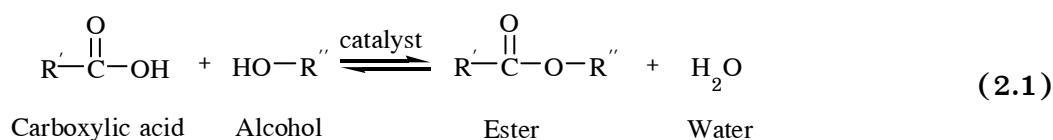# CHAPTER 2

THEORIES

2.1 History of Biodiesel

One hundred years ago, Rudolf Diesel (1885) tested ground-nut oil as a fuel with his diesel engine. Subsequently, petroleum was cheap and crude oil fractions were able to be distilled for producing diesel engine fuel, so vegetable oil was out of favour as a fuel in diesel engine development. Until 1930s, alternative diesel fuels were investigated because the world met an oil crisis for the first time. Today, the demand for fossil diesel fuel is more than its supply, the price of petroleum has increased, and petroleum fuel is a main source of air pollution (green house gases). Therefore, vegetable oils and animal fats are being investigated to produce alternative diesel fuels again.

Previously, non-modified vegetable oils were used directly in diesel engines. The direct utilization of vegetable oils 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 fossil diesel fuel (cetane number, density, and viscosity, etc.).

Microemulsion, pyrolysis, and transesterification are processes used to modify vegetable oils and animal fats to alternative diesel fuels now. Transesterification is the basic method 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 Esterification

In Equation 2.1 (Brown, *et al.*, 2003 and Peters, *et al.*, 2006), 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 a $R''O$ 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 reduce high FFA in oil by reacting it with alcohol using acid catalyst as shown in Equation 2.11 (Peters, *et al.*, 2006).
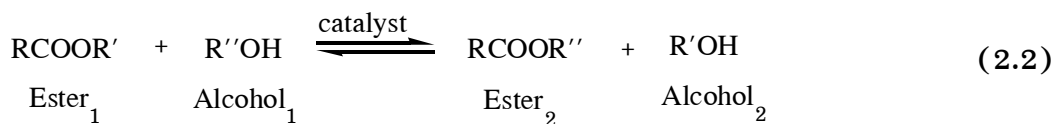
$$R'-\underset{\underset{O}{\|}}{C}-OH \ + \ HO-R'' \ \overset{\text{catalyst}}{\rightleftharpoons} \ R'-\underset{\underset{O}{\|}}{C}-O-R'' \ + \ H_2O \tag{2.1}$$

Carboxylic acid   Alcohol   Ester   Water

Where
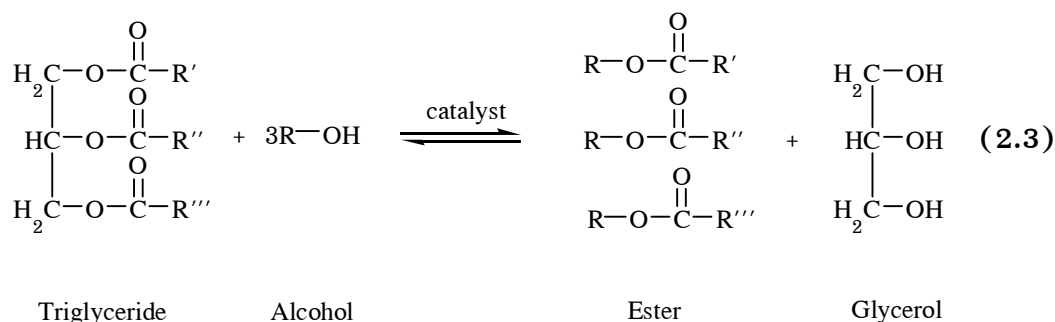
R' and R'' are alkyl group

2.3 Transesterification

Transesterification is a chemical process, which is similar to a hydrolysis process, but it uses alcohol only. The alcohol in ester is replaced with new alcohol molecule to generate new ester as show in Equation 2.2 (Meher, *et al.*, 2004). In the biodiesel production, transesterification is used to replace 1, 2, 3-propanetriol (glycerol) of triglycerides with methanol and ethanol using catalyst for generating new ester as shown in Equation 2.3 (Meher, *et al.*, 2004).

$$RCOOR' \ + \ R''OH \ \overset{\text{catalyst}}{\rightleftharpoons} \ RCOOR'' \ + \ R'OH \tag{2.2}$$

Ester$_1$ Alcohol$_1$ Ester$_2$ Alcohol$_2$

Where

R is alkyl group

$$\underset{\text{Triglyceride}}{\begin{array}{c} \text{H}_2\text{C}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}' \\[4pt] \text{HC}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}'' \\[4pt] \text{H}_2\text{C}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}''' \end{array}} + \underset{\text{Alcohol}}{3\text{R}-\text{OH}} \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} \underset{\text{Ester}}{\begin{array}{c} \text{R}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}' \\[4pt] \text{R}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}'' \\[4pt] \text{R}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R}''' \end{array}} + \underset{\text{Glycerol}}{\begin{array}{c} \text{H}_2\text{C}-\text{OH} \\[4pt] \text{HC}-\text{OH} \\[4pt] \text{H}_2\text{C}-\text{OH} \end{array}} \quad (2.3)$$
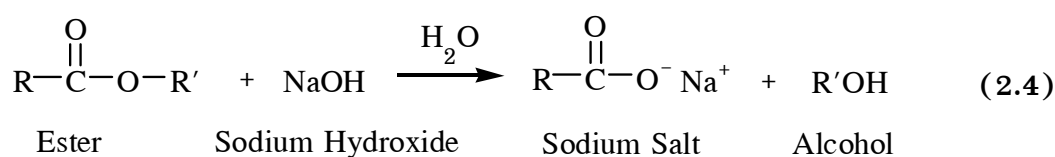
Where

R   is short chain alkyl groups

R′, R″ and R‴ are long chain alkyl groups

2.4 Saponification

Saponification is the hydrolysis reaction of an ester with strong base (NaOH, KOH). The ester is transferred into sodium salt of a long-chain carboxylic acid (soap) and alcohol as shown in Equation 2.4 (Brown, *et al.*, 2003). The strong base transfers the FFA to soap that forms gel 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 reduced ester yield in the biodiesel reaction.

$$\underset{\text{Ester}}{\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}-\text{R}'} + \underset{\text{Sodium Hydroxide}}{\text{NaOH}} \xrightarrow{\text{H}_2\text{O}} \underset{\text{Sodium Salt}}{\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}^-\text{Na}^+} + \underset{\text{Alcohol}}{\text{R}'\text{OH}} \quad (2.4)$$

2.5 Rate Law of Reversible Reaction (Fogler, 1999)

The general equation for reversible reaction:

$$\text{aA} + \text{bB} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{cC} + \text{dD} \quad (2.5)$$
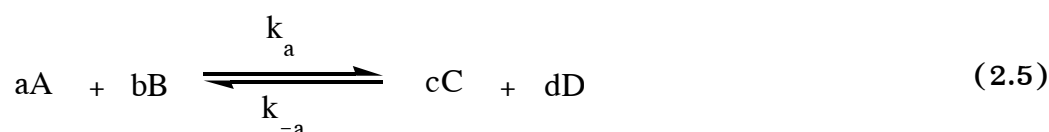
Where

A and B are the initial reagents

C and D are the products

a and b are the coefficient of reagents A and B, respectively

c and d are the coefficient of products C and D, respectively

k_a is   the rate coefficient of the forward reaction

k_{-a} is   the rate coefficient of the reward reaction

The rate of forward reaction $(r_{A, forward})$:

$$r_{A, forward} = -k_a [A]^a [B]^b \qquad (2.6)$$

Where

[A] is the molar concentration of reagent A

[B] is the molar concentration of reagent B

a   is order of reagent A

b   is order of reagent B

The rate of reverse reaction $(r_{A, reverse})$:

$$r_{A, reverse} = k_{-a} [C]^c [D]^d \qquad (2.7)$$

Where

[C] is the molar concentration of product C

[D] is the molar concentration of product D

c   is order of product C

d   is order of product D

The net rate (Equation 2.6+ Equation 2.7):

$$r_A = k_{-a} [C]^c [D]^d - k_a [A]^a [B]^b \qquad (2.8)$$

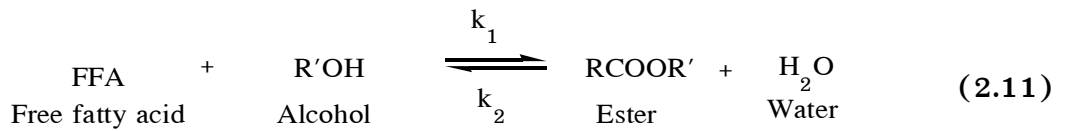The mole balance of the constant-volume batch reactor:

$$r_A = \frac{d[A]}{dt}$$

(2.9)

The rate law for reversible reaction:

$$\frac{d[A]}{dt} = k_{-a}[C]^c[D]^d - k_a[A]^a[B]^b$$

(2.10)

2.6 Kinetics of Esterification

Equation 2.11 shows the reaction of methanol and oil, which contains high FFA concentrations. FFA is converted to ester by alcohol in the presence of acid catalyst as shown in the reversible reaction. According to the theory, the esterification rate equation controlling of the FFA concentration is shown as Equation 2.12.

$$\underset{\text{Free fatty acid}}{\text{FFA}} + \underset{\text{Alcohol}}{\text{R'OH}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{Ester}}{\text{RCOOR'}} + \underset{\text{Water}}{H_2O}$$

(2.11)

$$\frac{d[FFA]}{dt} = -k_1[FFA]^a[A]^b + k_2[E]^c[WT]^d$$

(2.12)

Where

[A]   is the molar concentration of alcohol

[E]   is the molar concentration of ester

[FFA] is the molar concentration of free fatty acid

[WT]   is the molar concentration of water

a   is order of free fatty acid in reaction sequence

b   is order of alcohol in reaction sequence

c   is order of ester in reaction sequence

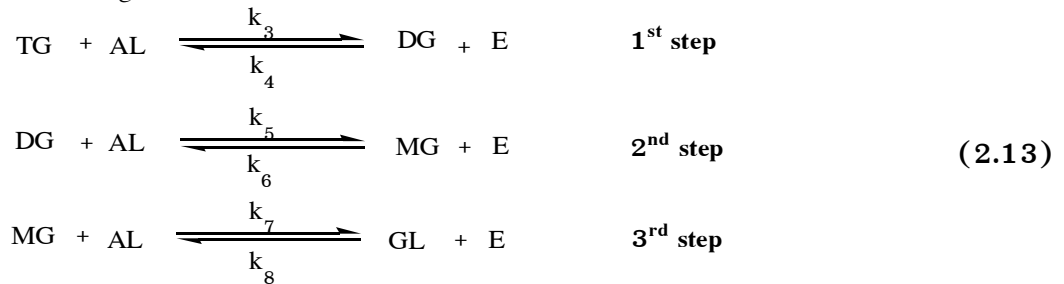d   is order of water in reaction sequence

k_1 is the rate coefficient of free fatty acid (forward reaction)

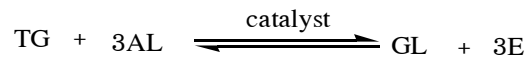k_2 is the rate coefficient of free fatty acid (reverse reaction)

2.7 Kinetics of Transesterification

The overall reaction shows three stages during the transesterification reaction (Equation 2.13) (Darnoko, *et al.*, 2000, Noureddini, *et al.*, 1997). There are two intermediate compounds, which occur during the mechanism of the transesterification reaction. Those are diglyceride (DG) and monoglyceride (MG), which explains the generation of three moles of ester (E) and one mole of glycerol (GL). All of reactions are reversible with different rate coefficients that are of pseudo-secondary order.

The 3 stages of transesterification :

$$TG + AL \underset{k_4}{\overset{k_3}{\rightleftharpoons}} DG + E \qquad \textbf{1}^{st} \textbf{ step}$$

$$DG + AL \underset{k_6}{\overset{k_5}{\rightleftharpoons}} MG + E \qquad \textbf{2}^{nd} \textbf{ step}$$

$$MG + AL \underset{k_8}{\overset{k_7}{\rightleftharpoons}} GL + E \qquad \textbf{3}^{rd} \textbf{ step}$$

$$(2.13)$$

The overall of transesterification:

$$TG + 3AL \overset{catalyst}{\rightleftharpoons} GL + 3E$$

Where

AL   is alcohol

DG   is diglyceride

E   is ester

GL   is glycerol

MG   is momoglyceride

TG   is triglyceride

k_3 is the rate coefficient of TG (forward reaction)

k_4 is the rate coefficient of TG (reverse reaction)

k_5 is the rate coefficient of DG (forward reaction)

k_6 is the rate coefficient of DG (reverse reaction)

k_7 is the rate coefficient of MG (forward reaction)

k_8 is the rate coefficient of MG (reverse reaction)

Three steps of transesterification used to create rate laws of transesterification as shown in Equation 2.14 (Allen, *et al.*, 2003). These reactions define the rate of the disappearance and the appearance of the several components.

$$\frac{d[TG]}{dt} = -k_3[TG][AL] + k_4[DG][E]$$

$$\frac{d[DG]}{dt} = k_3[TG][AL] - k_4[DG][E] - k_5[DG][AL] + k_6[MG][E]$$

$$\frac{d[MG]}{dt} = k_5[DG][AL] - k_6[MG][E] - k_7[MG][AL] + k_8[GL][E] \qquad (2.14)$$

$$\frac{d[GL]}{dt} = k_7[MG][AL] - k_8[GL][E]$$

$$\frac{d[E]}{dt} = k_3[TG][AL] - k_4[DG][E] + k_5[DG][AL] - k_6[MG][E] + k_7[MG][AL] - k_8[GL][E]$$

$$\frac{d[AL]}{dt} = -\frac{d[E]}{dt}$$

Where

[AL]   is the molar concentration of alcohol

[DG]   is the molar concentration of diglyceride

[E]   is the molar concentration of ester

[GL]   is the molar concentration of glycerol

[MG]   is the molar concentration of momoglyceride

[TG]   is the molar concentration of triglyceride

2.8 Activation Energy

In liquid-phase reactions, the rate coefficient depends on a function of total pressure, and other parameters such as the choice of solvent and the ionic strength. Actually, pressure has little effect on liquid reactions than the temperature because liquids are incompressible. Therefore, rate coefficients of reactions will be assumed to depend on the temperature only.

Arrhenius, a Swedish chemist, was the first to suggest the temperature dependence of the rate coefficient (k_A) as shown in Equation 2.15 (Fogler, 1999). This equation is known as the Arrhenius equation.

$$k_A = Ae^{-E_a/RT} \qquad (2.15)$$

Where

k_A is the rate coefficient

A   is pre-exponential factor or frequency factor

E_a is activation energy, J/mol or cal/mol

R   is gas constant = 8.314 J/mol K or 1.987 cal/mol K

T   is absolute temperature, K

Activation energy is a minimum energy that must be possessed by reacting molecules before the reaction will occur. The activation energy is experimentally determined by carrying out the reaction at several different temperatures. For the calculation of the activation value, the Arrhenius equation is changed to a logarithmic form by taking the natural logarithm as show in Equation 2.16 (Fogler, 1999). Then a plot of ln k_A against 1/T should show a straight line. If the Arrhenius equation is applicable, the slope of the straight line is proportional to the activation energy.

$$\ln k_A = \ln A - \frac{E_a}{RT} \qquad (2.16)$$

2.9 Raw Materials

2.9.1 Oils and Fats

Oils and fats, water-insoluble substance, consist of triglycerides, which are the combination of three molecules of fatty acids and one molecule of glycerol. Triglycerides have long chain of fatty acids, which 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.

MCPO, having high FFA, is a mixture of palm fibre oil and palm kernel oil. It was used to produce biodiesel containing many compounds such as TG, DG, MG FFA, complex lipid, and impurities. Although there are many fatty acids in MCPO (as shown in Table 2.2), palmitic acid, oleic acid, and linoleic acid are mainly fatty acids found in MCPO.

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	$C_{24}H_{48}O_2$

2.9.2 Alcohol

There are two main types of alcohol used to produce biodiesel, which are methanol and ethanol. Methanol is the most commercially used alcohol in biodiesel production because it is cheaper, easier to recover, easier to recycle, and denature. Moreover, the triglycerides react quickly with methanol and catalyst can be dissolved in it simply because it has short chain. However, methanol is usually manufactured from natural gas whereas ethanol can be made from wood, rice, and sugar, etc.

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	–	–	–	Cradde, *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

2.10 Effect of Parameter in Biodiesel Procedure

There are five parameters, which are significance on the biodiesel production, such as catalyst, the molar ratio of methanol to oil, the reaction temperature, the mixing intensity, and moisture and FFA content.

2.10.1 Catalyst

Many acid, base, and enzyme such as sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), and lipase can be used as catalyst in the transesterification. Alkali catalyst is the most frequently used because it gives faster rate than acid and enzyme catalysts. If the oil contains high FFA and moisture, acid catalyst is suitable in the transesterification reaction. As for the enzyme, it can effectively convert all of triglycerides to biodiesel, but the product cost of enzyme catalytic is more expensive than other catalysts.

2.10.2 Molar Ratio of Methanol to Oil

In Equation 2.3, the stoichiometric molar ratio of alcohol to oil is three molecules of alcohol to one molecule of triglyceride. Actually, the base-catalyzed transesterification requires higher molar ratio to drive the reaction to highest yield. Therefore, the molar ratio of alcohol to oil is frequently set to 6:1 or more.

Normally, the highest conversion biodiesel of oil, which holds high FFA, require the molar ratio of alcohol to oil in excess of 15:1 while using sulfuric acid as catalyst. When a high molar ratio is used to generate ester, it interferes with the glycerol separation because of increasing solubility. In addition, if the glycerol remains in solution, it can reverse the reaction. That is one cause of lower ester yields.

2.10.3 Mixing Intensity

The mixing intensity has quite a small effect on the rate of reaction. However, the mixing intensity has some influence on heterogeneous-solution reactions, which have slow reactions in the first period, where diffusion and mass transfer reactions control the overall rate of the reaction.

2.10.4 Reaction Temperature

The reaction temperature strongly influences the rate of the reaction. The biodiesel reaction will proceed to near completion even at the room temperature when it is given enough reaction time. Normally, the reaction is carried out nearly at the boiling point of methanol (64.8 degree Celsius) at the atmospheric pressure. In addition, the reaction temperature depends on catalyst so that, for example, a high temperature is used to produce biodiesel by using acid catalyst and no-catalyst.

2.10.5 Moisture and FFA Content

Raw materials (oil, alcohol, and catalyst) in transesterification must be anhydrous and have low FFA (< 1 %wt) content. Moisture and high FFA (more than 1 %wt) will cause gel to form by saponification (Equation 2.4), which results in lower yields and washing problems. However, 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.

2.11 Specifications and Properties of Biodiesel

Biodiesel is produced from various vegetable oils and animal fats by different methods, so the standardization of biodiesel quality was 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.

ASTM test methods and European test methods are used to measure performance parameters of biodiesel production in Thailand. These methods are enacted in the Royal Gazette for controlling production standards for trading (Table 2.3 and 2.4).

Table 2.3 The requirement of commercial biodiesel qualities and quantities in Thailand (Department of Energy Business, 2005)

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 ($^{\circ}$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	$\leq$ Number 1	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 /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.

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 $^{\circ}$C (kg/m^3)	$\geq$ 860 and $\leq$ 900	ASTM D 1298
Viscosity at 40 $^{\circ}$C (cSt)	$\geq$ 1.9 and $\leq$ 8	ASTM D 445
Flash point ($^{\circ}$C)	$\geq$ 120	ASTM D 93
Sulphur (%wt)	$\leq$ 0.0015	ASTM D 2622
Cetane Number	$\geq$ 47	ASTM D 613
Sulfated Ash (%wt)	$\leq$ 0.02	ASTM D 874
Water and Sediment (%vol)	$\leq$ 0.2	ASTM D 2709
Copper Strip Corrosion	$\leq$ Number 3	ASTM D 130
Acid Value (mg KOH/g)	$\leq$ 0.80	ASTM D 664
Free Glycerin (%wt)	$\leq$ 0.02	EN 14105
Total Glycerin (%wt)	$\leq$ 1.50	EN 14105
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.

2.12 Method of High Free Fatty Acid Oils and Fats

Generally, biodiesel is produced easily by using the base-catalyzed transesterification. Oils and fats, which are used in this technique, must contain free fatty acid less than 1 %wt. If they have free fatty acid more than 1 %wt/wt, base catalyst reacts with free fatty acids to produce soap. That is a major cause of lowering biodiesel yields. Therefore, more base catalyst is needed to neutralize the free fatty acid. In practice, oils and fats containing less than 3 %wt FFA can be processed but with some loss of product. For a feedstock that contains free fatty acids more than 4 %wt, there are at least 4 methods to convert free fatty acids to biodiesel like the enzyme method, the glycerolysis, the acid catalysis, the acid catalysis followed by the alkali catalysis.

This thesis focuses on the acid catalysis followed by the alkali catalysis. Adding acid catalyst in oil to convert free fatty acid into ester is the first step. This step avoids the saponification reaction when alkali catalyst is used in the second stage.

Advantages are that it takes less time than the enzymatic method, and that the reaction temperature is lower than either glycerolysis or the acid catalysis.

2.13 Runge-Kutta Method for Solving Ordinary Differential Equation (O.D.E) (Wongwises, 2005)

The fourth-order Runge-Kutta Method (RK4) is suitable and easy to analyze and to program data from experiment. This RK4 is derived from the Taylor series (method of order 4). The proof is algebraically complicated and results in a formula involving a linear combination of function values.

The interval [a, b] is divided in to (M) subintervals of equal width (h) starting with (x_0, y_0), four functions evaluations per step are required to generate the discrete approximations (x_i, y_i) as follows.

Solving the initial value problem (I.V.P.)

$y'= f(x, y(x))$ on [a, b]   with $y(x_0)=y_0$ Given a, b, y0, M, f(x, y)

h	:=	(b-a)/M
x(0)	:=	a
For	i	:= 1 to M do:
	x	:= x(i-1)
	y	:= y(i-1)
	k1	:= h*f(x,y)
	k2	:= h*f(x+h/2, y+0.5*k1)
	k3	:= h*f(x+h/2, y+0.5*k2)
	k4	:= h*f(x+h/2, y+k3)
	y(i)	:= y+[k1+2*k2+2*k3+k4]/6
	x(i)	:= x+h
(For	i	:= 1 to M)
Print	x(i), y(i)	

There are 2 types of Runge-Kutta Method order, which are used in MATLAB7: Order 2-3 (function ode23) and Order4-5 (ode45) as shown in the formulae presented as Equations 2.17 and 2.18, respectively. The parameters in ode23 are similar to those in ode45. Nevertheless, ode45 is more accurate than ode23 because the relative error of ode23 is 0.001 and of ode45 is 0.000001.

$$[x, y] = ode23('function', [a \; b], initial) \tag{2.17}$$

$$[x, y] = ode45('function', [a \; b], initial) \tag{2.18}$$