CHAPTER 4

TRANSESTERIFICATION OF PALM OIL ON SUPERCRITICAL ETHANOL CONDITION

The transesterification of palm oil and ethanol to biodiesel was studied at high pressure and temperature conditions. This study was carried out in the absence of catalyst in order to eliminate the separation process of catalyst from the product stream. Operating pressure and temperature ranges were 74.83-180.30 bar and 250-360°C. These conditions were in the range of supercritical condition. Other parameters were molar ratio of vegetable oil to ethanol 1:10 to 1:50 and reaction time 30 seconds to 360 seconds. The detail results of those effects and kinetic parameters will be discussed in the following parts.

4.1 Blank study

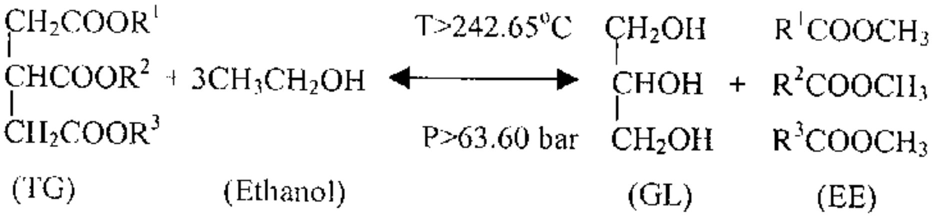
Palm oil and ethanol were placed into a stainless steel micro-batch reactor. The reactor was set at 100°C for 1 hour. After that the reactor was cooled down to room temperature. Chemical compositions after the reaction time were analyzed. It was not found any product of esters presented. Both palm oil and ethanol still separated at the same level input before. This meant that a reaction of palm oil and ethanol would not take place at mild condition of temperature and pressure in the absence of catalyst.

Further study was carried out similarly at higher pressure, like 100 bar. The chemicals after the reaction were found differently. The product was found to be in one single phase but later separated into 2 and 3 layers. This provided that the reaction would possibly take place at higher pressures.

However, it was hard to fix operating pressure. Temperature was then set, and used to control its saturated pressure.

4.2 Effect of molar ratio of palm oil and ethanol

Final products for the whole reaction in the transesterification reaction for biodiesel fuel production are ethyl esters with glycerine, as shown in Equation 4.1. According to thermodynamic, ethanol would not perform any dehydration reaction at this condition, and TG could only be decomposed at very high temperature. Other side reactions, then, would not be considered.



$$\begin{array}{lllll} CH_2COOR^1 & & & CH_2OH & R^1COOCH_3 \\ | & & & | & \\ CHCOOR^2 + 3CH_3CH_2OH & \xleftrightarrow[P>63.60\ bar]{T>242.65^{\circ}C} & & CHOH\ + & R^2COOCH_3 \\ | & & & | & \\ CH_2COOR^3 & & & CH_2OH & R^3COOCH_3 \\ (TG)\qquad (Ethanol) & & & (GL) & (EE) \end{array} \qquad (4.1)$$

According to the transesterification reaction, three moles of ethanol required to react with one mole of palm oil. Many literatures suggested that molar ratio of ethanol to palm oil is the most important parameter affecting the yield of ethyl esters converted.

In this work, the effect of the molar ratio of ethanol to palm oil was studied in the range between 10 and 50 on the yield of ethyl esters formed for supercritical ethanol treatments. We assumed the average molecular weight of palm oil was 847 [10] throughout our study. In this case we set the reaction at three different temperatures as 280, 310 and 350°C. According to the transesterification of rapeseed oil and methanol [3, 4], reaction would be finished within 60 seconds under critical conditions. For our reaction, we would like to examine the steady state conversion. 120 seconds, a fixed parameter, was selected as the reaction time.

The product after the reaction time was injected to analyze its chemicals by a gas chromatrography. Ethyl palmitate, ethyl stearate, ethyl oleate, ethyl linoleate, and ethyl linolenate were detected. A typical spectra was shown in Appendix A. The conversion was computed according to the disappeared amount of triglyceride (TG) as presented in Equation 4.2.

As shown, the amount of each ethyl ester was summarized together. The content of total ethyl esters produced in various molar ratios for 120 seconds and 350°C now is plotted shown in Figure 4.1.

The results showed that a molar ratio of 50 in ethanol provided the highest yield of esters. The highest conversion was approximately achieved in a yield of 90.97 % of ethyl esters.

$$X = \frac{M \times [1 - N]}{3 + N} \tag{4.2}$$

Where : $N = \dfrac{E * \mu}{(E * \mu) + [(100 - E - (\frac{e}{e+G})(100 - E))\phi] + [(\frac{e}{e+G})(100 - E)\varphi]}$

e = % area of esters

G = % area of glycerine

E = % area of ethanol

φ = Response factor of esters

ϕ = Response factor of glycerine

μ = Response factor of ethanol

M = Molar ratio (ethanol:vegetable oil)

Compared to a yield of molar ratio of 10 in ethanol, the reaction produced only 10.65 % (9 times less than a molar ratio of 50 as explained above). With a higher molar ratio of ethanol applied, the ethyl ester compounds were increased. The reason could be extracted that the higher ratio of ethanol to vegetable oil , the higher soluble amount of palm oil to ethanol would be. Since the solubility of palm oil to ethanol is very low [1, 3, 10, 12], excess amount of ethanol then was needed to improve the reaction.

The results operated at 280°C and 310°C were appeared in the similar fashion as shown in Figure 4.2. However, with the higher operating temperature, the higher conversions were obtained. This could explain that the higher temperature, the higher kinetic movement of ethanol was increased. Moreover, the solubility of vegetable oil on ethanol would be increased. This would provide higher activity ethanol to oil palm. These lines of evidences, indicate that the higher molar ratios of ethanol result in the better transesterification reaction.

Comparing to the similar work, 350°C, 240 seconds the transesterification of methanol to rapeseed oil, the molar ratio of 42:1 (methanol:rapeseed oil) was selected [3, 4]. Other reports, 10 hours, 235°C and the ratio of 21:1 (methanol:soy bean oil) was used in methyl ester from soy bean oil from methanol [12]. In our study, the ratio of ethanol to oil palm of 50 provided the highest conversion to ethyl esters. This ratio was used as a fixed parameter for the further study.

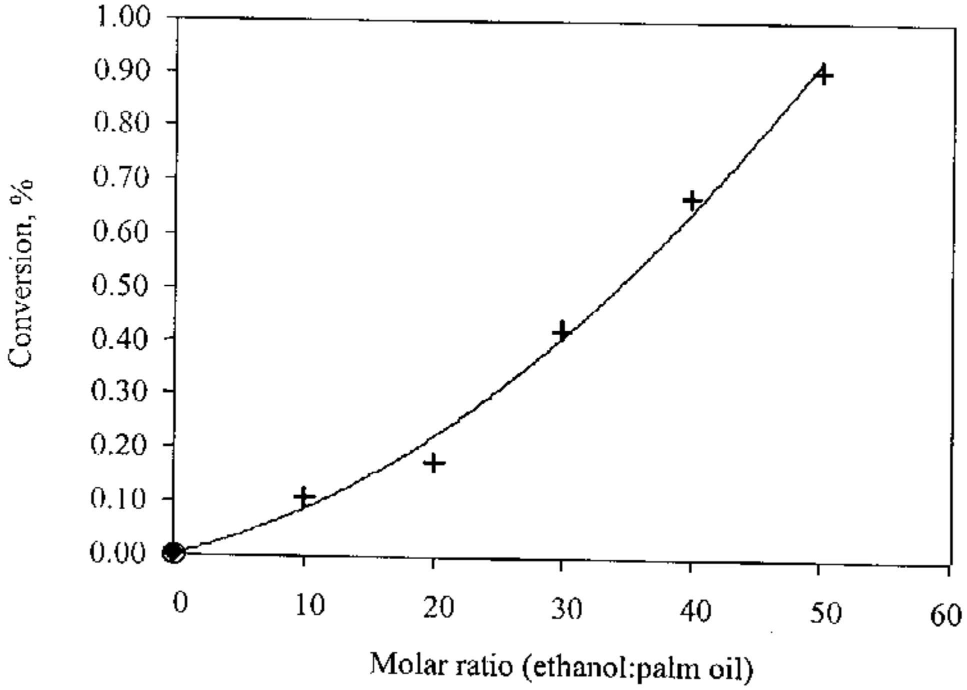


Figure 4.1 Effect of molar ratios of ethanol to palm oil in transesterification reaction on producing ethyl esters, treated at 350°C and 120 seconds.

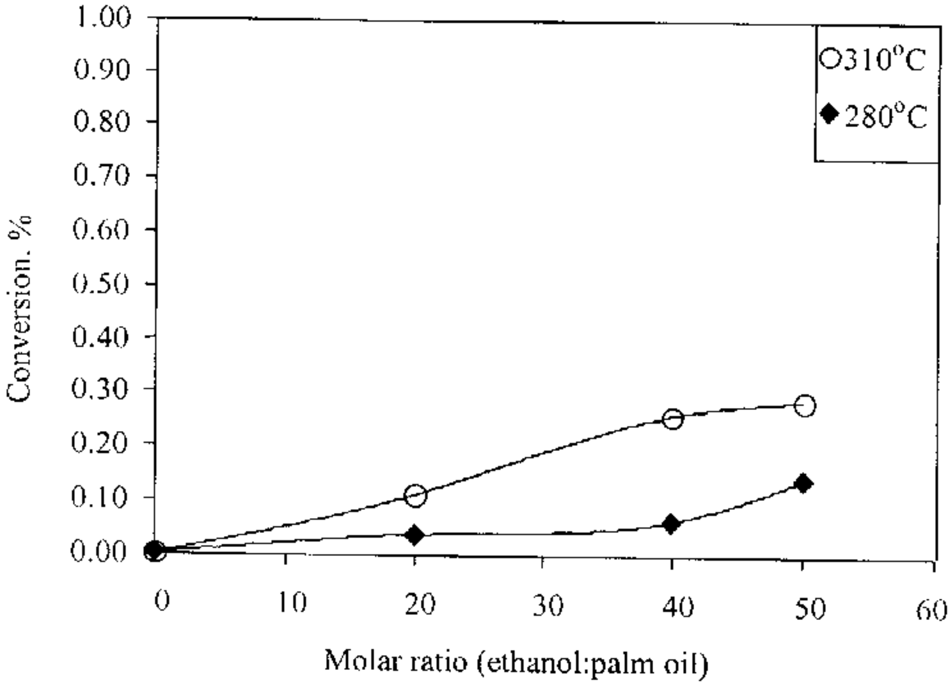


Figure 4.2 Effect of molar ratios of ethanol to palm oil in transesterification reaction on producing ethyl esters, treated at 280, 310°C and 120 seconds.

4.3 Effects of reaction time and temperature

4.3.1 Conversion to ethyl esters

Palm oil and ethanol were placed inside a reactor and set at 250°C for a certain time, the reaction was stopped immediately by imerging the reactor into ice-cool water (assuming at 0°C). The conversions computed following as Equation 4.2 of triglycerides (TG) to ethyl ester, computed following Equation 4.2, were then plotted versus with operating time, as shown in Figure 4.3. The reaction was carried out in a batch period of 30, 60, 120, and 240 seconds. It was found that conversion was increased as operating time. The conversion gradually increased with time and the highest conversion was found in small value of 14%. The reaction was not processed longer because this low conversion could not be practically used. Higher temperature operation was then recommended.

4.3.2 Temperatures

Figures 4.4 shows the conversion of palm oil to ethyl ester in term of operating time for 280, 310 and 350°C. It was found that the reaction provided conversions at 280°C (32.24%) little higher than those at 250°C (14.36%). However, at the temperature of 310°C and 350°C, the changes of conversion are quite large compared to lower temperatures. The conversions from 240 seconds operating time at 310°C and 350°C were 50% and 100%, respectively.

The appearance which can be found in the products was significant different by the temperature operating conditions. Figure 4.5 is the photo taken products of palm oil after setting for 24 hours. At even higher temperature of 350°C, the transesterification reaction is essentially completed for 240 seconds to convert almost all palm oil to their ethyl esters. However, in such a high reaction temperature, solids phase appeared in the sample after setting for an overnight. This indicated that decomposition reaction took place at temperature around 350°C due to the thermal degradation.

This could be explained that higher temperature could provide higher saturate pressure. The condition then was close to supercritical thermodynamic condition. Figure 4.6 refers to the operating conditions related to phases. It revealed that condition at 242.65°C, 63.6 bars fell into critical condition. As known that supercritical thermodynamic condition is the condition that chemicals inside the system are in the same phase of fluid. With the same phase, the higher solubility could take place. This would take into account of obtaining higher conversion at higher temperature and pressure.

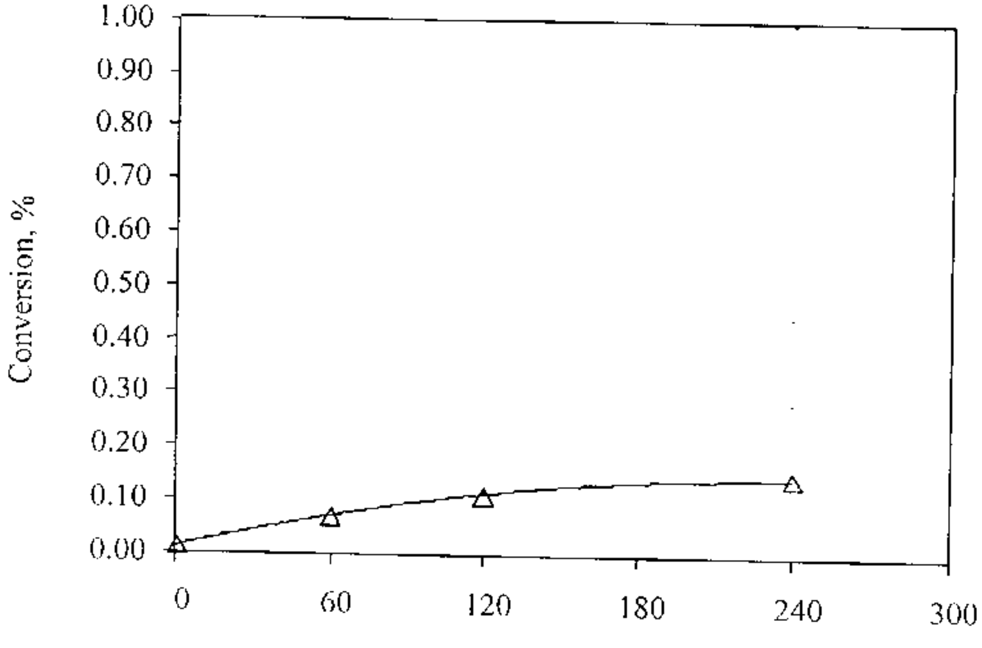


Figure 4.3 Effect of the reaction temperature on the ethyl esters formation at 250°C.

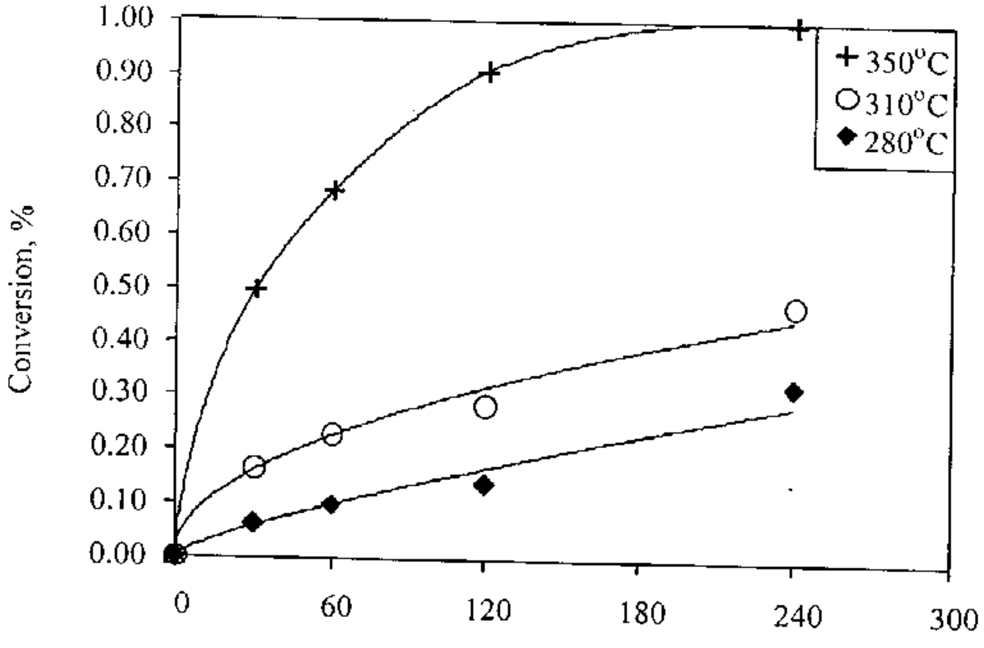


Figure 4.4 Effect of the reaction temperature on the ethyl esters formation at 280, 310, 350°C and molar ratio of 1:50 (palm oil:ethanol).

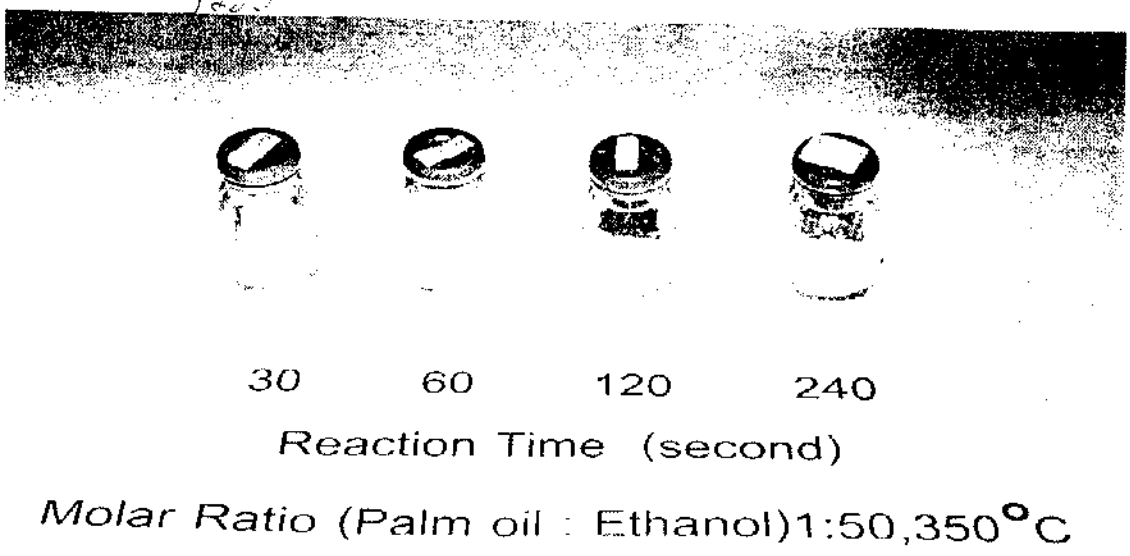


Figure 4.5 Product derived from palm oil after setting for 24 hours.

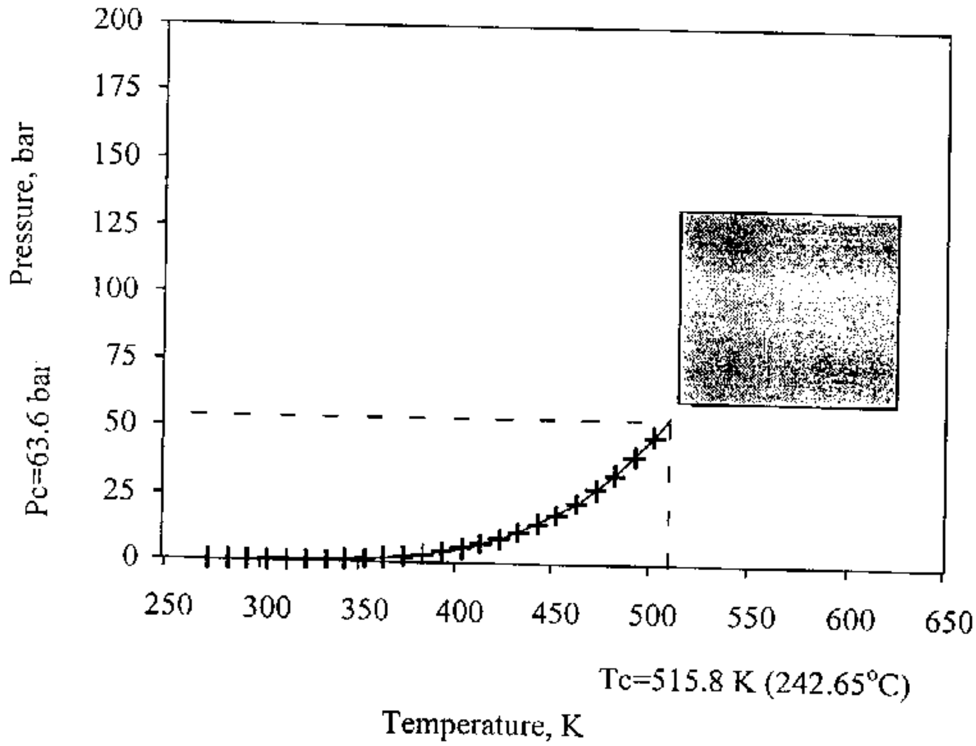


Figure 4.6 P-T phase diagram for ethanol.

4.4 Power rate laws

A rate law expression is the simplest expression to explain the reaction. It is useful in term of reactor design as well. In order to determine all kinetic parameters, a parameter of molar ratio of ethanol to palm oil was fixed, while temperature and operating time were varied.

To correlate experimental data and to quantify the temperature, reaction time and molar ratio effects, the experimental results were analyzed further in terms of the kinetics of palm oil to ethyl esters. The model will be based on overall reaction, as shown below.

$$rate = -\frac{d[TG]}{dt} \tag{4.3}$$

where [TG] refers to the content of palm oil used in this study.

The rate constant of the reaction can be determined based on the decreased amount of one reactant. In this work, the decreased amount of one reactant, that is TG, was chosen. In this supercritical ethanol method, three species were defined as ethyl esters [EE], glycerine [GL] and unethyl esterified compounds [uEE] which include triglycerides, diglycerides, monoglycerides and unreacted free fatty acids. An analysis in this section was based to our GC detection limitation. Most ethyl esters were detected. This reaction is assumed to proceed in the nth order reaction as a function of the concentration of trigrycerides (TG), ethanol, and reaction temperature.

$$\frac{-d[TG]}{dt} = k[TG]^n[EtOH]^m \tag{4.4}$$

However, the reaction was carried out in excess molar ratio of ethanol over palm oil. To be simplified the power rate expression, it could possibly consider that ethanol concentration kept stable over the reaction period. Equation (4.4) then can be simplified as:

$$\frac{-d[TG]}{dt} = k'[TG]^n \qquad (4.5)$$

$$[TG] = [TG]_0(1 - X)$$

$$\frac{[TG]_0 dX}{dt} = k'[TG]_0^n(1 - X)^n$$

$$\frac{dX}{dt} = k''(1 - X)^n$$

where $n = 0,\ X = kt$ (4.6)

$n = 1,\ \ln(1 - X) = kt$ (4.7)

$n = 2,\ \frac{X}{1 - X} = kt$ (4.8)

A consideration could be carried out in 2 ways, differential an integral methods. An integral method was not practicable in this work since the temperature range was quite large. A result of order would be deviated from the whole collecting data. Our work was based on differential method, by assuming the order of the reaction and proving for a straight line.

Figure 4.7 to 4.9 present the tests of order, proven for power rate law, starting from zero through second order, respectively. For zero order, X and t data were plotted for all temperatures. As shown in Figure 4.7. It was found that for lower temperature (250-280°C), X was corresponded to reaction time. However, when the temperature increased, X did not seem to correspond with reaction time. The reaction was converted automatically to other kinetic behavior at higher temperature. This confirmed that zero order was not proven to be reasonable order for this reaction.

Similar analysis was carried out for proving first order, ln(1-X) and t were plotted. It was found that data from all temperatures were fit straightly. It was shown a good agreement of first order as shown in Figure 4.8.

In contrast, a proving of second order did not agree with the experimental data, as shown in Figure 4.9.

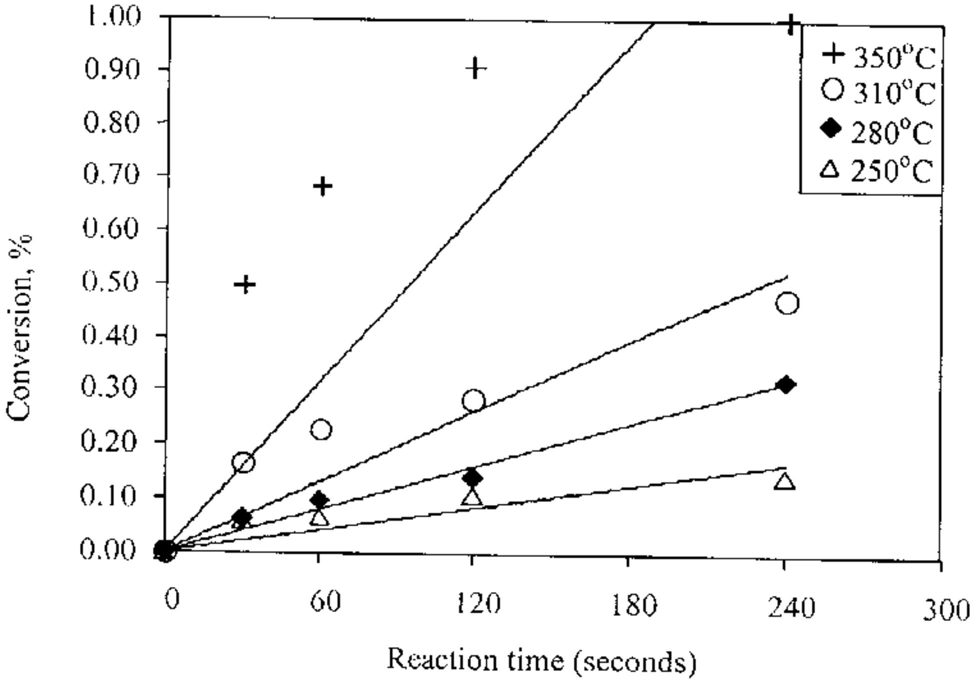


Figure 4.7 Proof of zero order (palm oil:ethanol ratio of 1:50).

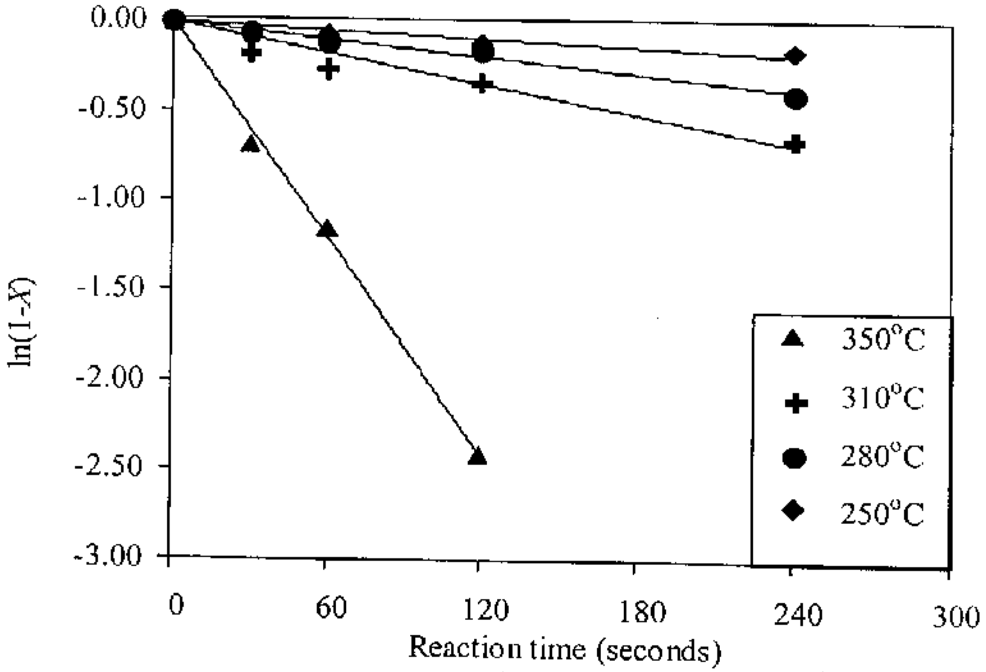


Figure 4.8 Proof of first order (palm oil:ethanol ratio of 1:50).

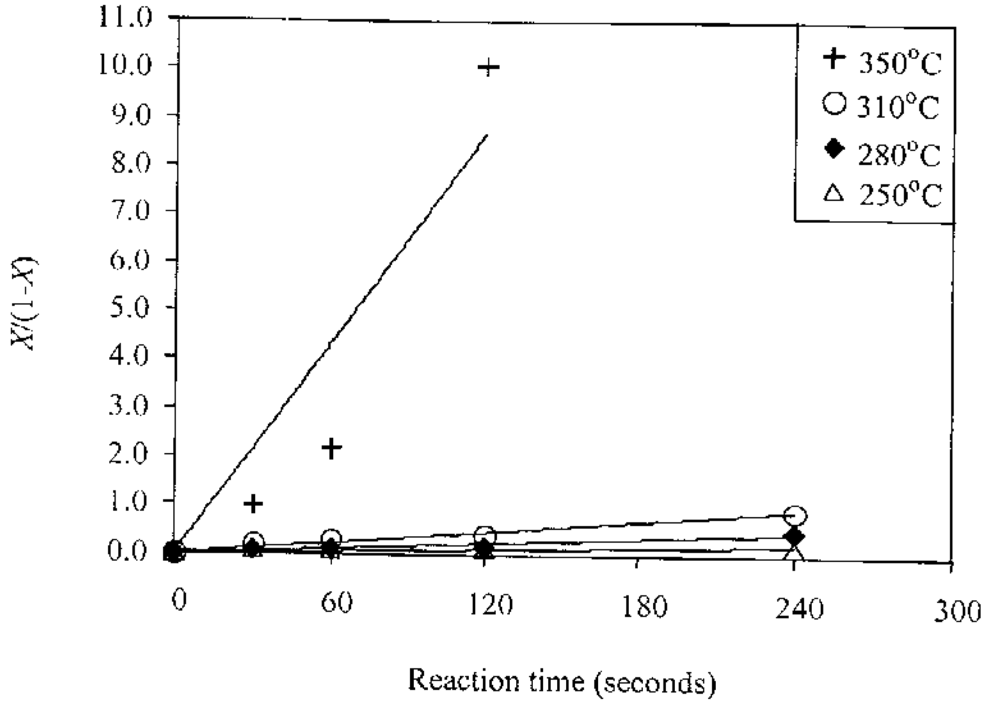


Figure 4.9 Proof of second order (palm oil:ethanol ratio of 1:50).

As shown, this reaction behaved kinetically appropiately to first order reaction (Equation 4.7). Only one parameter of rate constant for each temperature should be evaluated. According to Equation 4.7, k could be determined by the slope of each line in Figure 4.8, and its value of k was tabulated in Table 4.1. These k data would further be used for evaluating an activation energy of this reaction.

The k values were plotted as shown in Figure 4.10. From this line the apparent activation energy for transesterification of palm oil under supercritical ethanol condition was estimated to be 86.46 kJ/mol. Compared to the activation energy of 69.29 kJ/mol studied with rapeseed oil and methanol under supercritical condition[4], the activation energy for this study was higher. The kinetic constant k for this reaction can hence be expressed as:

$$k = (2.5271\times10^{5})\exp(\frac{-86461.443}{RT}) \qquad (4.9)$$

where: $R = 8.314\frac{J}{mol \bullet K}$

A parity plot for this model is presented in Figure 4.11, which indicates that the expression provides an adequate representation to the observed data.

Table 4.1 The rate constant of transesterification reaction of palm oil with respect to temperature.

Temperature (°C)	Rate constant, k (s^{-1})
250	0.0007447
280	0.0015641
310	0.0028315
350	0.0200171

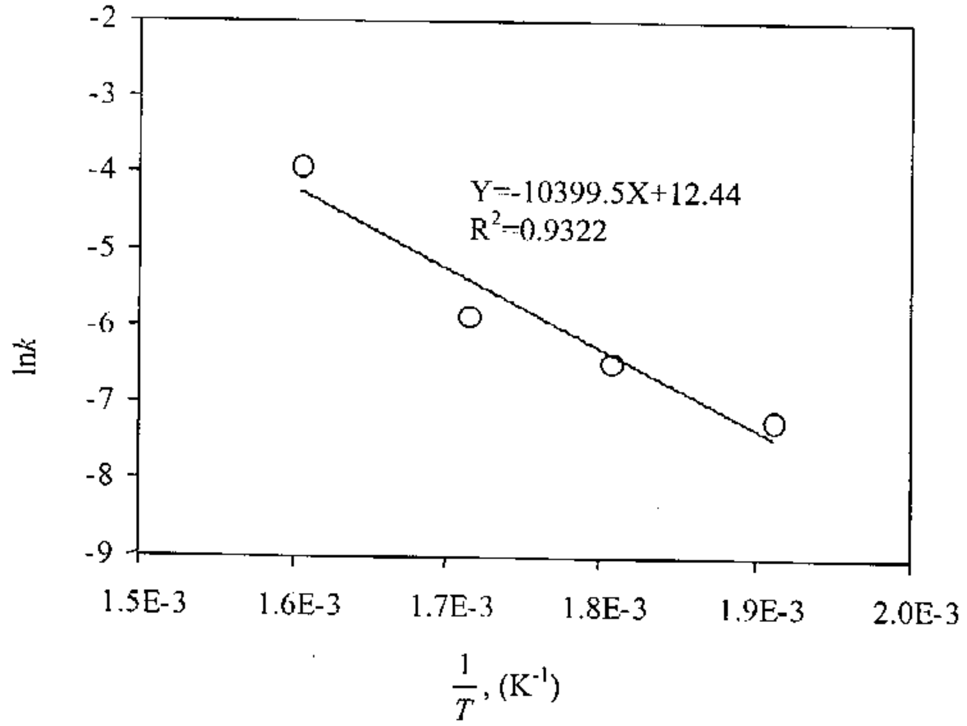


Figure 4.10 First order reaction rate constant in Arrhenius plot of palm oil in ethanol during transesterification reaction.

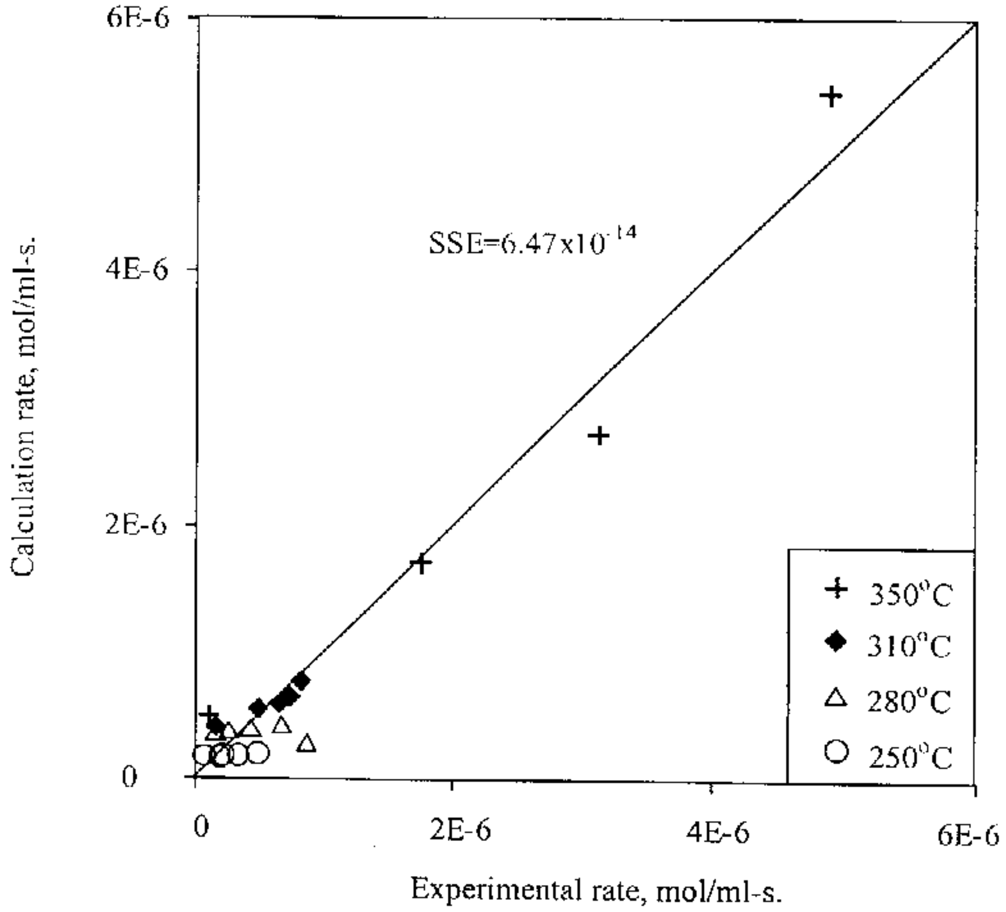


Figure 4.11 Parity plot for Equation 4.7 and experimental rate at different temperatures.

From the results in Figure 4.11 the sum square error was obtained to be 6.47×10^{-14}, which is very low.