CHAPTER II
LITERATURE REVIEW

Generally, diesel fuel is mainly referred to petroleum-based diesel, also called petrodiesel, or fossil diesel which used in diesel engines. Diesel is widely used in the industry and transportation section lead to high consumption in this fossil fuel. Due to the increasing energy demand and pollution problems caused by the use of fossil fuels, it has become necessary to develop alternative fuels as well as renewable sources of energy, such as biodiesel and renewable diesel, which are called bio-based diesel to replace the used of diesel fuel.

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 properties of feedstocks, chemical reaction, processing condition, and production process are described.

2.1 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.

2.1.1 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.

2.1.1.1 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 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.

- 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.

- 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.

2.1.1.2 Volatility

- 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.

- 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 is dependent on both the lean flammability limit of the fuel as well as the vapor pressure of the fuel constituents. The flash need not correspond to a sustained flame. The "fire point" is

sometimes used to designate the fuel temperature that will produce sufficient vapor to maintain a continuous flame.

2.1.1.3 Ignition Indices

One of the most important properties of a diesel fuel is its readiness to auto ignites 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.

- 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:

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

- 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.

Nowadays, the increasing energy demand and pollution problems caused by the use of fossil fuels have to be concerned. These concerns include feedstock availability, price volatility, continuing depletion of the reserves of non-renewable petroleum, and greenhouse gas emissions. From these problems, it has become necessary to develop alternative fuel as well as renewable sources of energy.

2.2 Bio-based Diesel

Bio-based diesel is one of the non-petroleum-based diesel which refers to any diesel-equivalent biofuel derived from vegetable oils or animal fats and other biomass-derived oils. The most prominent sources of bio-based diesel are biodiesel and renewable diesel or hydrogenated biodiesel. Biodiesel is defined as fatty-acid methyl ester or FAME which is obtained from vegetable oil or animal fats (bio-lipids) via tranesterification. Hydrogenated biodiesel is another category of diesel fuels which involve converting the triglycerides in vegetable oil and animal fats into alkanes by refining and hydrogenation. This produced fuel has many properties that are similar to synthetic diesel, and are free from the many disadvantages of FAME.

2.2.1 Feedstocks

Vegetable oils and animal fats are considered as raw materials for bio-based 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. These products, when compared to plant-derived oils, often offer an economical advantage as a feedstock. There is also some

indication that these sources, which are high in saturated fats, produce less nitrous oxide compared to plant-derived oils.

Both oils and fats are composed of molecules called triglycerides. Triglyceride, also called triacylglycerol (TAG), is a chemical compound formed from one molecule of glycerol and three fatty acids. 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. Vegetable oils contain free fatty acids (generally 1-5 %), carotenes, phosphatides, phospholipids, sulphur, tocopherols compounds, and traces of water. The fatty acid composition of some common edible fats and oils is also shown in Table 2.1.

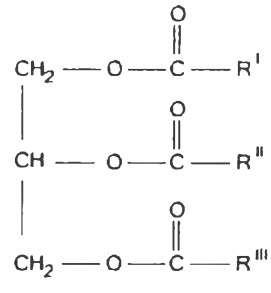

Figure 2.1 A chemical structure of triglyceride.

Table 2.1 Fatty acid composition of some fats and oils (Zamora, 2005)

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

Table 2.1 (Cont.) Fatty acid composition of some fats and oils (Zamora, 2005)

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
Butterfat (goat)	0.5	7	3	9	25	12	27	3	1
Canola Oil	15.7	-	-	-	4	2	62	22	10
Cocoa Butter	0.6	-	-	-	25	38	32	3	-
Cod Liver Oil	2.9	-	-	8	17	-	22	5	-
Coconut Oil	0.1	6	47	18	9	3	6	2	-
Corn Oil (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	-
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	-
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.

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

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

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

The cetane numbers of vegetable oils are in the range of 32 to 40. The cetane number is an engine-based test that follows ASTM standard D613. The primary reference fuel is n-cetane (n-hexadecane), which has a cetane number of 100. The normal alkanes have a high cetane number (above 98), whereas typical diesel fuel has a cetane number around 45. The normal alkanes also have good cold flow properties (Helwani, 2009). The cetane number of fatty esters depends on chain length and degree of unsaturation. The presence of polyunsaturated fatty esters is the cause of oxidative stability problems with biodiesel, and the presence of higher amounts of saturated fatty esters is the cause of cold flow problems.

Some physical properties of the most common fatty acids occurring in vegetable oils and animal fats are listed in Table 2.2.

Table 2.2 Selected properties of some common fatty acids (Gerhard *et al.*)

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	286100	$C_{18}H_{34}O_2$	2657.4 (25°)
Linoleic acid (9Z,12Z-Octadecadienoic acid); 18:2	280.45	-5	229-3016	$C_{18}H_{32}O_2$	-
Linolenic acid (9Z,12Z,15Z-Octadecatrienoic acid);18:3	278.44	-11	230-217	$C_{18}H_{30}O_2$	-
Erucic acid (13Z-Docosenoic acid);22:1	338.58	33-4	26515	$C_{22}H_{42}O_2$	-

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 (mmHg) at which the boiling point was determined.

Murugesan *et al.* (2009) studied the prospects and opportunities of introducing vegetable oils and their derivatives as fuel in diesel engines. The studied of the fuel properties of vegetable oil indicated that the average viscosity of vegetable oils is about 20 times higher than that of diesel fuel. The flash point of vegetable oil is very high (above 200 ^{o}C). The heating values are in the range of 39–40 MJ/kg when compared to diesel fuel (about 45 MJ/kg). The presence of chemically bound oxygen in vegetable oil lowers their heating values by about 10%. The cetane numbers are in the range of 32–40. Blending of vegetable oils with diesel fuel is more suitable for diesel engine than neat vegetable oil. They also studied the properties of biodiesel produced by tranesterification. In case of Methyl ester of bio-diesel (B100), it can be directly used in diesel engines without any modifications for short term with slightly interior performance than that of diesel and it can reduce the unwanted gas emission.

In 2010, Karmakar *et al.* studied physico-chemical properties of the plant and animal resources that are being used as feedstocks for biodiesel production by tranesterification. They found that the different physical and chemical properties of feedstocks like fatty acid composition, free fatty acid content, moisture, impurities and unsaponifiables, titre, etc. influence biodiesel production process as well as the properties of the product. Cetane number, flash point, oxidative stability, cloud point, and heat content of biodiesel depend on the chain length and unsaturation of the constituent fatty acids. Feedstocks with high MIU (Moisture, Impurities, and Unsaponifiables) and titre (the temperature at which oil changes from solid to liquid) require extra processing steps like filtration, centrifuging and heating. For high free fatty acid feedstocks, especially for waste oils and animal fats, an acid pretreatment step should be used before alkali catalyzed process.

There are many research works studied on vegetable oil but a few for animal fat. Some studied the co-processing between petro-diesel and bio-diesel. There are also literatures about using the pure vegetable oil as the feed for the production of hydrogenated biodiesel, but the pure animal fat is rarely studied. The price of animal fat is lower than vegetable oil and it can be used to produce

hydrogenated biodiesel, which has more value. Thus, this research focuses on using the pure animal fat as feedstock for the production of hydrogenated biodiesel.

In this research, the animal fats, i.e. beef fat, pork fat, and chicken fat, will be used as the model feedstocks for the production of hydrogenated biodiesel by deoxygenation process. As the fatty acid composition shown in Table 1, beef fat and pork fat consist of C_{14} - C_{18}. They all have about 3 % palmitoleic acids (C16:1). Normally, they are solid at the room temperature. Thus, we need to add dodecane as the additive in feedstock. The results from using these animal fats as feedstocks will be then compared with the results of the vegetable oils (jatropha oil and palm oil).

2.2.2 Biodiesel

Biodiesel, which is referred to mono-alkyl ester, is normally produced via the transesterification of vegetable oils or animal fats (triglycerides). 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. In this process, triglycerides react with alcohols, generally methanol or ethanol, in the presence of a catalyst to produce mono-alkyl esters and glycerol. The transesterification reaction can be catalyzed by bases, acids, or enzymes. The most common catalysts used are strong bases, such as sodium hydroxide, potassium hydroxide, and sodium methoxide. The typical transesterification process is shown in Figure 2.2.

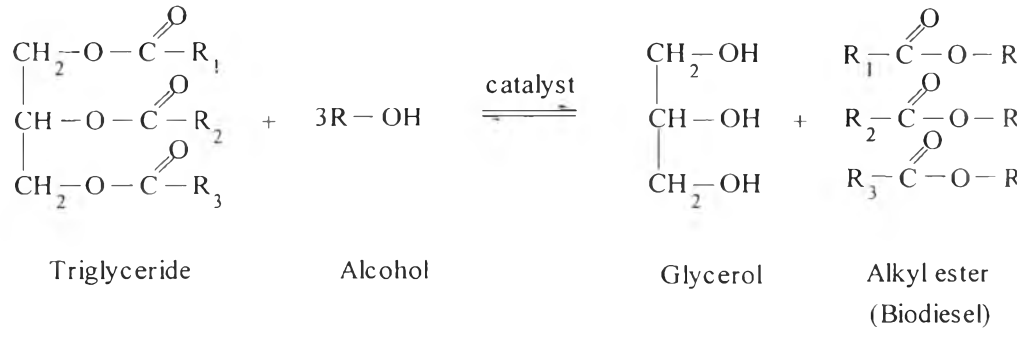

Figure 2.2 The production of biodiesel via transesterification of triglyceride.

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

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

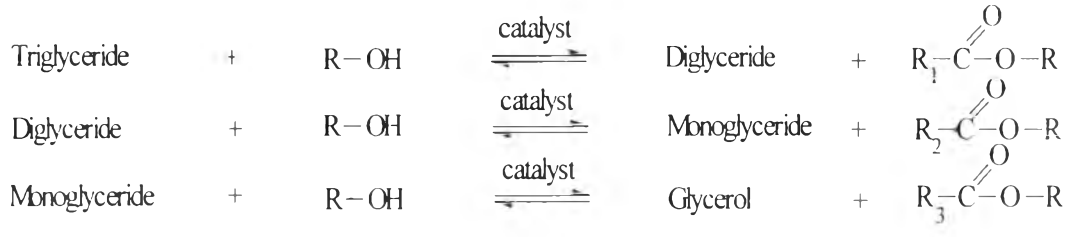

Figure 2.3 The transesterification reactions of triglyceride with alcohol to ester and glycerol (Srivastava and Prasad, 2000).

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 A. *et al.*, 2000)

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

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 obtained products from this process have high quality and have similar property to the conventional diesel fuel.

2.2.3 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 $NiMo/Al_2O_3$, $NiMo/\gamma\text{-}Al_2O_3$).

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 tri-glycerides into alkanes or renewable diesel is shown in Figure 2.4.

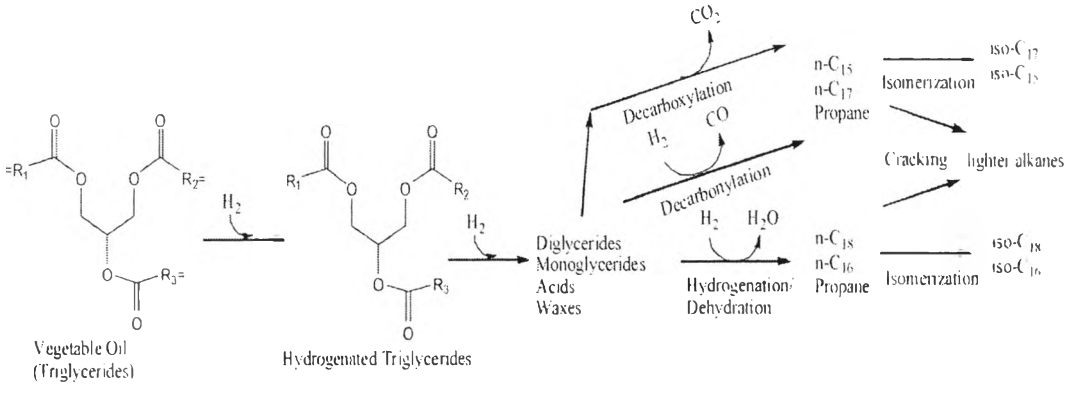

Figure 2.4 The reaction pathway for conversion of triglycerides to renewable diesel (Corma *et al.*, 2007).

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 2.5. 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 *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 (Corma *et al.*, 2007).

Liquid phase reactions						$\Delta G_{\text{[illegible]}}$ (kJ/mol)	$\Delta H_{\text{[illegible]}}$ (kJ/mol)
I	Decarboxylation:	R-COOH		$\longrightarrow$	R-H + CO_2 (g)	-83.5	9.2
II.	Decarbonylation:	R-COOH		$\longrightarrow$	R'-H + CO (g) + H_2O (g)	-17.0	179.1
III.		R-COOH	+ H_2 (g)	$\longrightarrow$	R-H + CO (g) + H_2O (g)	-67.6	48.1
IV.	Hydrogenation:	R-COOH	+ $3H_2$ (g)	$\longrightarrow$	R-CH_3 + $2H_2O$ (g)	-86.1	-115.0
		R – saturated alkyl group			*R' – unsaturated alkyl group*		

Figure 2.5 The possible liquid-phase reaction pathways for production of straight-chain hydrocarbons from fatty acids (Murzin *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 2.6.

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 2.6 Gas phase reactions of CO or CO_2 with H_2 or H_2O (Murzin *et al.*, 2006).

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

2.2.4 Influence of Condition

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

In 2005, deoxygenation reaction of vegetable oils over a carbon-supported metal catalyst was studied by Murzin *et al.* as a suitable reaction for production of dieselfuel-like hydrocarbons. Stearic acid, ethyl stearate, and tristearine representing model compounds of vegetable oils have been tested in separate deoxygenation experiments at 300–360 °C and overall pressure 17–40 bar. In order to determine the influence of hydrogen partial pressure on the conversion and products distribution, different reaction atmospheres, e.g. helium (He), hydrogen (H_2), and hydrogen (5 vol.%)– argon (H_2–Ar) mixture, were applied.

All of the feedstocks, stearic acid, ethyl stearate, and tristearine, was converted with high selectivity to n-heptadecane, corresponded to direct decarboxylation, which is supported by formation of carbon dioxide, detected in the gas phase. For the influence of temperature and hydrogen partial pressure, under slightly higher hydrogen pressure the formation of aromatic hydrocarbons, undesired product which contribute to catalyst deactivation, was suppressed. Further increase of the hydrogen partial pressure, however, suppressed the stearic acid conversion. As expected, higher temperature favoured conversion of ethyl stearate; however. increasing the temperature caused a decrease of the selectivity towards n-heptadecane and particularly promoted aromatization.

The temperature also has the effect to the product. The yield of straight-chain alkanes decreases at temperatures higher than 350 °C because the alkanes undergo cracking and isomerization at higher temperatures (Huber, 2007). Accordingly, the recent experiments carried out at different temperatures showed that the heptadecane yield decreases as the temperature rises, whereas the yield of light hydrocarbons becomes higher (Yakovlev *et al.*, 2009). It is possible that at higher temperatures, along with hydrogenation and HDO processes, the hydrocracking occurs, leading to the formation of CH_4 and hydrocarbons with a lower molecular weight. Besides, one should not ignore a possible occurrence of decarboxylation reaction with the CO_2 formation, although CO_2 and CO are absent in the gas products of the reaction.

2.2.5 Comparison of Biodiesel and Renewable diesel

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 2.3. 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 2.3 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, by dif. 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 NOx emission	-	+10	0 to -10

Figure 2.7 and Table 2.4 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.

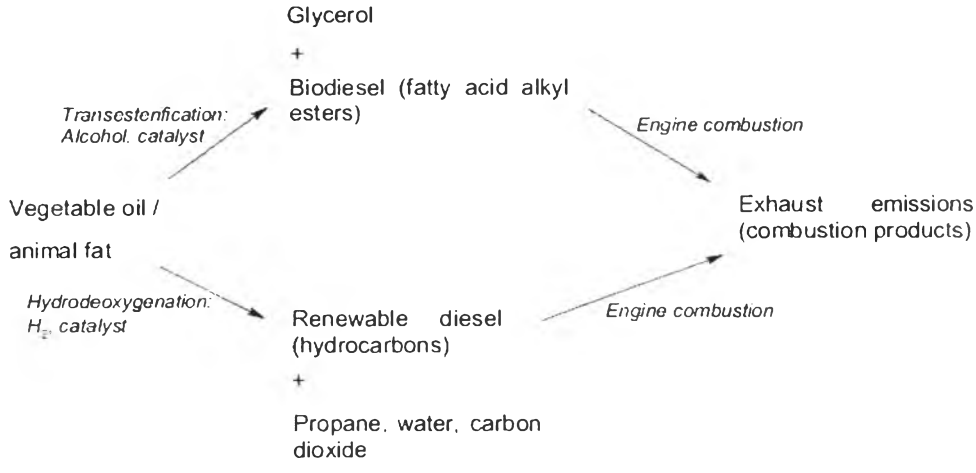

Figure 2.7 Flow chart for transformation of lipid materials (biodiesel and renewable diesel) to products of engine combustion (Knothe, 2010).

Table 2.4 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 2.5, 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 2.5 Green diesel and biodiesel yields

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

2.3 Solid Catalysts

2.3.1 Importance of Solid Catalysts

Catalysts play a key role in industry, as well as everyday life. A catalyst's main function is to increase the rate of a reaction without being consumed. Catalyst's increase productivity and efficiency, which translates into increase in profit, which is why finding more catalysts is such an important topic today.

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. 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 hydrodesulphurization (HDS) catalysis. 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.

In this research, focus on production of renewable diesel via hydrodeoxygenation which a solid heterogeneous catalyst plays the important role in this process. Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen). The total surface area of solid has an important effect on the reaction rate. The smaller catalyst particle size, the larger surface area for a given mass of particles is observed. The overall process of solid heterogeneous catalytic reaction can be classified into the sequence of individual steps, as shown in Table 2.6.

Table 2.6 Steps in a catalytic reaction (Fogler, 2006)

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

Normally, a solid heterogeneous catalyst with continuous processing technologies is expected to gain wider acceptance due to its potential effectiveness and efficiency, leading to reducing the cost of production. Moreover, when carrying

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

2.3.2 Influence of Active Metal and Catalyst Support

The influence of active metal and catalyst support is important for any catalysis process. Different metals or supports give different reactions and products. In Table 2.7, selected solid catalysts are shown together with their main used.

Table 2.7 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
CrO_x/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

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

as a desired product. The catalyst screening showed that the reaction can be effectively performed over palladium and platinum supported on activated carbons. Furthermore, the gas phase analysis indicated that the decarboxylation reaction was more preferable over the Pd/C catalyst, as the decarbonylation was more preferable over the Pt/C catalyst. The comparison with different metals on the equivalent supports by normalizing the results with metal content depicted that the beneficial effect of a metal in the deoxygenation reaction is in the decending order Pd, Pt, Ni, Rh, Ir, Ru, and Os.

2.3.3 Catalyst Deactivation

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

Table 2.8 Mechanisms of catalyst deactivation

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
Vapor–solid and solid–solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical-induced crushing of the catalyst particle

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

1) Surface diffusion
2) Solid-state diffusion
3) Evaporation/condensation of volatile atoms/molecules
4) Grain boundary diffusion
5) Phase transformation

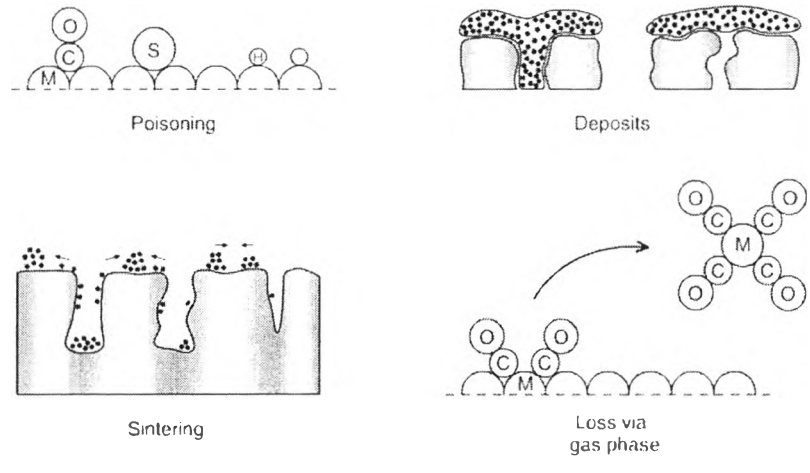

Figure 2.8 Mechanisms of catalyst deactivation (M = metal).

There are many research works studied on the influence of various catalyst poisons and other impurities on biodiesel production which reduce the activity of catalysts. Generally, all impurities reducing the catalyst activity have been termed "catalyst poisons," independent of their chemical nature or their origin. These impurities are either typical constituents of natural oils and fats or decomposition products or may be introduced during processing.

Helmut Klimmek (1984) studied the effect of various impurities which reduce the activity of nickel catalysts during fatty acid hydrogenation. A

refined and bleached tallow with free of catalyst poisons was used as a starting material. The impurities were prepared by adding the following compounds: 5-sulfosalicylic acid, hexachlorocyclohexane or aldrin, lecithin, and l-leucine or choline for S, Cl, P, and N respectively to the "poison-free" fatty acid (cLntrol). The influence of 0.2-0.5% sodium soaps or 0.5-2.5% oxidized fatty acid in tallow and soy fatty acids was also examined.

The impurities in fatty acids which affect the hydrogenation process were divided into three categories categories: catalyst poisons (S, N, P, Cl, and As), catalyst inhibitors (decomposition products, gums, alkali soaps, and oxidized fatty acids), and catalyst deactivators (acids, water, and carbon monoxide). The catalyst poisons are strongly attached to the Ni surface via electron donation which reduces the activity of catalyst. A second group, catalyst inhibitors, such as decomposition products, gums, oxidized fatty acids, or alkali soaps, which will be adsorbed, e.g., at the entrance of the pores of the catalyst surface. The third group, catalyst deactivators, decreases the hydrogenation reaction rate because the compounds can react chemically with the nickel crystallites.

Kubicka and Horacek (2011) studied the deoxygenation of several rapeseed oils with different degree of upgrading over sulfided CoMo/γ-Al_2O_3 catalyst. All hydrotreating experiments were carried out in an electrically heated fixed bed tubular reactor. The reaction temperature, hydrogen pressure, hydrogen-to-oil molar ratio, and WHSV were kept constant at 310 ^{o}C, 3.5 MPa, 100 mol/mol, and 2 h^{-1}, in that order. As the main objective of the experiments was to establish the role of vegetable oil impurities in catalyst deactivation, the experiments were performed under constant conditions for 100–150 h. The result showed that the presence of alkalis promoted catalyst deactivation due to their deposition on catalyst surface leading to blockage/poisoning of active sites. The effect of phosphorus was two-fold. When charge-compensating alkalis were present, corresponding phosphates were deposited above and at the beginning of catalyst bed leading to gradual build-up of deposits. On the other hand, in absence of alkalis decomposition of phospholipids yielded phosphoric acid that catalyzed oligomerization reactions leading to rapid catalyst deactivation by carbonaceous deposits. Presence of sulfur compounds was shown to be beneficial for the catalyst deoxygenation performance. While in absence

of DMDS gradual deactivation was observed, addition of DMDS resulted in a stable catalyst performance.

2.3.4 Synthesis of Solid Catalysts

Solid catalysts are composed of metals or metal oxides that form supports onto oxides and create metal particles with high surface areas. The goal is to form small metal particles with high surface areas, since reactions take place on the surface, so the more surface area, the more the reaction can take place.

Methods of catalyst preparation arc very diverse and each catalyst may be produced via different routes. Preparation usually involves several successive steps. Many supported metal and oxide catalysts are prepared by the succession of impregnation, drying, calcination, activation; zeolite catalysts are prepared by precipitation of gel, crystallization, washing, ion exchange, drying. The properties of heterogeneous catalysts depend on all their previous history.

Three fundamentals stages of catalyst preparation may be distinguished:

- Preparation of the primary solid (or first precursory solid) associating all the useful components (e.g., impregnation or co-precipitation, or, in the case of zeolites, crystallization).
- Processing of that primary solid to obtain the catalyst precursor, for example by heat treatment.
- Activation of the precursor to give the active catalyst: reduction to metal (hydrogenation catalysts), formation of sulfides (hydrodesulphurization), deammoniation (acidic zeolites). Activation may take place spontaneously at the beginning of the catalytic reaction (selective oxidation catalysts).

There are conventional approaches to prepare these materials. The methods that have found wide use (including industrial use) are impregnation and co-precipitation. In the last two decades, the greatest progress has been made in the sol–gel preparation of dispersed single component and multicomponent systems by the hydrolysis of solutions of metal alkoxides and in the synthesis of new, so-called mesophase mesoporous materials (Pakhomov and Buyanov, 2005).

2.3.4.1 Impregnation

Impregnation is a preparation technique, in which a solution of the precursor of the active phase is brought in contact with the support. Impregnation consists in contacting a solid with a liquid containing the components to be deposited on the surface. During impregnation many different processes take place with different rates. There are at least 8 different methods for impregnation but only 3 methods are discussed.

- Impregnation by soaking or excess solution impregnation (ESI)

Excess liquid is eliminated by evaporation or by draining. Deposition of the active element is never quantitative. The quantity deposited depends on the solid/liquid ratio. Deposition is slow, requiring several hours or days. Extensive restructuring of the surface (loss of surface area, etc.) may occur. However, the method allows the distribution of the species to be very well controlled and high dispersions may be obtained. The method works best if ion/solid interactions are involved.

A disadvantage of the ESI technique is the interaction that occurs between the surface of the support and the catalyst solution because the various catalytically active materials have different chemisorption rates or react at different rates and different equilibrium levels. This leads to "preferential loading" of some metals over others, and unit selectivity cannot be achieved.

- Dry or pore volume impregnation (PVI)

The required amounts of components are introduced in the volume corresponding to the pore volume of the support. The method is best suited to deposition of species which interact very weakly with the surface, and for deposition of quantities exceeding the number of adsorption sites on the surface. If the number of species which can adsorb on the surface is smaller, a chromatographic effect may occur, i.e. attachment to the mouth of the pores. Redistribution inside the pores is very slow.

Advantages of the PVI technique include easy determination of the catalyst volume solution required, and unit selectivity (i.e., the weight ratios of the catalytically active materials in the solution are equal to the weight ratios of the catalytically active materials in the substrate). However, pore volume impregnation

is not readily applicable to monolithic catalyst supports due to the complexity and rigidity of their shape. Simply absorbing the volume of solution equivalent to the volume of the support, generally results in very poorly distributed catalysts.

- Incipient wetness impregnation (IWI)

This method is used in present research. A procedure similar to dry impregnation, but the volume of the solution is more empirically determined to correspond to that beyond which the catalyst begins to look wet. All the comments under pore volume impregnation above can be applied.

After these methods, the catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface.

2.3.4.2 Sol-gel Method

Sol-gel processing is one of the routes for the preparation of porous materials by their solidification from a true solution phase. The method is characterized by the formation of stable colloidal solutions (''sol'') in the first step followed by anisotropic condensation of colloidal particles (micelles) producingpolymeric chains with entrapped solution of condensation by-products, resulting in the formation of a ''lio- or hydrogel'' or ''monolith'' when external solvent is not used. After washing out the by-products the solvent removal produces ''xero-'' or ''aerogels,'' depending on the drying mode, with distinct structure of the primary particles, and their packing manner (texture). In Figure 2.9, general scheme of sol-gel processing in the preparation of solid materials is shown.

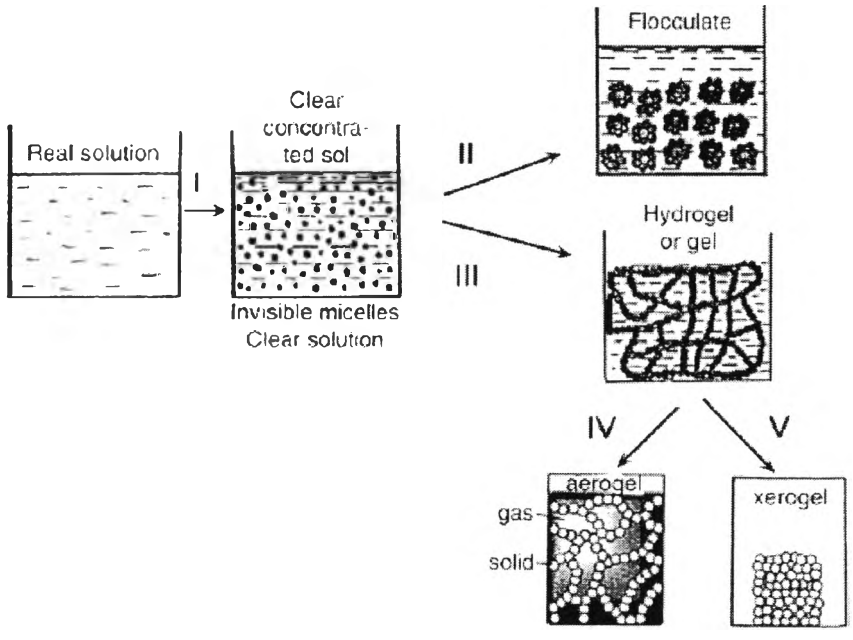

Figure 2.9 General scheme of sol-gel processing in the preparation of solid materials: I – colloidization; II – flocculation; III – gelation; IV – supercritical fluid processing; and V – drying by evaporation.

2.3.4.3 Co-precipitation

Co-precipitation is one of the routes for the preparation catalyst where one or more metals are precipitated together with the support or its precursor. However, for a number of catalysts, and especially at large scale, co-precipitation can be very attractive and indeed a large number of commercial catalysts.

A benefit of co-precipitation over impregnation is the high attainable metal loading of up to 60%, sometimes up to 80% or even higher, compared to typically <30% metal loading for impregnation. Because of these high metal loadings, co-precipitated catalysts are often referred to as ''bulk'' catalysts or ''self-supporting'' catalysts. Another benefit is the relatively high metal dispersion. As a result the weight and volume activities, which are a function of the product of both metal loading and dispersion, are generally higher than for an impregnated catalyst. Not only different metals and support (precursors) may be deposited in a single process, but also mixtures of metallic and/or even nonmetallic promoters, for example, sulfur, making co-precipitation a highly versatile process.