



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Theoretical Background

2.1.1. Biodiesel

Biodiesel or technically so called “mono-alkyl ester” is a renewable fuel that can be used instead of diesel fuel derived from petroleum. There are a number of options for biodiesel feedstock which can be vegetable oils, animal fats or even used cooking oils. Among the vegetable oils, sources are soybean, canola, palm, and rape. Animal fats are products of rendering operations. They include beef tallow, lard, poultry fat, and fish oils. Biodiesel usually blend with petroleum-based diesel in concentration of 2 percent (B2), 5 percent (B5), or 20 percent (B20). It can also be used as pure biodiesel (B100).

The advantages of biodiesel over petroleum-based diesel is renewable, simple to use, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Contribute to reduce serious air pollutants such as particulates, carbon monoxide, hydrocarbons, and other toxic matters.

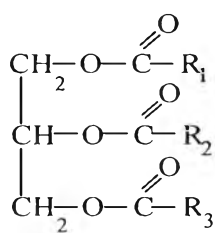
2.1.1.1 Feedstocks Used in Biodiesel Production:

Although biodiesel can be produced from any triglyceride, the popular fats and oils most commonly used worldwide are:

The predominant feedstock used is soybean oil. Other vegetable oils, such as corn, cottonseed, canola (rape seed), flax, sunflower and peanut, also can be used. These seed oils are generally more expensive than soybean oil.

Animal-derived products such as tallow, choice white grease (lard), poultry fat and yellow grease are also triglycerides and are used as biodiesel feedstocks. 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 oxides compared to plant-derived oils.

The third main source of triglycerides is recycled oil and grease, usually from restaurants and food processing plants. Although more pre-treatment is required for this feedstock compared to virgin vegetable oils, economically it can be a very attractive feedstock. The use of a recycled product such as used cooking oil is an environmentally friendly process since it solves a waste disposal problem.



Triglyceride

Figure 2.1 A Chemical structure of triglyceride.

2.1.2 Biodiesel Production

The production of biodiesel from renewable sources is generally done via a chemical reaction called transesterification. However, it can as well be done via the deoxygenation reaction.

2.1.2.1 Transesterification of Triglyceride

Most of the biodiesel produced today is done with the base catalyzed reaction because it require low temperature and pressure, can yields high conversion (98%) with minimal side reactions and reaction time, and is a direct conversion to biodiesel with no intermediate compounds.

In transesterification, one hundred pounds of fat or oil (such as soybean oil) are reacted with 10 pounds of a short chain alcohol in the presence of a catalyst to produce 10 pounds of glycerin and 100 pounds of biodiesel or stoichiometrically, one part vegetable oil with three parts methanol gives three parts methyl esters (biodiesel) and one part glycerin. In this process, the short chain alcohol like methanol, but sometimes ethanol is used by the reason of reactivity. To drive the equilibrium of reaction, alcohol is charged in excess amount usually 6 moles of alcohol are used for every mole of triglyceride. The catalyst is usually strong mineral bases such as sodium hydroxide (NaOH) and potassium hydroxide

(KOH) that has already been mixed with the methanol in order to promote the solubility alcohols via forming alkoxide species which make the reaction proceed at a reasonable rate. R_1 , R_2 , and R_3 indicate the fatty acid chains associated with the oil or fat which are largely palmitic, stearic, oleic, and linoleic acids for naturally occurring oils and fats. The formation of alkoxide species and the typical transesterification process is shown in Figure 2.2 and Figure 2.3, respectively.

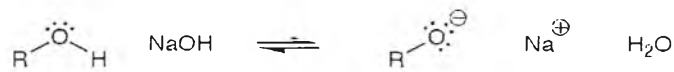


Figure 2.2 Alkoxide formation by base catalyze.

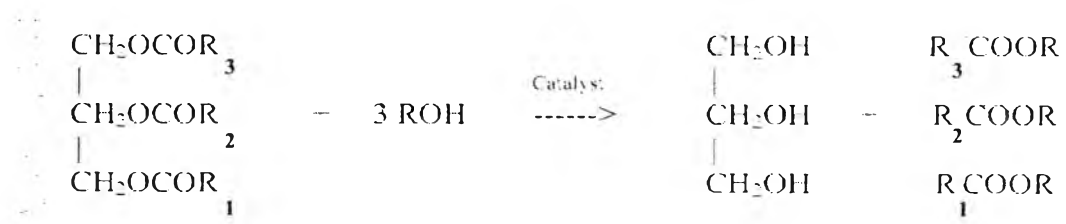


Figure 2.3 Chemical reaction of biodiesel production via transesterification of triglyceride.

During transesterification, Three main steps which can be reversible are believed to occur. In the first step, a triglyceride can be shown to react with methanol to produce diglycerides, the diglycerides react with another methanol molecule to produce monoglycerides and then these react with a third methanol molecule to produce glycerol, as illustrated in Figure 2.4

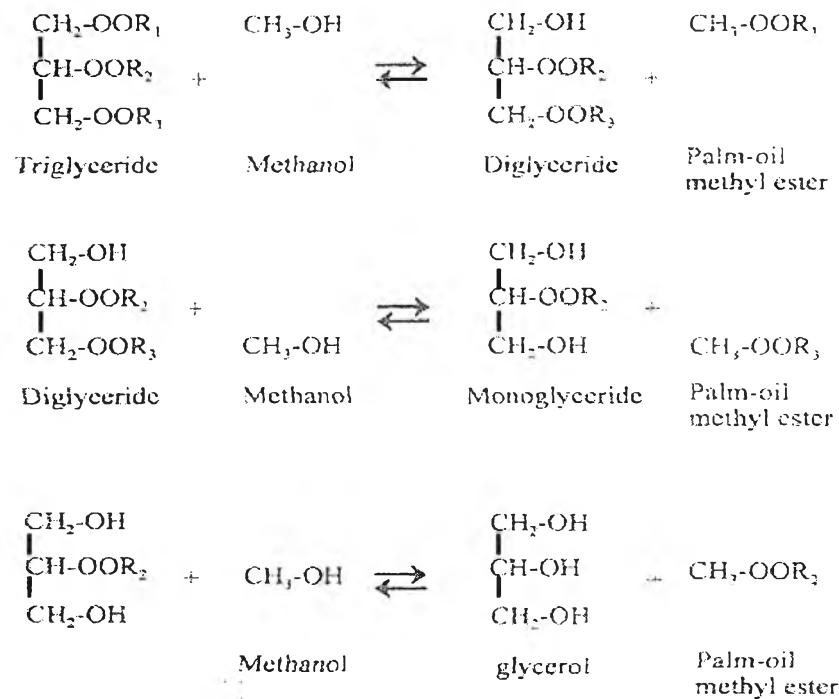


Figure 2.4 Transesterification of triglyceride.

An example of basic schemes for biodiesel production is depicted below.

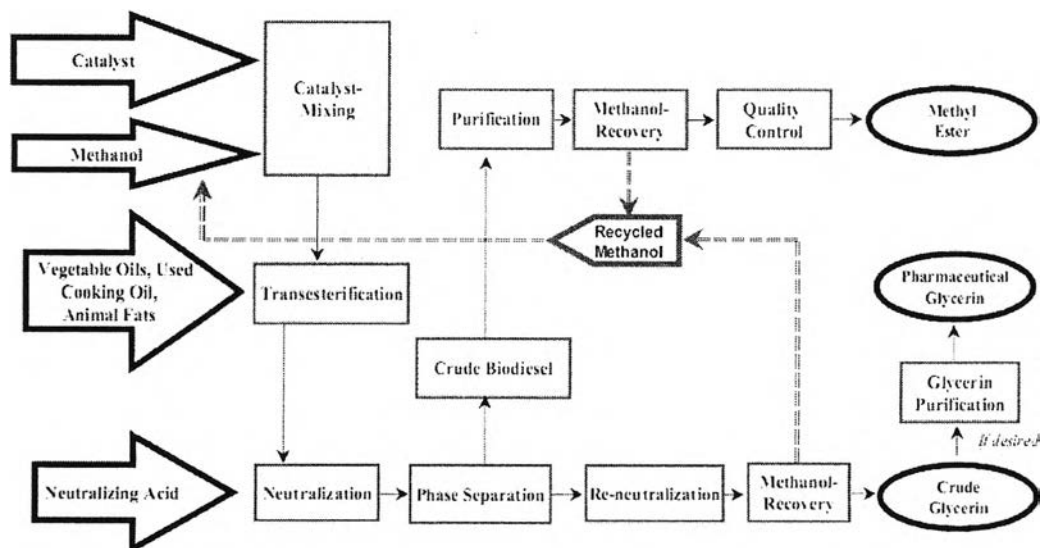


Figure 2.5 Process flow diagram of biodiesel production.

Biodiesel can be produced via either batch or continuous process. Figure 1.6 shows a process flow diagram for a typical batch system. The oil is first charged to the system, followed by the mixture of catalyst and methanol. The system is agitated during the reaction time. Then agitation is stopped. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge. The alcohol is removed from both the glycerol and ester stream using an evaporator or a flash unit. The esters will be washed and neutralized using warm, slightly acid water to remove residual methanol and salts, and then dried. The finished biodiesel is then transferred to storage. The glycerol stream is neutralized and washed with soft water. The glycerol is then sent to the glycerol refining section.

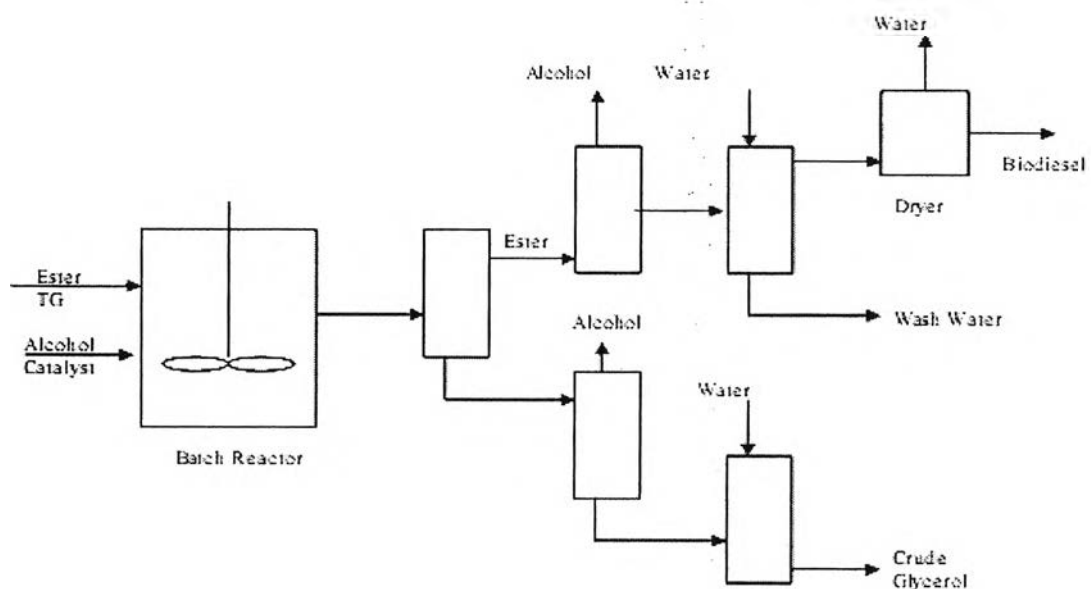


Figure 2.6 Batch reaction process for biodiesel production.

For continuous process, the plug-flow reactor (PFR) is usually used in order to achieve rather short residence times, as low as 6 to 10 minutes, for near completion of the reaction. The PFRs can be staged, as shown, to allow decanting of glycerol. Often this type of reactor is operated at an elevated temperature and pressure to increase reaction rate. A PFR system is shown in Figure 1.7

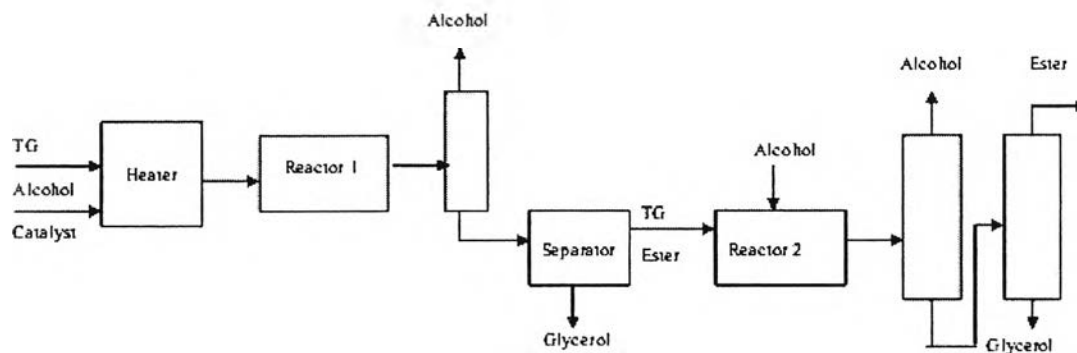


Figure 2.7 Plug flow reaction process for biodiesel production.

2.1.2.2 Deoxygenation of Fatty Acid

Diesel fuel can be produced via 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 deoxygenation reaction may be carried out in the presence of homogeneous or heterogeneous catalysts under controlled hydroprocessing conditions, known as hydrotreating or hydrocracking processes.

There are several possible reaction pathways for a production of straight-chain hydrocarbons, shown as Fig. 2.8. Fatty acids can be directly decarboxylated or decarbonylated. Direct decarboxylation removes the undesired oxygen by releasing carbon dioxide and producing aliphatic hydrocarbon chains with one carbon atom less than in the original feed, while 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 reactions III. (Murzin D.Yu. *et al.*, 2006)

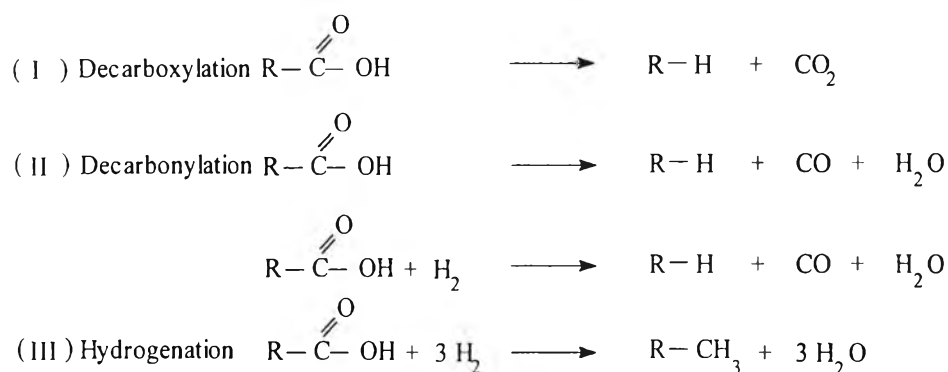


Figure 2.8 The possible liquid-phase reaction pathways for production of straight chain hydrocarbons from fatty acids.

In addition to the liquid-phase reactions, the water gas shift and methanation reaction are occurred 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 CO₂, while methanation reaction of fatty acids gives methane and water.

<i>Gas phase reactions</i>					$\frac{\Delta G_{573}}{(\text{kJ/mol})}$	$\frac{\Delta H_{573}}{(\text{kJ/mol})}$			
V. Methanation:	CO ₂	+	4H ₂	\rightleftharpoons	CH ₄	+	2H ₂ O	-61.2	-177.2
VI. Methanation:	CO	+	3H ₂	\rightleftharpoons	CH ₄	+	H ₂ O	-78.8	-216.4
VII. Water-gas-shift	CO	+	H ₂ O	\rightleftharpoons	H ₂	+	CO ₂	-17.6	-39.2

Figure 2.9 Gas phase reactions of CO or CO₂ with H₂ or H₂O (thermodynamic data for gas phase reaction are provided at 300 °C).

2.2 Literature Reviews

At the present, there are many researchers give more attention on hydrodeoxygenation of biomass-derived feedstock than the past due to its superior performance in cetane number and others property. But the exactly mechanism pathways of this reaction is still discussing.

Pestman *et al.*, (1995) studied relationship between structure and activity on the competitive formation of ketones and aldehydes from carboxylic acids by using oxide of iron, vanadium, and titanium as catalysts. Four carboxylic acids which have a different number of α -hydrogen atoms ranging from zero to three, which are pivalic, isobutyric, propionic, and acetic acid were tested in this study. The results obtained from all four catalysts showed similar trends, the selectivity toward aldehyde increases while ketone production is suppressed by decreasing the number of α -hydrogen atoms in the acid. In addition, the formation of ketone completely disappears when no α -hydrogen is present in the acid. There are 2 possible explanations for this phenomenon. First, there is no α -hydrogen atom which is an important in the formation of ketene, an intermediate in the reaction to ketone. Another explanation is effect of steric hindrance, the bulky methyl groups can obstruct the coupling of two acids to ketone by hinder the abstraction of the α -hydrogen atom on the surface. In order to observe effect of ketene on acetone production, the experiments was performed on acetic acid by varying the contact time. And the obtained data revealed that increasing of contact time suppress the production of ketene, while the production of acetone is favored. This indicates that ketene is a potential intermediate in the reaction to acetone under low pressure conditions. They also proposed the mechanism for ketonisation in the case of acetic acid. Carboxylic acid is adsorbed horizontally on the catalyst surface to form a carboxylate after that α -hydrogen atom will be abstracted from the carboxylate. With this orientation, a C unit can easily be split off, either from I₁ or I₂, then coupling with neighboring carboxylate to form acetone.

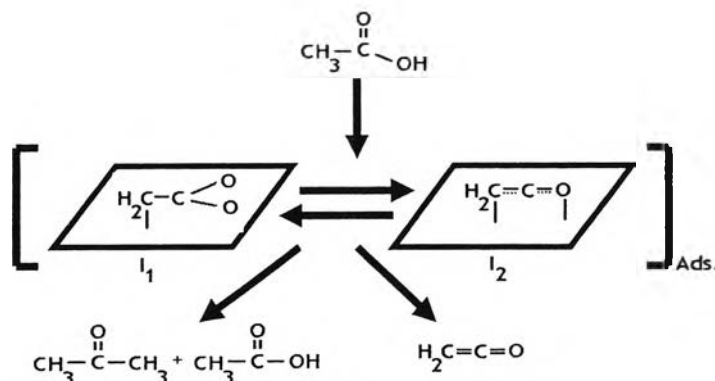


Figure 2.10 Formation of ketone and aldehydes from acetic acids.

In 1996, Deckers *et al.* prepared green catalyst, containing 25% to 50% by weight of (metallic) nickel, 10% to 35% by weight of nickel oxide, 4% to 12% by weight of magnesium oxide, 1% to 5% by weight of sodium oxide, and the rest is support material. They claim that this green catalyst is very useful for hydrogenation of propanal, n-butanal, and i-butanal, preferably at 110-160°C. The reaction can be carried out with simultaneous generation of steam under pressure to improve the economics of the process. With the selectivity greater than 99.5%, usually greater than 99.9%; about 0.01% of the aldehyde used remains in the final product. Less than 0.1% of the aldehyde is converted into carbon monoxide, ethers, acetals, and esters. For hydrogenation of propanal, the product comprises about 99.9% by weight of n-propanol and less than 0.1% by weight of unconverted propanal. By-products determined are less than 100 ppm of 2-methylpentan-3-one and less than 20 ppm of di-n-propyl ether.

In 2000, Van Druten *et al.* studied the hydrogenation of aldehydes and ketones using propanal and acetone as model for reactions to investigate the competitive hydrogenation over noble metal catalysts including Pt, Pt-Ga, Pd, and Rh, the reaction was performed at 100°C, 1000 psig for all sets of experiment. The results over 1wt% 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 lowering the conversion of acetone over Pd implied that propanal can inhibit

hydrogenation of acetone by adsorbed more strongly than acetone and this makes reactivity of propanal slower than that of acetone. Whereas, the addition of acetone does not influence significantly on hydrogenation of propanal but it can be converted to form 2-propanol, diisopropylether, and also 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 different in catalytic behavior of Pd compared with other platinum metals is usually explained by the formation of π -allyl complex of carbonyl compounds with Pd (Tanaka K., 1986).

Wang *et al.* also examined the active sites over reduced Ni-Mo/Al₂O₃ catalysts for hydrogenation of linear aldehydes. The characterization results revealed that the reduced Ni-Mo/Al₂O₃ catalysts exhibit a behavior comparable to that of sulfided Ni-Mo/Al₂O₃ catalysts in hydrogenation of linear aldehydes to alcohols. Similar to what has been previously reported. For sulfided catalysts, NO and CO₂ can be used over the reduced Ni-Mo catalysts as probe molecules for the active sites responsible for two competing reactions which are aldehyde hydrogenation to alcohols and condensation reactions to heavy products, respectively. Reduced catalysts have a higher aldehyde conversion activity and alcohol selectivity than their sulfided counterparts. The reduction temperature has a strong effect on the surface density of anion vacancies, which are responsible for alcohol formation. Reduction temperature also plays a role in determining the abundance of OH groups on the alumina surface. The effect of reduction temperature also manifests itself through the differences seen in the oxidation states of Mo and Ni species.

Ding *et al.* used a series of NiMo catalyst with different acidity supports which are NiMo/Al₂O₃, NiMo/Si-Al(10), NiMo/Beta(5), NiMo/Beta(10), NiMo/Beta(20), and NiMo/Y(10) to study performance of hydrogenation and hydrocracking reactions on the model compounds; 4,6-dimethyl dibenzothiophene (4,6-DMDBT), 1-methyl naphthalene, pyridine, and hexadecane. The results from catalyst characterizations showed that the distributions Mo species on surface are closely associated with the surface silica species distributions. The larger MoS₂ crystallines are preferably formed on Si-rich surfaces. During sulfidation, Mo and Ni

species tend to migrate into bulk, and more Mo species than Ni species were migrated which consistent with studied done by Wang *et al.*, (2005).

The effect of pre-treatment conditions both sulfidation temperatures and post-treatment degassing temperatures on the performance of sulfided Ni-Mo / γ -Al₂O₃ was performed by Wang *et al.*, (2005). The propanal hydrogenation was carried out in a fixed-bed flow reactor with 1/4 inch i.d. The amount of prepared 3% Ni -15% Mo/ γ -Al₂O₃ loaded into the reactor corresponded to a total surface area of 25 m². Reaction temperatures were in the range of 140–180°C and pressure was kept at 1000 psig. The effect of sulfidation temperatures was investigate by varying sulfidation temperatures from 300-600°C at all three reaction temperatures used 140, 160, and 180°C. The results revealed that catalyst sulfided at 300°C shows relatively low activity because sulfidation in not yet complete at this temperature. While increasing sulfidation temperature, both the conversion and the propanol yield substantially increase and achieve the plateau between 400 and 500°C, due to a highest the co-ordinatively unsaturated sites (CUS) which considered as the active sites for hydrogenation reaction. In addition, the yield of heavy product also increases, which promoted by OH groups on the exposed alumina surface, since the MoS₂ slabs are formed during the sulfidation contribute to an increase in exposed alumina surface. But Furthers increases in sulfidation temperatures, the catalyst will lost its activity since some active sites are lost due to sulfate formation confirmed by XPS analysis. Effect of post-sulfidation degassing temperatures had investigated by varying post-sulfidation degassing temperatures from 400-700°C at all three reaction temperatures used. From the obtained results, the improved performance observed as the degassing temperature is increased from 400 to 500°C as increases in propanol yield and decreases in heavy product yield which likely due to an increase in anion vacancies accompanied by a decrease in hydroxyl and sulfydyl groups on the surface. At higher degassing temperatures, 600-700°C lead to lowering in both activity and propanol yield due to increasing of growth in crystallite sizes. But do not affect much to the heavy product yield.

Senol *et al.* studied the influence of sulphiding agents which are H₂S and CS₂ on the hydrodeoxygenation (HDO) of aliphatic esters on NiMoS/ γ -Al₂O₃. The experiments was performed isothermally at 250°C under 1.5 MPa. The mixture of 5

vol% H₂S/H₂ and H₂ were feed simultaneously to the reactor by at various flow rates to obtain 140, 500, 1000, and 24000 ppm. Results indicate the promoting effect of H₂S on the reactions of the aliphatic oxygenates on the sulphided catalysts by the enhancement of total and HDO conversions and stabilized selectivities as a function of time in the presence of H₂S. For example, addition of 1000 ppm H₂S can enhance the HDO conversion of methyl heptanoate and ethyl heptanoate from 67 to 76% and 63 to 83%, respectively. Similarly, the H₂S also improved the HDO conversion of heptanol and heptanoic acid. For product distribution analysis of the outlet stream revealed the formation of carbon oxides (CO₂ and CO) in the reactions of the esters and the acid. In addition, methane and ethane were detected in the reactions of methyl heptanoate and ethyl heptanoate, respectively. But no gaseous product was found in the reactions of heptanol. Moreover, H₂S shifted the main products of the esters and the acids from C₇ to C₆ hydrocarbons, and the yields of C₆ hydrocarbons increased, led to an increase in the formation of carbon oxides (CO and CO₂). They also indicated that sulfiding agents considered to increase the acidity of sulfided catalysts through increasing of Brønsted acid sites, e.g. SH⁻ and H⁺ groups at the surface of the sulfided catalysts by dissociative adsorption of H₂S on sulfur anion vacancies or coordinatively unsaturated site in the MoS₂ phase, generally known as Lewis acid sites which are active sites for hydrogenation and carbon-heteroatom bond scission. Moreover, they had proposed that the aliphatic methyl esters are converted to hydrocarbons via three paths as shown in Figure 2.1. 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 alkanes formed from methyl heptanoate is n-heptane and from methyl hexanoate is n-hexane under all conditions.

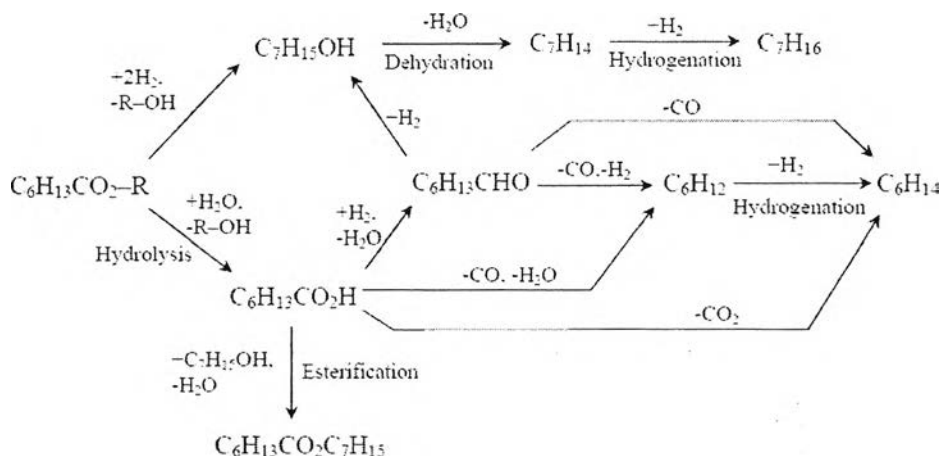


Figure 2.11 The hydrodeoxygenation reaction scheme of aliphatic methyl esters ($n=6$) for methyl heptanoate and $n=5$ for methyl hexanoate).

Since, The effect of water formed during hydrotreating of oxygen-containing feeds has been found to affect the performance of sulfided NiMo/ γ -Al₂O₃. They also conducted the experiments to investigate effect of water on the activity of sulfided NiMo/ γ -Al₂O₃ catalysts in hydrodeoxygenation (HDO) of aliphatic esters in a tubular reactor by varying the amount of water in the feed. The results showed that the total yield of the C₇ and C₆ hydrocarbons decreased with the amount of added water, while the concentrations of the oxygen-containing intermediates increased. The presence of H₂S improved the total hydrocarbon yield and shifted the main products towards the C₆ hydrocarbons. Thus, the addition of H₂S effectively compensated the inhibition by water.

Hydrotreating of pure sunflower oil were performed in a fixed bed reactor with a sulfided NiMo/ γ -Al₂O₃ catalyst. The reaction were done at temperature ranging from 300 to 450°C, pressure of 50 bar, LHSV 4.97 h⁻¹ and H₂ to feed ratio of 1600 ml H₂ /ml liquid feed. The gas inlet was 91% H₂ with the balance being Ar. The products obtained were analyzed by GC. It was found that the fraction distilled 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 involves hydrogenation of the C=C

bonds of the vegetable oils followed by alkane production by three different pathways: decarbonylation, decarboxylation and hydrodeoxygenation as shown in Figure 2.12. 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 the decarbonylation, decarboxylation and hydrodeoxygenation pathways. (Avelino Corma *et al.*, 2007).

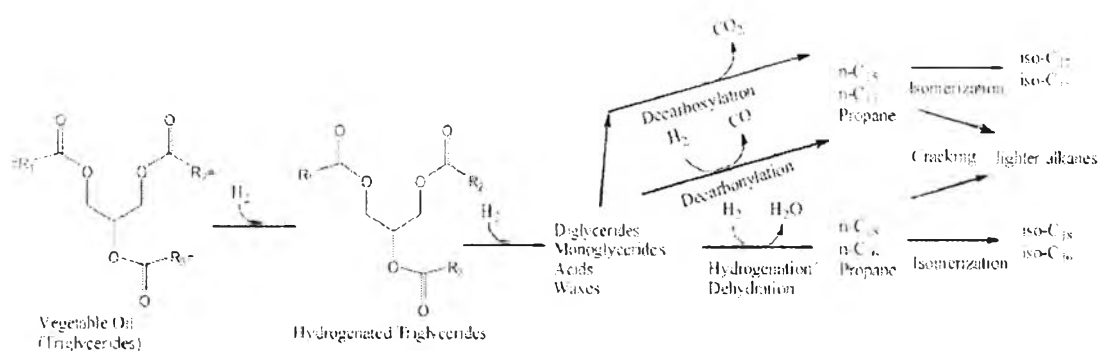


Figure 2.12 The reaction pathway for conversion of triglycerides to alkanes.

Catalytic deoxygenation including decarboxylation/decarbonylation of ethyl stearate over Pd supported on active carbons in a semi-batch reactor under a nitrogen atmosphere has been investigated by Murzin *et al.*, (2007). Three different types of 5wt% Pd on active carbon which are Pd/C (Aldrich), Pd/C (Degussa), and Pd/C (BAC) were used. The results shown that the initial reaction rates of ethyl stearate increased with an increasing pH of the catalyst slurry (see Table 2.1); i.e., alkalinity in the catalyst enhanced the initial reaction rate. In the study, Pd/C (Aldrich) which was the most alkaline Pd/C catalyst shows the highest yields of *n*-heptadecane product of ethyl stearate decarboxylation. However, the drawback in using an alkaline Pd/C catalyst was a substantial formation of aromatic side products. In addition, they also observed that over the most acidic catalyst, Pd/C (BAC), the main product was stearic acid and only trace amounts of aromatic side products were formed.

Table 2.1 Catalyst characterization results of catalysts in experiment

catalyst	BET-specific Surface area of the catalyst (m ² /g _{cat})	pH of the catalyst slurry	initial rate (mmol min ⁻¹ g ^{cat} -1)
Pd/C (Aldrich)	1126	10.2	0.411
Pd/C (Degussa)	715	7.2	0.115
Pd/C (BAC)	826	5.9	0.0948

Corma *et al.*, (2008) found that two molecules of carboxylic acid can transform into symmetrical ketones by coupling reaction or so called ketonic decarboxylation. For this kind of reaction, Two carboxylic acid are condensed, leads to the formation of symmetrical ketones with 2n-1 carbon atoms while one molecule of water and one molecule of CO₂ were produced as the by product (Figure 2.13). Furthermore, fatty ketones or their derivatives can also make excellent premium diesel and lubricants. The experiments of lauric acid were done over basic magnesium oxide catalyst in a fixed-bed continuous reactor. The result revealed that, complete conversion was achieved in less than one hour of contact time at 400°C. At 95% conversion, the desired ketone, laurone (C₁₁H₂₃COC₁₁H₂₃) was obtained with excellent selectivity (97 %). However, in order to make the premium diesel and lubricant, which consider as a valuable product, catalyst should able to perform hydrogenation of ketone group to alcohol followed by elimination of water and further hydrogenation to remove all the oxygen from the molecule to yield an alkane.

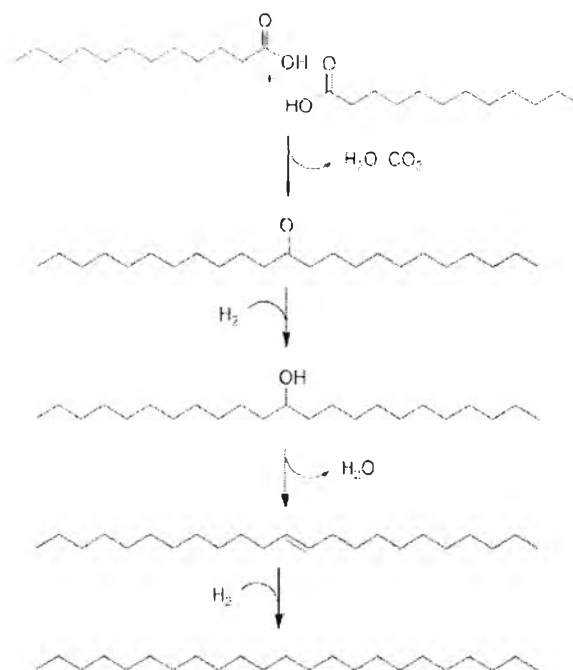


Figure 2.13 Formation of triocane from two molecules of lauric acid by ketonic decarboxylation with subsequent hydrogenation of the carbonyl group, the elimination of water, and hydrogenation of the olefin.