CHAPTER 4

RESULTS AND DISCUSSION

4.1 Methanolysis of Palm Oil

4.1.1 Temperature Survey Tests

The temperature survey tests were carried out at a fixed molar ratio of methanol-to-oil, 43:1, with various temperature and holding time between 150-400 °C and 10-55 min, respectively. As shown in Fig. 4.1, at the beginning, when the reactor temperature gradually increased, the pressure remained constant at the atmosphere for about 10 min. before starting to increase. Because of during this time the methanol did not boil. When the temperature was about 100 °C, Boiling of methanol occurred then the pressure increased with the temperature. It was found that the pressure could be held nearly constant during boiling. When the temperature cooled down, the pressure also dropped for all tests.

4.1.2.Effect of Temperature and Holding Time on Biodiesel Yield

The GC-MS analysis of products from the survey tests revealed that at 150 °C, the biodiesel yield was quite low which was around 21%, as shown in Fig.4.2. The yields were higher with the higher temperature. The maximum yield was 81%, at 300 °C and 35 min holding time. At 300°C, 10 min, the yield was at 76% which indicated that the reaction was not completed. At 350 °C, the yield was lower to be 41% due to the effects of the thermal decomposition and the dehydrogenation reactions (Saka and Kusdiana, 2001). However, the yield rebounded to be 78% at 400 °C due to the backward-reaction effect. However, from these survey tests, it could be concluded that

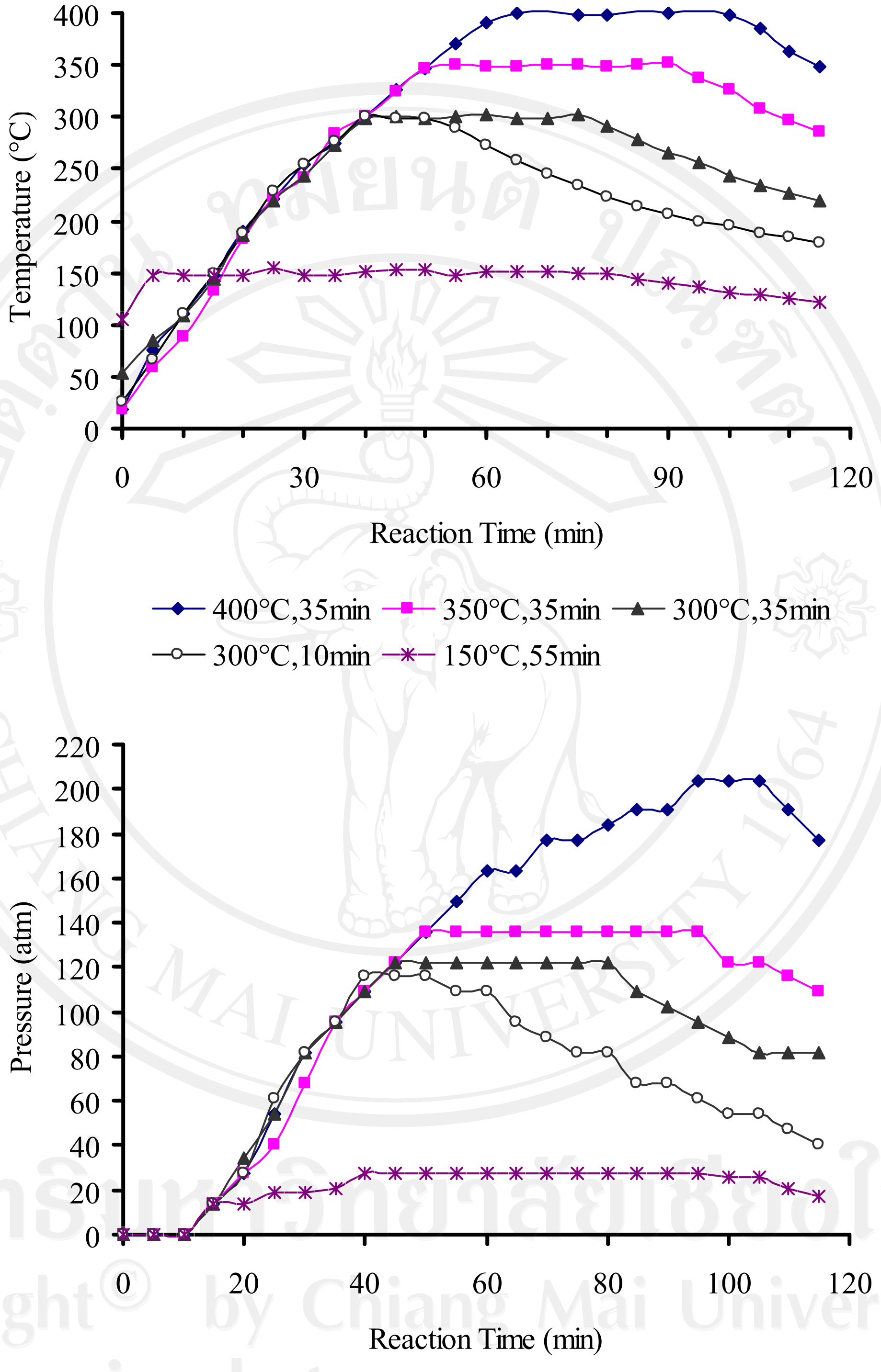

Fig. 4.1 Temperature and Pressure Evolutions During the Methanolysis Reaction (Molar ratio methanol-to-oil 43:1, Methanol 64 ml : Oil 36 ml)

the most suitable temperature was at 300°C since highest yield with lowest energy input was obtained.

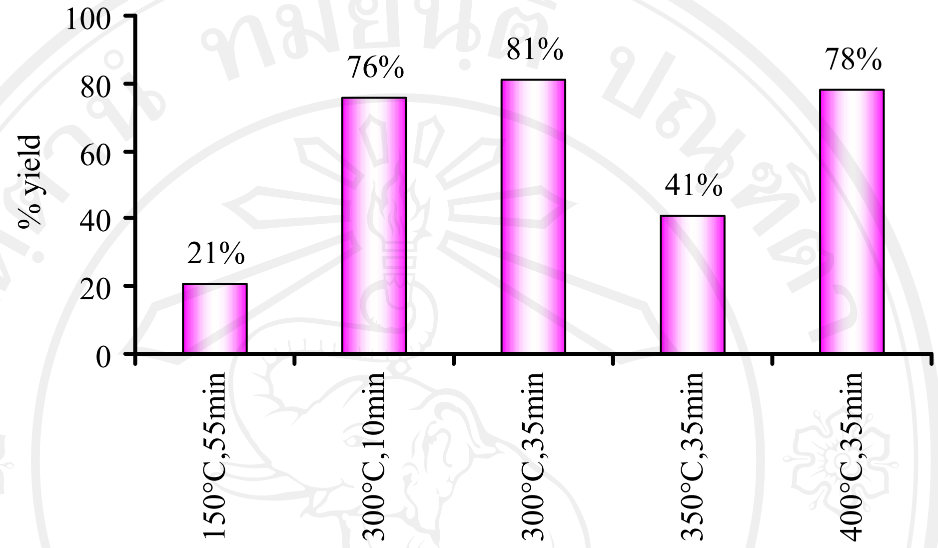

Fig. 4.2 Effect of Temperature and the Holding Time on the Biodiesel Yield (Molar ratio of methanol-to-oil at 43:1, Methanol 64 ml : Oil 36 ml)

4.1.3.Effect of the Molar Ratio and Holding Time on Biodiesel Yield

In this part the effect of molar ratio of methanol-to-oil and holding time were evaluated at temperature 300 °C. Three molar ratios of methanol-to-oil (8:1, 22:1 and 42:1) were carried out at 300°C and 105 holding time. The GC-MS analysis revealed the biodiesel yields, as shown in Fig. 4.3. The yield was highest at 97 % at the molar ratio of 22:1. However, at the 42:1 molar ratio, the yield was declined to 85%. The reduction of the yield at the higher molar ratio was due to the too long holding time. The maximum yield was occurred at an earlier time.

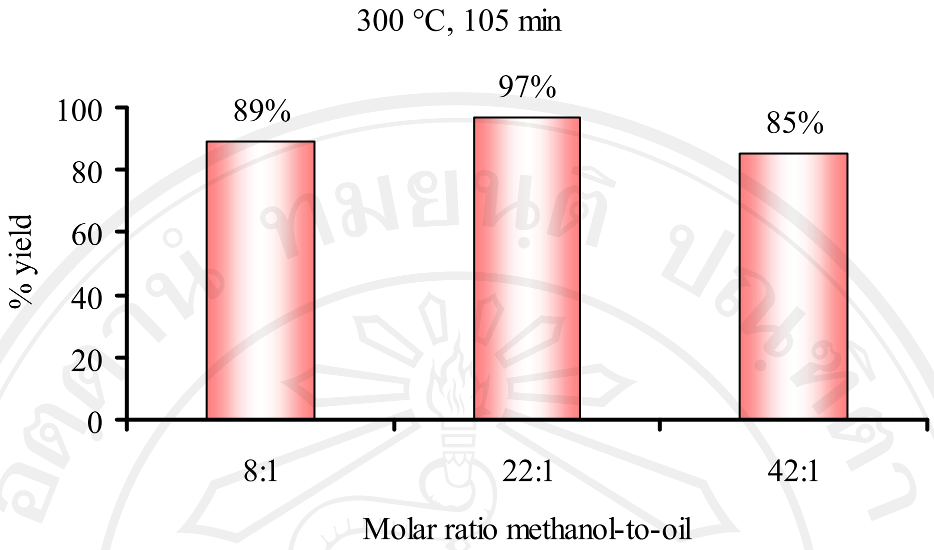

Fig. 4.3 Effect of the Molar Ratio on the Biodiesel Yield (300 °C and 105 min. Holding Time)

4.1.4 Effect of Holding Time on Biodiesel Yield

The biodiesel yield depended on the molar ratio and the holding time. The maximum yield took a shorter holding time for the higher molar ratio. For example, at the molar ratio 8:1, the maximum yield occured at 70 min. and at molar ratio 22:1, the maximum yield occurred at 10 min. At molar ratio of 42:1, it could occure at a shorter time as shown in Fig.4.4.

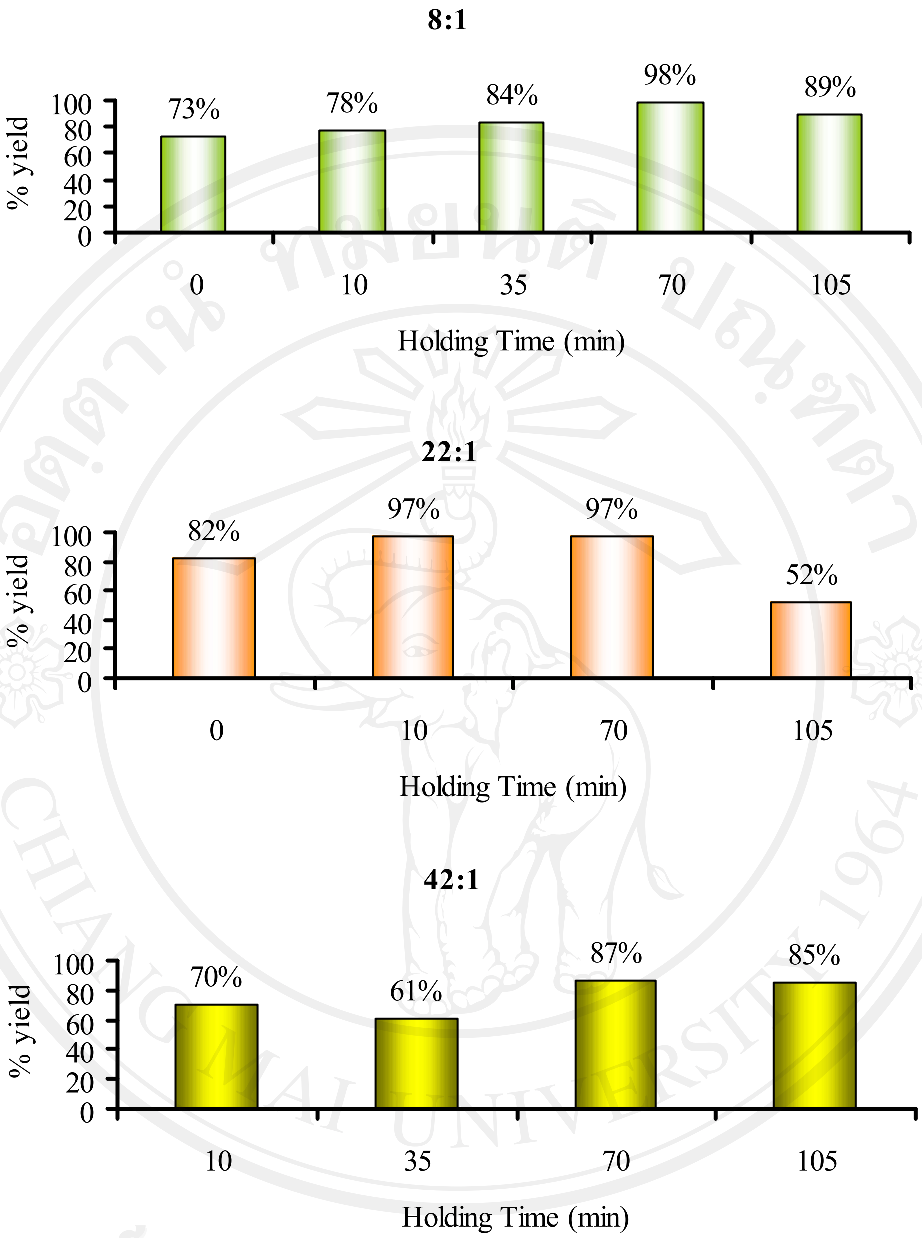

Fig. 4.4 Effect of the Holding Time on the Biodiesel Yield (Molar Ratio of Methanol-to-oil at 8:1, 22:1 and 42:1, Temperature at 300°C)

4.2 Kinetics of Reaction

According to the methanolysis of triglycerides reaction, one mole of triglycerides (TG) reacts with three moles of methanol (MeOH) yields one mole of glycerin (G) and three moles of methyl esters (ME), as

$$TG + 3MeOH \longrightarrow 3ME + G \ . \tag{4.1}$$

The reaction rate (r) can be expressed as;

$$r = -r_{TG} = \frac{-r_{MeOH}}{3} = -r_G = \frac{r_{ME}}{3} \ , \tag{4.2}$$

$$r = -\frac{dC_{TG}}{dt} = -\left(\frac{1}{3}\right)\frac{dC_{MeOH}}{dt} = \frac{dC_G}{dt} = \left(\frac{1}{3}\right)\frac{dC_{ME}}{dt} \ , \tag{4.3}$$

where r = reaction rate, $-r_{TG}$ = rate of disappearance of triglycerides, $-r_{MeOH}$ = rate of disappearance of methanol, r_G = rate of appearance of glycerine, r_{ME} = rate of appearance of methyl esters, C_{TG} = the concentration of triglycerides, C_{MeOH} = the concentration of methanol, C_G = the concentration of glycerin, and C_{ME} = the concentration of methyl esters, respectively.

The reaction rate (r) can be rewritten in term of rate constant (k) as

$$r = kC_{TG}^{m}C_{MeOH}^{n} \ . \tag{4.4}$$

In practice, the concentration of methyl esters which evaluated by the gas chromatography mass spectrometry (GC-MS) analysis could be represented with a non-unit term of methyl esters fraction (x) as

$$\frac{dC_{ME}}{dt} = k_p \frac{dx}{dt} \ , \tag{4.5}$$

where k_p is a proportionality constant.

4.2.1.Reaction Order Principle

Zero Order Reaction

Zero order reaction means the reaction rate (r) of the reaction is relied only on the rate constant (k) whereas the triglycerides concentration (C_{TG}) and the methanol concentration (C_{MeOH}) have no influence at all. The reaction rate is expressed in term of rate of increasing of methyl esters concentration $\left(\frac{dC_{ME}}{dt}\right)$ as

$$\begin{aligned} \frac{dC_{ME}}{dt} &= k \\ C_{ME,t} &= C_{ME,0} + kt \quad , \end{aligned} \tag{4.6}$$

where $C_{ME,t}$ = concentration of methyl esters at any t, $C_{ME,0}$ = concentration of methyl ester at initial time.

Therefore, a plot of the biodiesel concentration (C_{ME}) and time (t) is a straight line having a gradient k and an intercept $C_{ME,0}$ as shown in Fig. 4.5. It could be noted that that k is a constant at a specific temperature, T.

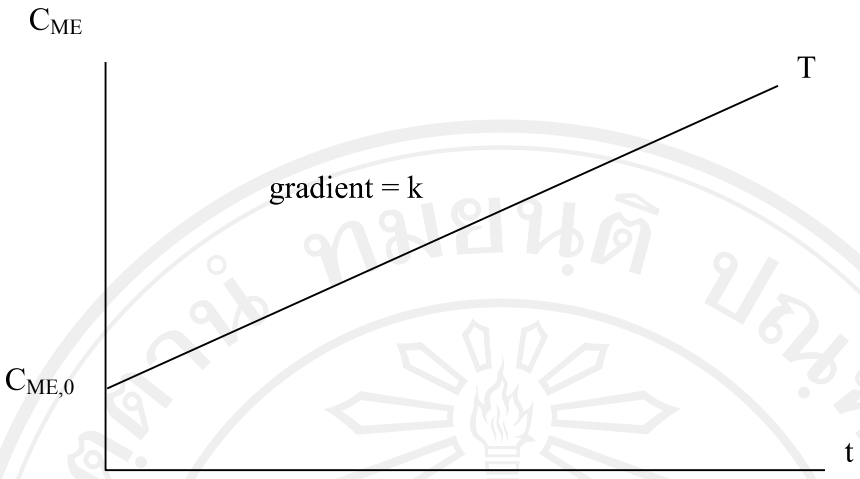

Fig. 4.5 A plot of Biodiesel Concentration (C_{ME}) and Reaction Time (t) for the Zero Order Reaction

First Order Reaction

First order reaction means the reaction rate (r) is relied on both the rate constant (k) and the triglycerides concentration. Rate of increasing of methyl esters concentration $\left(\frac{dC_{ME}}{dt}\right)$ is proportional to rate of decreasing of unmethyl esterified compound concentration $\left(\frac{dC_{uME}}{dt}\right)$ according to the eq. below

$$uME + x\,mole\,MeOH \xrightarrow{K} G + x\,mole\,ME\,. \tag{4.7}$$

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

$$r = -\frac{dC_{uME}}{dt} = k\ C_{uME}\ , \tag{4.8}$$

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

Rate of increasing of methyl esters concentration $\left(\frac{dC_{ME}}{dt}\right)$ is expressed in terms of rate of decreasing of unmethyl esterified compound concentration as

$$-\frac{dC_{uME}}{dt} = kC_{uME}$$

$$-\left(\frac{1}{C_{uME}}\right)dC_{uME} = kdt$$

$$\ln C_{uME,t} = -kt + \ln C_{uME,0} \,. \tag{4.9}$$

Therefore, a plot of eq. 11 is a straight line having a gradient -k and intercept at ln $C_{ME,0} = 0$ as shown in Fig. 4.6.

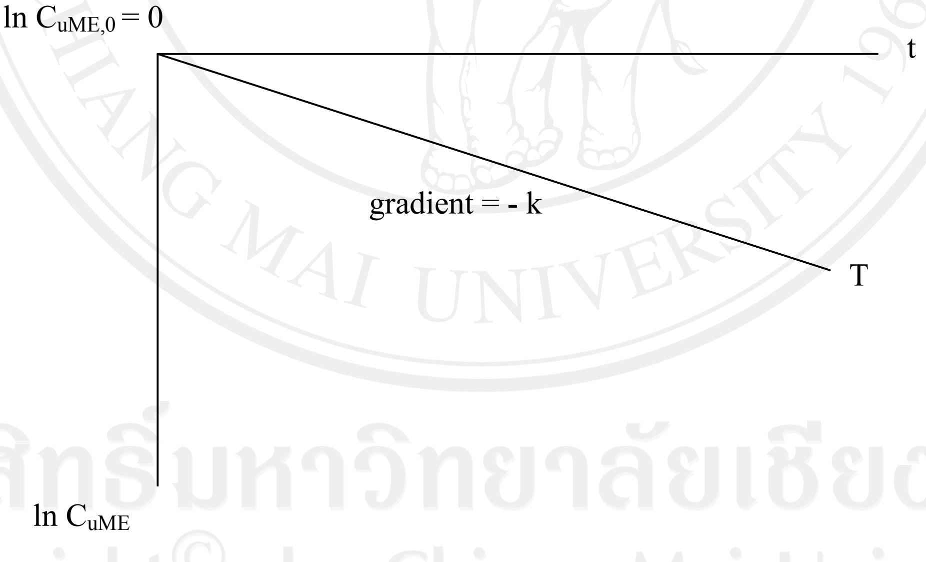

Fig. 4.6 A plot of unmethyl esterified compound concentration (C_{uME}) and reaction time (t) for the first order reaction

If we defined that

$$C_{uME,t} = C_{uME,0}(1-x) \quad , \tag{4.10}$$

where x is the methyl ester fraction, then

$$\ln(1-x) = -kt \ . \tag{4.11}$$

A plot of eq. 4.11 gave a straight line having a gradient -k and intercept at 0 as shown in Fig. 4.7.

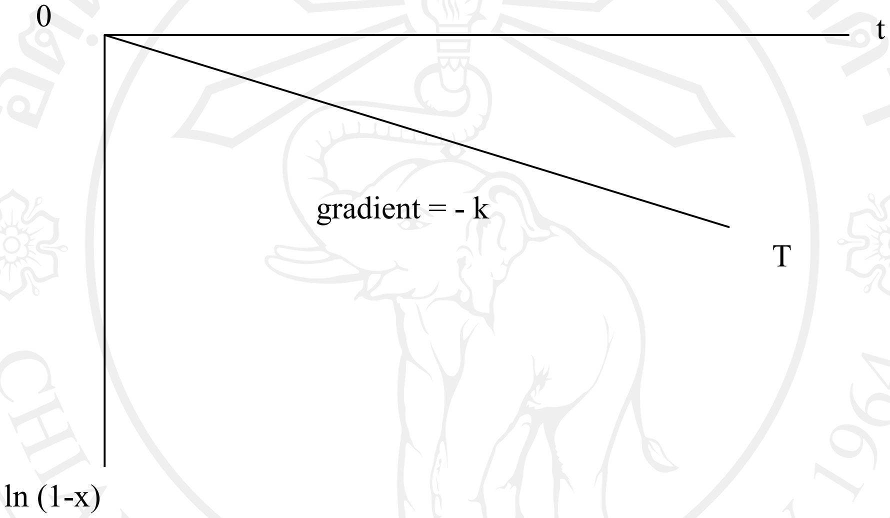

Fig. 4.7 A plot of ln(1-x) and Reaction Time (t) for the First Order Reaction

At the beginning of the reaction, there is no biodiesel presenting in the reactor, the methyl ester fraction is zero (x=0) or ln (1-x) = 0, and there is 100% of the unmethyl esterified compound ($C_{uME,0}$=1) or ln $C_{uME,0}$ = 0.

4.2.2. Rate Constant and Activation Energy

According to the Arrhenius equation, rate constant (k) is a function of temperature as

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

or

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

If we can find a rate constant (k) at any temperature, therefore, the activation energy (Ea) would be revealed.

To find the rate constant by the zero order model, at first we have to look at the methyl esters fraction (x) data in the experiments. The data came from the GC-MS analysis of the 22 samples which periodically ejected from the reactor during the test runs at temperature 146-210 °C, as shown in Fig.4.9. It was observed that all samples which ejected at various temperatures had many methyl ester fractions. At the beginning the mixing of the methanol and the oil were not complete miscible then the reaction performed with low temperature of about 146-170 °C and the methyl esters fractions did not changed significantly of around 0.1-0.2. After that, when the mixing was more completed, the values increased from 0.2 to 0.8, as the temperature increased from 170 to 200 °C. At the end of the reaction, even the temperature increased but the fraction changed only slightly. The results were shown in Figs. 4.8 and 4.9.

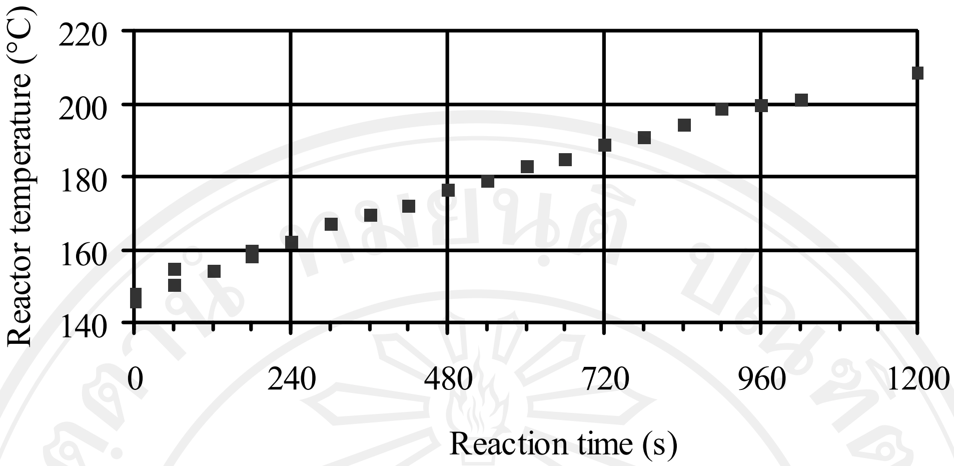

Fig. 4.8 Reactor Temperature (T) during the Reaction Time (t)

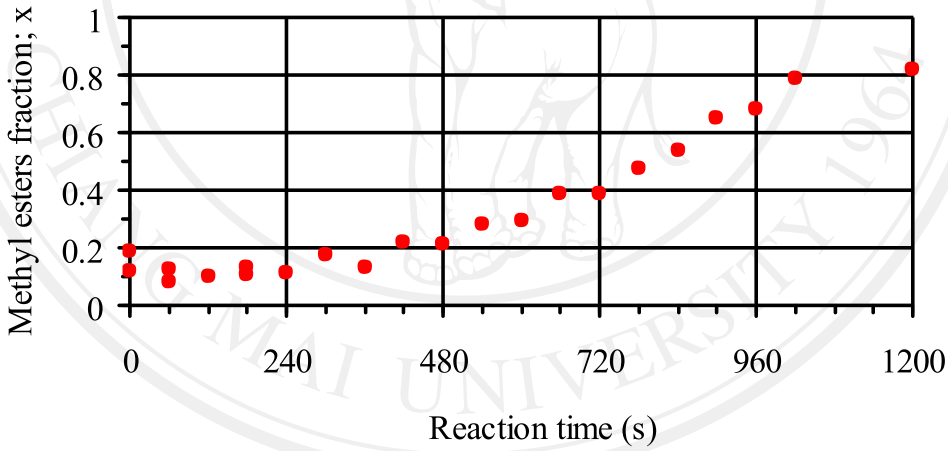

Fig.4.9 Methyl Esters Fraction (x) of Each Sample During the Reaction time (t)

Rate of increasing of methyl esters fraction (dx/dt) was determined and apparent rate constants (k1) were arrived by the zero order model as

$$r = k = \left(\frac{1}{3}\right)\frac{dC_{ME}}{dt} = \left(\frac{1}{3}\right)k_p\frac{dx}{dt}$$

At a specific temperature, $\frac{dx}{dt}$ was a constant (k_1). Therefore

$$k = \left(\frac{1}{3}\right) k_p k_1$$

$$k_1 = \frac{3k}{k_p}$$

The apparent rate constants were presented in Table 4.1.

Table 4.1 Apparent Rate Constants (k1) Derived from the Zero Order Model

$k_1 = \frac{dx}{dt}$ (s^{-1})	Temperature (°C)
0.0000330	146
0.0000330	148
0.0000988	150
0.0001645	154
0.0000988	155
0.0002303	158
0.0002303	160
0.0002960	162
0.0003618	167
0.0004276	170
0.0004933	172
0.0005591	177
0.0006248	179
0.0006906	183
0.0007564	185
0.0008221	189
0.0008879	191
0.0009536	194
0.0010194	199
0.0010852	200
0.0011509	201
0.0013482	209

Activation Energy by the Zero Order Model

Arrhenius plot of ln k1 against 1/T, where T is the absolute temperature was carried out. The apparent activation energy and the pre-exponential factor were found to be at 52 kJ/mol and 572, respectively, as shown in Fig.4.10.

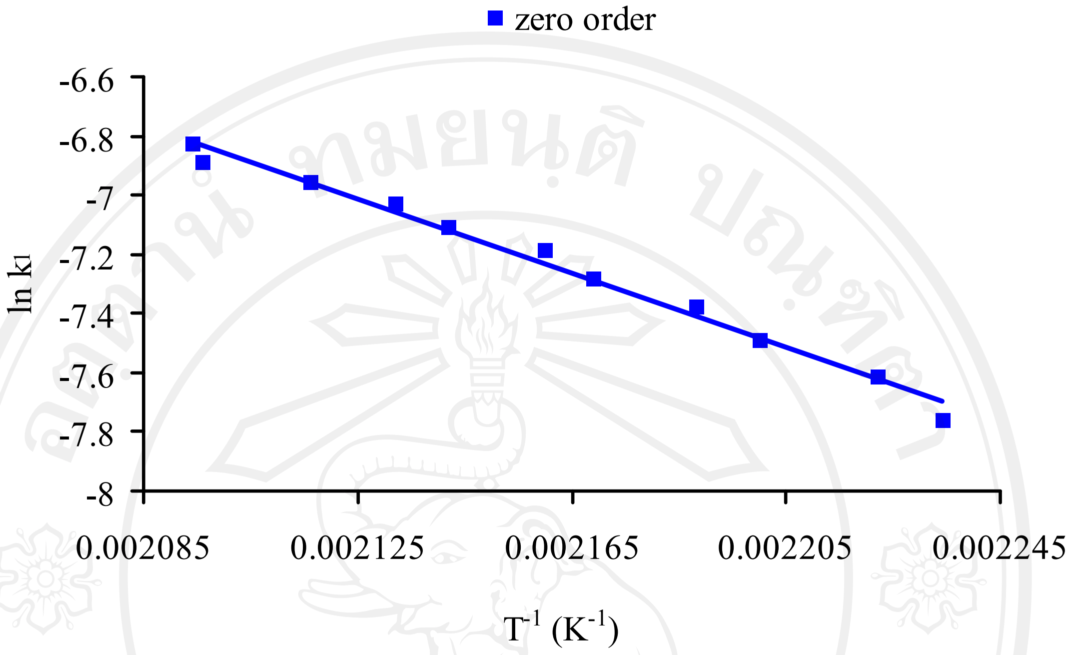

Fig. 4.10 Arrhenius Plot by the Zero Order Model (Temperature 170-200°C)

Activation Energy by the First Order Model

Similarly, for the first order model, numerical values of the apparent rate constants (k1) at various temperatures were calculated from eq. 4.11, as shown in Table 4.2. Therefore, Arrhenius plot can be made and the apparent activation energy (E_a) and the pre-exponential factor (k_0) were found to be at 56 kJ/mol and 1580, respectively, as shown in Fig.4.11.

Table 4.2 Apparent Rate Constants (k1) Derived from the Zero Order Model

$k_1 = \frac{\ln(1-x)}{t}$ (s^{-1})	Temperature (°C)
-	146
-	148
-0.00142	150
-0.00088	154
-0.00219	155
-0.00063	158
-0.00079	160
-0.0005	162
-0.00064	167
-0.0004	170
-0.00059	172
-0.00049	177
-0.00062	179
-0.00058	183
-0.00075	185
-0.00068	189
-0.00083	191
-0.00092	194
-0.00118	199
-0.0012	200
-0.00151	201
-0.00143	209

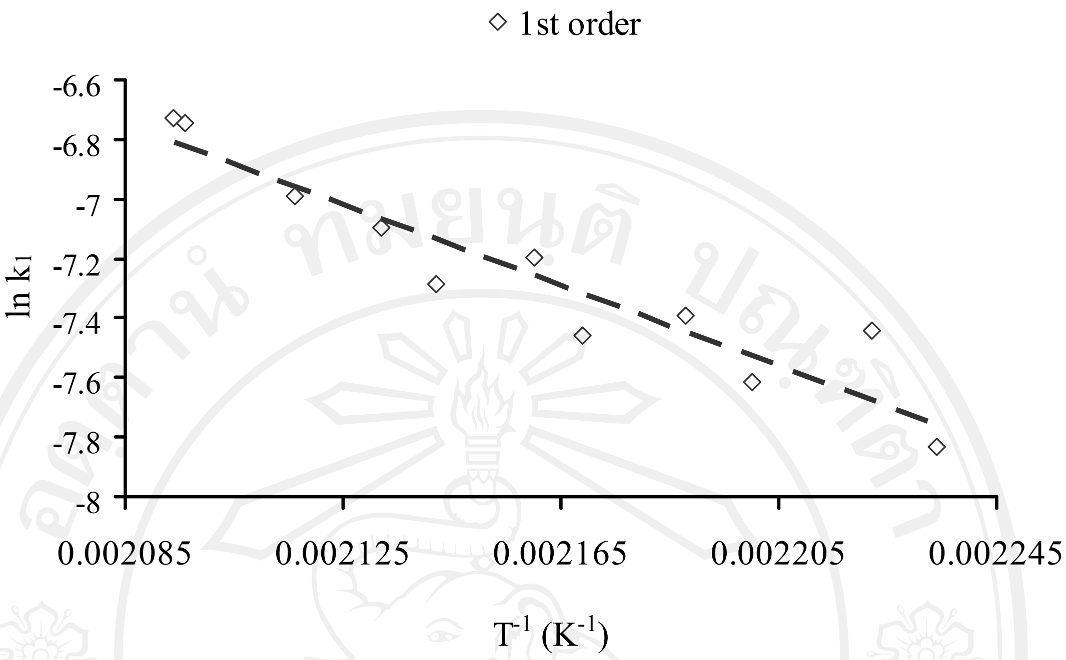

Fig. 4.11 Arrhenius Plot for the First Order Model (Temperature 170-200°C)

The kinetic data derived from the experiments with palm oil at 170-200°C are summarized in Tables 4.3. Two activation energies were estimated at 52 kJ/mol (from the zero order model) and at 56 kJ/mole (from the 1st order model). The values obtained were slightly higher than those reported by Kusdiana and Saka (2001) with E_a = 38.4 kJ/mol for rapeseed oil at 200-270°C, and by He *et al*. (2007) with E_a = 11.2 kJ/mol for soybean oil at 210-230°C. However, our Ea were lower than that of Song *et al*. (2008) which reported E_a of 105 kJ/mol for palm oil at 200-400°C. It should be noted that Song *et al*. (2008) assumed their reaction rates to be a second order model with respect to both oil and methanol concentrations. The effect of the immiscibility between methanol and oil revealed clearly in our study during the initial period of the reaction (temperature below 170°C). The gradient of the energy curve was reduced as temperature increased. The effect of the immiscibility was minimized when oil and methanol were completely homogeneous at temperature above 170°C.

The apparent rate constants of Dasari *et al*. (2003) were much lower than those of others including present study. This may be contributed to the fact that Dasari *et al*. (2003) carried out their experiments in glass reactors so that the catalytic effect of the reactor surface was eliminated while present study and others used metal reactors.

Table 4.3 Comparisons of the Present Study Results with literature

Reference	**Kinetics model:** $r = k_0 C_{TG}^{m} C_{MeOH}^{n} e^{-E_a/RT}$			
	m	n	k_0	E_a (kJ/mol)
Present study (zero order)	0	0	572	52
Present study (1st order)	1	0	1.58×10^{3}	56
Cheng *et al.* (2008)	1.5	0	12.45	28.9
Song *et al.* (2008)	0.96	1.05	4.30×10^{5}	105.3
Joelianingsih *et al.* (2008)	1	0	4.21	30.8
He *et al.* (2007)	1	0	1.94×10^{-3}	11.2
He *et al.* (2007)	1	0	170	56.0
Kusdiana and Saka (2001)	1	0	3.33	38.4(a)
Kusdiana and Saka (2001)	1	0	145	47.1(b)

C_{TG} = triglycerides concentration, C_{MeOH} = methanol concentration, k_0 = pre-exponential factor, E_a = activation energy, R = the universal gas constant = 8.314 J/mole.K, T = absolute temperature, (a) = for 200-270°C, (b) = for 300-487°C

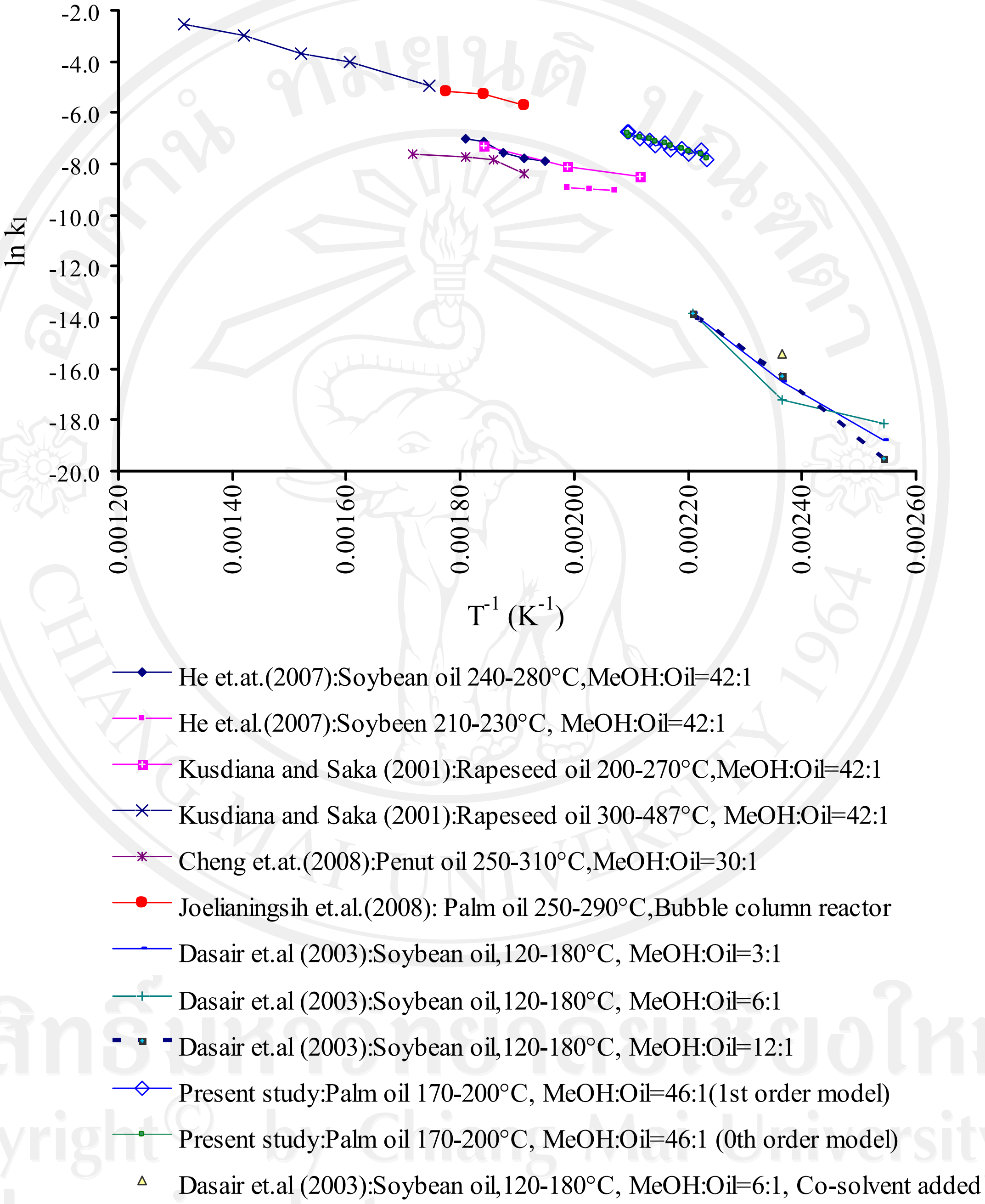

Fig. 4.12 Comparison of Various Arrhenius Plots between Present study and Literature