

CHAPTER II

THEORETICAL CONSIDERATIONS

2.1 Alternative renewable energy

While the energy demand is continually increasing, the fossil fuel resources (e.g. crude oil, natural gas, coal) are reduced and finite. So the alternative renewable energy becomes interesting and the researches are directed toward solar tower, dams and alternative energy. Biofuel with low molecular weight can be used for engine fuel instead of diesel fuel. More than one hundred years ago, a brilliant inventor named Rudolf Diesel designed the original diesel engine to run on vegetable oil. He used peanut oil to fuel one of his engines at the Paris Exposition of 1900 [7]. In 1930s and 1940s vegetable oils were used as diesel fuel but usually in emergency situation only. Recently, due to increase of crude oil prices, limited resources of fossil fuel and environmental concerns, there has been focusing on vegetable oils and animal fats to make biodiesel.

Biodiesel is a type of the alternative diesel fuel manufactured from vegetable oil and animal fats. Biodiesel is defined as consisting of monoalkyl esters which formed by transesterification or alcoholysis of the triglyceride from the vegetable oils or animal fats with a monovalent low-molecular weight alcohol such as methanol or ethanol. This reaction can be activated in presence of catalyst and without catalyst. Generally, the manufacture uses a strong base such as sodium or potassium hydroxide as catalyst because the reaction uses a short time. It produces new chemical compound called esters which these esters have come to be known as *biodiesel* [8].

Vegetable oils are primarily water-insoluble hydrophobic substances that are made of one mole glycerol and three moles of fatty acids and are commonly called triglycerides [9]. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The fatty acids found in vegetable oils and typical fatty acid compositions of common oil sources are summarized in Table 2.1 and Table 2.2, respectively. Table 2.3 showed the names, in a variety of formats, of common fatty acids.

Table 2.1 Fatty acid compositions of vegetable oil [9, 10^a, 11^b]

Vegetable oil	Fatty acid composition, % by weight								
	16:0	18:0	20:0	22:0	24:0	18:1	18:2	18:3	22:1
Corn	11.67	1.85	0.24	0.00	0.00	25.16	60.60	0.48	0.00
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	57.51	0.00	0.00
Crambe	2.07	0.70	2.09	0.80	1.12	18.86	9.00	6.85	58.51
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.40	22.30	8.23	0.00
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	55.53	6.31	0.00
Sunflower seed	6.08	3.26	0.00	0.00	0.00	16.93	73.73	0.00	0.00
Canola oil^a	5.50	2.20	0.70	0.50	0.30	55.00	24.00	8.80	0.40
Palm^b	43.50	4.30	0.20	0.00	0.00	39.80	10.20	0.30	0.00

Table 2.2 Typical fatty acid composition-common oil sources [9]

Fatty acid	Soybean	Cotton	Palm	Lard	Tallow	Coconut seed
Lauric, C12:0	0.1	0.1	0.1	0.1	0.1	46.5
Myristic, C14:0	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic, C16:0	10.2	20.1	42.8	23.6	23.3	9.8
Stearic, C18:0	3.7	2.6	4.5	14.2	19.4	3.0
Oleic, C18:1	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic, C18:2	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic, C18:3	8.6	0.6	0.2	0.4	0.9	0.0

Natural vegetable oils and fats were commonly extracted or pressed to obtain crude oils or fats. These usually contain FFAs, phospholipids, sterols, water, odorants and other impurities.

Table 2.3 Names and structures of the most common fatty acids [12]

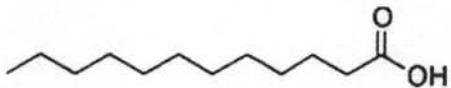
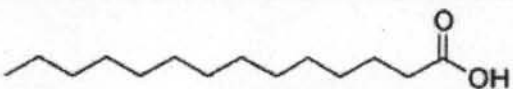
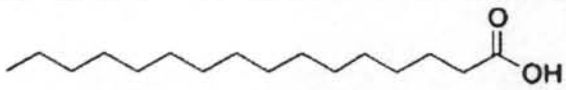
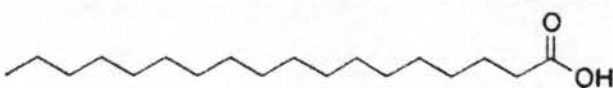
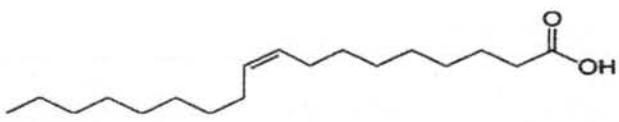
No. of C:No. of double bond	Molecular formula (Molecular mass)	Systematic name	Other names
C12:0	C ₁₂ H ₂₄ O ₂ (200.32)	Dodecanoic acid	Lauric acid, n-Dodecanoic acid
			
C14:0	C ₁₄ H ₂₈ O ₂ (228.38)	Tetradecanoic acid	Myristic acid
			
C16:0	C ₁₆ H ₃₂ O ₂ (256.43)	Hexadecanoic acid	Palmitic acid, hexadecylic acid cetylic acid
			
C18:0	C ₁₈ H ₃₆ O ₂ (284.48)	Octadecanoic acid	Stearic acid
			
C18:1 ^{Δ9}	C ₁₈ H ₃₄ O ₂ (282.46)	(9Z)-octadec-9-enoic acid	(9Z)-Octadecenoic acid, (Z)-Octadec-9-enoic acid, <i>cis</i> -9-octadecenoic acid, <i>cis</i> -Δ9-octadecenoic acid, Oleic acid, 18:1 <i>cis</i> -9
			

Table 2.3 Names and structures of the most common fatty acids (*Continued*)



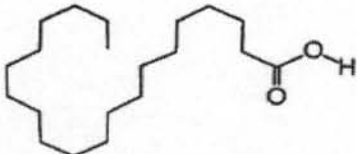
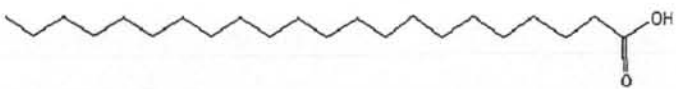
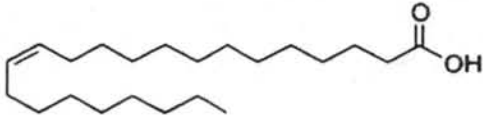
No. of C:No. of double bond	Molecular formula (Molecular mass)	Systematic name	Other names
C18:2 ^{Δ9,12}	C ₁₈ H ₃₂ O ₂ (280.46)	(9Z,12Z)- Octadecadienoic acid	Linoleic acid, <i>cis-cis</i> -9,12- Octadecadienoic acid
			
C18:3 ^{Δ9,12,15}	C ₁₈ H ₃₀ O ₂ (278.44)	(9Z,12Z,15Z)- Octadecatrienoic acid, <i>all-cis</i> -9,12,15- octadecatrienoic acid	α-Linolenic acid, <i>cis,cis,cis</i> -9,12,15- Octadecatrienoic acid, (Z,Z,Z)-9,12,15- Octadecatrienoic acid, Industrene 120
			
C20:0	C ₂₀ H ₄₀ O ₂ (312.54)	Icosanoic acid	eicosanoic acid, <i>n</i> -eicosanoic acid, arachidic acid, arachic acid,
			
C22:0	C ₂₂ H ₄₄ O ₂ (340.60)	Docosanoic acid	Behenic acid
			

Table 2.3 Names and structures of the most common fatty acids (*Continued*)

No. of C:No. of double bond	Molecular formula (Molecular mass)	Systematic name	Other names
C22:1	C ₂₂ H ₄₂ O ₂ (338.58)	Z-13-Docosenoic	<i>cis</i> -13-Docosenoic Erucic acid
			

2.2 The appropriate oils or fats for production of biodiesel

The quality of the biodiesel from fatty acid depends on the composition of the fatty acid in the vegetable oil. Various types of fatty acids have an effect on the physical properties related to the biodiesel produced. Saturated fatty acids such as stearic and palmitic acids, improve Cetane number, CN (See definition, p.xvi) and stability and reduce NO_x emissions, but create significant cold weather performance issues. Due to the high CNs of many fatty compounds, especially saturated ones, even exceeding the cetane scale, the term 'lipid combustion quality number' was suggested for use with those compounds. The effects of structure of fatty compounds on CN were also predicted. The structure of fatty esters can also influence emissions with, for example, NO_x emissions being reduced by increasing saturation. The highly saturated fatty acid level in fact proves to be advantageous in terms of storage stability as compared to the more unsaturated vegetable oil-based fuels, which are more susceptible to the chemical deterioration (e.g. autoxidation and polymerization) under certain conditions of storage temperature, moisture, ultraviolet radiation, and packaging materials [13]. Contrary to this, polyunsaturated fatty acids such as linoleic or linolenic acids provide good performance cold weather, but reduce stability. Cetane number lead to high levels of NO_x emissions. The number of double bonds appears to be a key factor in the performance of these fuels (polyunsaturated fatty acids have too many; saturated fatty acids have too few). Short chain fatty acids

(C6-C14) have a negative effect on flash point (See definition, p.xvi) since flash point is increased by increasing the molecular weight. Long chain fatty acids (C14-C22) are an obvious rejection to the biodiesel industry because they increase the viscosity of the biodiesel and responsible for insecurity of biodiesel in cold weather [4]. The main relationships between fatty acid composition and biodiesel properties are summarized in Table 2.4 [14]. Otherwise, various fatty acid contents have effect to cloud and pour points (See definition, p. xvi).

The appropriate fats and oils were picked through accessing their physical and chemical properties. Table 2.5 was showed the significance of parameters on the properties of biodiesel.

Table 2.4 Relationships between biodiesel properties and fatty acids composition

Fatty acid	Positive Effect	Negative Effect
Saturated	Cetane value Oxidation stability	Cold Stability
Polyunsaturated	Cold stability	Oxidation stability
Short chain fatty acid	Distillation curve	Flash point
Long chain fatty acid	Viscosity	Cold stability

Table 2.5 Interaction between the chemical parameters and behavior [14, 15, 16, 17]

Parameters	Effect on:
Acidity	Corrosion properties Cold stability Hydrolytic stability Fire resistance Thermal stability
Partial ester (high hydroxyl value)	Cold stability Thermal stability Corrosion properties Hydrolytic stability

Table 2.5 Interaction between the chemical parameters and behavior (*Continued*)

Parameters	Effect on:
Free monoalcohol	Flash point
Free polyalcohol	Formation of insolubles
Free methyl esters (in polyolesters)	Low viscosity Fire resistance Thermal stability
Catalyst residue	Soap formation Insolubles Hydrolytic stability Thermal stability Oxidation stability
Free fatty acids (FFAs)	Acid number Soap formation Gum formation

2.3 The production of biodiesel

The production of biodiesel typically uses transesterification process. Transesterification is the general term used to describe organic reactions where an ester is transformed into another ester through interchange of the alkoxy moiety as shown in Figure 2.1. When the ester is reacted with an alcohol, this process is called alcoholysis.

**Figure 2.1** General equation for transesterification reaction

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of strong acid or base to give a mixture of fatty acids alkyl esters and glycerol as shown in Figure 2.2 [18].

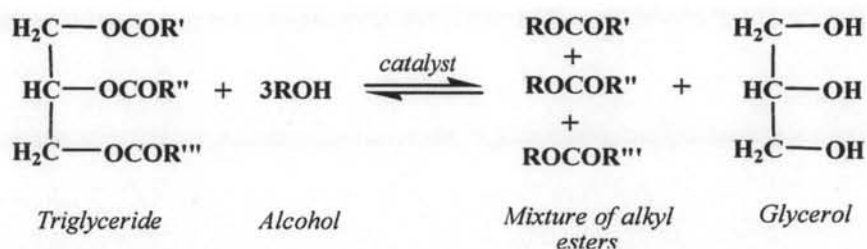


Figure 2.2 Transesterification of vegetable oils

Alcohols can be used in the transesterification process which short chain such as methanol, ethanol, propanol and butanol. Methanol and ethanol were used most frequently, especially methanol because of its low cost and its physical and chemical advantages [7]. Generally methanol can quickly react with triglyceride in the presence of sodium hydroxide (NaOH).

A catalyst is usually used to improve the reaction and yield transesterification. Because the reaction is reversible (the overall process is a sequence of three consecutive, in which di- and monoglycerides are formed as intermediates), excess alcohol is used to shift the equilibrium to product side. To complete a transesterification stoichiometrically, 3:1 molar ratio of alcohol to triglyceride is required. Alkyl group (R) in triglyceride refers to fatty acids, for example, palmitic acid, linoleic acid or linolenic acid.

The general aspects of these processes and the applicability of different types of catalysts can be used [18] consisting of:

2.3.1. Acid-catalyzed processes

The processes are catalyzed by Brønsted acids, preferably by sulfonic acid, sulfuric acid and hydrochloric acid. These catalysts give very high yields in alkyl esters but the reactions are slow and requiring temperature above 100°C and more than 3 h to reach the complete conversion. Transesterification process under acid-catalyzed condition needs to be done in absence of water because the water reduces the yield alkyl ester. The alcohol/oil molar ratio is one of the main factors that influence the transesterification. An excess alcohol favors the formation of products. On the other hand, an excessive amount of alcohol makes the recovery of glycerol difficult.

2.3.2. Base-catalyzed processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction and is most often used commercially. Due to the fact that alkaline catalysts are less corrosives, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium or potassium carbonate. They give very high yields in short reaction times and relatively cheap. But it has disadvantage, the process is added these catalysts into feedstocks, the FFAs react with the catalyst to form soap and water if the oil or fat contains amounts of FFAs. The reaction was showed below:

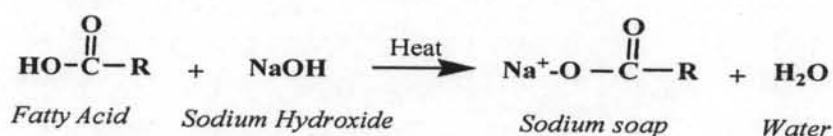


Figure 2.3 The reaction of sodium soap [8]

This reaction is called “saponification”. So in this process, glyceride and alcohol must be anhydrous because the reaction will change to saponification in the presence of water. The presence of soap effect to yield of esters and makes the separation of ester, glycerol and water difficult.

2.3.3. Lipase-catalyzed processes

The use of this type of catalyst is unfavourable compared to using base catalyst in transesterification process but immobilized lipase in esterification process had important advantage. Due to the yield of ester were almost 100% and no problem with contaminated glycerol [19]. The few advantages of using lipase catalysts can tolerate organic solvents, are stable and are readily available. The example of lipase catalysts includes PS 30 [20], Novozym 435-catalyzed [21-23]. Recent studies have indicated the use of biocatalyst on the production of biodiesel. The use of whole cell biocatalyst immobilized within biomass support particle, like lipase is of advantage to the biodiesel industry. Immobilized *Pseudomonas fluorescense* lipases is very popular as a biocatalyst relative to mobilized biocatalyst as its activity is more effective and it can be repeatedly used without any decrease activity [24]. Further studies to genetically engineer of this product are being done [25].

2.3.4. Non-ionic base-catalyzed processes

A great number of organic bases has been developed and used as catalyst or reactant for organic synthesis. These provide for a mild reaction condition to simplify manipulation of the factors involved in increasing the yield of the alkyl ester. Bases were used in this process including amines such as triethylamine, piperidine; amidines such as 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN); guanidines such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,1,3,3-tetramethylguanidine (TMG) and amino- and nitroguanidines such as tris(dimethylamino)methyliminophosphorane (Me_7P).

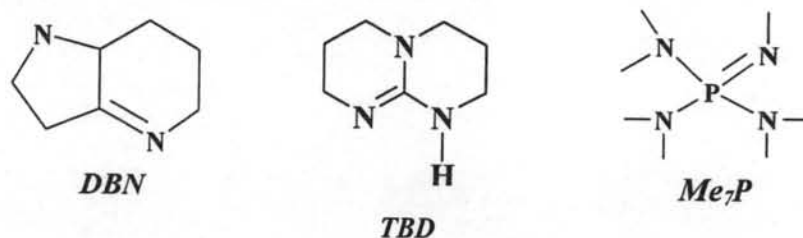


Figure 2.4 Samples of non-ionic base-catalysts

The reaction yields obtained with TBD were close to observed with NaOH and no unwishful by-product such as soaps (easily formed when alkaline metal hydroxides are used) were observed.

2.3.5. Heterogeneously catalyzed processes

Although transesterification using a conventional base-catalyzed process gives high conversion levels of triglycerides to their corresponding alkyl esters in short times, the reaction has several drawbacks: it is energy intensive; recovery of glycerine is difficult; the catalyst has to be removed from the product; alkaline waste-water requires treatment and FFAs and water interfere with reaction. In order to minimize problems, attempts to use heterogeneous catalyst system in alcoholysis of triglycerides have been made. They can be easily separated from the system at the end of the reaction and could also be reused even they could not be used for a long duration of time as they leach out and the reaction is incomplete and the phases are difficult to separate. However, the performance is still unfavourable compared to the based catalysts. The heterogeneous catalysts have been reported in the literature, such as zeolites, clays, guanidines heterogenized on organic polymers, ion exchange resins, oxides, etc [26].

2.3.6. Noncatalytic transesterification process

In addition, a catalytic reaction which produce biodiesel through transesterification, several processes like the recovery of unreacted reactants and catalysts, purification of the esters and separation is involved. These processes make the production of biodiesel through catalytic transesterification system complicated (separation of catalyst from the reaction mixture is very difficult), thus giving a reason to investigate production of alkyl esters from vegetable oils via non-catalytic reactions. Supercritical alcohols have been explored as a reactant for the transesterification process and have proven a conversion rate of triglyceride to be 80-100% as called non-catalytic transesterification process. Transesterification process can also be done without the aid of a catalyst, high temperature, high pressure and less excess alcohol is required in absence of catalysts [27]. We can summarize the preparation of biodiesel according to used process, as shown in Table 2.6.

Table 2.6 Classification of processes use different catalysts for the preparation of biodiesel

Homogeneous processes	Heterogeneous processes
Acid-catalyzed process	Lipase-catalyzed process
Base-catalyzed process	Heterogeneous process
Non-ionic base-catalyzed process	
Noncatalytic process	

Normally, transesterification of vegetable oils is used base-catalyst processes in commercial due to give a very high yields and very active. After transesterification of vegetable oils, the product is a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglyceride. It is not easy to gain pure ester without impurities such as di- and monoglycerides [28]. The by-product, glycerol needs to be recovered because of its value added for important applications, in cosmetics, toothpastes, pharmaceuticals, lacquers, plastics, alkyl resins, foods and beverages, explosives, cellulose processing, etc. The separation of glycerol can be done by gravitational settling.

Transesterification consists of a number of successive and reversible reactions. Triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol

[29] as shown in Figure 2.5. A mole of ester is released at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol which overall reaction referred to above. The process of biodiesel production is shown in Figure 2.6.

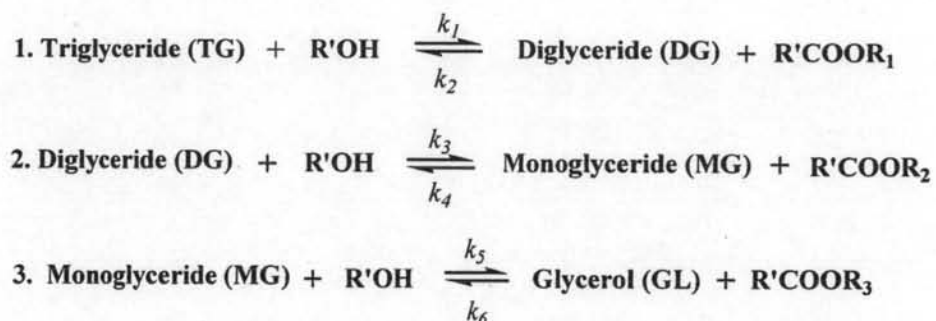


Figure 2.5 The transesterification reactions of vegetable oil with alcohol to ester and glycerol [7]

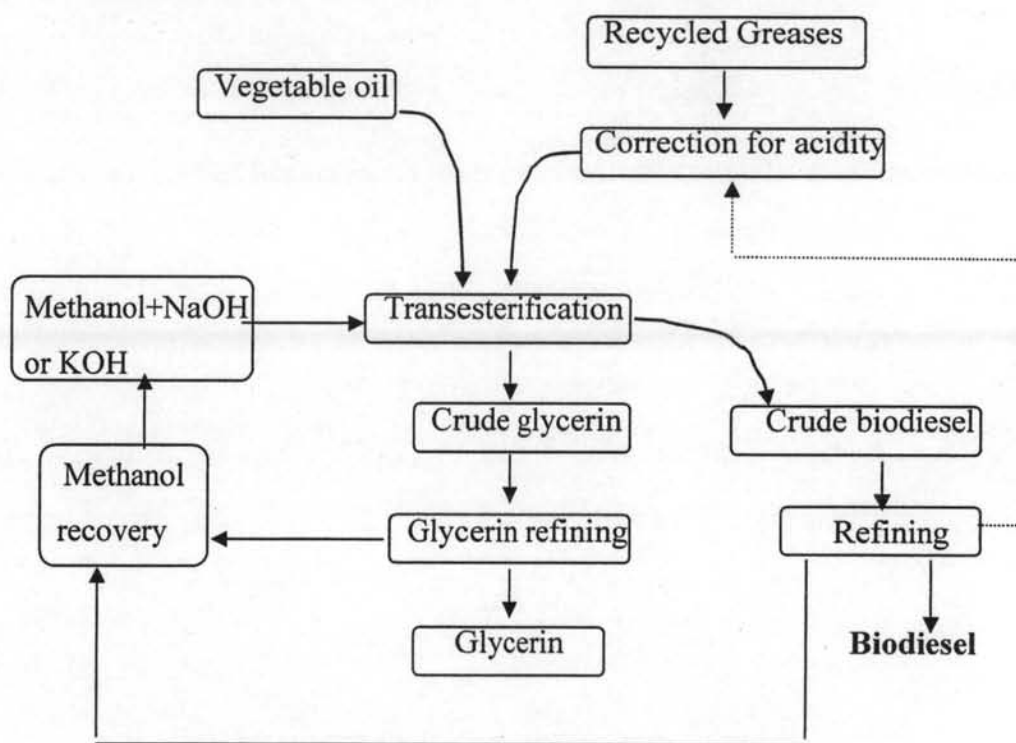


Figure 2.6 Process for biodiesel production [27]

The physical properties of primary chemical products of transesterification are summarized in Tables 2.7 and 2.8. The boiling points and melting points of the fatty acids, methyl esters, mono-, di- and triglyceride increase following up the increasing of carbon atoms in the carbon chain. However, these properties will decrease with the

increase of number of double bonds. The melting points also increase when tri-, di- and monoglyceride increase, because the polarity of the molecules and hydrogen bonding increase.

Table 2.7 Physical properties of chemical related to transesterification [9]

Name	Specific gravity (g/ml)	Melting point (° C)	Boiling point (° C)
Methyl laurate ^a	-	5.2	262.0
Methyl myristate	0.875	18.8	295.0 ^a
Methyl palmitate	0.825	30.6	196.0
Methyl stearate	0.850	38.0	215.0
Methyl oleate	0.875	-19.8	190.0
Methyl linoleate ^a	-	-35.0	215.0
Methanol	0.792	-97.0	64.7
Glycerol	1.260	17.9	290.0

^aData from [12]

Table 2.8 Melting points of fatty acids, methyl esters and mono-, di- and triglyceride [30]

Fatty acid		Melting point (° C)				
Name	Carbon	Acid	Methyl	1-Mono glyceride	1,3-Di glyceride	Triglyceride
Myristic	14:0	54.4	18.8	70.5	66.8	57.0
Palmitic	16:0	62.9	30.6	77.0	76.3	63.5
Stearic	18:0	69.6	39.1	81.5	79.4	73.1
Oleic	18:1	16.3	-19.8	35.2	21.5	5.5
Linoleic	18:2	-6.5	-35.0	12.3	-2.6	-13.1

2.4 Combustion, emission, engine problems and deposit [13]

Generally, similar types of compound are observed in the exhaust emission of conventional Diesel Fuel (DF) and vegetable oil-derived fuels. This is proof of the suitability of fatty compounds as diesel because there presumably are similarities in their combustion behavior.

Emissions from any kind of engine are the result of the proceeding combustion within in the engine. The combustion process, in relation to the properties of the fuel, and its completeness are responsible for any problems associated with the use of biodiesel, such as formation of deposits, etc. To comprehend the formation of emissions, deposits, and possibly direct the combustion to suppress undesirable emissions and deposits.

Ideally, the products of complete combustion of hydrocarbons are CO₂ and water according to the equation which show for alkanes (saturated hydrocarbon):



Combustion in a diesel engine occurs mainly through a diffusion flame and is therefore incomplete. This causes the formation of partially oxidized materials such as carbon monoxide (CO), other oxygenated species (aldehydes, etc.) and hydrocarbon.

In the case of biodiesel, release of CO₂, as indicated above, from the ester moiety of methyl ester occurs besides combustion formation of CO₂ from hydrocarbon portions of biodiesel. The formation of CO₂, an incombustible compound despite its high oxygen content (although mistakenly assumed that it can serve as a combustion enhancer because of its high oxygen content), shows that one has judicious in choosing oxygenated compound as combustion enhancer for the combustion-enhancing properties will depend on the nature of the oxygen (such as bonding, etc.) in those compounds. So, the higher oxygen content of biodiesel does not necessarily imply improved combustion compared to conventional DF because of removal of this oxygen from the combustion process by liberation of CO₂, but CO₂ may contribute to combustion in other ways.

Exhaust emissions observed in the combustion of conventional DF and biodiesel are smoke, particulates polyaromatic hydrocarbons (PAHs), hydrocarbons, CO and oxides of nitrogen (NO_x; referred to as nitrous oxides or nitrogen oxides).

Important differences are sulfur-containing emissions which are not formed from biodiesel due to its lack of sulfur.

Engine problem is used neat vegetable oil fuel. At least in short-term trials, neat oils gave satisfactory engine performance and power output, often equal to or even slightly better than DF. However, vegetable oils cause engine problems. This was recognized in the early stages of renewed interest in vegetable oil-based alternative DFs.

Generally, most emissions observed for DF are reduced when using esters. In early reporting emissions with methyl and ethyl soyate as fuel, it was found that CO and hydrocarbons were reduced while NO_x were produced consistently at a higher level than the reference DF. The differences in exhaust gas temperatures corresponded with the differences in NO_x levels. Similar results were obtained on the emissions of rapeseeds oil methyl ester. NO_x emissions were slightly increased, while hydrocarbon, CO, particulate and PAH emissions were in ranges similar to the DF reference. The study on PAH emissions, where also the influence of various engine parameters was explored, found that the PAH emissions of sunflower ethyl ester were situated between DF and the corresponding neat vegetable oil.

Biodiesel has great advantages compared with the DF. It is functionally identifying standard petro diesel, and from an emissions and exhaust stand-point it has a number of major advantages [31]:

- Biodiesel contributes no sulfur at all to the atmosphere (diesel uses sulfur as a lubricant).
- Biodiesel adds no new carbon dioxide to the atmosphere.
- Biodiesel has cetane ratings slightly higher than diesel.
- Biodiesel is both non-toxic and fully-biodegradable.
- Biodiesel has a higher flash point than diesel and is therefore much safer to store.
- Biodiesel can be made from waste restaurant oils and animal fats.
- Biodiesel can be blended in any proportion with petroleum diesel fuel.

Although biodiesel has several advantages but it has disadvantages too. Such as currently more expensive, gel at low temperature, more nitrogen oxide emissions, degrade rubber compounds impacting fuel hose and pump. Problems appear only after

the engine has been operating on biodiesel for longer periods of time and storage as included [32]:

- Corrosion of FIE components
- Elastomeric seal failures
- Low pressure fuel system blockage
- Fuel injector spray hole blockage
- Increased dilution and polymerisation of engine sump oil
- Pump seizures due to high fuel viscosity at low temperatures

2.5 Biodiesel quality

Due to the fact that biodiesel is produced in quite differently scaled plants from vegetable oils, it was necessary to install a standardization of fuel quality to guarantee engine performance. Generally, it use ASTM D6751 but several countries in Europe did establish standards for biodiesel such as Austria, Sweden. When compared properties of diesel fuel and biodiesel, there is a standard for describing the chemical composition and purities of fatty acid methyl ester (FAME) as shown in Table 2.9. For Thailand, it has set legislative assembly characteristic and quality of biodiesel as shown in Table 2.10.

Table 2.9 Selected fuel properties for diesel and biodiesel fuels [33]

Fuel Property	Diesel	Biodiesel (B100)
Fuel Standard	ASTM D975	ASTM D6751
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower Heating Value, Btu/gal	131,295	117,093
Kinematic viscosity, @ 40 °C	1.3-4.1	1.9-6.0
Specific Gravity kg/l @ 60 °F	0.85	0.88
Density, lb/gal @ 15 °C	7.079	7.328
Water, ppm by wt	161	0.05% max
Carbon, wt%	87	77
Hydrogen, wt%	13	12
Oxygen, by dif. wt%	0	11
Sulfur, wt%	0.05 max	0.0-0.0024
Boiling Point, °C	188-343	182-338
Flash Point, °C	60-80	100-170
Cloud Point, °C	-15 to 5	-3 to 12
Pour Point, °C	-35 to -15	-15 to 10
Cetane Number	40-55	48-65
Stoichiometric Air/Fuel Ratio, wt/wt	15	13.8
BOCLE Scuff, grams	3,600	>7,000
HFRR, microns	685	314

Table 2.10 Characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand [34]

Characteristic	Value	Method of standard
Methyl ester, %wt.	>96.5	EN 14103
Density at 15°C, kg/m ³	860-900	ASTM D 1298
Viscosity at 40°C, cSt	3.5-5.0	ASTM D445
Flash Point, °C	>120	ASTM D 93
Sulphur, %wt.	<0.0010	ASTM D 2622
Carbon Residue, on 10% distillation residue, %wt	<0.30	ASTM D 4530
Cetane Number	>51	ASTM D 613
Sulfated Ash, %wt.	<0.02	ASTM D 874
Water, %wt.	<0.050	ASTM D 2709
Total Contaminate, %wt.	<0.0024	ASTM D 5452
Copper Strip Corrosion	<96.5	ASTM D 130
Oxidation Stability at 110°C, hours	>6	EN 14112
Acid Value, mg KOH/g	<0.50	ASTM D 664
Iodine Value, g Iodine/100 g	<120	EN 14111
Linolenic Acid Methyl Ester, %wt.	<12.0	EN 14103
Methanol, %wt.	<0.20	EN 14110
Monoglyceride, %wt.	<0.80	EN 14105
Diglyceride, %wt.	<0.20	EN 14105
Triglyceride, %wt.	<0.20	EN 14105
Free glycerin, %wt.	<0.02	EN 14105
Total glycerin, %wt.	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	<5.0	EN 14538
Phosphorus, %wt.	<0.0010	ASTM D 4951

2.6 History of biofuel in Thailand [35]

King Rama 9 was the first to realize the country's energy problem and he initiated the biofuel program in 1995 because of the consumption of gasoline and diesel is overabundance. In 1997, gasohol 95, a mixture of gasoline and 10% ethanol, was introduced to Thai consumer in a pilot area in Bangkok. By December 2004, there were more than 200 gas stations supplying gasohol 95. 'Diesohol', which is mixture of diesel and ethanol, was also initiated and developed in a project with royal patronage in 1998. However, diesohol is still at the experimental stage and is reported to have some disadvantages such as fuel instability and engine corrosion.

Biodiesel was introduced in Thailand in 1971 and has been much discussed since 2001. As mentioned earlier, biodiesel is obtained from vegetable oils and animal fatty acids. Biodiesel is still at the experimental stage and is not yet being produced for commercial use. By contrast, palm diesel (mixture of 2% refined bleached deodorized palm oil and 98% diesel) is available at two Petroleum Authority of Thailand (PTT) gas stations in Bangkok. So, palm oil is the alternative path for produce biodiesel.

2.7 Palm oil

The oil palm is a monocotyledon belonging to the genus *Elaeis*. The genus *Elaeis* comprises two species, namely *E. guineensis* and *E. oleifera*. But refer to *E. guineensis* which originating from West Africa was first introduced to Brazil and other tropical countries in the 15th Century by the Portuguese. It did not take off until the 19th Century when the Dutch brought seeds from West Africa to Indonesia resulting in four seedlings planted in Bogor, Indonesia in 1848 [11]. It is a perennial tree crop and the highest oil producing plant. The crop is unique in that it produces two type of oil. The mesocarp produces palm oil, which is used mainly for its edible properties and the kernel produces palm kernel oil, which has wide application in the oleochemical industry. Each palm tree produces approximately one fruit bunch, containing as many as 3000 fruitlets, per month. A brunch of fruits may contain a weight of 10-90 kilogram of fruits. In addition, each palm tree continues producing fruit economically for up to 25 years.

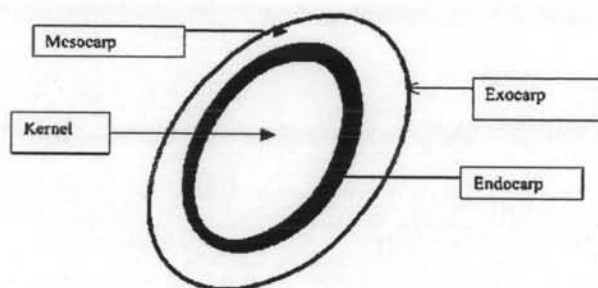


Figure 2.7 Composition of palm oil fruit

Palm oil is available in a variety of forms: crude palm oil (CPO, the production of crude palm oil showed in Figure 2.8), palm olein, refined, bleached and deodorized (RBD) palm oil, fractionated palm olein, palm stearin and palm mid-fraction. The extracted oil is known as CPO which until quite recently was known as the golden commodity [36]. Palm oil like all natural fats and oils comprises mainly triglycerides, mono- and diglycerides. There are minor components of palm oil such as phosphatides, sterols, pigments, tocopherols, tocotrienols and trace metals. Although less than 1% of the palm oil constituents, these components play an important role in the stability and quality of the oil. Carotenoids and vitamin E (tocopherols and tocotrienols) are important nutritional [37]. Other components in palm oil are FFAs, moisture and dirt.

The oil palm being extracted can be used in two different ways, the first part which contains 90% is used for food and food derivatives and the rest is used for non food products. The use of non-food product is rather small but it has high value.

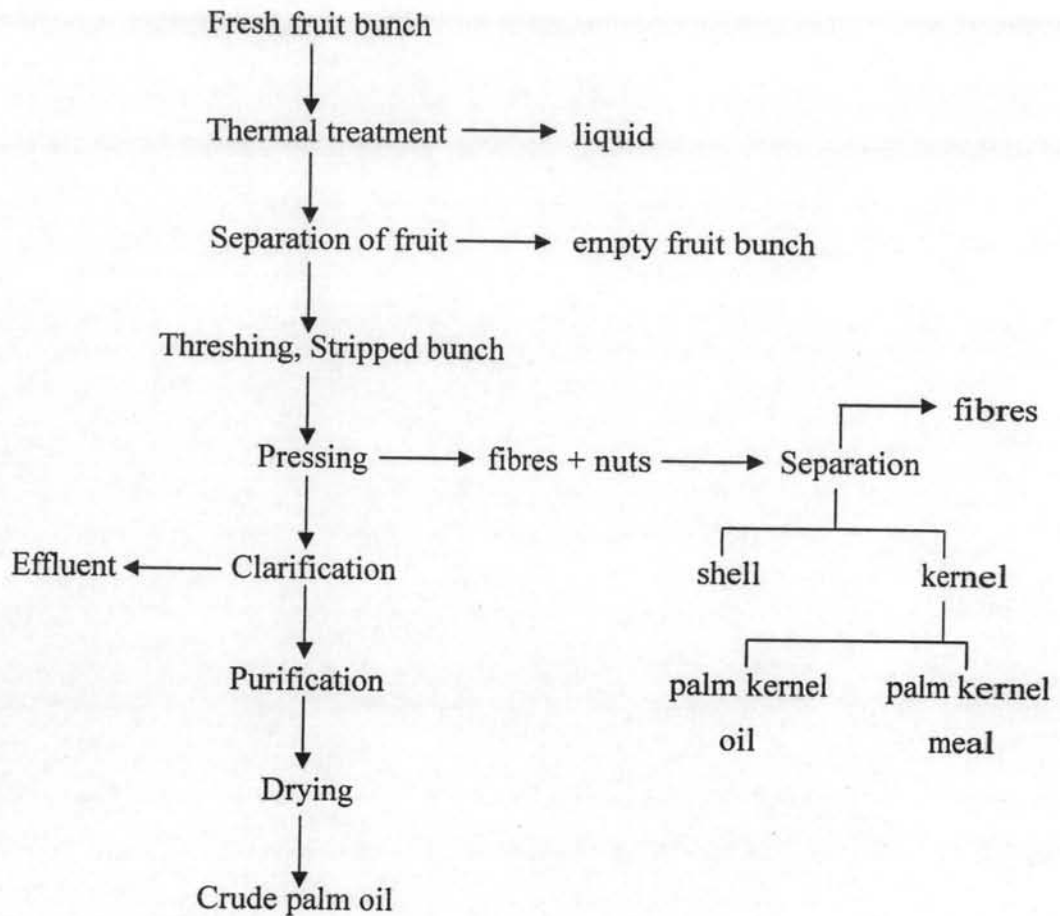


Figure 2.8 Diagram of the production of crude palm oil [39].

2.8 Chemical composition and properties of palm oil

Biodiesel typically contains up to 14 different types of fatty acids that are chemically transformed into fatty acid alkyl ester. Compositions of palm oil are within the range of those types of fatty acids as shown in Table 2.11.

Table 2.11 Typical (%) fatty acids composition of palm oil and palm kernel oil
[33]

Fatty acids	Carbon & Double Bond	%Fatty acid content	
		Palm Oil	Palm Kernel Oil
Caprylic	C8		2-4
Capric	C10		3-7
Lauric	C12		45-52
Myristic	C14	1-6	14-19
Palmitic	C16:0	32-47	6-9
Palmitoleic	C16:1		0-1
Stearic	C18:0	1-6	1-3
Oleic	C18:1	40-52	10-18
Linoleic	C18:2	2-11	1-2
Linolenic	C18:3		
Arachidic	C20:0		1-2
Eicosenoic	C20:1		
Behenic	C22:0		1-2
Euricic	C22:1		

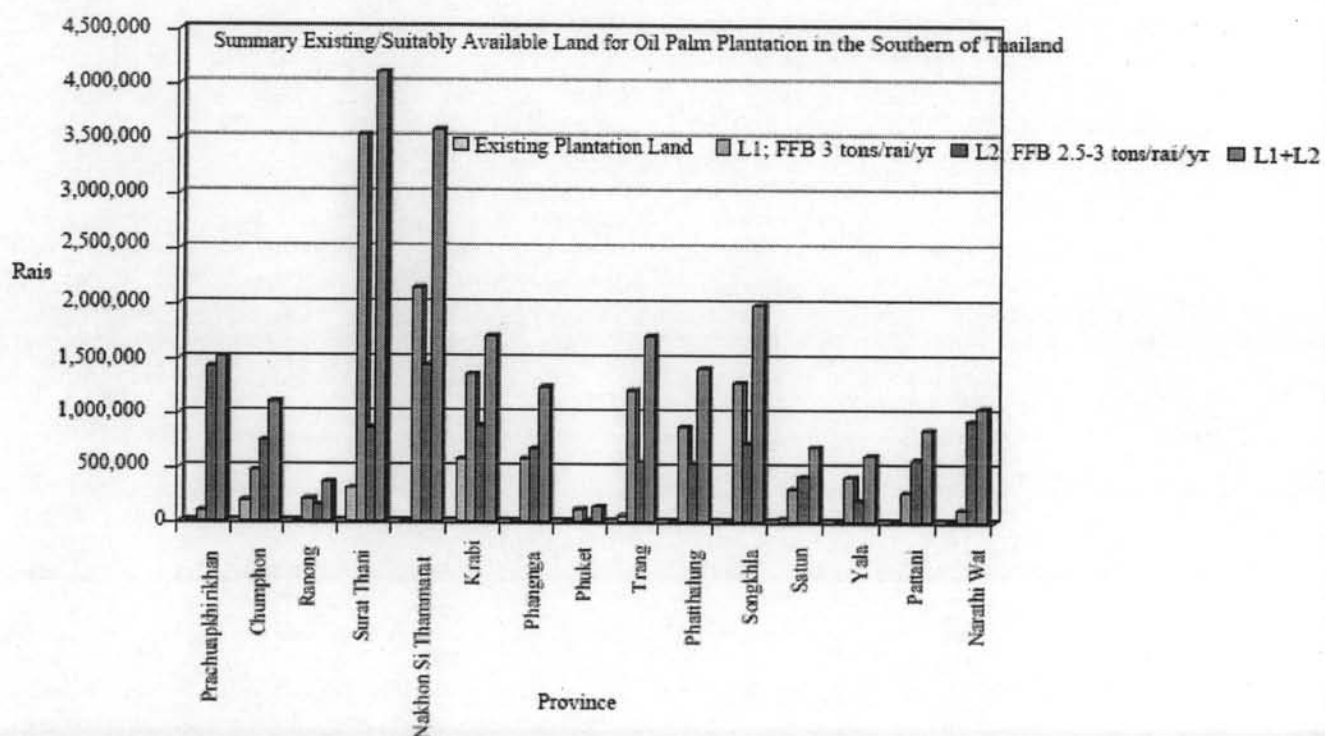
CPO has a rich orange-red colour because of its high content of carotene (700-800 ppm). The major carotenoids in palm oil are β - and α -carotene, which account for 90% of the total carotenoids. Carotenoids are the precursors of vitamin A, with β -carotene having the highest provitamin A activity [11].

2.9 Suitably obtainable area for oil palm plantation in Thailand

Oil palm was brought and grown in Thailand before World War II; consequently, the first commercial plantation started at Krabi and Satun provinces in 1968. The composition of FFAs from crude palm oil in Thailand was showed in Table 2.12. Currently, the government initiated a coordinative program with private sector and established the first refinery building in Krabi Province. Sarakoon et al. (1998) had conducted a study on the analysis and classification of suitably available land in

14 provinces in Southern Thailand, including Prachuap Khirikhan for oil plantation. The areas were excluded forest, existing plantation and communities or residential areas [39].

The oil palm plantation in the southern of Thailand is showed in Figure 2.9. Suratthani (~4 million rais) and Nakorn Si Thammarat (~3.5 million rais) have the largest suitable land remaining, respectively.



FFB- Fresh fruit bunches

Figure 2.9 Summary of existing and suitably available lands for oil palm plantation among studied provinces [39]

Table 2.12 Typical FFAs composition (%) of crude palm oil in Thailand [40]

Types of FFAs	% weight of FFAs
Saturated Fatty Acids	
Lauric acid (C12)	Little
Myristic acid (C14)	2
Palmitic acid (C16)	43
Stearic acid (C18)	7
Arachidic acid (C20)	Little
Unsaturated Fatty Acids	
Oleic acid (C18:1)	39
Linoleic acid (C18:2)	9
Linolenic acid (C18:3)	Little
Total	100

Thailand will never be able to produce enough palm oil to meet its energy needs. One palm tree can yield about 27 kilograms of palm oil per year. So, the government has strategic plan on palm cultivation area in 2004-2029 for aims to production and export palm oil as Malaysia and Indonesia. It puts up to increase areas as 10 million-rai in 2029. In 5 first years, it expands 40,000 rai palm plantation area [41].

From referred to the front, three raw important materials of production of biodiesel are animal fats and vegetable oils such as beef tallow, soybean oil, rapeseed oil, pork lard including low-molecular weight alcohols and catalyst. Especially, palm oil has highest yield oil of oil plant (See Appendix A). So, the government wants to increase palm cultivation to produce alternative energy to replace diesel and use in other industrial enterprise. Furthermore, there are several factors encouraging research on biodiesel and its development in Thailand. These include: 1) problems of oil price hikes that Thailand, being an oil importing country, has been facing; 2) continuous price drops of agricultural products causing troubles for farmers; 3) increasing transportation costs of agricultural products due to increasing prices of diesel; and 4) the environmental impact resulting from diesel combustion. It is interesting to purify biodiesel with adsorbents before uses in engine.

2.10 Other sources of biodiesel

Animal fats. The most prominent animal fat to be studied for potential biodiesel use is tallow. Tallow contains a high amount of saturated fatty acids, and it has therefore a melting point above ambient temperature. Generally, blends of tallow esters (methyl, ethyl, and butyl) with diesel fuel were studied. A study on blend of tallow with diesel fuel in short-term engine tests was carried out. The deposits were softer than those formed with cottonseed oil but still excessive. The deposits caused ring sticking and cylinder wear. Thus animal fats, like vegetable oils, were not suitable for long-term use unless modified.

Waste vegetable oils. Vegetable oils have many other applications, notably as food ingredients and cooking oils. Especially the latter use produces significant amounts of waste vegetable oils. However, analyses of used vegetable oils claimed that the differences between used and unused fats are not very great and in most cases simple heating and removal by filtration of solid particles suffices for subsequent transesterification. Filtered frying oil was transesterified under both acidic and basic conditions with different alcohols (such as methanol, ethanol, 1-propanol). The formation of methyl esters with base catalysis (KOH) gave the best yields.

2.11 Adsorption [42]

Adsorption is a process with which uses a solid to remove particles from a liquid or gas that passes across it. The particles stick to its surface.

Adsorption has been in use for thousands of years. Its first application was probably the use of bone ashes to remove colour by syrups or alcohol. At present, adsorbent materials are widely used; example, drinking water at water treatment plants is passed through activated charcoal to purify it.

All compounds are adsorbent to some extent. In order for a solid to be a good adsorbent, it must have a surface composed of molecules which provide a good attractive force. When molecules in the gas or liquid pass near the surface of the solid, they stick. This can happen in one of two ways:

1. Physisorption (by van der Waals and electrostatic forces)

This is the most common form of adsorption. The molecules are attracted by van der Waals forces, and attach themselves to the surface of the solid. The molecules remain intact, and can be freed easily (the forces are small, and short-range).

2. Chemisorption (by chemical bonding)

The molecules undergo a chemical bonding with the molecules of the solid, and this attraction may be stronger than the force holding the solid together. If the molecules are removed, they may form different compounds.

Another feature of a good adsorbent is a large surface area. The bigger its surface area, the more molecules it can trap its surface. Generally this means that a good adsorbent will be very porous; full of many tiny little holes on its surface that effectively increase its surface area by many times.

2.12 Impacted parameters of adsorption

- Type, physical properties and chemical properties of adsorbents such as surface area, pore size and chemical composition of adsorption.
- Type, physical properties and chemical properties of substances such as size, polar and chemical composition of molecule.
- Pressure or density of substance.
- Conditions of adsorption such as pH, temperature and time etc.

- Activated charcoal

Activated charcoal is the most commonly used adsorbent. It is full of holes, which makes its total surface area very large. There is lots of surface to hole molecules, which remain in place by van der Waals forces (physisorption). Activated charcoal is made by heating wood without oxygen. This removes the impurities, but leaves all the carbon in the wood mostly unburnt. About 25% of the original volume remains, and it's mostly carbon. Charcoal can then be burned itself, and very little smoke will result, because mostly it's just carbon combining with oxygen to produce CO₂ and CO (invisible gases). Activated charcoal is charcoal made from wood, sawdust, coconut shell, or bone, which has been treated with oxygen to remove all the impurities sticking to its surface inside the pores.

- Alumina (aluminium oxide)

Aluminium oxide is a chemical compound of aluminium and oxygen with the chemical formula Al_2O_3 . It is also commonly referred to as alumina in the mining, ceramic, and materials science. It has three types: acidic, basic and neutral and occurs in two forms: crystalline and powder. In its crystalline form, called corundum, its hardness makes it suitable for use as an abrasive and as a component in cutting tools. Powdered aluminium oxide is frequently used as a medium for chromatography. Alumina is the most widely used adsorbent because of the chemical properties of its surface and its ability to be shaped with well-defined pores defined as follows [43]:

- Macropores ($>1000 \text{ \AA}$) to enhance diffusion into the pore system.
- Mesopores (30 to 1000 \AA) to accommodate medium size molecules.
- Micropore ($<30 \text{ \AA}$) to accommodate small molecules like water.

- Molecular Sieves

The discovery of molecular sieves can be traced back to 1956 when the word zeolite was first used. It came from the Greek meaning "boil" and "rock" after the observation was made that minerals lost their content of water when heated. The term "molecular sieve" was originated by J.W. Mcbain to define porous solid materials, which have the property of acting as sieves on a molecular scale. Molecular sieves are adsorbents composed of aluminosilicate crystalline polymers (zeolites), which can trap molecules by adsorption into their pores. They efficiently remove low concentrations of polar or polarizable contaminants such as H_2O , methanol, H_2S , CO_2 , mercaptans, sulfides, ammonia, aromatics and mercury down to trace concentrations. They have various forms: beads, granules and extrudates, including pellets. The molecular sieve type (such as zeolites A and X, the most common commercial adsorbents), size and particle shape selected by the application [43].

- Clay Minerals

Clay minerals are layer silicates that are formed usually as products of chemical weathering of other silicate minerals at the earth's surface. They are found most often in shales, the most common type of sedimentary rock. In cool, dry, or temperate climates, clay minerals are fairly stable and are an important component of soil. Clay minerals act as "chemical sponges" which hold water and dissolved plant

nutrients weathered from other minerals. Clay has many uses today including, pottery, ceramic, lining for landfills, computer chips, cosmetics and pharmaceuticals. Clay minerals are important because of the negative charge they contribute for cation exchange. So, they act as “chemical sponges” which hold and dissolved plant nutrients weathered from other minerals. They have the ability to attract water molecules at surface area (because the ion and water is not attracted sink inside the clay). For prehistoric times, clay has been essential in industry architecture and agriculture. There are many types of known clay minerals. Some of the more common types and their used economic are described below :

- Kaolinite (the mineral name for kaolin or china clay) is economically important in the ceramic and paper industries. It has a white, powdery appearance.
- Illite, along with other clay minerals may also be used in ceramics.
- Montmorillonite is the chief constituent of fuller’s earth, and is also used in drilling muds (muds used cool and lubricate drilling equipment). This clay mineral is the weathering product of mafic silicates, and is stable in arid, semi-arid, or temperate climates. It has the ability to adsorb large amounts of water, forming a water-tight barrier (where it is known as **bentonite**).
- Vermiculite (similar to montmorillonite) will expand on heating to produce a material used in insulation. This clay mineral has the ability to adsorb water, but not repeatedly. It is used as a soil additive for retaining moisture in potted plants, and as a protective material for shipping packages.

Especially adsorbent, Bentonite is used very in the oil industry as drilling muds to protect the cutting bit while drilling, filtering and deodorizing agents in the refining of petroleum [44].

Moreover, the other adsorbent materials which may be employed in the present invention include silica gel, magnesium silicate, metal hydroxides metal carbonates etc. For the adsorbent which is used in commerce as magnesium silicate or “Magnesol[®]”. It is a register trademark of The Dallas Group of America. Inc. that a synthetic, amorphous and hydrous form of magnesium silicate. Magnesol[®] has a porous internal structure and enormous activated surface.

2.13 Literature review

Schuchardt *et al.* [18] studied transesterification process used different types of catalysts (acids, alkaline metal hydroxides enzymes, non-ionic bases, such as amines, guanidine and guanidine heterogenized on organic polymers) are described. However, the anchored catalysts show leaching problems.

Siegfried *et al.* [45] had reported the method for producing esters from triglyceride which obtained from animal fats or vegetable oils by transesterification with a low-molecular weight alcohol in the presence of homogeneous or heterogeneous catalyst. Heterogeneous catalysts have an advantage over the homogeneous catalyst in that they can more easily be separated from the reaction mixture. The formed esters are extracted from the reaction mixture by means of a near-critical extractant. In this way esters are obtained at high yield and worthy purity. As the extractant preferably a low pressure gas having a reduced temperature at 20° C of about 0.7, equal or great than 0.7, is employed. The preferred extractant are carbon dioxide, butane, methyl acetate therefore.

Kumar *et al.* [7] studied transesterification process which is the most commonly used method for producing biodiesel from vegetable oil and animal fats in presence of NaOH and H₂SO₄ at 70° C. The transesterification was affected by the mode of the reaction, molar ratio of the glycerides to alcohol, type and quality of catalyst, reaction time, reaction temperature and purity of oil and fats. They gave high yield in different condition. Furthermore, they were summarized the other methods for preparation of biodiesel with different oils and catalysts.

Maskan and Bağcı [46] studied the refining of used sunflower seed oil by various adsorbents (CaO, MgO, Mg₂CO₃, magnesium silicate, activated charcoal and permez earth). Permez earth, magnesium silicate and bentonite exhibited the highest abilities in decreasing oil viscosity, FFAs reduction and colour recovery, respectively.

Ahmad *et al.* [48] synthesized rubber powder which was used to adsorb the residual oil in palm oil mill effluent which is the wastewater in the palm industry. The adsorption process was studied by varying parameters affecting the process, such as adsorbent dosage, mixing speed, mixing time and pH. It was found that removal of residual oil was attained with an adsorbent dosage of 30 mg dm⁻³ and mixing speed of 150 rpm for 3 h at pH 7.

Tatsumi *et al.* [48] studied method of producing fatty acid ester. Fatty acid ester was produced from fat and oil with an alcohol in the presence of carbon dioxide or hydrocarbon. The reaction was used in subcritical or supercritical state. The use of carbon dioxide or hydrocarbon gave a high yield fatty acid ester because they could be decreased the solubility of glycerin in oil.

Bertram *et al.* [49] noted that methods of purifying biodiesel fuel by using at least one adsorbent, such as magnesium silicate, silica gel, metal hydroxides and other materials. Impurities which occurred during the production such as soap, is formed during the transesterification which the base-catalyst is present to speed the reaction. Because the fuel would leave a residual ash if any soap were present, it is normal to use a "water wash" to remove the soap. The soap can cause emulsification between water and methyl ester. The water and any impurities contained therein are separated from the biodiesel by gravimetry. When a large amount of soap is present, the water-washing causes emulsion problems, such as FAME will not separate from the water. Besides, water-washing does not effectively get rid some of the other contaminants.

Choo *et al.* [50] had reported that other alkyl esters, ethyl and isopropyl ester of crude palm oil and crude palm stearin were synthesized via chemical transesterification. They evaluated for their fuel properties that these alkyl esters have high viscosity than petroleum diesel, low sulfur content.

Yong *et al.* [51] studied method of producing waste cooking oils which contain large contents of FFAs from restaurants. Two-step catalyzed process was adopted to prepare biodiesel from waste cooking oil. The FFAs of waste cooking oils was esterified with methanol catalyzed via ferric sulfate in the first step and the triglycerides were transesterified with methanol catalyzed via potassium hydroxide. The conversion of FFA reached 97.22% when the parameters were as follows: amount of ferric sulfate 2 wt%, molar ratio of methanol to triglycerides 10:1 and reacted at 95°C for 4 h. The remained triglycerides in transesterification stage was performed at 65°C for 1 h in a presence of 1 wt% of potassium hydroxide and 6:1 molar ratio of methanol to triglycerides. The final product gave 97.02% of biodiesel after the two-step catalyzed process. The new process had many advantage compared with the acid or alkaline catalyzed process, such as high efficiency, no acidic waste water and easy recovery of the catalyst.