CHAPTER 2
THEORIES

2.1 History of Biodiesel

One hundred years ago, ground-nut oil was tested as fuel for the internal combustion diesel engine by Rudolf C. Diesel in 1885. However, vegetable oil was out of favour as a fuel in diesel engine because petroleum at that time was cheap. Until 1930s, alternative diesel fuels were investigated because it is the first time that the world met an oil crisis. Presently, the demand for fossil diesel fuel in this world is more than its supply and the price of petroleum has increased. In addition, petro-diesel is a main source of air pollution (green house gases: carbon dioxide and acid rain: sulfur dioxide). Therefore, vegetable oils and animal fats have returned to be used as an alternative diesel fuels.

Previously, if non-modified vegetable oils were used directly in diesel engines, they caused carbon deposits in the engine, decreased the durability of the engine, and caused lubricating oil contamination. In addition, animal fats could not be directly used as fuel because they were forming solid at ambient temperatures. Consequently, modified vegetable oils and animal fats were proposed as alternative fuels for diesel engines because their properties were similar to petro-diesel such as cetane number, density, and viscosity.

Microemulsion, pyrolysis, and transesterification are processes used to modify vegetable oils and animal fats to alternative diesel fuels now. However, transesterification is the basic method preferable used to generate biodiesel from vegetable oils and animal fats, because it is easier to produce biodiesel and to find suitable raw materials.

2.2 Biodiesel Production

In biodiesel production, biodiesel quality may not be reached the standard requirement. There is a possibility that the low quality of raw materials is used to produce biodiesel by transesterification. In addition, the reaction and other parameters such as mixing intensity, temperature and reaction time are not suitable for produce biodiesel from some materials. In order to obtain the standard biodiesel quality of Thailand, main parameters such as quality of raw materials, reactions and other parameter effects should be investigated.

2.2.1 Raw Materials

2.2.1.1 Fats and Oils

Oils and fats, water-insoluble substance, consisted of mono-, di- and tri-glycerides, which are the combination of one-three molecules of fatty acids and one molecule of glycerol, respectively. Chains of fatty acids in mono-, di- and tri-glyceride structure are specified by two numbers with a colon. The first numeral is a number of atoms of carbon in the chain that comprise carboxylic carbon at the end of fatty acid (the carbon atom has a double bond with the oxygen atom). The second numeral is the number of the double bonded atom (carbon atom to carbon atom) in fatty acid chain as shown in Table 2.1. In Table 2.2, vegetable oil and animal fats have variable saturation, chain length, and steric hindrance, which cause different rate coefficients to occur in the transesterification reaction.

Table 2.1 Fatty acid structure (Srivastava, *et al.*, 2000)

Fatty acid	Systematic name	Structure	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradacanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Oleic	*cis*-9-Octadecanoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9,*cis*-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Erucic	*cis*-13-Docosenoic	22:1	$C_{22}H_{42}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$

To meet the requirement of Thai government strategy, MCPO, having high FFA and un-degumming, a mixture of palm fibre oil and palm kernel oil, will offer to be used as a raw material in this work. Palm oil, like other edible oils, is an organic compound which is called a glyceryl ester because each molecule is comprised of a glycerol

Table 2.2 The percentage of common fatty acids in oils and fats

Oils and fats	**Type of fatty acid composition (%wt/wt)**											**References**
	12:0	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	**20:0**	**22:0**	**22:1**	**24:0**	
Cottonseed oil	-	-	28.33	0.89	13.27	57.51	0.00	0.00	0.00	0.00	0.00	Ma, *et al.*, 1998
Mahua oil	-	-	16.00- 28.20	20.00- 25.10	41.00- 51.00	8.90- 13.70.	-	0.00- 3.30	0.00	0.00	0.00	Srivastava, *et al.*, 2000
Peanut oil	-	-	11.38	2.39	48.28	31.95	0.93	1.32	2.52	0.00	1.23	Ma, *et al.*, 1998
Crude palm oil	0.00	0.30	46.70	3.10	42.60	9.50	0.20	0.40	-	-	-	Crabbe, *et al.*, 2001
Rapeseed oil	-	-	3.49	0.85	64.40	22.30	8.23	0.00	0.00	0.00	0.00	Ma, *et al.*, 1998
Crude rice bran oil	0.10- 0.30	0.70- 0.90	12.40- 23.00	2.05-2.35	39.88- 41.37	35.04- 36.16	1.58- 2.10	0.10- 0.30	0.20- 0.40	-	0.34- 0.86	Zullaikah, et al.,2005
Soy bean oil	-	0.00- 0.10	10.00- 10.70	3.80-4.30	23.40- 26.70	49.70- 53.90	6.80- 8.50	0.30- 0.50	0.30- 0.40	-	-	Liberty Vegetable Oil Company, 2000
Lard	0.10	1.40	23.60	14.20	44.20	10.70	0.40	-	-	-	-	Ma, *et al.*, 1998
Beef tallow	-	2.00- 8.00	24.00- 37.00	40.00- 50.00	-	1.00- 5.00	-	-	-	-	-	Ma, *et al.*, 1998

molecule bonded to a maximum of three fatty acid (carboxylic acid) residues. Each of the three fatty acid groups in palm oil is long chains comprising several carbon atoms (normally 14-20 atoms in length) but palmitic acid, oleic acid, stearic acid and linoleic acid are mainly fatty acids, which are found in MCPO.

2.2.1.2 Alcohols

Many several primary and secondary monohydric aliphatic alcohols having one to eight carbon atoms such as methanol, ethanol, buthanol, and amyl alcohol are suitable for being used in transesterification process. There are two main types of alcohol (methanol and ethanol), which are more preferred to be used as a reagent in biodiesel production. In fact, although the reaction that used methanol as a reagent is controlled by mass transfer, methanol is more commercially used as a raw material in biodiesel production than ethanol because it is cheap, easy to recover, easy to recycle, and denature. Moreover, glycerides can react quickly with methanol, catalyst can be simply dissolved in it and it does not promote strong emulsion form after finishing the reaction. Presently, although single alcohol is used in the biodiesel production, the mixture of two or more alcohols is offered because the obtained product can be used as fuel in diesel engine at low temperature. Most of all, the low moisture content in a raw material is required in process; therefore, the purity of alcohol at least 98 wt% must be used.

2.2.1.3 Catalysts

There are many several types of acid, base, and enzyme such as sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), and lipase which can be used as a catalyst in the transesterification. Alkali catalyst is the most frequently used to catalyze the reaction because it gives faster rate than acid and enzyme catalysis. However, if the oil containing high FFA and/or high moisture is used to produce biodiesel, saponification will be formed. That causes reduction in the biodiesel yield.

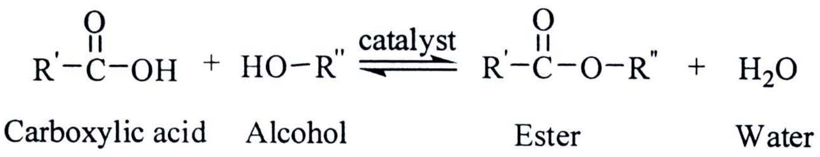
For solving saponification problem, acid catalyst is preferred to be used as a catalyst to produce biodiesel from the oil having high FFA and/or high moisture by transesterification reaction. In addition, acid catalyst is not only used as a catalyst in esterification but also as a main reagent for de-gumming or reducing phosphatide compound instead of phosphoric acid when the un-degummed crude oil (having high FFA) is used as a raw material in biodiesel production,. Therefore, the reaction time for preparing crude oil will be reduced.

As for the enzyme, it can effectively convert all of glycerides to biodiesel, but the product cost of enzyme catalytic is much expensive than other catalysts and the reaction time is much longer. Therefore, the process for producing biodiesel has not been popular with enzyme catalyst.

2.2.2 Relative Reactions

2.2.2.1 Esterification

In Equation 2.1, carboxylic acids react with alcohol to produce esters, which identify the reaction of esterification. Esters are compounds in which the hydroxyl group of carboxylic acid is substituted by an R"O group of alcohol. When ester is treated with acid or base in aqueous solution, the molecule of the ester divides into alcohol and an acid compound by hydrolysis. As for biodiesel production by a two-stage process, esterification is used to convert high FFA in oil to biodiesel by reacting it with alcohol using acid catalyst as shown in Equation 2.1.

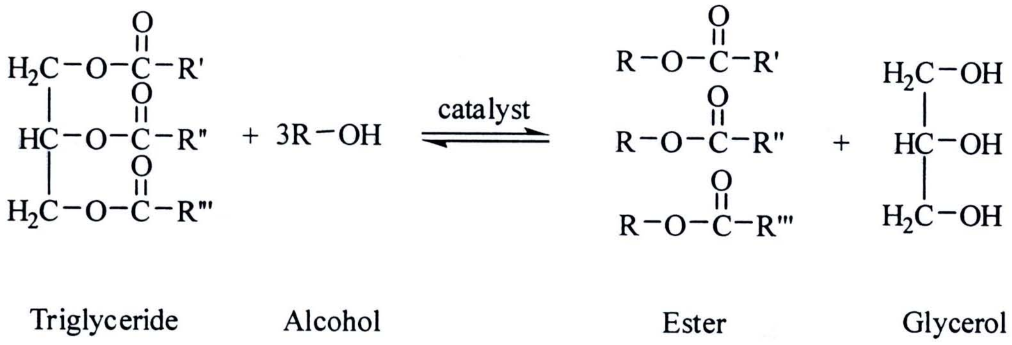


$$R'-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HO-R'' \xrightleftharpoons{\text{catalyst}} R'-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'' + H_2O \qquad (2.1)$$

2.2.2.2 Transesterification

Transesterification is a chemical process used to replace alcohol in ester with new one to generate new ester as shown in Equation 2.2. In the biodiesel production, 1, 2, 3-propanetriol (glycerol) of triglycerides is replaced with methanol or ethanol using catalyst for generating new ester (biodiesel) via transesterification as shown in Equation 2.3.

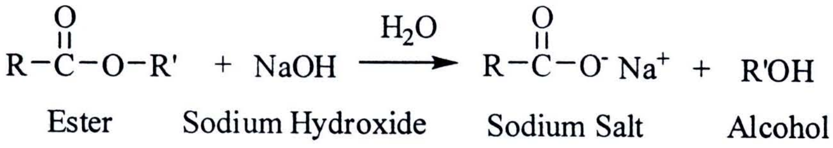
$$\underset{\text{Ester}_1}{RCOOR'} + \underset{\text{Alcohol}_1}{R''OH} \xrightleftharpoons{\text{catalyst}} \underset{\text{Ester}_2}{RCOOR''} + \underset{\text{Alcohol}_2}{R'OH} \qquad (2.2)$$



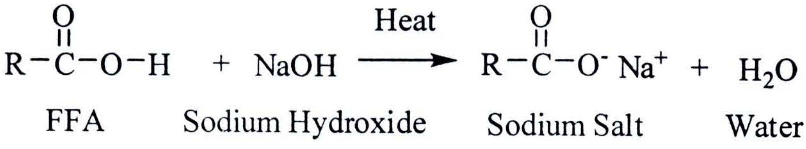
(2.3)

2.2.2.3 Saponification

Saponification is the hydrolysis reaction of an ester with strong base (NaOH and KOH). The ester is transferred into sodium salt of a long-chain carboxylic acid (soap) and alcohol as shown in Equation 2.4. In addition, the strong base transfers the FFA to soap and water as shown in Equation 2.5 during the reaction and emulsifies the mixture of glycerol and ester. It is difficult to recover ester from gel and to separate ester from the emulsion. Therefore, saponification is a significant cause of ester yield reduction in the biodiesel reaction.



$$\underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-O-R'} + \underset{\text{Sodium Hydroxide}}{NaOH} \xrightarrow{H_2O} \underset{\text{Sodium Salt}}{R-\overset{O}{\overset{\|}{C}}-O^- Na^+} + \underset{\text{Alcohol}}{R'OH} \qquad (2.4)$$

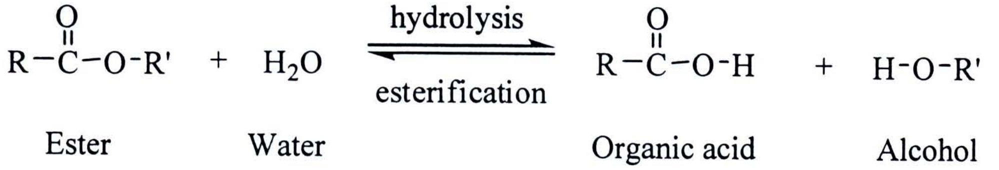


$$\underset{\text{FFA}}{R-\overset{O}{\overset{\|}{C}}-O-H} + \underset{\text{Sodium Hydroxide}}{NaOH} \xrightarrow{\text{Heat}} \underset{\text{Sodium Salt}}{R-\overset{O}{\overset{\|}{C}}-O^- Na^+} + \underset{\text{Water}}{H_2O} \qquad (2.5)$$

2.2.2.4 Hydrolysis

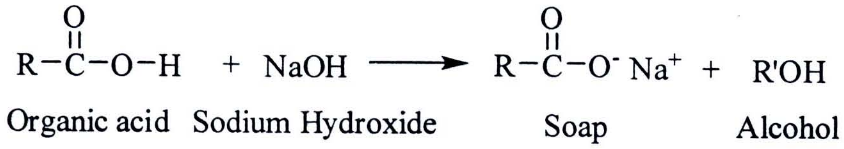
Hydrolysis (reversible reaction of esterification) is the reaction between ester and water catalyzed by sulfuric acid to produce organic acid and alcohol as shown in

Equation 2.6. Therefore, this reaction depends on the amount of water, if the raw material has a lot of water; a lot of organic acid and alcohol are obtained.

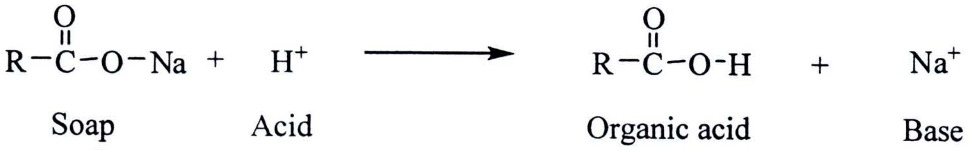


$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'} + \mathrm{H_2O} \underset{\text{esterification}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}H} + \mathrm{H{-}O{-}R'} \tag{2.6}$$

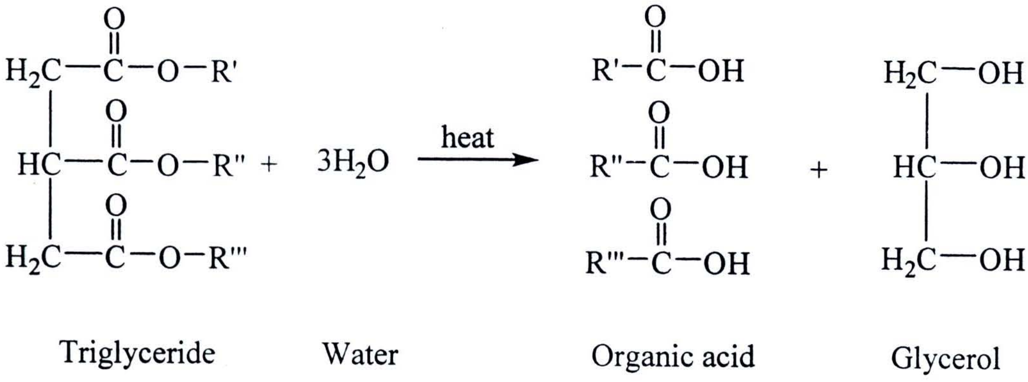
In addition, if alkali catalyst (sodium hydroxide and/or potassium hydroxide) is used as catalyst in hydrolysis reaction instead of acid catalyst, organic acid and alcohol are also occurred. After that, organic acid is reacted with alkali catalyst to produce soap and alcohol, which can be separated from solution as shown in Equation 2.7. This soap can be converted to organic acid again when it reacts with acid such as sulfuric acid and hydrochloric acid as shown in Equation 2.8. As for alcohol, it can be recovered by distillation during the hydrolysis reaction.



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}H} + \mathrm{NaOH} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O^{-}\,Na^{+}} + \mathrm{R'OH} \tag{2.7}$$



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}Na} + \mathrm{H^{+}} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}H} + \mathrm{Na^{+}} \tag{2.8}$$



(2.9)

In biodiesel procedure, hydrolysis converts the structure of glycerides or of esters into FFA, and glycerol or alcohol as shown in Equation 2.9. Therefore, this reaction can be protected by using the raw material, which contain low moisture, and by draining water formed during esterification reaction.

Moreover, hydrolysis reaction is used to separate FFA, methanol and glycerol out of crude glycerol and to separate FFA out of soap. Separated free fatty acid can be used as a raw material in esterification or blended with oil to use as a raw material in the two-stage process. As for methanol and glycerol, they are purified by distillation.

2.2.3 Effect of Parameters in Biodiesel Production

2.2.3.1 Methanol Ratio

According to theory of biodiesel production, the stoichiometric molar ratio of alcohol to oil is three molecules of alcohol to one molecule of triglyceride in transesterification and is one molecule of alcohol to one molecule of free fatty acid in esterification. Practically, using the stoichiometric molar ratio of alcohol, the requirement of ester conversion can not be achieved. Therefore, to drive the forward reaction for getting the highest yield of the product according to Le Châtelier's Principle, higher molar ratio is required in the reaction. In addition, reaction temperature nearly methanol boiling point atmospheric pressure is used; therefore, methanol can continuously evaporate during the reaction.

Generally, it was found that the molar ratio of alcohol to oil at 6:1 or more is frequent used in biodiesel procedure by transesterification. In addition, the molar ratio of alcohol to oil in excess of 15:1 or more is required to get the highest conversion in biodiesel production in esterification. For two-stage process, FFA in oil was treated under a (2.5-20):1 molar ratio of alcohol to oil and TG could be converted to biodiesel under a (3-9):1 molar ratio of alcohol to oil. However, although a high methanol ratio is required to generate biodiesel, the glycerol separation is interfered with alcohol because of increasing solubility. Moreover, remained glycerol in biodiesel can promote the reversible reaction. That is one cause of lower ester yields. Consequently, to reduce the problem, the suitable molar ratio of methanol to oil, which is required in each reaction, should be investigated.

2.2.3.2 The Amount of Catalyst

Even though the catalyst was not added in biodiesel production, the reaction between oil and methanol is still continuing. The reason was that methanol has high polarity. However, the reaction time for driving the reaction to reach the highest yield is too long. For reducing reaction time (increasing the initial reaction rate); therefore, it is necessary to add the catalyst in the process.

In transesterification, sodium hydroxide is frequently used as a catalyst because it is cheaper and biodiesel can be generated under the small amount of it. In principle, if the amount of alkali catalyst is increased, the high percentages of biodiesel purification are also obtained. However, it causes to reduce biodiesel yield by gravity separation. In the same way, sulfuric acid is also usually used as a catalyst in esterification more than other acid. Due to a strong acid and toxicity, the reaction can be reached under the small. From literature reviews, it was showed that the amount of sodium hydroxide at 0.4-2.0 wt% of oil and of sulfuric acid at 2-3 wt% of oil was used as a catalyst in biodiesel production by transesterification and by esterification, respectively.

2.2.3.3 Mixing Intensity

In the first period of reaction, mixing is important for driving the reaction into forward side because it reduces diffusion and mass transfer reactions that control the overall rate of the reaction. Since oils and methanol are immiscible reagent, the reaction for producing biodiesel requires the suitable mixing intensity for promoting the homogeneous solutions. The mixing intensity, generally, around 150-600 rpm is suitable for producing biodiesel, however, all this is due to the physical and types of reactor.

2.2.3.4 Reaction Temperature

The reaction temperature strongly influences the rate of the biodiesel production because the reaction is typically endothermic reaction. When the temperature increases, the final conversion also increases. Therefore, to drive the reaction reached in the short period of reaction time, the reaction should be reacted under the suitable reaction temperature though the reaction will proceed to near completion even at the room temperature.

Although, the reaction is carried out nearly the boiling point of methanol (64.8°C) at the atmospheric pressure, from literature reviews, Ma, *et al.* (1998) indicated that the reaction temperature at 60°C is suitable for producing biodiesel by transesterification. However, the effect on the reaction temperature is not only the boiling point of alcohol but also the type of catalyst; for example, a high temperature is used to produce biodiesel by using acid catalyst and no-catalyst. As the two-stage process, both reactions are carried out at 60°C.

2.2.3.5 Moisture and FFA content

Raw materials (oil, alcohol, and catalyst) in transesterification must be anhydrous and had low FFA (< 1 wt%) content. Moisture and high FFA will cause gel to form by saponification, which results in lower yields and washing problems.

Therefore, before producing biodiesel, generally, the water content and FFA should be checked by titration technique. After that the oil is prepared by heating up to120 °C in order to de-moisture and then the FFA in oil is de-acidified by saponification. In addition, problems of high moisture and high FFA content of vegetable oils and animal fats can be solved by using the acid-catalyzed transesterification, the enzyme-catalyzed transesterification, supercritical CO_2 techniques or a two-stage process.

2.2.4 Specifications and Properties of Biodiesel

Biodiesel is produced from various vegetable oils and animal fats by different methods; therefore, the standardization of biodiesel quality is introduced to guarantee biodiesel for using in diesel engines without any problems. Some countries such as Germany, Italy, France, The Czech Republic, Australia, United States and Thailand have defined and approved standards for guideline biodiesel properties.

Table 2.3 The requirement of commercial biodiesel qualities and quantities in Thailand (Department of Energy Business, 2009)

Parameters	Corresponding Value	Method [1]
Methyl Ester (%wt)	≥ 96.5	EN14103
Density at 15°C (kg/m^3)	≥ 860 and ≤ 900	ASTM D 1298
Viscosity at 40°C (cSt)	≥ 3.5 and ≤ 5	ASTM D 445
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	EN ISO 12937
Total Contaminate (%wt)	≤ 0.0024	EN 12662
Copper Strip Corrosion	≤ Number 1	ASTM D 130
Oxidation Stability at 110°C (hours)	≥ 10	EN 14112
Acid Value (mg KOH/g)	≤ 0.50	ASTM D 664
Iodine Value (g iodine /100g)	≤ 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) mg/kg	≤ 5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg) mg/kg	≤ 5.0	prEN 14538
Phosphorus (%wt)	≤ 0.0010	ASTM D 4951

Note: 1.The biodiesel quality can be verified with another method, but these methods used to obviate the argument.

ASTM test methods and some EN test methods are used to measure performance parameters of biodiesel production in Thailand. These methods are enacted in the Royal Gazette for controlling standards of production. The standard of biodiesel production in Thailand can be categorized in two groups which is the standard for commercial biodiesel production and for agriculture engine as shown in Table 2.3 and 2.4.

Table 2.4 The requirement of biodiesel qualities and quantities for agricultural engines in Thailand (Department of Energy Business, 2006)

Parameter	Corresponding Value	Method[1]
Density at 15°C (kg/m^3)	≥ 860 and ≤ 900	ASTM D 1298
Viscosity at 40°C (cSt)	≥ 1.9 and ≤ 8	ASTM D 445
Flash point (°C)	≥ 120	ASTM D 93
Sulphur (%wt)	≤ 0.0015	ASTM D 2622
Cetane Number	≥ 47	ASTM D 613
Sulfated Ash (%wt)	≤ 0.02	ASTM D 874
Water and Sediment (%vol)	≤ 0.2	ASTM D 2079
Copper Strip Corrosion	≤ Number 3	ASTM D 130
Acid Value (mg KOH/g)	≤ 0.80	ASTM D 664
Free Glycerin (%wt)	≤ 0.02	ASTM D 6584
Total Glycerin (%wt)	≤ 1.50	ASTM D 6584
Colour	Purple[2]	Eyesight
Additive	According to Department of Energy Business	

Note: 1.The biodiesel quality can be verified with another method, but these methods used to obviate the argument.

2. 1.4-dialkylamino anthraquinone and alkyl derivatives of azobenzene-4-azo-2-naphthol are used as the analytical regents.

2.3 Types of reactor

In batch process, the large reactor, high capital investment, high energy consumption and product quality control difficulty are unavoidable; therefore, the continuous reactor was investigated. The investigation found that continuous reactor, present, can be classified into 3 types: continuous stirred tank reactors (CSTRs), plug flow reactor (PFR) and packed bed reactor (PBR) as shown the detail of each type as followed:

2.3.1 Continuous Stirred Tank Reactors (CSTRs)

CSTRs connected in series (Figure 2.1 and 2.2) consist of one or more tanks (dependent on the kinetics of reaction) and an impeller in each tank. The process of CSTRs is similar to the process of batch reactor but for the CSTRs, the reagents are feeding into the reactor and product is transferred out of the reactor all the time. When the reagents pass through each tank of reactor, the reagents are homogeneous mixing under the similar reaction temperature and the retention time.

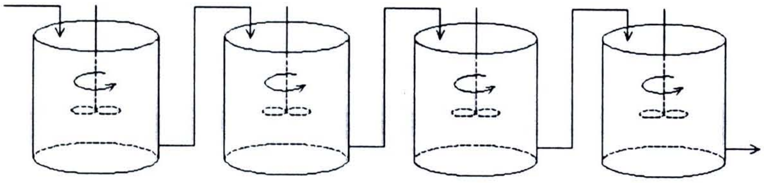


Figure 2.1 Continuous stirred tank reactors in series (Fogler, 2006)

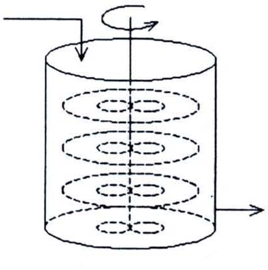


Figure 2.2 Continuous stirred tank reactors in vertical series (Fogler, 2006)

2.3.2 Plug Flow Reactor (PFR)

The characteristic of plug flow reactor (Figure 2.3) is a blank column in straight line whose length depended on the reaction rate. When un-reacted reagents are fed into PFR flowing through cross-sectional area, it is found that the concentration of reagent in perpendicular and in horizontal must be equal. Conversely, reagents in parallel flow are not equivalent in concentration when the reacted reagents are fed in to PFR. This reactor is frequent used in gas phase reaction.

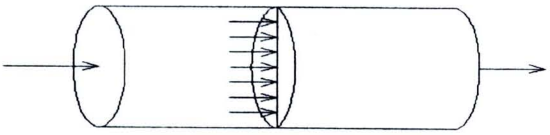


Figure 2.3 Plug flow reactor (Fogler, 2006)

2.3.3 Packed Bed Reactor (PBR)

Although the characteristic of PBR is similar to plug flow reactor, inside of reactor is packed with solid catalyst for promoting the reaction as shown in Figure 2.4. The reagents can be reacted inside column by counter-flow feeding. The advantage of reactor is high efficiency, low investment cost but the reactor must be fabricated in the large size.

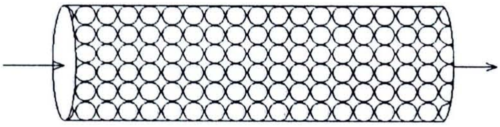


Figure 2.4 Pack bed reactor (Fogler, 2006)