CHAPTER 2

THEORY

2.1 Vegetable Oil

Vegetable oil is derived from oil crop such as palm oil which comes from palm fruits and soybean oil which comes from soybean seeds. Most vegetable oils can be used as food, like palm oil, soybean oil, sunflower oil, rapeseed oil and peanut oil. The idea of using vegetable oils in diesel engines is not new. Diesel (1894) showed that the invented engine could run with peanut oil. This show was performed in the International Exposition, in Paris, France. In 1912, he gave a speech: “The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time.” So far, this speech has been proven to be true. There are three methods using vegetable oils in diesel engine; direct use, dilution and emulsion, and transesterification. The direct use is the simplest method. It saves time and cost of fuel preparation. But the engine is suffered from the injector deposition, ring sticking and lubricant thickening. The dilution and emulsion method involves with little process and consumes little time and cost. It is done by adding low viscosity liquids into oils. If the liquids are miscible with oil called dilution, if immiscible called emulsion. Engine problems reveals after a long run. The problems include injector deposition and high wear rating. The transesterification is a process of changing the chemical structure of vegetable oils from triglycerides to new substances that have properties similar to the diesel fuel. These substances are recognized today as biodiesel.

2.2 Biodiesel

2.2.1 Definition

Biodiesel is defined as mono alkyl ester of long chain fatty acids derived from vegetable oil or animal fat (Marchetti et al. 2007). Biodiesel and diesel fuel are miscible in any fraction. B5 is a mixture by volume of 5% biodiesel with 95% diesel fuel whereas B100 is a 100% biodiesel.

2.2.2 Specification

Specifications of biodiesel from various standards are available for evaluation the quality of pure biodiesel (B100), They are slightly different from country to country, as shown in Table 2.1.

2.2.3 Fuel Property

A study (Bala,2005) revealed fuel properties of biodiesel in terms of heating value, viscosity , density and cetane number, as shown in Fig.2.1. The heating value of biodiesel and vegetable oil are about 0.9 of diesel. Biodiesel viscosity is around 2.5 times of that diesel viscosity whereas vegetable oil viscosity is around 12-15 times of the diesel one. The density of biodiesel is around 870 kg/m^3 which is slightly higher than that of the diesel. The cetane number of biodiesel and diesel are quite similar at 45-48 whereas that of vegetable oil is quite low at 37-38.

Table 2.1 Specification of Biodiesel from Selected Countries

Property (units)	Malaysia	Indonesia	Thailand	USA[1]	EU[2]	Brazil[3]
Flash point (°C)	min 182	min 100	min 120	min 130	min 120	min 100
Viscosity at 40 °C (cSt)	4.415	2.3–6.0	3.5–5	1.9–6	3.5–5	–
Sulfated ash (% mass)	max. 0.01	max. 0.02	max. 0.02	max.0.02	max.0.02	max. 0.02
Sulfur (% mass)	min 0.001	min 0.001	min 0.001	min 0.001	min 0.001	–
Cloud point (°C)	15.2	max. 18	–	–	–	–
Copper corrosion (3 h, 50 °C)	Class 1	Class 3	Class 1	Class 3	Class 1	Class 1
Cetane number	–	min 51	min 51	min 47	min 51	–
Water and sediment (% vol)	max.0.05	max. 0.05	–	max. 0.05	–	max. 0.05
CCR 100% (% mass)	–	–	max. 0.3	max. 0.05	–	max. 0.1
Neutralization value (mg, KOH/g)	–	–	–	0.05	0.05	0.08
Free glycerin (% mass)	max. 0.01	max. 0.02	max. 0.02	max. 0.02	max. 0.02	max. 0.02
Total glycerin (% mass)	max. 0.01	max. 0.24	max. 0.25	max. 0.24	max. 0.25	max.0.38
Phosphorus (% mass)	–	max. 10 ppm (mg/kg)	max. 0.001	max. 0.001	max. 0.001	–
Distillation temperature	–	<360 °C	–	< 360 °C	–	<360 °C
Oxidation stability (h)	–	–	6	3	6	6

[1]ASTM D6751, [2]E 14214 , [3]ANP 42,
source: (Jayed et al.,2009)

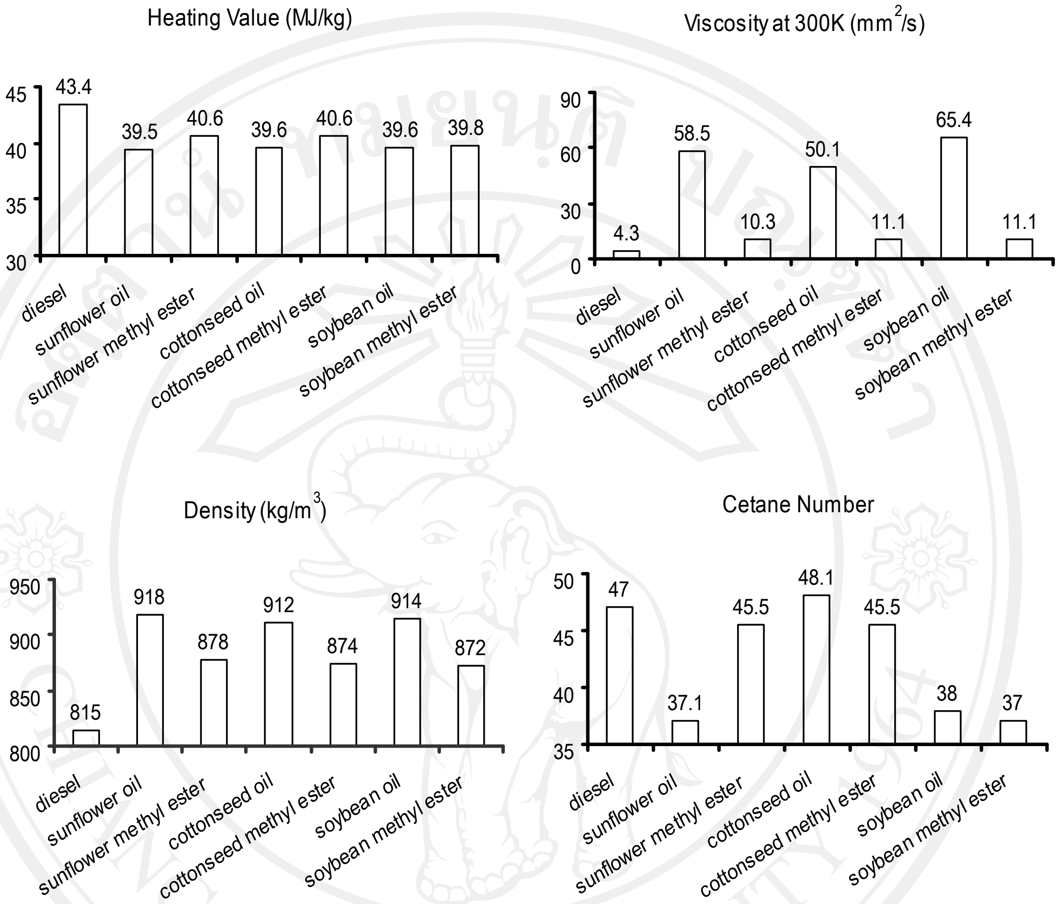


Fig. 2.1 Fuel properties of various biodiesels
source : (Bala 2005)

2.3 Biodiesel Production

Biodiesel production involves with three aspects; input materials, chemical reactions, and methods. The input materials are fixed oils and alcohols. The fixed oils are vegetable oils or animal fats. Alcohols such as methanol and ethanol are frequently used. The chemical reactions are alcoholysis, esterification and transesterification. The methods are catalytic and non-catalytic. Outline of the biodiesel production is shown in Fig.2.2.

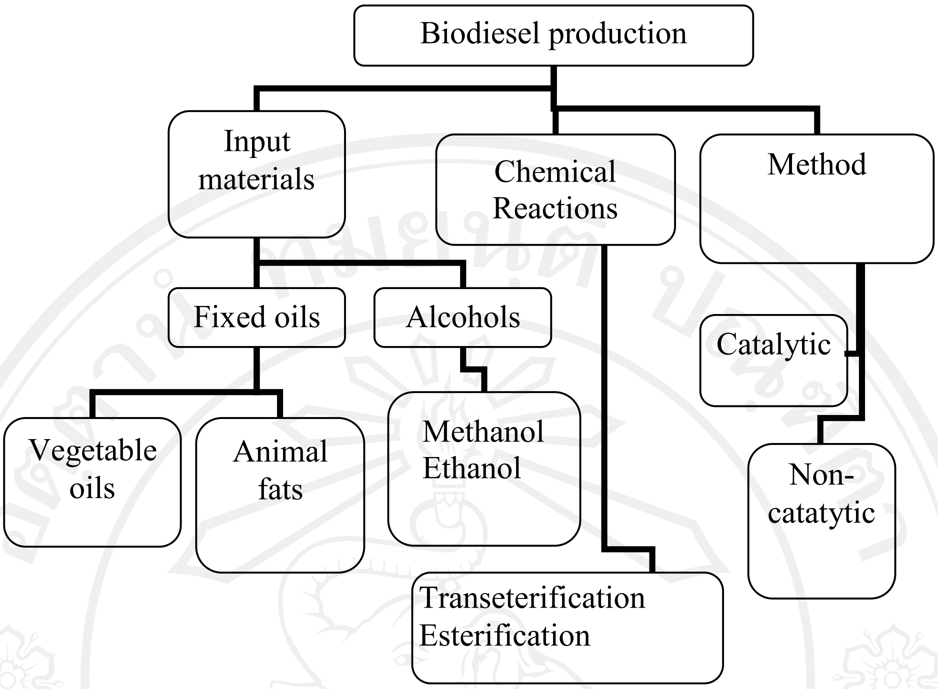


Fig.2.2 Outline of Biodiesel Production

2.3.1 Input Material

a) Fixed oil

Fixed oil contains fatty acids which found in vegetable oils and animal fats. The fatty acids in the fixed oil are presented in various forms e.g. triglycerides, di-glycerides, mono-glycerides and free fatty acids. The high quality fixed oil is triglycerides.

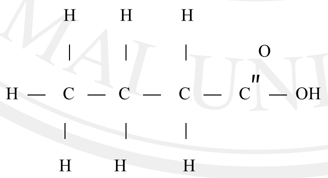
b) Triglycerides

Triglycerides are the main compositions of all fixed oils. A molecule of triglycerides called “triglycerol” or “triacylglycerol”. Triglycerol has one head and three tails. The head is glycerol part and the tails are fatty acids parts. If the three tails are similar, it is called simple-triglycerol otherwise called mixed-triglycerol. Simple-triglycerol is rarely found in nature.

c) Fatty Acids

Fatty acid is the essential parts of the triglycerol (a molecule of triglycerides called triglycerol). To produce fatty acid, a triglycerol must be cracked by the hydrolysis reaction (reaction with water). Three molecules of water react with a triglycerol and yield a glycerol and three free fatty acids. There are many types of fatty acid according to the number of carbon atom. Butyric acid (C4:0) has four carbon atom with zero double bond. Palmitic acid (C16:0) has 16 carbon atom with zero double bond. Nervonic acid (C24:1) has 24 carbon atom with one double bond. Fatty acids that have at least one double bond called unsaturated fatty acid. Fatty acid that has zero double bond called saturated fatty acid. Saturated fatty acid is more stable than unsaturated fatty acid. All fatty acids contain carboxyl group (COOH). The general formula of fatty acid is R′COOH. The R′ represents alkyl group as shown in Table 2.2.

Table 2.2 Example of a Fatty Acid

Fatty acid name	Structure	Formula	General formula
Butyric acid (C4:0)	 $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH}$	$CH_3(CH_2)_2COOH$	R′COOH

d) Glycerol

Glycerol is a trinary alcohol (alcohol that contains three OH groups). The OH groups make glycerol dissolve well with water (hydrophilic). The glycerol structure and it general formula is given in Table 2.3. Chemical reaction of glycerol called glycerolysis. The glycerolysis of fatty acid yields triglycerol and water as shown in Table 2.4.

Table 2.3 Glycerol structure

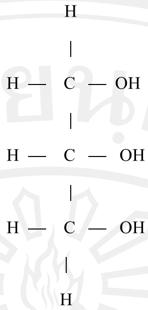
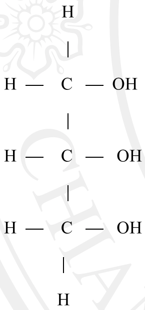
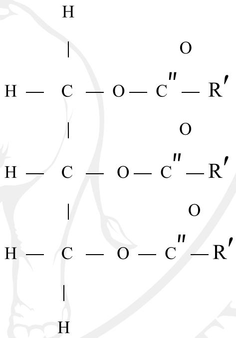
	Structure	Formula
Glycerol	 $\begin{array}{c} H \\ \vert \\ H - C - OH \\ \vert \\ H - C - OH \\ \vert \\ H - C - OH \\ \vert \\ H \end{array}$	$C_3H_5(OH)_3$

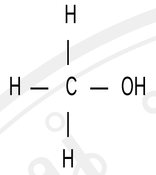
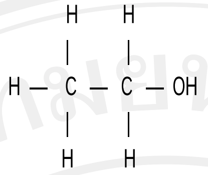
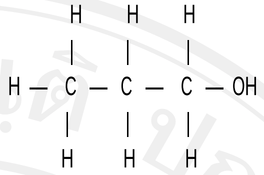
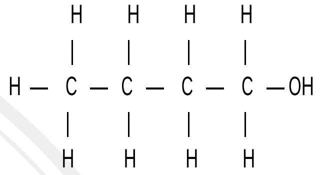
Table 2.4 Glycerolysis of fatty acids yields triglycerol and water

Glycerol	Fatty acids		Triglycerol	Water
 $\begin{array}{c} H \\ \vert \\ H - C - OH \\ \vert \\ H - C - OH \\ \vert \\ H - C - OH \\ \vert \\ H \end{array}$	$R'COOH$ $R'COOH$ $R'COOH$	→	 $\begin{array}{l} \quad\; H \\ \quad\; \vert \\ H - C - O - \overset{O}{C}'' - R' \\ \quad\; \vert \\ H - C - O - \overset{O}{C}'' - R' \\ \quad\; \vert \\ H - C - O - \overset{O}{C}'' - R' \\ \quad\; \vert \\ \quad\; H \end{array}$	H_2O H_2O H_2O

e) Alcohol

Methanol and ethanol are the most common alcohols used in the biodiesel production. They are straight-chain primary alcohols, details of these alcohols are given in Table 2.5. Other types of alcohol are branched-chain, cyclic, secondary, trinary and etc. Primary alcohols contain one hydoxy (OH) group. Secondary alcohols contain two OH groups. Trinary alcohol (such as glycerol) contains three OH groups. Normal butanol (n-butanol) and normal propane (n-propanol) are also straight-chain primary alcohols. Iso-butanol is a branched-chain alcohol which contains four carbons as n-butabol.

Table 2.5 Examples of straight-chain primary alcohols

No. Carbon	1	2	3	4
Symbol	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH
Structure	 $H-\overset{H}{\underset{H}{C}}-OH$	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$
Molecular Mass	32	46	60	74
Full name	Methyl alcohol	Ethyl alcohol	Propyl alcohol	Butyl alcohol
Short name	Methanol	Ethanol	Propanol	n-Butanol
Very short	MeOH	EtOH		BtOH

2.3.2 Chemical Reaction

a) Alcoholysis

Alcoholysis means the reaction of alcohol. After alcoholysis, the input materials (triglycerides, di-glycerides, monoglycerides and free fatty acids) are converted to biodiesel, glyceride and water. In the biodiesel production this reaction sometimes recognized as transesterification.

b) Transesterification

In the biodiesel production, transesterification and alcoholysis are interchangeable terms. However, in general chemistry, transesterification covers four types of reaction; alcoholysis, acidolysis, interesterification and aminolysis

c) Esterification

Esterification is reaction of acid and alcohol. Therefore, when considering the free fatty acids as acid, the reaction of alcoholysis can be recognized as the esterification as well. The reaction products are biodiesel and water.

2.3.3 Catalytic and Non-catalytic Method

a) Catalytic Method

Under atmospheric pressure, fixed oils and alcohol are immiscible. But in the present of suitable catalyst, they are miscible, therefore, chemical reaction develops. Catalyst increases reaction rate by reducing the reaction barrier energy or the activation energy. A common condition of catalytic method is at molar ratio of methanol-to-oil 6:1, with potassium hydroxide (KOH) or sodium hydroxide (NaOH) as catalyst at 1% of oil mass, and at temperature 60 °C. Although the rate of the reaction of the catalytic method is very fast, soap formation is unavoidable. Soap is product of saponification. To avoid the soap, raw materials must contain no free fatty acid and water. In practice, if raw material has high level of free fatty acids, the free fatty acids must be converted to biodiesel using the esterification reaction. The esterification develops faster under acid catalyst such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). Water in the fixed oil also promotes soap. Triglycerides after reacting with water become free fatty acids and glyceride. This reaction called hydolysis.

b) Non-catalytic Method

Non-catalytic method involved with a very high pressure and high temperature conditions. Such conditions, the alcohol is in the sub or the supercritical state. At this state, the oil and alcohol are mixed well and become a single phase. Therefore, the alcoholysis develops at a fast rate.

2.4 Supercritical Fluid

Supercritical fluid is fluid that in the supercritical state, its temperature and pressure is above the critical point. The fluid shows a single phase which is neither gas nor liquid. Fig.2.3 shows phase diagram of a common fluid; carbon dioxide. It is clearly seen that at pressure and temperature over critical point, carbon dioxide becomes supercritical fluid or supercritical carbon dioxide. Fig.2.4 shows carbon dioxide density at various conditions. It is observed that liquid-vapor density gap, dotted line, is smaller at higher

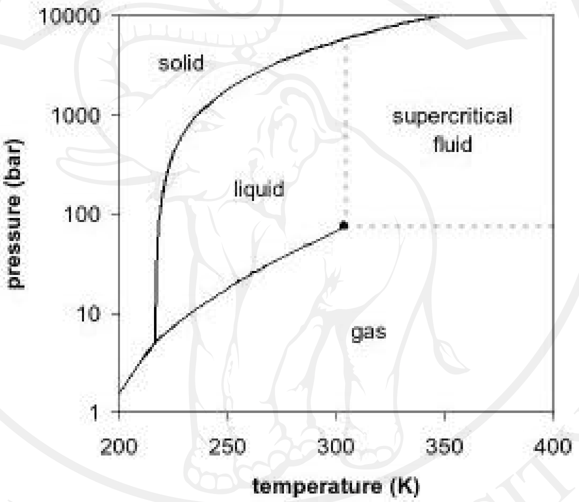


Fig.2.3 Phase diagram of carbon dioxide

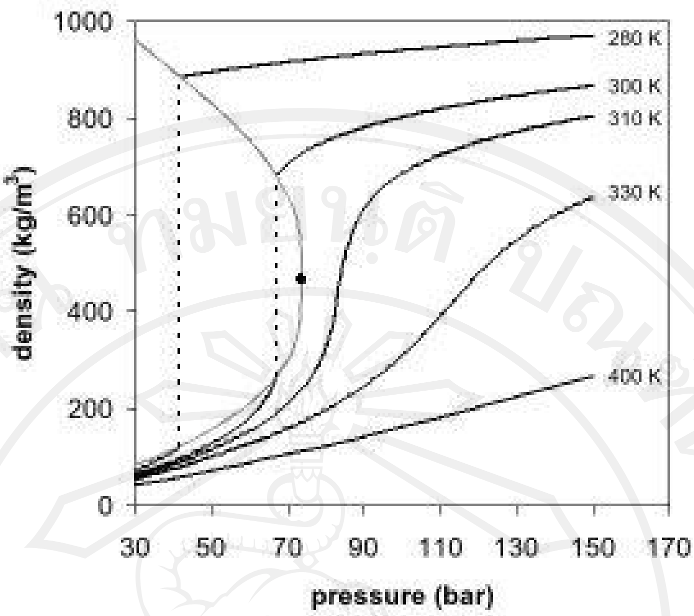


Fig.2.4 Density of carbon dioxide at various conditions

temperature. At a certain point, the line disappeared and only a dot presented. This dot is at 73.8 bar and 304.1 K which is the carbon dioxide critical point. Each substance has a specific critical point as shown graphically in Fig.2.5 and numerically in Table 2.8.

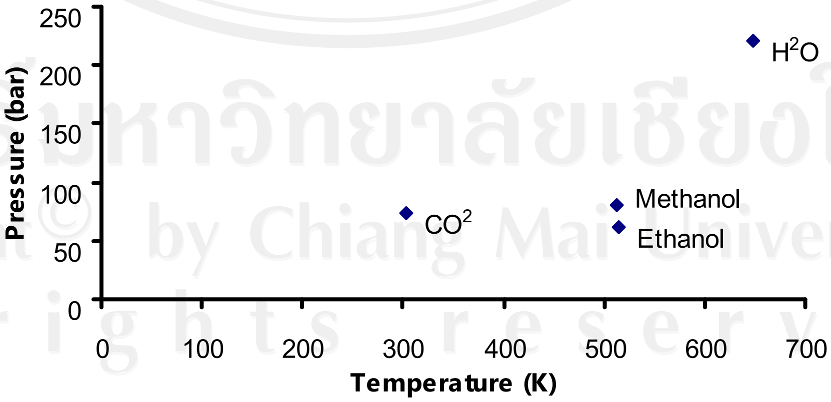


Fig.2.5 Critical points of methanol, ethanol, water and carbon oxide

Table 2.6 Critical temperature, critical pressure and density of some substances

Substance	Molar mass	Critical temperature	Critical pressure		Density at critical point
	(g/mol)	(K)	(MPa)	(bar)	(g/cm³)
Carbon dioxide (CO_2)	44.01	304.1	7.38	73.8	0.469
Ethanol (C_2H_6O)	46.07	513.9	6.14	61.4	0.276
Methanol (CH_4O)	32.04	512.6	8.09	80.9	0.272
Water (H_2O)	18.02	647.3	22.12	221.2	0.348

2.5 Percent Yield

Percent yield is defined as the ratio of the actual yield and the theoretical yield as

$$\%yield = 100\,x\,\frac{actual\ yield}{theoretical\ yield} \quad . \tag{2.1}$$

Where the actual yield is the mass of the interesting agent found in the product and the theoretical yield is the mass of that agent can be perfectly produced which is derived by calculation from the chemical equation as

$$\begin{array}{ccccccc} (1mole)\,Triglyceride & + & (3mole)(CH_3OH) & \rightarrow & (3mole)(methyl\ esters) & + & (1mole)C_3H_8O_3 \\ 851.3\text{ g} & + & 96.0\text{ g} & \rightarrow & 855.3\text{ g} & + & 92.0\text{ g}\,. \end{array} \tag{2.2}$$

For example, if 851.3 g (1 mole) of palm oil triglycerides is used for making biodiesel (methyl esters). The theoretical yield is 855.3 g (3 moles of the methyl esters). If 800 g biodiesel is found in the product of an experiment. The percentage yield of this experiment is 93.5 (100x800/855.3=93.5).

2.6 Percent Conversion

The percent conversion is defined as

$$\%\,conversion = 100\,x\,\frac{\left(C_{uME,0} - C_{uME,t}\right)}{C_{uME,0}}\ , \tag{2.3}$$

where $C_{uME,0}$ is the concentrations of unmethyl esterified compound (uME) at initial time. $C_{uME,t}$ is the concentrations of the unmethyl esterified compound (uME) at any time. The unmethyl esterified compound is a mixture of triglycerides, diglycerides, monoglycerides and unreacted free fatty acids which is a starting material of biodiesel production (Joelianingsih et al.,2008).

2.7 Kinetics of Reaction

2.7.1 Kinetics Rate Law

Kinetics rate law states that rate of chemical reaction between substances A and B could be formulated as

$$r = kC_A^{\alpha} C_B^{\beta} , \tag{2.4}$$

where r is the rate of reaction, k is rate constant which is a function of temperature. C_A and C_B are concentrations of A and B, respectively. α and β are the reaction orders of A and B, respectively. For A and B are triglycerides and methanol, respectively, there are three models of the kinetics reaction to get methyl esters as follow:

$$r = kC_A^{0.9565} C_B^{1.0493} \qquad \text{(Song Model) ,} \tag{2.5}$$

$$r = kC_A^{1.5} C_B^{0} \qquad \text{(Cheng Model),} \tag{2.6}$$

$$r = kC_A^{1} C_B^{0} \qquad \text{(Kusdiana and Saka Model).} \tag{2.7}$$

Cheng and Kusdiana and Saka assumed that methanol concentration do not influence the rate because the reaction was carried out under excessive methanol (molar ratio of methanol to triglycerides above 40:1).

2.7.2 Arrhenius equation

Arrhenius equation is the relationship of the rate constant (k) and temperature as

$$k = (k_0)(e^{-\frac{E_a}{RT}}), \tag{2.8}$$

where k_0 is pre-exponential factor having unit similar to the k, E_a is activation energy (kJ/mol), R is the universal gas constant (8.314 J/mol.K), T is absolute temperature (K).

By taking the natural logarithm on each side

$$\ln k = \ln(k_0)(e^{-\frac{E_a}{RT}}),$$
$$\ln k = \left(-\frac{E_a}{R}\right)\frac{1}{T} + \ln k_0.$$

Therefore, if we plot a graph of ln k against 1/T, we will get E_a and k_0 from the graph, as (-Ea/R) is the graph gradient, and ln k_0 is the intercept point on the y axis, as shown in Fig 2.6.

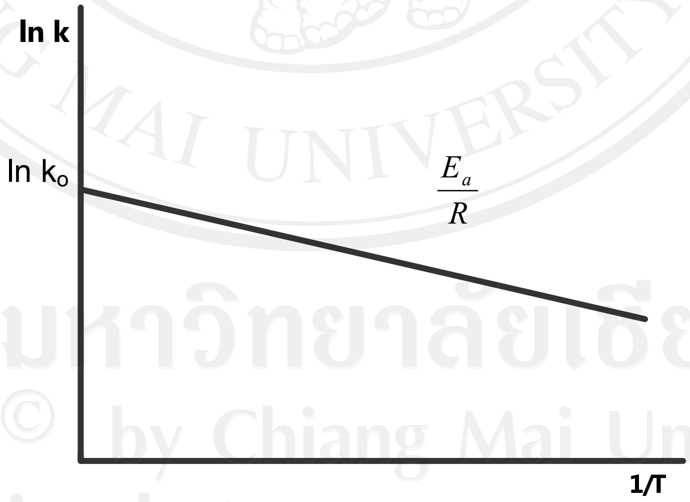


Fig. 2.6 Arrhenius plot of ln k and 1/T

a) Activation Energy

Activation energy is a minimum energy required in a chemical reaction. This energy is a barrier of the reaction development. A high activation energy reaction refers to a reaction that has a high energy barrier. This reaction needs a high external energy to make molecules of the reactants having high potential energy to overcome the barrier. If the molecules energy is lower than the activation energy, no reaction develops.

b) Pre-exponential Factor

This factor represented by k_0 in the Arrhenious equation. It is sometimes called frequency factor. A high frequency factor means a high number of molecules which having potential energy over the barrier. Consequently, the rate constant (k) is appeared high.

2.7.3 Kinetics of Triglycerides to Methyl Esters

a) Diasakou Model

Diasakou (1998) explained reaction mechanisms of thermal (non-catalytic) transesterification as:

$$\begin{aligned} &1st\ step; && TG + MeOH \xrightarrow{K_1} DG + ME \\ &2nd\ step; && DG + MeOH \xrightarrow{K_2} MG + ME \\ &3rd\ step; && MG + MeOH \xrightarrow{K_3} G + ME \end{aligned} \tag{2.9}$$

The mechanisms have three steps. The 1st step, triglycerides (TG) react with methanol and yield diglycerides (DG) and methyl esters (ME). The 2nd step, the diglycerides then react with methanol and yield monoglycerides (MG) and methyl esters. The 3rd step, the monoglycerides then react with methanol and yield glycerine (G) and methyl esters. Two assumptions are made; firstly, the reactions are irreversible because of the high content of methanol. Secondly, each reaction step is the first order with respect to the reacting component. Differential equations which represented the reaction rate of each step are:~~;~~

$$\begin{aligned}\frac{dC_{TG}}{dt} &= -K_1 C_{TG} C_{MeOH} \\ \frac{dC_{DG}}{dt} &= -K_2 C_{DG} C_{MeOH} + K_1 C_{TG} C_{MeOH} \\ \frac{dC_{MG}}{dt} &= -K_3 C_{MG} C_{MeOH} + K_2 C_{DG} C_{MeOH}\end{aligned} \tag{2.10}$$

where K_1, K_2, and K_3 are the rate constants.

b) Kusdiana and Saka Model

Kusdiana and Saka (2001) reduced Diasakou mechanisms from three steps to one step as

$$TG + 3MeOH \xrightarrow{k} G + 3ME \tag{2.11}$$

They carried out experiments with rapeseed oil in excessive methanol so that the methanol concentration can be assumed a constant. They also assumed that the reaction was in a first order respected to triglycerides concentration, therefore, the reaction rate (r) can be written in terms of the disappearing of triglycerides concentration over a period of time as

$$r = -\frac{dC_{TG}}{dt} = -kC_{TG}\,. \tag{2.12}$$

They define a new term “unmethyl esterified compound; uME” as a mixture of triglycerides, diglycerides, monoglycerides and unreacted free fatty acids. Therefore, eq.6 can be

$$uME + x\,mole\,MeOH \xrightarrow{K} G + x\,mole\,ME\,. \qquad (2.13)$$

If the reaction takes place under excessive methanol, the concentrations of the unmethyl esterified compound (uME), glycerine (G), and methyl esters (ME) are changed with time. Therefore, the reaction rate will be

$$r = -\frac{dC_{uME}}{dt} = -kC_{uME} \qquad , \qquad (2.14)$$

where C_{uME} is the concentration of the uME, k is rate constant.

c) Song Model

Song (2008) applied the one step mechanism in his model. Song carried out experiment with palm oil in methanol and his experiment was quite similar with that of Kusdiana and Saka. However, the activation energy of Song experiment was found to be 105 kJ/mol which was closed to that of Diasakou.

d) Joelianingsih Model

Joelianingsih et.al.(2008) studied the non-catalytic methanolysis of palm oil in a semi batch bubble column reactor. A kinetics model was developed from that of Kusdiana and Saka as follows:

$$-\frac{dC_{TG}}{dt} = kC_{TG}^{m}C_{MeOH}^{n} \quad . \qquad (2.15)$$

Assumed C_{MeOH} a constant, and m=1, therefore

$$-\frac{dC_{TG}}{dt} = k_1 C_{TG}$$

$$-\left(\frac{1}{C_{TG}}\right) dC_{TG} = k_1 dt$$

$$\int_{C_{TG,0}}^{C_{TG,t}} \frac{1}{C_{TG}} dC_{TG} = -\int_0^t k_1 dt$$

$$\ln\left(\frac{C_{TG,t}}{C_{TG,0}}\right) = -k_1 t$$

$$\ln C_{TG,t} - \ln C_{TG,0} = -k_1 t$$

$$-\ln C_{TG,t} + \ln C_{TG,0} = k_1 t$$