



CHAPTER II

LITERATURE REVIEW

2.1 Theoretical Background

Diesel fuel is referred to fuel oils which are intended for compression ignition diesel engines. Generally, diesel fuel is mainly referred to petroleum-based diesel. However, biodiesel which is an alternative to petroleum-based diesel can also be used as diesel fuel. Biodiesel has received more interests in the past several decades because of the depleting fossil fuels and the rapidly increasing petroleum prices. Nowadays biodiesel is increasingly being developed and adopted.

2.1.1 Petroleum-based Diesel

Petroleum-based diesel, also called petrodiesel or fossil diesel is a mixture of hydrocarbons, including paraffins, naphthenes, olefins, and aromatics, in the range of carbon numbers from 12 to 18. Normally, it is composed of about 75% saturated hydrocarbons (primarily paraffins including *n*, *iso*, and cycloparaffms), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approx. $C_{10}H_{20}$ to $C_{15}H_{28}$. Petroleum-based diesel is immiscible in water. It has the density of about 850 g/dm^3 and typically releases about 40.9 MJ/dm^3 when it is burnt.

2.1.2 Biodiesel

Biodiesel is an alternative to petroleum-based diesel fuel. It is defined as fatty acid methyl esters (FAMEs) or mono-alkyl esters of fatty acids derived from bio-oils such as vegetable oils and animal fats. It is a liquid which is immiscible in water. Its color varies from golden to dark brown depending on type of feedstock. Biodiesel usually can be blended with conventional diesel. This blending can improve lubricity and reduce emissions (Pandey, 2009). Biodiesel blends are denoted as “BXX” with “XX” representing the percentage of biodiesel contained in mixing process, such as B5 in Thailand, a blend of 5% biodiesel with 95% conventional diesel.

The advantages of biodiesel over petroleum-based diesel are renewable, biodegradable, non-toxic, low green house gas emission (Pandey, 2009), and essentially free of sulfur and metal (Gandarias *et al.*, 2008). One of the main benefits is the carbon dioxide (CO₂) neutrality which is described by the fuel production with no net output CO₂. The released CO₂ from fuel combustion is consumed during the photosynthesis of vegetables.

2.1.2.1 Biodiesel Feedstock

There are various types of feedstock for biodiesel production. The main feedstock is triglyceride-containing materials, including vegetable oils, animal fats, and used cooking oils. 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. The chemical structure of triglyceride is shown in Figure 2.1 where R₁, R₂, and R₃ may be the same or different, represent long chain fatty acids which are mostly palmitic, stearic, oleic, linoleic, and linolenic acids.

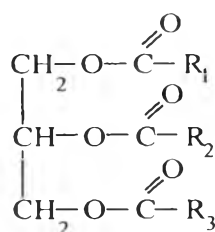


Figure 2.1 A chemical structure of triglyceride.

First of all, vegetable oils are the major feedstock for biodiesel production since they are widely available from several sources. For example, jatropha, palm, coconut, and sunflower are commonly grown in Thailand. In addition, vegetable oils have good heating value and provide exhaust gas with low sulfur and aromatic polycyclic compounds content (M. Balat and H. Balat, 2008). Generally, vegetable oils are not used directly as fuels in diesel engines because their viscosities are high. Therefore, modifications of automotive engines are required before using these oils as fuels. However, instead of modification engines, it is more attractive to improve properties of vegetable oils by converting them to biodiesel.

Second, animal-derived products such as tallow, lard, poultry fat, yellow grease, and beef oil are also triglycerides and are used as biodiesel feedstock. Finally, used cooking oil or recycled oil and grease, usually from restaurants and food processing plants also can be used. Although more pretreatment is needed for this feedstock compared to vegetable oils, but it is a very economically attractive feedstock. Furthermore, the use of used cooking oil is an environmentally friendly process because it can solve a waste disposal problem.

2.1.2.2 Biodiesel Production

The most common process for biodiesel production is transesterification process. Biodiesel is produced via transesterification of triglyceride-containing feedstock such as vegetable oils with alcohol i.e. methanol, ethanol, and butanol in the presence of catalysts. Glycerol is also produced as main co-product. Both base and acid catalysts can be used to catalyze the reaction in order to increase the reaction rate and to improve the product yield of the process. However, base catalysts like sodium hydroxide (NaOH) and potassium hydroxide (KOH) are usually used in the reaction because catalytic activity of base catalysts is approximately 4000 times higher than that of acid catalysts (Perego and Bianchi, 2010). Chemical reaction of biodiesel production via transesterification is shown in Figure 2.2.

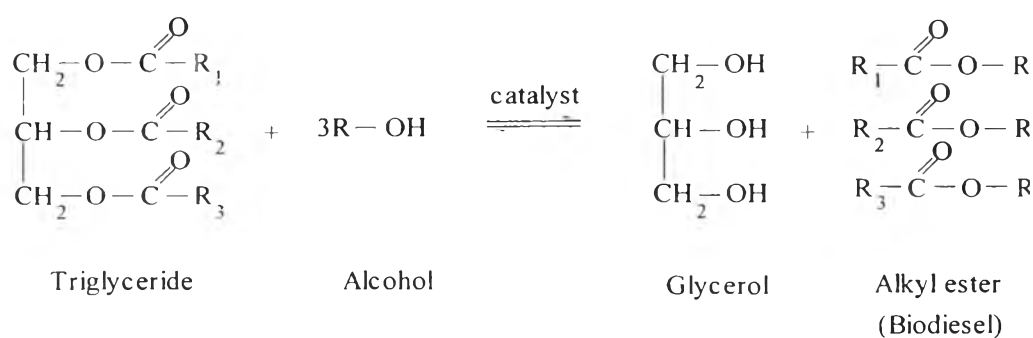


Figure 2.2 Chemical reaction of biodiesel production via transesterification of triglyceride.

Transesterification reaction composes of three consecutive steps, which are reversible reactions, as illustrated in Figure 2.3. In the first step, a

triglyceride reacts with alcohol to produce a diglyceride, followed by the reaction of the diglyceride with another alcohol molecule to produce a monoglyceride. The last step, the monoglyceride is converted to glycerol, and one alkyl ester molecule also is produced from each step (Srivastava and Prasad, 2000).

The stoichiometric relation between triglyceride and alcohol is a one mole of triglyceride reacts with three moles of alcohol. However, for the transesterification to take place, usually 6 moles of alcohol are used for every mole of triglyceride, which is more than the equation indicates. 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.

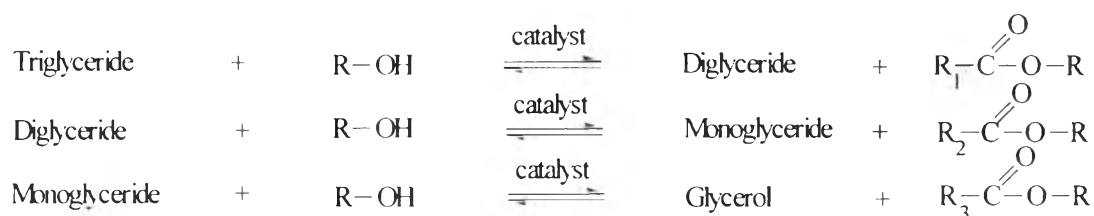


Figure 2.3 Three consecutive steps of transesterification reaction.

2.1.2.3 Drawbacks of Biodiesel

Although biodiesel produced from transesterification process has a lot of advantages over conventional diesel but it also has some drawbacks that limit its utilization. Due to high oxygen content in biodiesel, it results in high viscosity, corrosiveness because of high solvency, poor thermal and chemical stability, immiscibility with fossil fuels, low heating value (Yang *et al.*, 2009), low volatility, a tendency to polymerize under exposure to air during storage and transportation, the formation of carbon deposits in part of automotive engines upon combustion (Nava *et al.*, 2009), and increased engine-out NO_x emission (Hancsok *et al.*, 2007). Biodiesel also has cloud point and pour point higher than conventional diesel. These result in poor performance of biodiesel in cold conditions which might lead to engine problems (Kubickova *et al.*, 2005). Moreover, this production route

has several economic considerations mainly attributed to the price and availability of the main by-product, glycerin. Importantly, feedstock containing high concentrations of free-fatty acids can lead to operational problems because of saponification reactions with the base catalyst. Therefore newer FAME units include costly technology to remove or treat free fatty acids (Holmgren *et al.*, UOP, 2007). Several disadvantages of biodiesel production via transesterification process and many poor properties of biodiesel due to high oxygen content result in the development of new diesel processing technology.

Accordingly, bio-oils upgrading by removal oxygen from oxygenated molecules is the key challenge to improve quality of bio-fuel. The catalytic deoxygenation of triglycerides is the promising process for hydrogenated biodiesel or renewable diesel production. This process has several advantages over transesterification process, including compatibility with infrastructure of conventional refinery process, compatibility with engines and fuel standards, lower processing costs and raw materials flexibility (Stumborg *et al.*, 1996). In addition, this process can operate in the presence of free-fatty acids containing in feedstock without operational problems (Holmgren *et al.*, UOP, 2007). The obtain products from this process also have similar or even better properties to conventional diesel.

2.1.3 Hydrogenated Biodiesel

Hydrogenated biodiesel or renewable diesel refers to petrodiesel-like fuels derived from biological sources such as vegetable oils (Knothe, 2010). It is a paraffin-rich mixture of hydrocarbons (Hancsok *et al.*, 2007) which can be produced by directly converting triglyceride-containing feedstock to alkanes via catalytic deoxygenation reaction over conventional hydrotreating sulfided catalyst like NiMo/Al₂O₃ and CoMo/Al₂O₃.

2.1.3.1 *Hydrogenated Biodiesel Production*

Hydrogenated biodiesel can be produced via catalytic deoxygenation reaction of triglycerides. The hydrocarbon chain of triglycerides is broken and undesired oxygen is removed, leading to a production of straight-chain hydrocarbons suitable for diesel fuel. A proposed reaction pathway for conversion of triglycerides into alkanes or renewable diesel is shown in Figure 2.4.

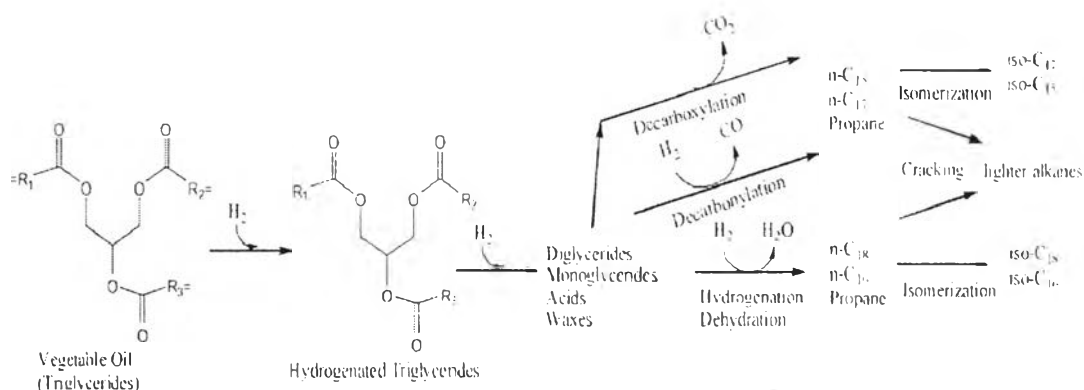


Figure 2.4 The proposed reaction pathway for conversion of triglycerides to renewable diesel (Huber *et al.*, 2007).

In the first step of this reaction pathway the triglyceride is hydrogenated and broken down into various intermediates which are monoglycerides, diglycerides and carboxylic acids. These intermediates are then converted into alkanes by three different pathways: decarboxylation, decarbonylation, and hydrodeoxygenation (or dehydration/hydrogenation). Moreover, the straight chain alkanes can undergo isomerization and cracking to produce lighter and isomerized alkanes. In addition, Huber *et al.* (2007) proposed that the catalyst and reaction condition play an important role to determine the yield of the decarbonylation, decarboxylation and hydrodeoxygenation pathways.

2.1.3.2 Comparison of Biodiesel and Hydrogenated Biodiesel

Hydrogenated biodiesel or renewable diesel has excellent fuel properties. It is useful to compare biodiesel and hydrogenated biodiesel properties and process since they represent two different approaches for making diesel fuel from vegetable oils. Their selected properties are compared in Table 2.1. The cloud point and specific gravity of biodiesel are high which can limit blending of lower-value products including hydrotreated light-cycle oil (LCO) into the refinery diesel pool. Moreover, biodiesel has lower heating value than petrodiesel and green diesel because of its oxygen content. For green diesel, renewable diesel named by UOP, a Honeywell company, it has extremely higher cetane number and lower density compared to the other two products, which will allow blending LCO into the typical

refinery diesel pool. The heating value of green diesel is also very close to that of conventional petrodiesel. It is clear that green diesel appears to be a superior product (Holmgren *et al.*, UOP, 2007).

Table 2.1 Comparison of petrodiesel, biodiesel, and green diesel properties (Holmgren *et al.*, UOP, 2007)

	Petrodiesel (ultra-low-sulfur diesel)	Biodiesel, FAME	Green diesel
O, %	0	11	0
Specific gravity	0.84	0.88	0.78
Sulfur content, ppm	<10	<1	<1
Heating value, MJ/kg	43	38	44
Cloud point, °C	-5	-5 to +15	-10 to +20
Distillation, °C	200 to 350	340 to 355	265 to 320
Cetane number	40	50 to 65	70 to 90
Stability	Good	Marginal	Good

The processes which produce biodiesel and green diesel also are compared, as illustrated in Table 2.2. The biodiesel process is fairly complicated, requiring multiple distillations and purifications. Green diesel is totally feed flexible and can handle low cost feedstocks like brown grease with high free fatty acid content without operational problems. Biodiesel requires methanol as feed and produces glycerol as a byproduct. Glycerol price is expected to drop significantly to \$.10/lb as biodiesel production increases. Green diesel only requires hydrogen as a feed and produces only diesel and propane as a product so its value is not affected by methanol or glycerol price. Biodiesel requires a homogeneous catalyst, resulting in higher chemical costs and higher separation costs (Marker *et al.*, UOP, 2005).

Table 2.2 Comparison of biodiesel and green diesel production processes (Marker *et al.*, UOP, 2005)

	Biodiesel	Green diesel
Complexity	High multistage	Low
Feedstocks	Sensitive to level of FFA	No sensitivity to FFA
Requires	Methanol 10%	H ₂ 2-3 %
Byproduct	Glycerol	Propane
Catalyst	Homogeneous	Heterogeneous

2.2 Literature Reviews

Nowadays, research work on deoxygenation of biomass-derived feedstock such as vegetable oils and animal fats for hydrogenated biodiesel or renewable diesel production has received much attention because its superior performance in cetane number, heating value, and other properties. Many researchers revealed that conventional hydrotreating catalysts like NiMo/Al₂O₃ and CoMo/Al₂O₃ can be used to remove oxygen from bio-feedstock for hydrogenated biodiesel production. Moreover, the development of new catalysts is also investigated.

2.2.1 Deoxygenation Process over Conventional Hydrotreating Catalysts

Catalytic deoxygenation of heavy gas oil was researched by Furimsky (1977). Hydrocracked gas oil (HCGO) with boiling range of 345-525 °C from thermal hydrocracking of Athabasca bitumen was used as feedstock. It was catalytically hydrotreated over a series of catalysts in a fixed-bed reactor. The catalysts studied in this work are unpromoted molybdate and promoted molybdate with Ni and Co supported on alumina. The concentrations of the active components (MoO₃ and NiO or CoO) were systematically increased. The results showed that 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 MoO₃ (6 wt.%) on the alumina support. However, further increasing

in the MoO_3 concentration does not appreciably increase the oxygen removal. Moreover, he also found that the deoxygenation reaction is also improved by the addition of cobalt and nickel oxides to the molybdate catalysts.

The hydrodeoxygenation of methyl esters, methyl heptanoate and methyl hexanoate, on sulphided $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ and sulphided $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ catalysts was also studied. The reactions were carried out in a tubular continuous flow reactor under isothermal conditions 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 yielded mainly the alkenes. For sulphided catalysts, sulphidation greatly increased the selectivity of the catalyst. The sulphided $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst is more active than the sulphided $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$. Moreover, the aliphatic methyl esters are converted to hydrocarbons via three paths as shown in Figure 2.5. 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 one 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 NiMo catalyst is consistent with its higher hydrogenation activity. The most alkane formed from methyl heptanoate is n-heptane and from methyl hexanoate is n-hexane under all conditions (Senol *et al.*, 2005).

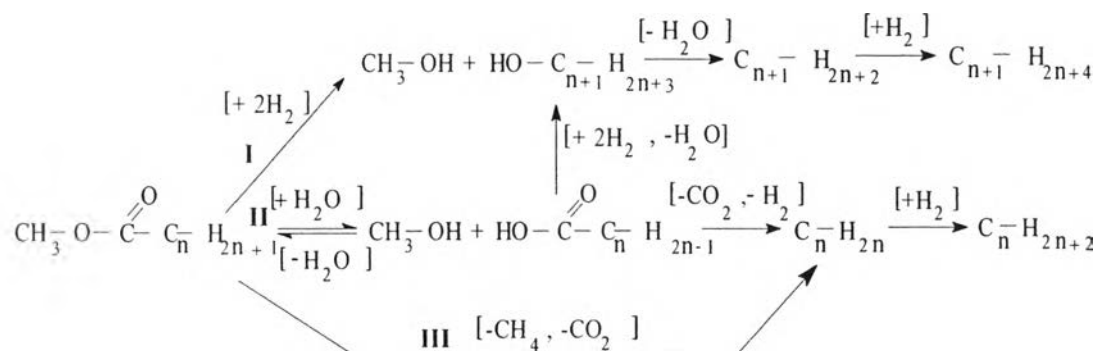


Figure 2.5 The hydrodeoxygenation reaction scheme of aliphatic methyl esters ($n=6$ for methyl heptanoate and $n=5$ for methyl hexanoate) (Senol *et al.*, 2005).

Huber *et al.* (2007) studied hydrotreating of pure sunflower oil over a sulfided NiMo/ γ -Al₂O₃ catalyst. The reaction were done in a fixed bed reactor at temperature ranging from 300 to 450°C, pressure of 50 bar, LHSV of 4.97 h⁻¹ and H₂ to feed ratio of 1600 ml H₂ /ml liquid feed. The gas inlet was 91% H₂ with the balanced with Ar. The products obtained were analyzed by GC. The results revealed that the fraction of the major products is a hydrocarbon mixture which has distillation temperature in the range from 250 to 380°C. This fraction is mostly n-C15, n-C16, n-C17, and n-C18 straight chain alkanes. The maximum in this fraction occurred at reaction temperature of 350°C with a yield of 71% on a carbon basis (which is 75% of the maximum theoretical yield for these products). Huber *et al.* suggested that the reaction pathways involves hydrogenation of the C=C bonds of the sunflower oil followed by alkane production by three different pathways: decarbonylation, decarboxylation and hydrodeoxygenation as shown previously in Figure 2.4. Moreover, the straight chain alkanes can undergo isomerization and cracking to produce lighter and isomerized alkanes. The selectivity to the decarbonylation and decarboxylation products increases with increasing reaction temperature as compared to the hydrodeoxygenation pathway. 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.

Gandarias *et al.* (2008) examined the role of commercial advanced NiMo and NiW catalysts developed for hydrodesulfurization (HDS) purposes in a hydrodeoxygenation (HDO) reaction using phenol as a model compound of pyrolyzed biomass. Furthermore, product distribution and catalyst stability are studied against changes in the feed composition, the solvent, and the catalyst pretreatment. The reaction was carried out under the reaction temperature in the range between 473 and 623 K at 1.5 MPa. They concluded that the NiMo catalyst had a higher activity than the NiW catalyst for the phenol HDO reactions in all the temperature range studied and the product aromatics content originated was lower, whereas the NiW catalyst had a higher isomerization activity resulting in higher conversions to methyl-cyclopentane. They also found that a phenol conversion increased with increasing of a reaction temperature, but aromatics content also increased. Moreover, the results showed that in the case of the NiMo catalyst the H₂S acted as an inhibitor, while it had no effect on the NiW catalyst at low temperatures but it was a promoter at high temperatures. For all the cases, the H₂S/H₂ addition did not improve the catalyst stability and changed the process selectivity. The effect of the H₂S addition on the selectivity could be used to control the aromatic content in the obtained product.

The effect of reaction temperature on product distribution in the organic liquid product (OLP) of the hydroprocessing of rapeseed oil for production of biocomponents in diesel fuel range was studied by Simacek *et al.* (2009). The reaction was carried out in the temperature range of 260–340 °C at pressure 7 MPa over three difference composition of Ni–Mo commercial hydrorefining catalysts with alumina. The results showed that at low reaction temperatures (260–300 °C depending on the catalyst used), the products contain triglycerides (especially tristearin), free carboxylic acids (especially stearic acid), a small amount of mono- and diglycerides, and trace of n-octadecanol. On the other hand, at a sufficiently high reaction temperature (above about 310 °C), the mentioned reactants and intermediates are not present in the obtained organic liquid product (OLP). These results can be concluded that the content of reactants and intermediates (mainly triglycerides and free fatty acids) decreased with increasing reaction temperature. Moreover, they found that reaction temperature has a relatively strong effect on

content of alkanes n-C18 and n-C17 which are the main component in the OLP. The content of n-heptadecane increases with temperature for all catalysts used, whereas the content of n-octadecane decreases with increasing temperature and there are larger differences in n-octadecane content between the catalysts used, especially at the highest reaction temperature (340 °C). It is clear that the reaction prefer to proceed via decarboxylation route when the reaction temperature increases. Furthermore, the formation of i-alkanes from isomerisation reaction also increases with increasing temperature for all tested catalysts.

The hydrodeoxygenation of crude palm oil (CPO) over an industrial hydrotreating catalyst, NiMo/ γ -Al₂O₃ was investigated at pilot plant scale by Guzman *et al.* (2010). They studied the reaction variables which are hydrogen pressure and time of stream (TOS). The purpose of studying time of stream is to observe the stability of the catalyst to the reaction by-products. The reaction was conducted in a trickled-bed reactor unit continuously operated using pure CPO as feed. They varied H₂ pressure and TOS as follows: pressure = 15–90 bar and TOS = 0–14 days using in all experiments a volume (STP) ratio hydrogen/CPO = 484 (20:1 molar). The results showed that crude palm oil (CPO) can be deeply converted into paraffins in the diesel range at 40-90 bar hydrogen pressure, whereas at low pressure hydrodeoxygenation cannot be fully reached. The intermediates of reaction as C16–C18 alcohols, C16–C18 acids and esters also presented in the obtained product. For times of stream (TOS) experiments, the results revealed that conventional hydrotreating catalyst suffers of slight deactivation as the reaction proceeds because of the presence of heavy oxygen containing components as octadecanol, n-hexadecanoic acid, octadecanal, and the esters hexadecyl hexadecanoate and octadecyl hexadecanoate. This catalyst deactivation results in a gradual lost of selectivity to the main C15–C18 products that constitute the renewable diesel.

Recently, Kubicka and Kaluza (2010) investigated the activity and selectivity of sulfide Ni/Al₂O₃, Mo/Al₂O₃ and NiMo/Al₂O₃ for triglyceride deoxygenation. The catalysts were prepared by conventional impregnation method. The loadings of MoO₃ and NiO in the monometallic catalysts were 21.8 and 12.7 wt.%, respectively, whereas the bimetallic catalysts had the atomic ratio Ni/(Ni + Mo) in the range 0.2-0.4. The results showed that the activity of the catalysts

decreased in the order $\text{NiMo}/\text{Al}_2\text{O}_3 > \text{Mo}/\text{Al}_2\text{O}_3 > \text{Ni}/\text{Al}_2\text{O}_3$ indicating the synergy between Ni and Mo. NiS phase acts in synergy with MoS_2 resulting in increasing the catalyst deoxygenation activity. It can be concluded that Ni functions as an activity promoter of Mo catalysts in deoxygenation of triglycerides. The different product distributions of the three catalysts provided evidence of the differences in reaction pathways over the tested catalysts. The bimetallic NiMo catalysts showed higher yields of hydrocarbons than the monometallic catalysts. They also found that the transformation of rapeseed oil over $\text{Ni}/\text{Al}_2\text{O}_3$ proceeded only via decarboxylation of fatty acid intermediates producing hydrocarbons with odd numbers of carbon atoms in their molecules (n-heptadecane), whereas over $\text{Mo}/\text{Al}_2\text{O}_3$ the reaction proceeded mainly via hydrodeoxygenation pathway with even hydrocarbons production (n-octadecane). For $\text{NiMo}/\text{Al}_2\text{O}_3$, the obtain products were from both decarboxylation and hydrodeoxygenation reaction. The molar ratio of hydrodeoxygenation and decarboxylation products increased with increasing conversion. The reaction pathways in conversion of triglycerides into hydrocarbons were illustrated in Figure 2.6. In addition, the influence of Ni/(Ni + Mo) ratio on activity and selectivity for triglycerides conversion was not considerable.

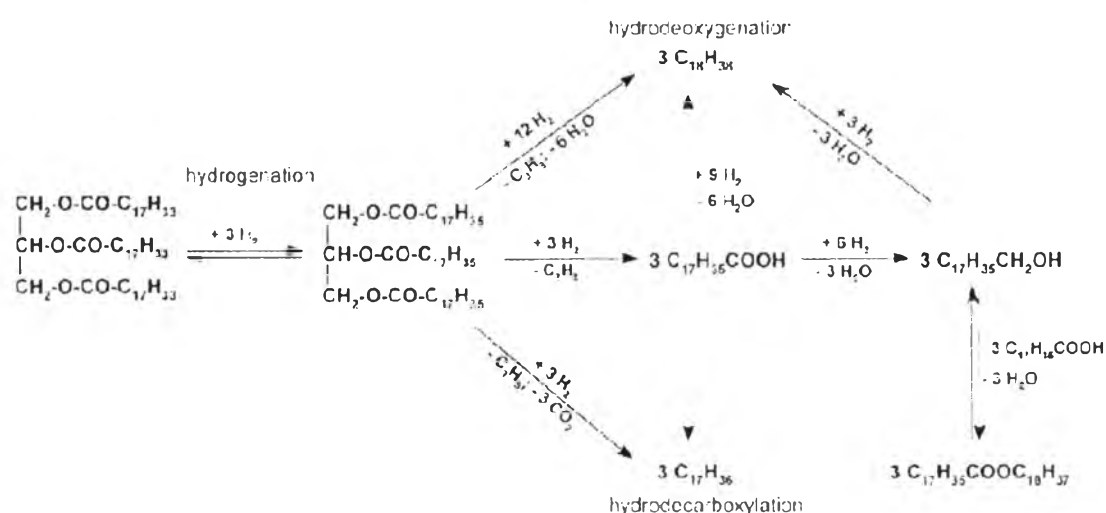


Figure 2.6 The reaction pathways involved in conversion of triglycerides into hydrocarbons (Kubicka and Kaluza, 2010).

2.2.2 Development of New Catalysts for Deoxygenation Reaction

Ferrari *et al.* (2001) studied hydrodeoxygenation of oxygen-containing compounds over a sulfided CoMo catalyst on activated carbon support. They considered influences of the hydrogen sulfide partial pressure on the activity of a sulfide CoMo/Carbon catalyst. The experiments were carried out in the fixed bed continuous flow tubular reactor under partial pressure of H₂S varied from 10 to 150 kPa (a total pressure of 7 MPa) at 200 and 270 °C. 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 results indicated that the activity of sulfided CoMo/C catalyst was rarely affected by the hydrogen sulfide partial pressure. Hydrogen sulfide did not affect the activity of sulfided CoMo/Carbon catalyst for the overall conversion of GUA. 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 H₂S.

Later, in 2002 they also studied hydrodeoxygenation over carbon supported molybdenum–cobalt catalysts. They considered the influence of the active phase loading on the physico-chemical properties and on the hydrodeoxygenation (HDO) activity of catalysts. Catalysts tested in this work are four molybdenum catalysts (Mo), with a MoO₃ loading ranging from 6 to 15 wt.% and four cobalt promoted molybdenum catalysts (CoMo), with a total oxide content (MoO₃ + CoO) ranging from 7.2 to 18 wt.% (with constant Co/(Co + Mo) ratio). A mixture of model compounds: 4-methylacetophenone (MA), ethyldecanoate (ED), guaiacol (GUA) was used as feed. The XPS results showed that both series of catalysts exhibit a non-uniform distribution of the active elements between the inside and outside of the carbon particles. The dispersion decreases with increasing metal loading. Moreover, cobalt is mainly impregnated on the external particle surface and to be responsible for a partial remobilization of molybdenum which migrates towards the external part of the particles where cobalt is impregnated. The formation of bulk cobalt or molybdenum oxides was not detected. They found that micropore blocking occurs in the case of MoO₃ contents higher than 6 wt%, whereas for MoO₃ content lower than

6 wt%, most of the molybdenum is located in the microporous structure with good dispersion and strong attachment to the support. The CoMo catalysts were tested in HDO reactions. The results indicated that the catalytic activity does not increase proportionally with the amount of active phase due to the decrease of the dispersion. They can conclude that the most important parameter for the reaction of MA and ED is the dispersion of the active phase. However, other factors like the accessibility of the active phase and the Co/(Co + Mo) atomic ratio probably play a crucial role in the conversion of GUA (Ferrari *et al.*, 2002).

Deoxygenation reaction of vegetable oils over a carbon-supported metal catalyst for diesel fuel-like hydrocarbon production was researched by Kubickova *et al.* (2005). Stearic acid, ethyl stearate, and tristearine were used as model compounds and dodecane was used as a solvent. The deoxygenation experiments were performed in semi-batch reactor over commercial activated carbon supported palladium (5 wt%) at 300–360 °C and overall pressure 17–40 bar. The main product that obtained from converting the three model reactants are the same product, n-heptadecane with high selectivity. The formation of carbon dioxide which was detected in gas analysis can be used to confirm that the reaction proceeded via decarboxylation. Ethyl stearate transformation occurs via stearic acid as an intermediate. The concentration of unsaturated C17 hydrocarbons was extensively higher than in case of stearic acid. The results showed that hydrogen partial pressure and reaction temperature affect on the product distribution of converting ethyl stearate. The formation of aromatic hydrocarbon was suppressed under slightly higher hydrogen pressure, whereas further increase of the hydrogen partial pressure suppressed the stearic acid conversion. Increasing the reaction temperature significantly improved the conversion of ethyl stearate, leading at the same time to enhanced formation of undesired aromatics.

Pd supported on active carbons also was further investigated by Maki-Arvela *et al.* (2007). They studied catalytic deoxygenation of fatty acids and their derivatives over Pd/C catalysts for the production of linear hydrocarbons in semi-batch reactor. The main studied parameters were catalyst acidity, effect of solvent, and gas atmosphere. In addition, several feeds were used to explain the reaction mechanism. The feeds that were tested are stearic acid, ethyl stearate,

behenic acid, nonanoic acid, and oleic acid. Analysis of gaseous components also was done in order to get information on reaction mechanism. The decarboxylation of stearic acid over the Pd/C catalyst at 300 °C under a helium atmosphere gave mainly *n*-heptadecane with high yield (97%) and small amount of unsaturated and aromatic C17 compounds. For the transformation of ethyl stearate, the highest yields of *n*-heptadecane were attained over the most alkaline Pd/C catalyst. However, using an alkaline Pd/C catalyst had a disadvantage which was a considerable formation of aromatic side products. The reactions in two different solvents revealed that the initial rate of the reaction of ethyl stearate in dodecane slightly higher than that in mesitylene. Furthermore, *n*-heptadecane was favored in dodecane, whereas in mesitylene, an intermediate product, stearic acid, was not reacting further to *n*-heptadecane. For the study of the effect of gas atmosphere, the results showed that under hydrogen the decarbonylation of ethyl stearate is more prominent to produce *n*-heptadecane, whereas under an inert atmosphere more stearic acid is formed. Gas analysis results revealed that the main gaseous product from the reaction of ethyl stearate was carbon monoxide, opposite to carbon dioxide observed for stearic acid. These results indicated that the catalytic transformation of fatty acids proceeded mainly via decarboxylation, whereas decarbonylation was the main route for esters. When different feeds in the catalytic decarboxylation reaction were compared, it can be concluded that, the longer the carbon chain, the slower the reaction. The conversion level was the highest after 360 min for stearic acid, followed by behenic acid and ethyl stearate. Additionally, the decarboxylation of unsaturated fatty acids results in hydrogenated products, which reacted further to hydrocarbons.

According to the two previous works, a Pd/C catalyst was demonstrated to be efficient for deoxygenation of saturated fatty acids and esters. The possibility to deoxygenate unsaturated renewable yielding diesel-like hydrocarbons over a commercial Pd/C catalyst (5 wt.%) was investigated by Snare *et al.* (2008) as well. The model compounds examined were the monounsaturated fatty acid, oleic acid, the diunsaturated fatty acid, linoleic acid and the monounsaturated fatty acid ester, methyl oleate. The chemical structures of these reactants are illustrated in Figure 2.7. The results showed that the deoxygenation reaction was achieved via initial isomerization and hydrogenation of double bonds followed by

further deoxygenation of saturated acid. The deoxygenation is carried out via direct formation of olefins from unsaturated acid as well. The main deoxygenation product is n-heptadecane, but minor amounts of unsaturated positional isomers (1-, 3-, and 8-heptadecene) and C17 aromatics are detected. The comparison of all feeds illustrated that the diunsaturated linoleic acid exhibited the lowest conversion level (34%) after 6 h, while monounsaturated oleic acid and methyl oleate displayed higher conversion after 6 h, 78% and 84%, respectively. The low conversion for linoleic acid resulted from an additional hydrogenation step from diunsaturated to monounsaturated and catalysts deactivation due to coke formation. The effect of reaction atmosphere also was investigated. They found that under hydrogen rich atmosphere the hydrogenation was enhanced and the deoxygenation reaction became predominant. Moreover, isomerisation occurred prior to hydrogenation and deoxygenation. Additionally, the conversion of unsaturated acids under hydrogen increased compared to experiments under inert atmosphere.

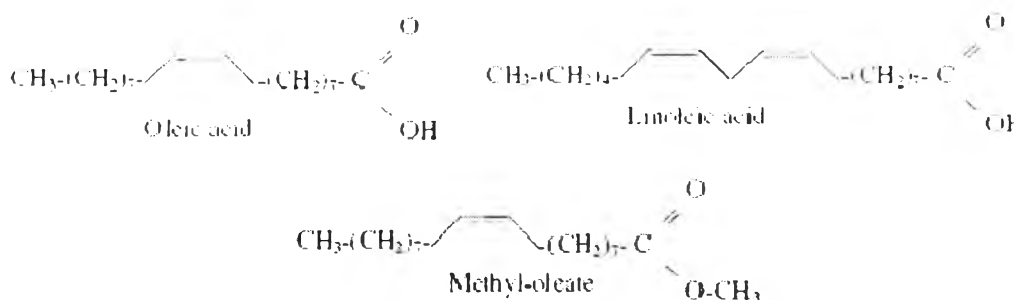


Figure 2.7 Chemical structures of the unsaturated model compounds, oleic acid, linoleic acid and methyl oleate (Snare *et al.*, 2008).

Recently, catalytic deoxygenation over a Pd/C catalyst was studied again by Boda *et al.* (2010). Promoted molybdena–alumina (Ni,Mo/ γ -Al₂O₃) catalyst also was investigated in order to compare the product distribution and reaction mechanism with a Pd/C catalyst. The main objective of this paper is to learn more about the direct conversion of triglycerides and fatty acids into hydrocarbons over commercial non-sulfide catalysts, palladium on activated carbon (Pd/C) and promoted molybdena–alumina (Ni,Mo/ γ -Al₂O₃). Tricaprylin (TC) and caprylic acid

(CA) were used as model reactants. The product distribution was also determined as a function of reaction parameters. Catalytic HDO of TC and CA were carried out in a high-pressure flow-through reactor under reaction temperature in the range of 300–400 °C at total pressure 21 bar. The results showed that a large variety of products such as carboxylic acids, alcohols, aldehydes, alkanes, alkenes, CO₂, CO, CH₄ and H₂O existed in the product mixture. They suggested that products can be formed in a series of consecutive reactions including, hydrogenolysis, decarboxylation, hydrodecarbonylation, hydrogenation, and parallel side reactions such as the water gas shift (WGS) reaction or methanation of CO. A series of consecutive reactions was illustrated in Figure 2.8. For hydroconversion of TC, the reaction steps are hydrogenolysis (HYS) of TC to CA and propane, followed by hydrodeoxygenation (HDO) of the CA intermediate. The rate determining step that governed the overall reaction rate was the HDO step. Consequently the concentration of the fatty acid intermediate was quite high in the product mixture. The product distributions suggest that distinct HDO mechanisms: (i) hydrodecarbonylation and (ii) reduction of oxygen prevail over the two catalyst types. They indicated that the decarbonylation was preferred over Pd/C giving C7 alkane (heptane) as the major product, and the reaction passes through formic acid intermediate that rapidly decomposes to CO and H₂O. In case of Ni,Mo/g-Al₂O₃ catalysts, the HDO proceeded in consecutive H₂ addition and dehydration steps giving predominantly C₈⁼ alkenes (octene), C₈ alkanes (octane), and water, while alcohol and traces of aldehyde also were detected as acid-to-alkane intermediates. Moreover, they found that the hydrocarbon yields were higher at higher temperatures.

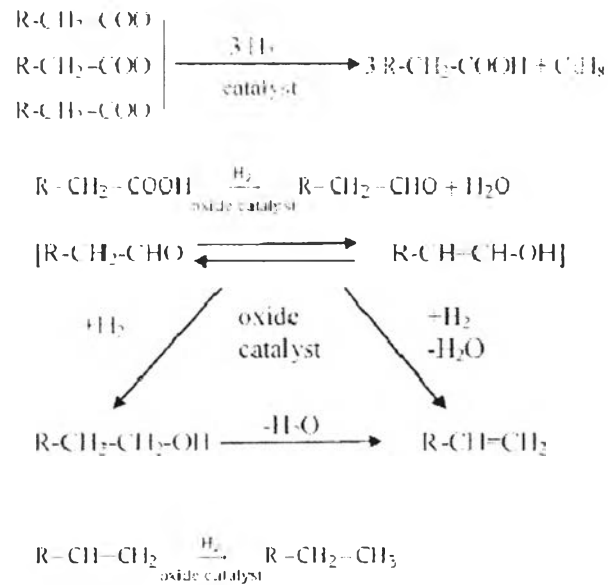


Figure 2.8 A series of consecutive reactions of hydroconversion of triglycerides (Boda *et al.*, 2010).

Deoxygenation of fatty acids over a variety of catalysts (Pd, Pt, Ru, Mo, Ni, Rh, Ir, and Os supported on carbon and metal oxides) resulting in straight-chain hydrocarbons by using stearic acid as a model compound were investigated by Snare *et al.* (2006). The reaction was carried out in a semibatch reactor under constant temperature and pressure, 300 °C and 6 bar, respectively in order to screen catalysts that active and selective in the deoxygenation reaction. They found that highly active and selective catalysts are palladium and platinum supported on activated carbons which can convert stearic acid completely with selectivity toward deoxygenated C17 products. Moreover, the gas phase analysis demonstrated that the decarboxylation reaction was more profound over the Pd/C catalyst, while the decarbonylation reaction was more evident over the Pt/C catalyst.

Fisk *et al.* (2009) studied the liquid phase upgrading of a model bio-oil over a series of supported Pt catalysts. Pt catalysts (1% wt) were prepared via incipient wetness impregnation with the metal precursor on several supports: γ -Al₂O₃, TiO₂, ZrO₂, SiO₂-Al₂O₃, CeO₂ and Ce_{0.7}Zr_{0.3}O₂. Upgrading experiments were carried out under inert atmosphere at 350 °C in a slurry reactor. The results showed that all of the Pt catalysts increased activity for deoxygenation in comparison with

the blank experiment. Pt/Al₂O₃ had the highest activity for deoxygenation, the oxygen content of the model oil decreasing from an initial value of 41.4 wt% to 2.8 wt% after upgrading. The main oil products after upgrading of bio-oil are alkyl-substituted benzenes and alkylcyclohexanes. The gaseous products contained predominantly CO₂ with small amount of H₂ and C1-C6 hydrocarbons.

Gutierrez *et al.* (2009) investigated hydrodeoxygenation (HDO) reaction for upgrading of pyrolysis oils from biomass by using guaiacol (GUA) as model compound. Hydrodeoxygenation of GUA was carried out over zirconia-supported mono- and bimetallic noble metal (Rh, Pd, Pt) catalysts. Moreover, the results for noble metal catalysts are compared with those for commercial conventional HDO catalyst (Al₂O₃-supported sulfided CoMo). The monometallic catalysts were prepared by impregnation, whereas the bimetallic catalysts RhPt and RhPd were prepared by co-impregnation method. All catalysts were tested under the experimental conditions, at temperature 100 and 300°C at pressure 8 MPa. The results showed that for the conventional sulfide CoMo/Al₂O₃ catalyst, the products were contaminated with sulfur, and the catalyst deactivated due to carbon deposition. These are common problems with conventional sulfided hydrotreating catalysts. In contrast, the ZrO₂-supported noble metal catalysts did not encounter these problems. They also found that at 100°C these noble catalysts are active and selective in the hydrogenation of GUA, while at 300°C the catalysts are active and selective in the HDO of GUA. At 100 °C GUA conversions with the monometallic Pd and Pt catalysts were similar to the conversion achieved with the sulfided CoMo/Al₂O₃ catalyst (13.8%), and complete conversion of GUA was obtained with the monometallic Rh catalyst. However, the combination of Pd or Pt with Rh improved the GUA conversion from values around 10% for the monometallic catalysts to 32.7% on the RhPd and 98.7% on the RhPt catalyst. The products at 100 °C were predominantly hydrogenated oxygen-containing compounds with all catalysts tested. In the experiments at 300 °C, all the noble metal catalysts gave complete or almost complete conversion of GUA and the deoxygenation of GUA was catalyzed. The main product was benzene, and also small amounts of cyclohexanol. Rh-containing catalysts give good HDO performance.

Yakovlev *et al.* (2009) also developed non-noble and non-sulfided catalysts for upgraded biodiesel production via oxy-organic hydrodeoxygenation (HDO) processes. They used biodiesel produced from the rapeseed oil (mainly C18 ester) as the initial oxygen-containing substrates for studies of the HDO processes. The catalysts that were investigated in this work were Ni-based catalysts on ZrO₂, CeO₂, and CeO₂-ZrO₂ supports. The single Ni catalysts contained 38 wt.% of nickel, whereas Ni-Cu catalysts had total 38 wt.% of Ni and Cu with the Ni:Cu molar ratio equal to 3:1. The results showed that Ni-Cu catalysts are more attractive than single Ni catalysts in HDO under mild conditions. High content of light hydrocarbons C6-C12 was gained from single Ni catalyst but the copper addition to the catalyst prevented the formation of light products and led to the heptadecane formation as a main product. According to the results, heptadecane was obtained as the main product, therefore they can conclude that the HDO of biodiesel proceeds via decarboxylation (DCO) reaction. Furthermore, copper that was added to the single Ni catalysts helps reduce the reduction temperature of nickel oxide lower than 300°C and it also prevents methanization of oxy-organics at 280–350 °C. Additionally, they also studied the effect of the reaction temperature. The results showed that hydrocracking process increases with temperature, leading to declining of heptadecane yield. Analysis of the products reveals that the hydrocracking of hydrocarbons chain takes place predominantly by the end -CH₂- group removal.