CHAPTER II
LITERATURE REVIEW

2.1 Diesel Fuel

Diesel fuel refers to a liquid fuel which is appropriate for compression ignition engines or diesel engines. Generally, diesel fuel is mainly referred to petroleum-based diesel but alternative non-petroleum-based diesel is increasingly being developed and adopted. Non-petroleum-based diesel refers to synthetic diesel, biodiesel and renewable diesel.

Synthetic diesel is diesel fuel that made by processing natural gas through a technology called the Fischer-Tropsch process, which converts the natural gas into Synthetic Diesel or gas-to-liquid (GTL). Synthetic diesel may also be produced out of biomass in the biomass-to-liquids (BTL) process or out of coal in the coal-to-liquid (CTL) process. Synthetic diesel has 30% lower particulate emissions than conventional diesel (US- California).

Biodiesel refers to any diesel-equivalent biofuel derived from vegetable oils or animal fats and other biomass-derived oils. Normally, biodiesel is defined as mono-alkyl ester. However, alkane (non-oxygenate) biodiesel is also available. The bio-based diesel-like hydrocarbon is called renewable diesel, green biodiesel or hydrogenated biodiesel.

In this section, the basic overviews of petroleum-based diesel and the more detail of bio-based diesel, biodiesel and renewable diesel which related to this work, in term of chemical reaction, processing condition and production process are described.

2.2 Petroleum-based Diesel

Petroleum diesel, also called petrodiesel or fossil diesel is produced from the fractional distillation of crude oil between 200 °C (392 °F) and 350 °C (662 °F) at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule. Normally, it is composed of about

75% saturated hydrocarbons (primarily paraffins including *n*-, *iso*-, and cycloparaffins), 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.

2.2.1 ASTM Specifications for Diesel Fuel Oils (D 975)

Diesel fuel is characterized in the United States by the ASTM standard D 975. This standard currently identifies five grades of diesel fuel as described below.

Grade No. 1-D and Low Sulfur 1-D (LS 1-D): A light distillate fuel for applications requiring a higher volatility fuel for rapidly fluctuating loads and speeds as in light trucks and buses. Low sulfur fuel is required for on-highway use with sulfur level < 15 ppm.

Grade No. 2-D and Low Sulfur 2-D (LS 2-D): A middle distillate fuel for applications that do not require a high volatility fuel. Typical applications are high-speed engines that operate for sustained periods at high load. Low sulfur fuel is required for on-highway use with sulfur level < 15 ppm.

Grade No. 4-D: A heavy distillate fuel that is viscous and may require fuel heating for proper atomization of the fuel. It is used primarily in low and medium speed engines.

ASTM D 975 specifies the property values shown in Table 2.1 for these grades of diesel fuel. It defines the property values needed to provide acceptable engine operation and safe storage and transportation (Tyson *et al.*, 2006).

Table 2.1 Requirement for diesel fuel oils (ASTM D 975)

Property	**Grade LS 1-D**	**Grade LS 2-D**	**Grade No. 1-D**	**Grade No. 2-D**	**Grade No. 4-D**
Flash point °C, min	38	52	38	52	55
Water and sediment, % vol, max.	0.05	0.05	0.05	0.05	0.50
Distillation temp. ,°C, 90%					
Min	--	282	--	282	--
Max	288	338	288	338	--
Kinematic Viscosity, mm^2/s at 40°C					
Min.	1.3	1.9	1.3	1.9	5.5
Max.	2.4	4.1	2.4	4.1	24.0
Rams bottom carbon residue on 10%, %mass, max	0.15	0.35	0.15	0.35	--
Ash, % mass, max	0.01	0.01	0.01	0.01	0.10
Sulfur, % mass, max	15 ppm	15 ppm	0.50	0.50	2.00
Copper strip corrosion,					
Max 3 hours at 50 °C	No. 3	No. 3	No. 3	No. 3	--
Cetane Number, min	40	40	40	40	30
One of the following Properties must be met:					
(1) Cetane index	40	40	--	--	--
(2) Aromaticity, % vol, max	35	35	--	--	--
Cloud point, °C, max	Determined by local climate Should be 6°C higher than the tenth percentile minimum ambient temperature for the region.				

2.2.2 Important Characteristics of Diesel Fuels

The essential characteristics of diesel fuels and requirement for diesel fuel and biodiesel in Thailand will be described in the following paragraphs and Table 2.1 respectively.

2.2.2.1 Cold Flow Properties

Operators of diesel equipment are well aware of the tendency of diesel fuel to gel or solidify at low temperatures. Some of the long chain hydrocarbons in number 2 diesel fuel, known as waxes, will usually start to develop crystals at around –9.4° C (15° F). If allowed to agglomerate, these crystals will grow large enough to plug fuel filters and fuel lines.

a) Cloud Point

The cloud point is the temperature at which a cloud of wax crystals first appears in a fuel sample that is cooled under conditions described by ASTM D 2500.

b) Pour Point

The pour point 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 D 97.

The cloud point is the highest temperature used for characterizing cold flow and the pour point is the lowest.

2.2.2.2 Volatility

a) Distillation Curve (ASTM D 86)

The distillation curve is determined by relating the fraction of a fuel sample that is removed by heating a fuel sample to progressively higher temperatures. Typically, the curve is characterized by the initial point, the temperature at which the first drop of liquid leaves the condenser, the temperatures at each 10% of the liquid, and the end point. Since diesel fuel consists of hundreds of different compounds, a distillation curve provides important information about the composition of the fuel.

b) Flash Point (ASTM D 93)

The flash point is the lowest temperature at which a combustible mixture can be formed above the liquid fuel. It depends on both the lean flammability limit of the fuel as well as the vapor pressure of the fuel constituents. The flash need not corresponds 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.

2.2.2.3 Ignition Indices

One of the most important properties of a diesel fuel is its readiness to auto ignite at the temperatures and pressures present in the cylinder when the fuel is injected. The *cetane number* is the standard measure of this property. The *cetane index* is derived from correlation equations based on large numbers of cetane number tests. These quantities are described below.

a) Cetane Number

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 fuels are n-cetane (n-hexadecane), which has a cetane number of 100 and heptamethylnonane (HMN), which has a cetane number of 15. When the ignition delay is restored to 13 degrees, the cetane number is computed from the following relationship:

$$\text{Cetane Number} = \%\ \text{n-cetane} + 0.15\ (\%\text{HMN})$$

b) Cetane Index

The cetane index is a calculated quantity that is intended to approximate the cetane number. It is much cheaper to determine than the engine-based cetane number but its accuracy is limited to the type of fuel on which it is based. It generally does not provide an accurate indication of cetane number if the fuel contains cetane-improving additives or for non-petroleum-based alternative fuels. Two methods are available for computing the Cetane Index.

ASTM standard D 976 gives the following empirical equation for the Cetane Index:

$$\text{Cetane Index} = 454.74 - 1641.416\,D + 774.74\,D^2 - 0.554\,T_{50} + 97.803[\log_{10}(T_{50})]^2$$

where D = fuel density at 15°C in g/ml.

T_{50} = the temperature corresponding to the 50% point on the distillation curve in degrees C.

2.3 Bio-based Diesel

Biodiesel is defined as any diesel-equivalent biofuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and other biomass-derived oils that meets the fuel specification requirements of the American Society of Testing and Materials (ASTM) D6751. In an article on proposed ASTM standards, biodiesel was defined as “the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines.” Biodiesel can be used as a pure fuel (B100). Moreover, it can be blended with the conventional diesel. 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.

Renewable diesel is defined in the Internal Revenue Code (IRC) as diesel fuel produced from biological material using a process called “thermal depolymerization” that meets the registration requirements for fuels and fuel additives established by the Environmental Protection Agency (EPA) under section 211 of the Clean Air Act (42 U.S.C. 7545); and meets the requirements of the American Society of Testing and Materials (ASTM) D975 (petroleum diesel fuel) or D396 (home heating oil). Normally, renewable diesel is referred to hydrocarbons that do not contain oxygen in their molecular structure.

Thermal depolymerization is a process for the reduction of complex organic materials through the use of pressure and heat to decompose long-chain polymers of hydrogen, oxygen, and carbon into short-chain hydrocarbons with a maximum length of around 18 carbon atoms. A process may qualify as thermal depolymerization even if catalysts are used in the process.

Vegetable oils and animal fats are considered as raw materials for biodiesel and renewable diesel production because they are broadly available from a variety of sources, and they are renewable. The example of vegetable oils use for production are palm oil, sunflower oil, corn oil, coconut oil, jatropha oil, olive oil, canola oil, cottonseed oil, castor oil, soybean oil, etc. As well as animal fats, include Beef oil Lard, Chicken oil, recycled cooking oil, 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.

Both oils and fats are composed 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. The chemical structure of a triglyceride is shown in Figure 2.1 where R^{I}, R^{II}, and R^{III}, which may be the same or different, represent long chain fatty acids which are mostly palmitic, stearic, oleic, linoleic, and linolenic acids.

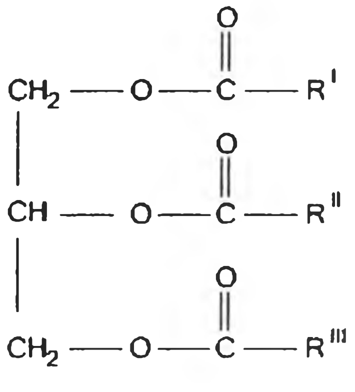

Figure 2.1 A chemical structure of triglyceride.

Some physical properties of the most common fatty acids occurring in vegetable oils and animal fats are listed in Table 2.2. Besides these fatty acids, numerous other fatty acids occur in vegetable oils and animal fats, but their abundance usually is considerably lower. Table 2.3 summarizes the fatty acid composition of some vegetable oils. The fatty acids which are commonly found in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic acids. Vegetable oils contain free fatty acids (generally 1 to 5%), phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds and traces of water. Table 2.4 shows fatty acid concentrations in subcutaneous adipose tissue of steers and cows produced in the U.S.,Australian crossbred cattle, Japanese Black steers, and Hanwoo steers fed under different production conditions. This table shows that beef oil mainly contains monosaturated oleic acid (C18:1).The fatty acid compostions of some other edible fats and oils are summarized in Table 2.5.

Table 2.2 Selected properties of some common fatty acids (Knothe *et al.*, 1997)

Trivial (Systematic) name[a] ; Acronym[b]	**Mol. wt.**	**m.p. (°C)**	**b.p.[c] (°C)**	**Formula**	**Heat of Combustion (kg-cal/mole)**
Caprylic acid (Octanoic acid); 8:0	144.22	16.5	239.3	$C_8H_{16}O_2$	-
Capric acid (Decanoic acid); 10:0	172.27	31.5	270	$C_{10}H_{20}O_2$	1453.07 (25°)
Lauric acid (Dodecanoic acid); 12:0	200.32	44	131^{1}	$C_{12}H_{24}O_2$	1763.25 (25°)
Myristic acid (Tetradecanoic acid); 14:0	228.38	58	250.5^{100}	$C_{14}H_{28}O_2$	2073.91 (25°)
Palmitic acid (Hexadecanoic acid); 16:0	256.43	63	350	$C_{16}H_{32}O_2$	2384.76 (25°)
Stearic acid (Octadecanoic acid); 18:0	284.48	71	360d	$C_{18}H_{36}O_2$	2696.12 (25°)
Oleic acid (9Z-Octadecenoic acid); 18:1	282.47	16	286^{100}	$C_{18}H_{34}O_2$	2657.4 (25°)
Linoleic acid (9Z,12Z-Octadecadienoic acid); 18:2	280.45	-5	$229\text{-}30^{16}$	$C_{18}H_{32}O_2$	-
Linolenic acid (9Z,12Z,15Z-Octadecatrienoic acid);18:3	278.44	-11	$230\text{-}2^{17}$	$C_{18}H_{30}O_2$	-
Erucic acid (13Z-Docosenoic acid);22:1	338.58	33-4	265^{15}	$C_{22}H_{42}O_2$	-

a) Z denotes cis configuration.

b) The numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.

c) Superscripts in boiling point column denote pressure (mm Hg) at which the boiling point was determined.

Table 2.3 Fatty acid composition in vegetable oils (Fangrui *et al.*, 1999)

Vegetable Oil	**Fatty Acid Composition (wt. %)**								
	14:0	**16:0**	**18:0**	**20:0**	**22:0**	**24:0**	**18:1**	**18:2**	**18:3**
Corn	-	11.67	1.85	0.24	-	-	25.16	60.60	0.48
Cottonseed	0.70	28.33	0.89	-	-	-	13.27	57.51	-
Peanut	-	11.38	2.39	1.32	2.52	1.23	48.28	31.95	0.93
Rapeseed	-	3.49	0.85	-	-	-	64.40	22.30	8.23
Soybean	0.10	11.75	3.15	-	-	-	23.26	55.53	6.31
Sunflower	-	6.08	3.26	-	-	-	16.93	73.73	-
Palm	1.00	42.8	4.50	-	-	-	40.50	10.10	0.20
Jatropha	0.06	13.81	6.89	0.22	0.04	0.05	45.84	31.77	0.21

Table 2.4 Fatty acid concentrations in subcutaneous adipose tissue of steers and cows produced in the U.S., Australian crossbred cattle, Japanese Black steers, and Hanwoo steers fed under different production conditions (Smith *et al.*, 2009)

Item	**Cattle group/dieta (g/100 g total fatty acids)**					
	Brahman	**Hereford**	**Angus**	**Australian J.**	**Black**	**Hanwoo**
Age (months)	54	54	16	22	27	28
14:0	4.3	4.0	3.0	1.5	1.3	3.2
14:1n-5	3.2	2.4	1.1	0.1	1.3	1.0
16:0	22.7	26.0	27.4	24.2	24.2	27.9
16:1n-7	10.7	9.4	5.6	1.6	5.2	4.6
18:0	7.6	8.9	8.8	26.1	7.6	9.6
18:1*trans*-11			1.6	2.3	0.7	
18:1n-9	49.6	47.8	41.3	39.8	52.9	47.3
18:1n-7			2.0	1.0	3.0	
18:2n-6	4.3	1.7	1.9	1.6	2.0	4.2
18:3n-3	0.9	0.7	0.1	0.5	0.2	0.4
16:1:18:0	1.41	1.06	0.19	0.06	1.86	0.48

Table 2.5 Fatty acid of some edible fats and oils

Oil or Fat	Unsat./Sat. ratio	Saturated					Mono unsat.	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 Tallow	0.9	-	-	3	24	19	43	3	1
Butterfat (cow)	0.5	3	3	11	27	12	29	2	1
Butterfat (goat)	0.5	7	3	9	25	12	27	3	1
Butterfat (human)	1.0	2	5	8	25	8	35	9	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 (Maize 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	-
Illipe	0.6	-	-	-	17	45	35	1	-

Table 2.5(Cont.) Fatty acid of some edible fats and oils

Oil or Fat	Unsat./Sat. ratio	Saturated					Mono unsat.	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
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	-
Peanut Oil	4.0	-	-	-	11	2	48	32	-
Safflower Oil*	10.1	-	-	-	7	2	13	78	-
Sesame Oil	6.6	-	-	-	9	4	41	45	-
Shea nut	1.1	-	1	-	4	39	44	5	-
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

* Not high-oleic variety. Percentages may not add to 100% due to rounding and other constituents not listed. Where percentages vary, average values are used.

2.4 Biodiesel

Biodiesel refers to any diesel-equivalent biofuel derived from vegetable oils or animal fats and other biomass-derived oils. Normally, biodiesel is defined as mono-alkyl ester which is a liquid varies in color, golden to dark brown, depending on type of feedstock. It is immiscible in water. Most of mono-alkyl ester has high boiling point (in the range of 620-630 K) and low vapor pressure (less than 1 mm Hg). Its flash point is higher than 130 °C, significantly higher than that of the conventional diesel (64 °C), and its density is in the range of 0.86 to 0.90 g/cm^3, less than the density of water. The production of biodiesel from bio-oils is a chemical reaction called transesterification.

2.4.1 Chemistry of Transesterification Process

Normally, mono-alkyl ester is 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 (biodiesel) and glycerol (Jon Van Gerpen *et al.*, 2004). 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.

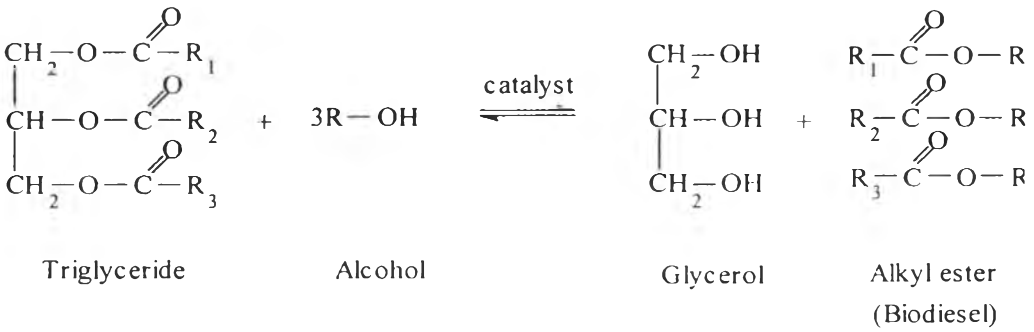

Figure 2.2 The production of biodiesel via transesterification of triglyceride.

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. These reactions are given in Figure 2.3.

$$\text{Triglyceride} + \text{ROH} \overset{\text{catalyst}}{\rightleftarrows} \text{diglyceride} + \text{R}'\text{COOR}$$

$$\text{Diglyceride} + \text{ROH} \overset{\text{catalyst}}{\rightleftarrows} \text{monoglyceride} + \text{R}''\text{COOR}$$

$$\text{Monoglyceride} + \text{ROH} \overset{\text{catalyst}}{\rightleftarrows} \text{glycerol} + \text{R}'''\text{COOR}$$

Figure 2.3 The transesterification reactions of triglyceride with alcohol to ester and glycerol.

The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. In the last step, the conversion of monoglycerides to glycerol, yielding one methyl ester molecule from each step (Srivastava *et al.*, 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 occur, 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.

The most popular mono-alkyl ester is methyl esters, resulting from the reaction of triglyceride with methanol, shown as Figure 2.4.

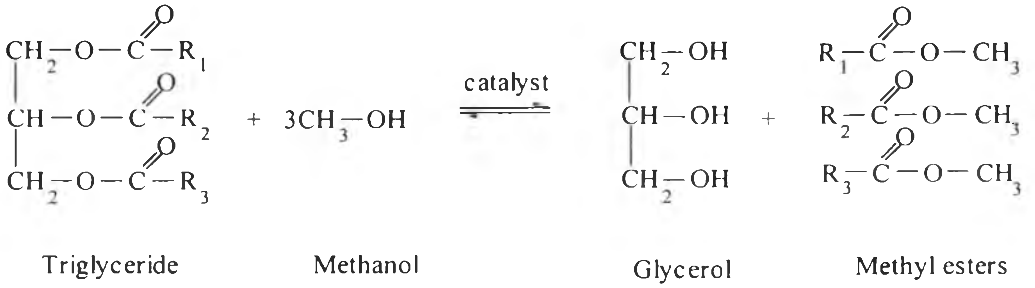

Figure 2.4 A chemical reaction of triglyceride with methanol.

The conversion of triglycerides into mono-alkyl esters through the transesterification reaction reduces the molecular weight to one-third that of the triglyceride and slightly increases the volatility.

2.4.2 Biodiesel Production Process

Most processes for making biodiesel use a catalyst to initiate the esterification reaction. The catalyst is required because the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate.

Typical proportions for the chemicals used to make biodiesel are:

Reactants	•Fat or oil (e.g. 100 kg palm oil)
	•Primary alcohol (e.g. 10 kg methanol)
Catalyst	•Mineral base (e.g. 0.3 kg sodium hydroxide)
Neutralizer	•Mineral acid (e.g. 0.25 kg sulfuric acid)

An example of basic scheme for biodiesel production is shown in Figure 2.5.

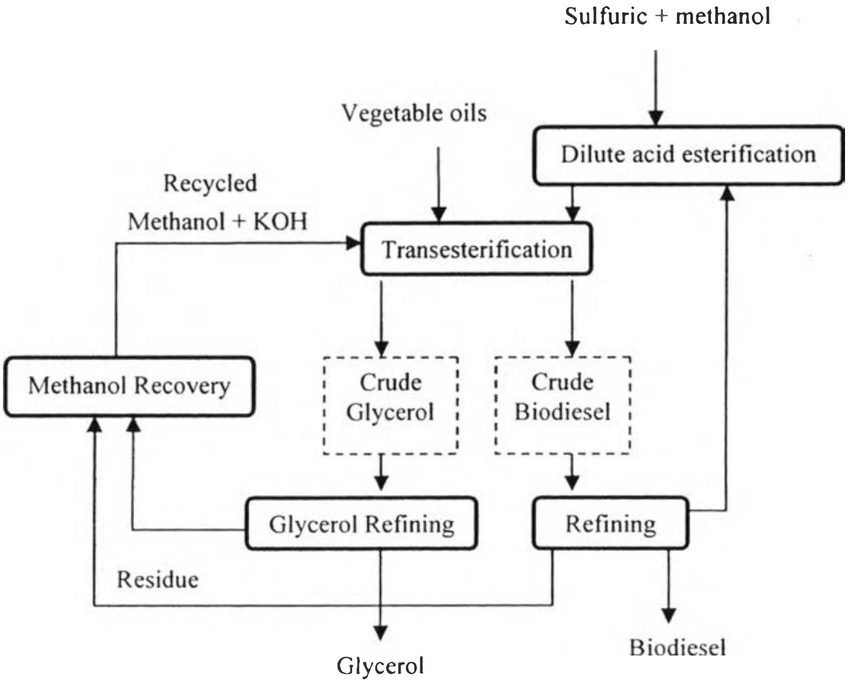

Figure 2.5 A basic schemes for biodiesel production.

Although mono-alkyl ester is considered as a potential sustainable alternative fuel but there are still disadvantages associated with its use. There are several properties of mono-alkyl ester that limit their uses. First, mono-alkyl ester has cloud point and pour point higher than conventional diesel, the performance of biodiesel in cold conditions is poorer than petroleum diesel, which might be caused engine problems and increased nitrogen oxide emissions. Biodiesel has been shown to increase nitrogen oxide (NO_x) emissions in many engines on engine stand tests. Biodiesel does not contain nitrogen so the increasing NO_x phenomenon is not related to fuel nitrogen content. NO_x is created in the engine as the nitrogen in the intake air reacts with oxygen at the high in-cylinder combustion temperatures. Second, mono-alkyl ester is a good solvent, it can dissolve rubber and some plastics, remove paint, and oxidize the metals. Third, the hydrophilic property of mono-alkyl ester might cause the corrosion of the engine. Lastly, mono-alkyl ester contains oxygen which may be undesirable for certain applications. The presence of oxygen lowers the heat content as shown by the volumetric heating values of it, which are 9-13% lower than conventional diesel (Demirbar, 2003). Moreover, this production route has several economic considerations mainly attributed to the price and availability of the main byproduct glycerin. Another drawback is the demand for large biodiesel production units requiring large investments (Knothe *et al.*, 2005).

Therefore, the deoxygenation 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, lower processing costs and raw materials flexibility (Stumborg *et al.,* 1996). Moreover, the obtain products from this process have high quality and have similar property to the conventional diesel fuel.

2.5 Renewable Diesel

Renewable diesel 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.

Renewable liquid alkanes or renewable diesel can be produced by hydrotreating of vegetable oils at standard hydrotreating conditions (i.e. 300–450 °C) with conventional hydrotreating catalysts (sulfided NiMo/Al_2O_3, NiMo/γ-Al_2O_3). Avelino Corma *et al.*, (2007) studied hydrotreating of pure sunflower oil in a fixed bed reactor with a sulfided NiMo/γ-Al_2O_3 catalyst. The reaction were done at temperature ranging from 300 to 450°C, pressure of 50 bar, LHSV 4.97 h^{-1} and H_2 to feed ratio of 1600 ml H_2 /ml liquid feed. A reaction pathway for conversion of triglycerides into alkanes or renewable diesel is shown in Figure 2.6.

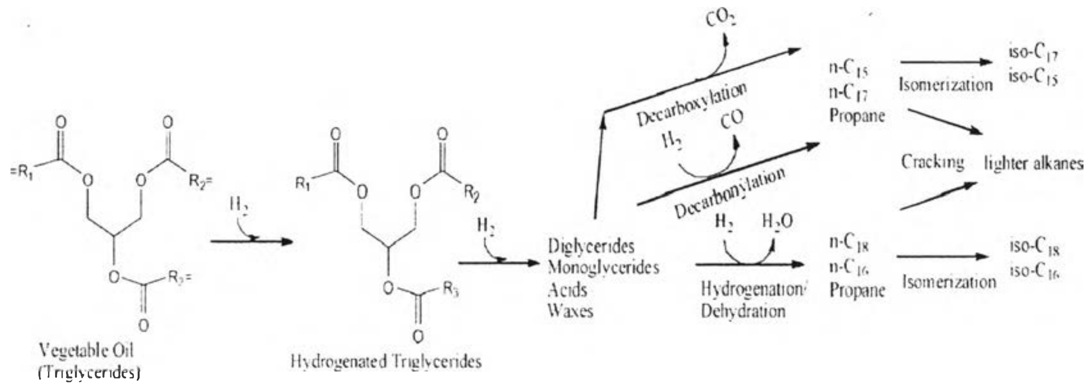

Figure 2.6 The reaction pathway for conversion of triglycerides to renewable diesel (Avelino Corma *et al.*, 2007).

In the first step of this reaction pathway the tri-glyceride 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 hydrodexogenation (or dehydration/hydrogenation). 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.

There are several possible reaction pathways for a production of straight-chain hydrocarbons, shown as Figure 2.7. Carboxylic acids have used to represent feedstock and similar equations can be written for alkane production from mono-, di or tri-glycerides. 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). This pathway involves bifunctional catalysis 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 > decarbonylation pathway > decarboxylation pathway (Avelino Corma *et al.*, 2007).

Liquid phase reactions

		Reaction	ΔG_{573} (kJ/mol)	ΔH_{573} (kJ/mol)
I.	Decarboxylation:	$R\text{-}COOH \longrightarrow R\text{-}H + CO_2(g)$	-83.5	9.2
II.	Decarbonylation:	$R\text{-}COOH \longrightarrow R'\text{-}H + CO(g) + H_2O(g)$	-17.0	179.1
III.		$R\text{-}COOH + H_2(g) \longrightarrow R\text{-}H + CO(g) + H_2O(g)$	-67.6	48.1
IV.	Hydrogenation:	$R\text{-}COOH + 3H_2(g) \longrightarrow R\text{-}CH_3 + 2H_2O(g)$	-86.1	-115.0

R – saturated alkyl group   *R' – unsaturated alkyl group*

Figure 2.7 The possible liquid-phase reaction pathways for production of straight-chain hydrocarbons from fatty acids (Snare *et al.*, 2006).

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 CO_2, while methanation reaction of fatty acids gives methane and water, shown as Figure 2.8.

Gas phase reactions		ΔG_{573} (kJ/mol)	ΔH_{573} (kJ/mol)
V. Methanation:	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	-61.2	-177.2
VI. Methanation:	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-78.8	-216.4
VII. Water-gas-shift	$CO + H_2O \rightleftharpoons H_2 + CO_2$	-17.6	-39.2

Figure 2.8 Gas phase reactions of CO or CO_2 with H_2 or H_2O (snare *et al.*,2006).

2.5.1 Renewable Diesel Production Process

Hydrotreating is a process traditionally used by petroleum refineries to remove sulfur impurities from diesel fuel. Renewable diesel produced using this process can either be produced in a "bio-only" unit that uses only bio-oil (vegetable oils or animal fats) as feedstock or where oils or fats are co-processed with the distillate fractions (diesel fuel) derived from petroleum. Both processes produce a mixture of hydrocarbons that has been reported to meet the ASTM standard for petroleum diesel (D975). The renewable diesel fuel produced through these processes, consequently, could utilize the existing infrastructure currently used for blending and transporting petroleum fuels. Any fuels containing the products produced from either process must be registered with the EPA as a fuel or fuel additive before being sold as diesel fuel in the U.S.

2.5.1.1 Processing in a Stand-alone Process Unit ("Bio-only" Hydrotreating)

Neste Oil, a company that is 50% owned by the Finnish government, has developed a "bio-only" process that produces non-ester renewable diesel fuel through its NExBTL^{TM} technology, a thermal/hydrotreating process. The process uses vegetable oils and/or animal fats as sole feedstock. The product obtained from this technology is called NExBTL renewable diesel or Green diesel.

NExBTL renewable diesel, which is a mixture of hydrocarbons similar to petroleum diesel fuel, is essentially sulfur, oxygen, nitrogen and aromatic free. It can be combined with petroleum diesel at any blend level but requires a lubricity additive, as do very low sulfur petroleum diesels. Using NExBTL also helps improve overall air quality, as it generates significantly less nitrogen oxide and particulate emissions as well. The schemes for NExBTL process is shown in Figure 2.9. The production process can apparently be adjusted to produce a fuel with a cloud point anywhere between -5 °C and -30 °C.

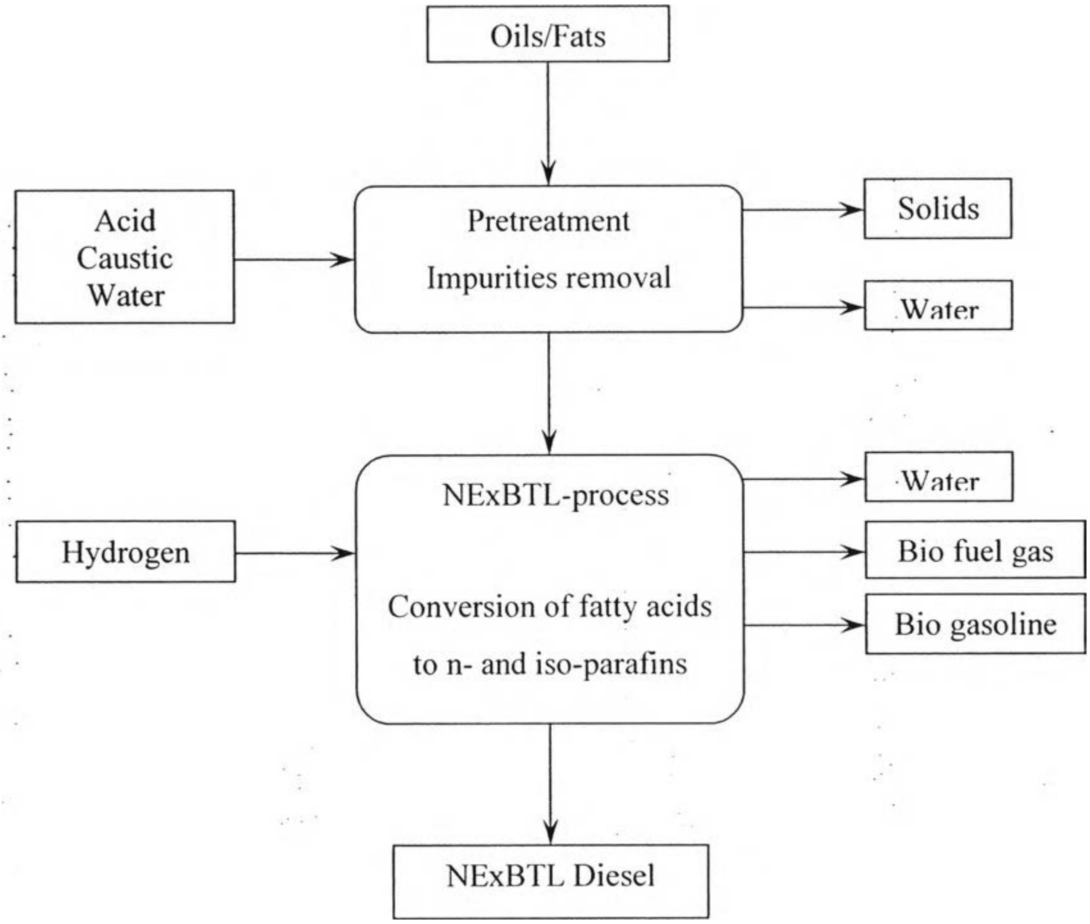

Figure 2.9 The scheme for NExBTL process.

Dynamic Fuels, a joint venture between Tyson Foods and Syntroleum, has recently announced plans to construct a 75 million-gallon per year facility to produce renewable diesel using catalytic hydrotreating of fats and oils feedstock, with production expected in 2010. The fuel produced from this process is presumably similar in composition to the NExBTL fuel produced by the Neste process.

UOP, a Honeywell company, also recently announced that ENI, an Italian refining company intends to build a production facility at an existing refinery in Italy using UOP catalytic hydrotreating technology to convert vegetable oils to renewable diesel. It is expected to begin production in 2009, at a capacity of about 95 million gallons per year.

The potential for using bio renewable feedstocks in oil refineries was studied. The study considered the production green diesel from vegetable oils and greases via catalytic hydrotreating technology.

In a standalone unit, a pre-processing step would remove contaminants from the biofeedstock by using a combination of technologies such as hydrocyclones, desalting, acid washing, ion exchange, or fixed guard bed catalyst systems. One possible flow scheme for standalone production of green diesel is shown in Figure 2.10. Feed and a hydrogen-rich gas are contacted with a regenerable hydrotreating

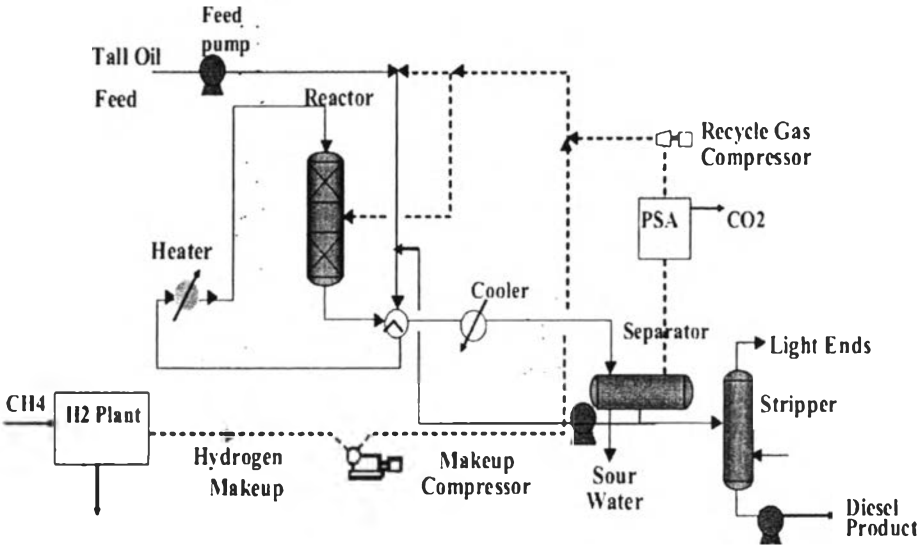

Figure 2.10 Proposed flow scheme for standalone production of green diesel (Marker *et al.*, 2005).

Catalyst in vessel at typical hydrotreating conditions, e.g., temperature of 350-400 °C, and 500-2000 psia then reactor products and unreacted hydrogen are cooled and separated. The liquid product is stripped to remove light components and hydrogen sulfide, or fractionated to recover multiple liquid products (R.L. Bain, UOP, 2007).

The experiments performed in this project showed that both hydro-deoxygenation and decarboxylation occur, with the results summarized in

Table 2.6. Decarboxylation is favored at lower pressures and hydrodeoxygenation increased with increasing pressure. Decarboxylation ($DeCO_2$) results in odd number paraffin production and CO_2 formation whereas hydrodeoxygenation (HDO) results in even carbon number paraffin production; therefore the ratio of n-C17 to n-C18 is a measure of the $DeCO_2$/HDO ratio. Standard hydrotreating catalysts of NiMo, CoMo and Pd all showed activity for both reactions. Furthermore it was demonstrated that the process could be run at lower temperatures than cited in the Arbokem patent and heavy material boiling above diesel range, which Arbokem produced, could be eliminated or reduced with proper choice of catalyst and conditions. Also, most experiments were done at 500 psi which is well below the pressures cited in the Arbokem patent. (Marker *et al.*, 2005)

Table 2.6 Green diesel experimental summary

	524	531	1316-C3	1316-C4
Feed	Vegetable oil	Vegetable oil	Vegetable oil	Vegetable oil
Catalyst	HCT (NiMo)	N200 (CoMo)	HCT (NiMo)	HCT (NiMo)
Test Unit	Autoclave	Autoclave	Plt 1316-B1	Plt 313-B1
WHSV	1.9	1.7	0.8	0.3
Temperature (°c)	300-350	300-350	325	310
Pressure (psia)	500	500	500	500
Products				
% water	1.7	1.2	4.9	9.9
% CO_2+ CO	12.7	13.4	2.6	1.9
% Light HC	7.0	5.2	3.4	3.9
% diesel +	79.0	80.0	88.3	84.0
% heavy	0	3.2	0.3	0.3
% deoxygenation	90+	91+	85.0	99.0
n C17/ nC18	3.0	2.1	0.6	0.49

Snare *et al.* (2006) studied on heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel. The deoxygenation reaction is carried out in a semibatch reactor under constant temperature and pressure, 300 °C and 6 bar, respectively. A thorough catalyst screening was performed to obtain the most promising metal and support combination.The metals studied were Ni, Mo, Pd, Pt, Ir, Ru, Rh, and Os on Al_2O_3, Cr_2, O_3, MgO, and SiO_2 as well as on activated carbons.

Metal-supported carbon catalysts were very selective toward deoxygenation products. All the palladium and the platinum on carbon catalysts achieved >90% selectivity toward deoxygenation products (n-heptadecane, 1-heptadecene, and sum of other C_{17} products) after 6 h. Additionally Rh, Ru, and Os on carbon catalysts exhibited relatively high selectivity toward deoxygenation products. Apart from the above-mentioned supported carbon catalysts, the following catalysts displayed high selectivity toward deoxygenation products: Ni/SiO_2 and Ni/Cr_2O_3. Moreover, the Ni/Cr_2O_3 catalyst was particularly selective toward n-heptadecane.

The catalytic deoxygenation of stearic acid over heterogeneous catalysts was successfully achieved with high activity and selectivity to the desired product, heptadecane. Even though this reaction can be effectively performed over a variety of catalysts, the catalyst screening results revealed that the reaction is preferably carried out over palladium and platinum supported on activated carbons. Furthermore, the gasphase 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.

Mikulec *et al.* (2010) also studied on renewable diesel. The studies are devoted to the issue of direct transformation of triacylglycerols (TAG) to diesel fuels applying a commercial and synthesize NiMo and NiW supported on Al_2O_3, TiO_2, and ZrO_2. It was proved that during the hydrodesulphurization, hydrodeoxygenation also occurs. TAG can be converted to the fuel biocomponent by adding 6.5 % vol. of TAG to atmospheric gas oil. After hydroprocessing at tested conditions (temperature of 320–360 °C, pressure of 3.5–5.5 MPa, LHSV of 1.0 h^{-1} and H_2:HC ratio of 500–1000 Nm^3/m^3), diesel fuel containing 5–5.5% of biocomponent was obtained. The products were analyzed for their standard diesel specifications.

Catalyst acidity had no significant effect on isomerization of n-alkanes being formed. As the reaction gave rise to higher n-alkanes with a higher melting point, it was helpful that gas oil worked as a solvent. NiW containing catalysts exhibit an extraordinary hydrogenation activity and at lower reaction temperature (320–340°C) wax like insoluble product were formed. In cases of catalyst supports with low specific surface (ZrO_2), the level of desulphurization was much lower when compared to the commercial catalyst. At temperatures 360-380 °C and with high hydrogen excess, a greater quantity of reaction water was formed, pointing out to a more significant proportion of the HDO reaction. Total aromatics content was decreased in comparison with base atmospheric gas oil. The decreasing of total aromatic content was caused by transformation of TAG in a reaction mixture to the alkanes.

Key factor of successful hydrodesulphurization and hydrodeoxygenation/ hydrodecarboxylation is in appropriate selection of the catalyst and technological condition. The selectivity to hydrodeoxygenation/ hydrodecarboxylation products increases with increasing temperature.

2.5.1.2 Co-processing with Petroleum

The process unit for the biofeedstock co-processing is a distillate hydrotreater for ultra-low sulfur diesel (ULSD) as shown in Figure 2.11. The objective of the co-processing is to produce a “G5” diesel pool in which 5% of the diesel pool contains “green diesel”. The hydroprocessing conditions are assumed to completely favor hydrodeoxygenation (HDO). In other words, oxygen in the biofeedstock is removed by reaction with hydrogen to form water and the C_{18} n-paraffin.

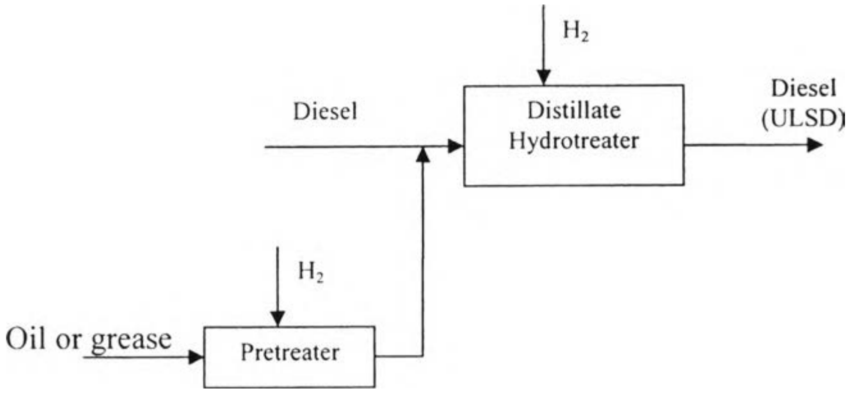

Figure 2.11 Pretreated and co-processing oil or grease in an existing hydroprocessing unit (Marker *et al.*, 2005).

From the experiments, co-processing of biomasses in a typical refinery distillate hydrotreating unit has some drawbacks for green diesel production such as the chemical nature of the biofeedstocks significantly increases hydrogen requirements under conditions that favor hydrodeoxygenation, the heat release from these feeds substantially reduces the catalyst cycle length, typical hydrotreating unit configurations do not permit remediation of increased cloud point due to n-paraffins in the green diesel component of the diesel pool, and the process conditions for hydrotreating units for ultra-low sulfur diesel production favor HDO, producing water that may adversely affect catalyst performance. In conclusion, standard refinery distillate hydrotreating units do not appear to be suitable for green diesel production in a co-processing scheme (Marker *et al.*, 2005).

Mikulec et al. (2010) reported that the standard refinery distillate hydrotreating units are suitable for renewable diesel production in a co-processing scheme, but co-processing of biomass such as vegetable oils and/or animal fats may be processed in a revamp refinery distillate hydrotreating unit. Flow scheme are illustrated in Figure 2.12 and Figure 2.13.

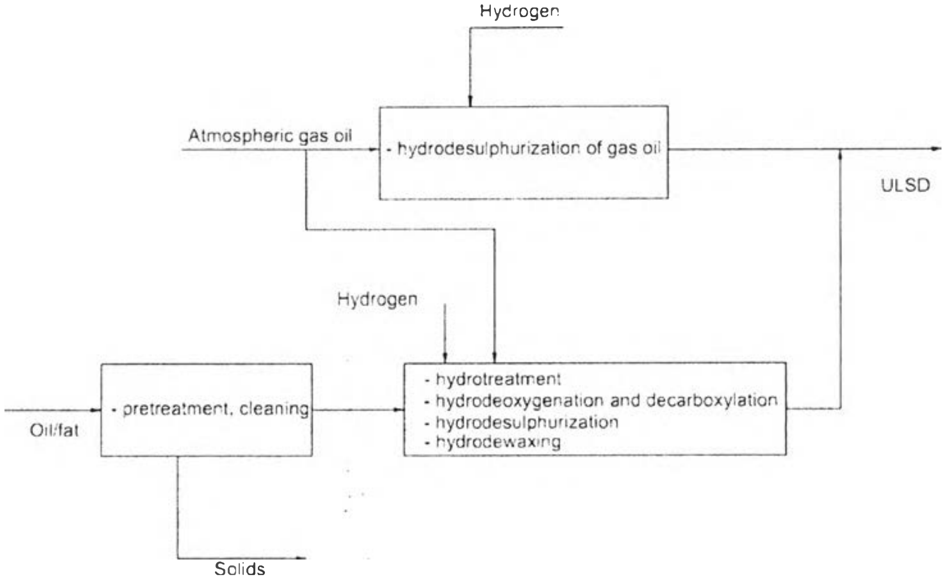

Figure 2.12 Renewable diesel productions – co-processing of biofeed in hydrodesulphurization unit (Mikulec *et al.*, 2010).

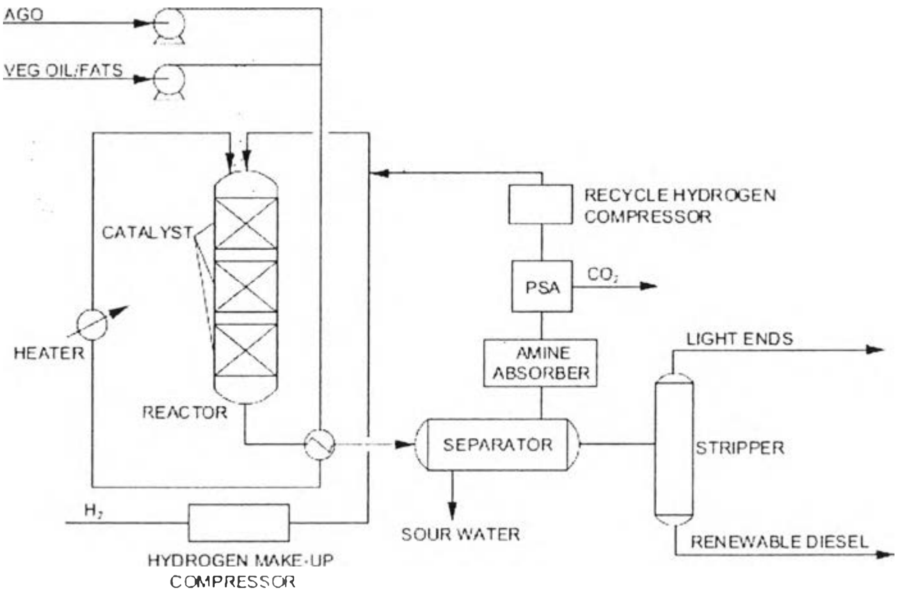

Figure 2.13 Flow scheme proposal for co-processing hydrodesulphurization of atmospheric gas oil with hydrodeoxygenation and hydrodecarboxylation of renewable biocomponent (Mikulec *et al.*, 2010).

2.6 Comparison of Biodiesel and Renewable Diesel Process and Properties

It is useful to compare biodiesel and renewable diesel in terms of properties and processes since they represent two different approaches for making diesel fuel from vegetable oil/animal fat. Selected properties are compared in Table 2.7. Green diesel has excellent diesel fuel properties including an extremely high cetane number. Biodiesel has lower heating value because of its oxygen content. Biodiesel also has other undesirable properties such as high density, and high NO_x emissions. Overall, green diesel appears to be a superior product (Marker *et al.*, UOP, 2005).

Table 2.7 Petroleum diesel, biodiesel and green diesel properties

	Petroleum Diesel	**Biodiesel (FAME)**	**Green Diesel**
Low Heating Value (MJ/kg)	42	38	44
KinematicViscosity,40 °C (mm^2/s)	1.3 to 4.1	4.0 to 6.0	-
Specific Gravity, 60 °F (kg/L)	0.85	0.88	-
Density, 15 °C (lb/gal)	7.079	7.328	6.509
Water and Sediment, vol%	0.05 max	0.05 max	-
Carbon, wt.%	87	77	-
Hydrogen, wt.%	13	12	-
Oxygen, wt.%	0	11	0
Sulfur, wt.%	<15ppm	<10ppm	<10ppm
Boiling Point, °C	180 to 340	315 to 350	265 to 320
Flash Point, °C	60 to 80	100 to 170	-
Cloud Point, °C	-15 to 5	-3 to 12	-5 to -30
Pour Point, °C	-35 to -15	-15 to 10	-
Cetane Number	40 to 55	48 to 65	80 to 90
% change in NO_x emission	-	+10	0 to -10

Figure 2.14 and Table 2.8 are comparing the processes by which biodiesel and green diesel are produced. 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 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.

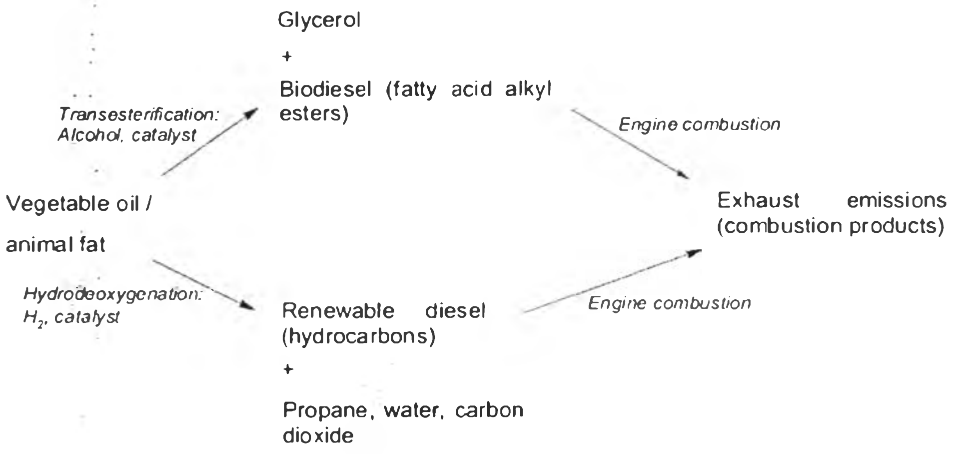

Figure 2.14 Flow chart for transformation of lipid materials (biodiesel and renewable diesel) to products of engine combustion (Knothe, 2010).

Table 2.8 Comparison of biodiesel and green diesel production processes

	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

As shown in Table 2.9, biodiesel does have an advantage in yields of diesel product per lb of vegetable oil feed. This is due to the fact that the oxygen in vegetable oil is retained in the biodiesel product where as the oxygen in vegetable oil is rejected green diesel as water or CO_2. However, the overall cost of biodiesel production is projected to be nearly twice that of green diesel. (Marker *et al.*, 2005)

Table 2.9 Green diesel and biodiesel yields

Feed	**Biodiesel**	**Green Diesel**
% Oil or Grease	100	100
% H_2	-	1.5-3.8
% methanol	8.7	-
Products		
% water,CO_2	-	12-16
% Lt HC	-	2-5
% diesel	96	83-86
% glycerol	12	-
Operating cost $/gal	0.05	0.025

2.7 Heterogeneous Catalysis

2.7.1 Importance of Solid Catalysts

Catalysis is essential to modern energy conversion, chemicals manufacture, and environmental technology. From the start, oil refining and bulk chemicals manufacture have relied largely on the application of solid catalysts. In the meantime, in specialty and fine-chemicals production catalysis is used frequently too. According to current estimates about 85% of all chemical processes make use of catalysis, while all molecules in modern transportation fuels have been confronted with one or more solid catalysts. Moreover when use catalyst, amount of energy and raw materials needed for fuels and chemicals manufacture is much reduced by using catalysts. In fact today, many products could not be obtained without catalysis.

Although sulfur removal from oil products started as extraction processes, today's low-sulfur diesel and gasoline could not be produced in an acceptable manner without hydrodesulfurization (HDS) catalysis. Exhaust catalysis has enabled the widespread use of cars, while selective catalytic reduction of nitrogen oxides has removed the brown plumes from power and chemical plants. In the future, the importance of catalysis will grow as raw materials for chemicals diversify and alternative energy sources and end use come into play. Building blocks in new energy chains, such as water electrolysis and fuel cells, also rely on solid catalysts.

2.7.2 Development of Solid Catalysts

In Table 2.10, selected solid catalysts are shown together with their main used. Bulk and supported catalysts as well as zeolite-based catalysts are listed. Many of the examples shown have been known for decades. However, a continuous and spectacular progress over the years is noted for many catalytic processes.

Table 2.10 Survey of selected catalysts with their main applications

Catalyst	**Applications**
Ni/SiO_2	Hydrogenation
$K_2O/Al_2O_3/Fe$	Ammonia synthesis
$Ag/\alpha\text{-}Al_2O_3$	Epoxidation
$CrOx/SiO_2$	Polymerization
$CoMoS_2/\gamma\text{-}Al_2O_3$	Hydrotreating
Co/SiO_2	Fischer–Tropsch synthesis
$Cu/ZnO/Al_2O_3$	Methanol synthesis
Zeolite Y composite	Catalytic cracking
Pt/Mordenite	Hydroisomerization of light alkanes
V_2O_5/TiO_2	NO*x* abatement
Pt/C	Hydrogenation; fuel cell

2.7.3 Synthesis of Solid Catalysts

2.7.3.1 Impregnation

The simplest way to execute impregnation is by contacting a previously dried support, of pore volume VPT, with a volume V = VPT of solution containing the precursor of the active phase. The solution is drawn into the pores by capillary suction (hence ''capillary impregnation'') (Neimark *et al.,* 1981, and Lee *et al.*, 1985, and Lekhal *et al.*, 2001). In the case of proper wetting no excess of solution remains outside the pore space and the procedure is also called ''dry'' or ''incipient wetness'' impregnation.

The penetration of the liquid phase requires the elimination of air from the pores. If the pore radius is very small, capillary pressure is much larger than the pressure of the entrapped air; compressed air dissolves or escapes from the solid through larger pores (Lee *et al.,* 1985, and Lekhal *et al.,* 2001). Sometimes, the mechanical strength of the support is not sufficient to withstand forces imposed by the transitory formation of bubbles and the catalyst grains may burst (Lee,et al, 1985). This can be remedied by impregnation under vacuum or addition of a surfactant to the solution.

Heat is generally released when a solid/gas interface is replaced by a solid/liquid interface. This might influence the quality of impregnation if the precursor solubility decreases when the temperature increases or if detrimental reactions involving the support take place due to a temperature rise. These drawbacks can be avoided by exposing the support to water vapor before impregnation and thus stabilizing the interface with a hydrous film. Impregnation can also be carried out in diffusional conditions, that is, by immersing a water-filled support in the precursor solution (wet impregnation) (Neimark *et al.*,1981, and Lee *et al.*, 1985, and Lekhal *et al.*, 2001). Before water filling, air can be replaced by a watersoluble gas like ammonia to avoid gas bubbles in the pores (Lee *et al.*, 1985). Wet impregnation should be avoided when the interaction between precursorand support is too weak to guarantee the deposition of the former (Gavriilidis *et al.*,1993) For powders, it can be convenient to suspend the support in an excess of solution and evaporate the solvent under regular stirring. Such a method can be used for the introduction of poorly soluble compounds, but leads to a dispersed phase only if seeds serving the subsequent growth of the particles have time to form all over the support surface before crystallization starts. It is thus advised to check by microscopic methods if the final distribution of the active phase is homogeneous at the scale of the support grain. So as to combine conventional stirring and the use of a low volume of precursor solution, a two-solvent method has been proposed, in which a dry hydrophilic support is first suspended into a large volume of an organic solvent with a relatively low surface tension (Lopes *et al.*, 2006). A volume VPT of precursor solution in water is then poured into the suspension. It moves into the pores where it replaces the organic solvent that has a lower affinity for the support surface.

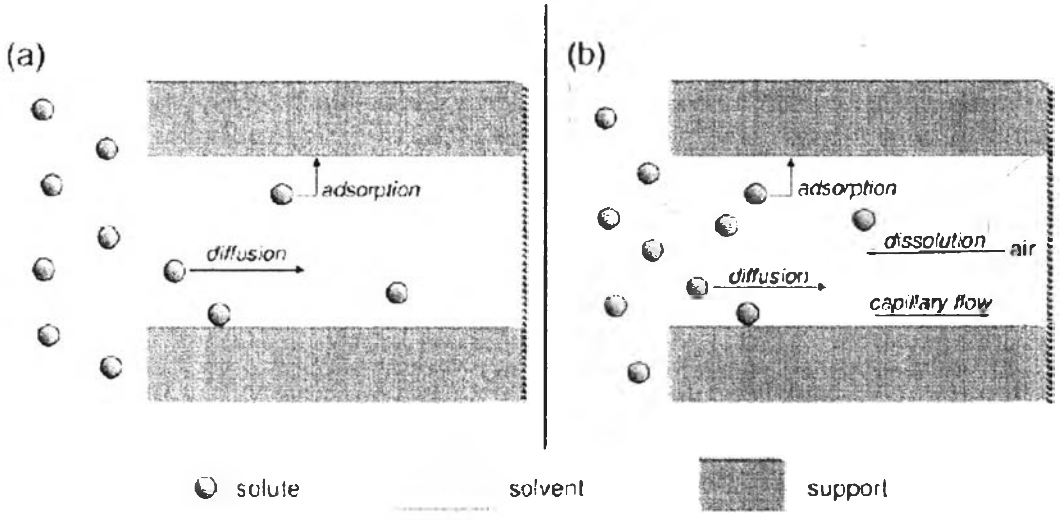

Figure 2.15 Phenomena of transport involved in (a) wet impregnation and (b) dry impregnation. The solute migrates into the pore from the left to the right of the figures.

2.7.3.2 Drying

The step after impregnation is the elimination of the solvent. Typically, the impregnated system, spread in fine layers, is heated in an oven up to the boiling point of the solvent or at a lower temperature for gentle drying, in static conditions or under a flow of gas. The elimination of water from the pores leads to an increase of the precursor concentration up to saturation and crystallization, preferably on seeds resulting from the interactions with the support, if one wants to obtain a highly dispersed phase. However, hydrated salts like nitrates melt at moderate temperature which may cause the coalescence of their initially dispersed particles, or even their exclusion from the pores.