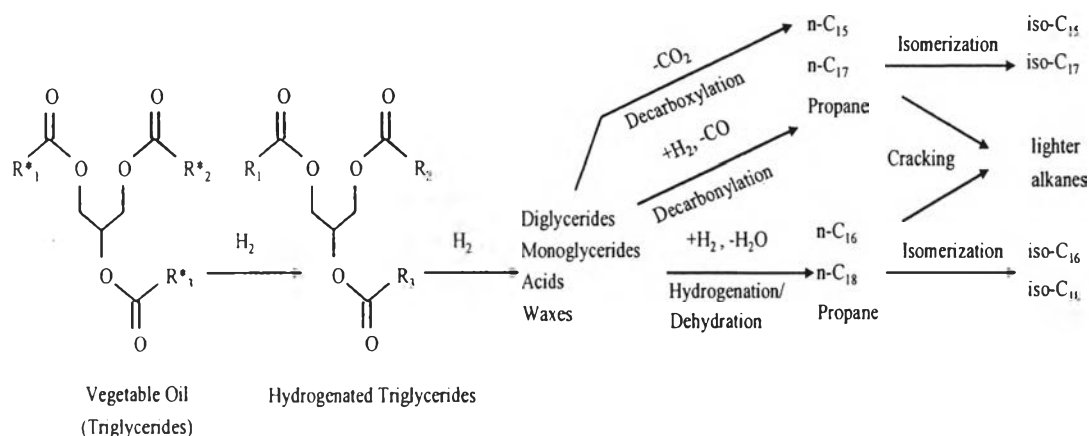
O O O O
R*₁ O   O   R*₂   R₁   O   O   R₂

Decarboxylation -CO₂   n-C₁₅
                        n-C₁₇   Isomerization   iso-C₁₅
                                                    iso-C₁₇
+H₂, -CO   Propane
Decarbonylation   Cracking   lighter alkanes

Diglycerides
Monoglycerides   +H₂, -H₂O   n-C₁₆
Acids   n-C₁₈   Isomerization   iso-C₁₆
Waxes   Hydrogenation/   iso-C₁₈
        Dehydration   Propane

$$R*_1 \quad \xrightarrow{H_2} \quad R_1 \quad \xrightarrow{H_2}$$

Vegetable Oil   Hydrogenated Triglycerides
(Triglycerides)

Figure 2.9 The reaction pathways for conversion of triglycerides to renewable diesel (Huber *et al.*, 2007).

In 2000, Druten *et al.* studied the hydrogenation of aldehydes and ketones using propanal and acetone as model reactants to investigate the competitive hydrogenation over noble metal catalysts, including Pt, Pt-Ga, Pd, and Rh. The reaction was performed at 100 °C and 1000 psig for all sets of experiment. The results over 1 wt.% Pd/aerosil revealed that the main product of propanal and acetone is di-n-propylether and 2-propanol, respectively. The main mechanism on palladium is hydrogenation of carbonyl groups to yield alcohol, followed by ether formation via condensation of two alcohol molecules. The addition of propanal to acetone can lower the conversion of acetone over Pd. This implied that propanal can inhibit hydrogenation of acetone by adsorbing more strongly than acetone, and this makes reactivity of propanal slower than that of acetone. Whereas the addition of acetone does not influence significantly to hydrogenation of propanal, but it can be converted

to form 2-propanol and diisopropylether, and react with propanol to form n-propyl isopropyl ether. From this study, they concluded that palladium is very efficient in ether formation while it much less efficient catalyst for hydrogenation of carbonyl groups compared to those noble metal catalysts, e.g. Pt, Pt-Ga, and Rh, due to the difference in catalytic behavior of Pd compared with other platinum metals. This is usually explained by the formation of p-allyl complex of carbonyl compounds with Pd (Tanaka, 1986).

Fluorided aluminas have been used as catalysts in several important industrial reactions because of the increase in the strength of their Brønsted sites caused by the incorporation of F^-. As catalyst supports, they are used in hydrotreatment (HDT) catalysts, where an increased acid functionality is needed. In these types of catalysts, alumina fluoridation helps increase the hydrogenating function of NiMo hydrotreatment catalysts (Ramirez et al., 1990).

The need of processing heavier petroleum cuts with high levels of contaminants and the more strict environmental regulations on the sulfur content in transportation fuels makes the use of hydrotreatment catalysts with enhanced hydrogenating and acid functionalities more necessary in order to improve the removal of the most refractory sulfur compounds from the different petroleum fractions. Fluoride-modified HDT catalysts present these characteristics.

Zeolites are widely used as catalysts in the petrochemical industry, for instance in fluid catalytic cracking and hydro-cracking. Nowadays, zeolites are used for the production of biodiesel. Zeolites confine molecules in small spaces, which causes changes in their structure and reactivity. The hydrogen form of zeolites (prepared by ion-exchange) is powerful solid-state acids. ZSM-5 catalysts have a strong acidity, high activities, and shape selectivities, which can convert the oxygenated bio-oil to light hydrocarbons C1–C10 by dehydration and deoxygenation reactions (Williams and Horne, 1995). In previous studies about the upgrading of a fast pyrolysis bio-oil with different catalysts in a fixed bed micro-reactor, it has been found that acidic zeolite catalysts, especially H-ZSM-5, were more effective in converting the bio-oil to hydrocarbons than the less acidic silica–alumina and non-acidic silicalite. Zeolite beta catalysts have a medium acidity and larger pore size

than zeolite ZSM-5, which make easier the access to active sites, located inside its pores, for large molecules of biomass origin.

Zeolite L is known as a good support for a catalyst used in aromatization of the C6-hydrocarbons. It has been reported to have high catalytic activity and high selectivity to benzene for conversion of n-hexane. The research about this zeolite in the deoxygenation field has not been studied widely, but this zeolite might be proper for the deoxygenation process due to its properties and structure. The crystal structure of zeolite L was determined initially by Barrer and Villiger (1969). The zeolite L has one-dimensional pores of about 0.71 nm apertures, leading to cavities of about 0.48×1.24×1.07 nm, and its Si/Al ratio is typically 3.0. The framework structure (Figure 2.10) consists of 12-ring channels (Baur and Fischer, 2006).
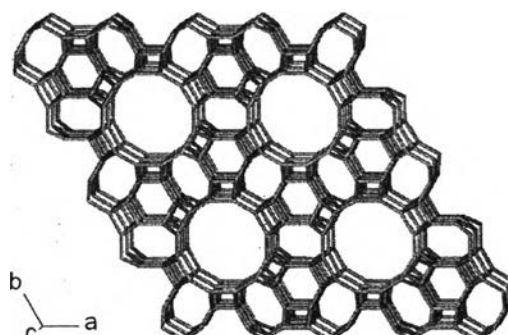

Figure 2.10 The framework structure of LTL-type compounds in the highest possible topological symmetry $P\ 6/mmm$. View parallel [001] rotated by 5 about [100] and [120].

2.4.3 Influence of Catalyst Support

The different catalyst formulations have the effect on the reaction efficiency, nature of product, etc. Therefore, the catalyst support plays an important role in the reaction. There are many research works about the effect of the catalyst support in deoxygenation process. Some are discussed as follows:

Laurent and Delmon (1994) studied the effect of catalyst metal and support. They mentioned that $NiMo/\gamma$-Al_2O_3 has a higher decarboxylation activity

than CoMo/γ-Al$_2$O$_3$ with hydrogenation of carboxylic groups, requiring temperatures around 300 °C. Carboxylic acids and esters react at similar rates with similar reactivity. Alumina-supported catalysts exhibited higher rates of decarboxylation and deesterification compared to carbon and silica, although the overall effect is complex. The acidity of the support influences the formation of active sites for decarboxylation and hydrogenation of carboxyl groups (Centeno *et al.*, 1995).

Kreuzer and Kramer (1997) also studied the effect the catalyst support. In the hydrogenolysis of tetrahydrofuran on supported platinum, the primary product is n-butanol. On unsupported platinum, the primary reaction proceeds distinctly slower than on supported platinum, and on these catalysts, the activity increases in the order of Pt/SiO$_2$ < Pt/Al$_2$O$_3$ < Pt/TiO$_2$. Thus, it is deduced that for the C–O bond scission, the presence of a support enhances the activity, with titania exhibiting an excellent ability to activate the C–O single bond. The primary product, butanol, undergoes two different secondary reactions, either by a hydrodeoxygenation to butane or by a decarbonylation to propane. The selectivity toward these products depends again on the supporting material, changing form about 0 % deoxygenation by unsupported platinum to almost 100 % deoxygenation by Pt/TiO$_2$. Again, the supported catalysts are more active in C–O bond scission and therefore more selective for butane formation.

In 2005, Senol *et al.* studied the hydrodeoxygenation of methyl esters, methyl heptanoate, and methyl hexanoate, on sulphided NiMo/γ-Al$_2$O$_3$ and sulphided CoMo/γ-Al$_2$O$_3$ catalysts. The reactions were carried out in a tubular continuous flow reactor under isothermal condition at 250 °C. The products obtained were analyzed by GC. The results showed that both methyl esters yielded a number of alkanes, alkenes, alcohols, and carboxylic acids. The oxide NiMo catalyst showed more activity for the reaction of aliphatic methyl ester than the oxide CoMo catalyst. However, oxide NiMo yieled mainly the alkenes. Moreover, the aliphatic methyl esters are converted to hydrocarbons via three paths, as shown in Figure 2.11. 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 alcohol and 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 carbon atom less than in the acyl group in the third path. The hydrogenation of the formed alkenes takes place following this deoxygenation.
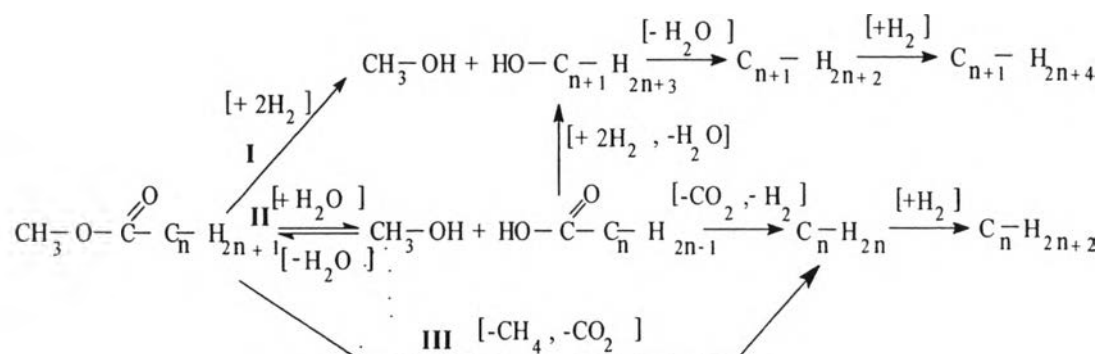
$$CH_3-OH + HO-C_{n+1}H_{2n+3} \xrightarrow{[-H_2O]} C_{n+1}H_{2n+2} \xrightarrow{[+H_2]} C_{n+1}H_{2n+4}$$

$$\xrightarrow[\text{I}]{[+2H_2]} \qquad \uparrow [+2H_2, -H_2O]$$

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

$$\text{III} \quad [-CH_4, -CO_2]$$

Figure 2.11 The hydrodeoxygenation reaction scheme of aliphatic methyl esters (n=6) for methyl heptanoate and n=5 for methyl hexanoate) (Senol *et al.*, 2005).

Yakovlev *et al.* (2009) studied the influence of the catalyst support properties in the HDO of aliphatic and aromatic oxy-organics. Rh-, Rh–Co-, Ni- and Ni–Cu-containing catalysts were tested in the HDO. SiO_2, Al_2O_3, ZiO_2, CeO_2, and CeO_2–ZrO_2 were used as catalyst supports. The Ni-based CeO_2–ZrO_2 mixed oxide support was suggested to be the most appropriate material since the valence of these metals can change under the biodiesel HDO conditions. Thus, there is an additional activation of oxy-organics. The main reaction product was heptadecane, and they mentioned that the heptadecane yield decreases as the temperature rises, whereas the yield of light hydrocarbons becomes higher.

Murzin *et al.* (2006) studied the deoxygenation of stearic acid over the heterogeneous catalysts for production of biodiesel. A variety of metals (Pd, Pt, Ru, Mo, Ni, Rh, Ir, and Os) supported on Al_2O_3, Cr_2O_3, MgO, and SiO_2, as well as activated carbons, were studied. The deoxygenation experiments were carried out in a semi-batch reactor under constant overall pressure and temperature at 600 kPa and 300 °C, respectively. In case of noncatalytic deoxygenation, it was found that less than 5 % of stearic acid was converted within 6 h of reaction, and the main products formed were linear C17 hydrocarbons. The heterogeneous catalytic deoxygenation of

stearic acid was achieved with high activity and selectivity to n-heptadecane (n-C17), as a desired product. The catalyst screening showed that the reaction can be effectively performed over palladium and platinum supported on activated carbons. Furthermore, the gas phase analysis indicated that the decarboxylation reaction was more preferable over the Pd/C catalyst, as the decarbonylation was more preferable over the Pt/C catalyst.