CHAPTER 5

TRANSESTERIFICATION OF RICE BRAN OIL ON SUPERCRITICAL ETHANOL CONDITION

The transesterification reaction of rice bran oil and ethanol under a supercritical condition was studied in this chapter. This study was to determine the range of reasonable conditions for producing its ethyl esters. We chose to use rice bran oil because it is one of Thailand's most important oilseeds. The conditions were selected in this study as in Chapter 4. The detail results of those effects and kinetic parameters will be discussed in the following parts.

5.1 Blank study

Rice bran oil and ethanol were placed into a stainless steel micro-batch reactor and operating as in Chapter 4. After that, chemical compositions after the reaction time were analyzed. It was not found any product of esters presented. Both rice bran oil and ethanol still separated at the same level input before. This meant that a reaction of rice bran 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 was found differently. The product was found to be in only one phase. 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.

5.2 Effect of molar ratio of rice bran oil and ethanol

In this work, the effect of the molar ratio of ethanol to rice bran 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 rice bran oil was 250 [11] throughout our study. In this case we set the reaction at three different temperatures as 280, 310 and 350°C. 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 as in Chapter 4. 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 5.1. 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 78.88 % of ethyl esters.

The results operated at 280°C and 310°C were appeared in the similar fashion as shown in Figure 5.2. 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. This would provide higher activity of ethanol to rice bran oil. These lines of evidences, indicate that the higher molar ratios of ethanol result in the better transesterification reaction.

For the rice bran oil, the ratio of ethanol to rice bran oil of 50 provided the highest conversion to ethyl esters. This ratio was used as a fixed parameter for the further study.

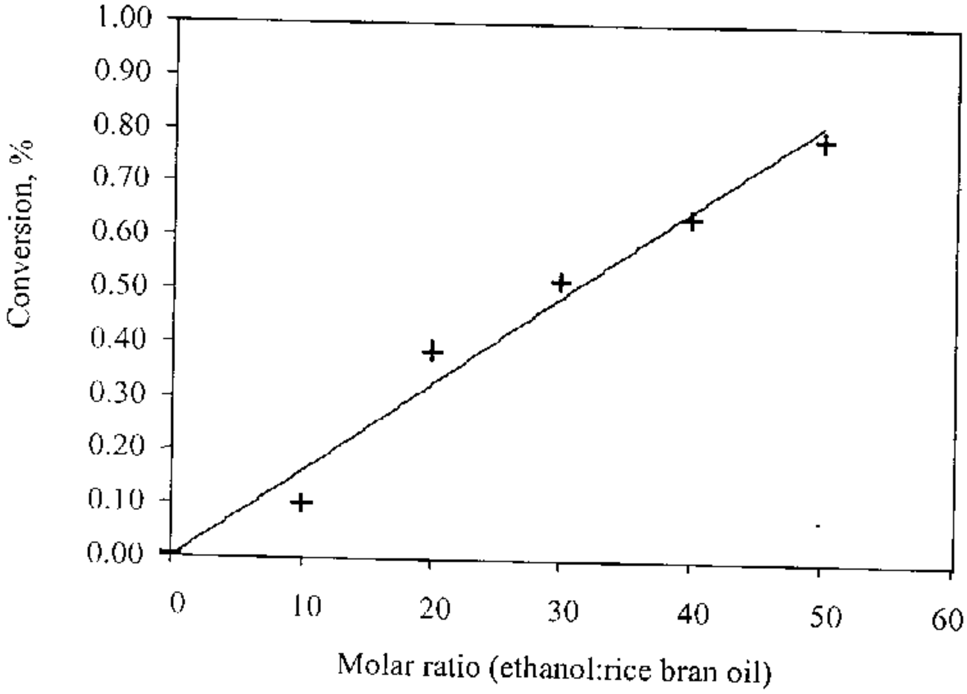

Figure 5.1 Effect of molar ratios of ethanol to rice bran oil in transesterification reaction on producing ethyl esters, treated at 350°C and 120 seconds.

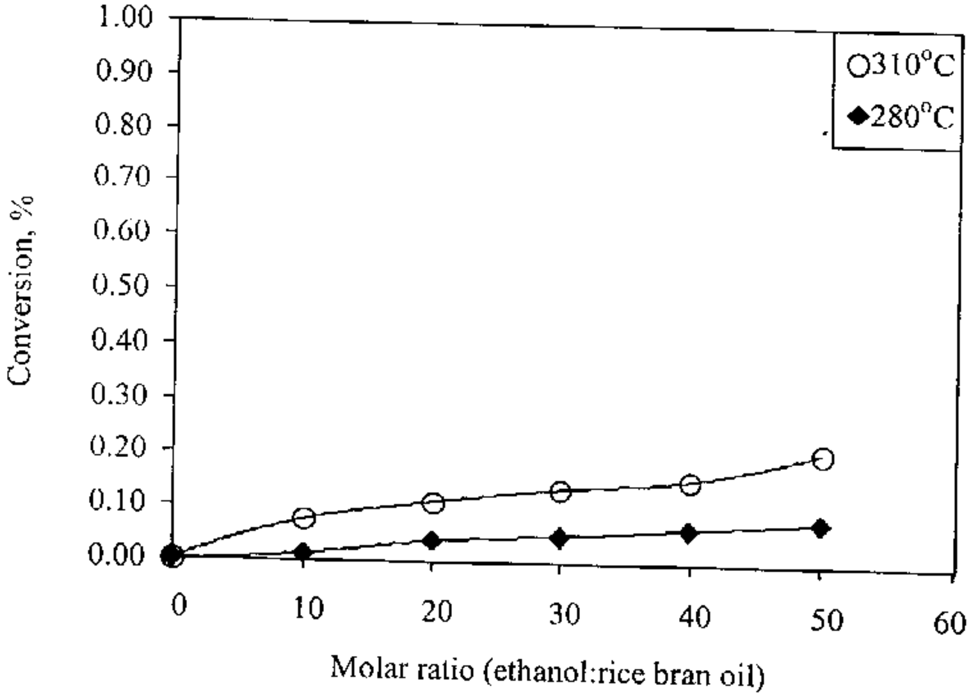

Figure 5.2 Effect of molar ratios of ethanol to rice bran oil in transesterification reaction on producing ethyl esters, treated at 280°C and 310°C 120 seconds.

5.3 Effects of reaction time and temperature

5.3.1 Conversion to ethyl esters

Rice bran oil and ethanol were placed inside a reactor and set at 250°C for a certain time, the reaction was stopped immediately by immerging 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 5.3. 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 3.28%. The reaction was not processed longer because this low conversion could not be practically used. Higher temperature operation was recommended.

5.3.2 Temperatures

Figures 5.4 shows the conversion of rice bran 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 (9.72%) little higher than those at 250°C (3.28%). 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 32.98% and 100%, respectively.

The appearance which can be found in the products was significant different by the temperature operating conditions. Figure 5.5 is the photo taken products of rice bran oil after setting for 24 hours, the product was found to be in only one phase. The reason for this would be related with the supercritical condition in which higher temperature and pressure of the reaction were employed. The transesterification reaction is essentially completed for 240 seconds to convert almost all rice bran oil to their ethyl esters.

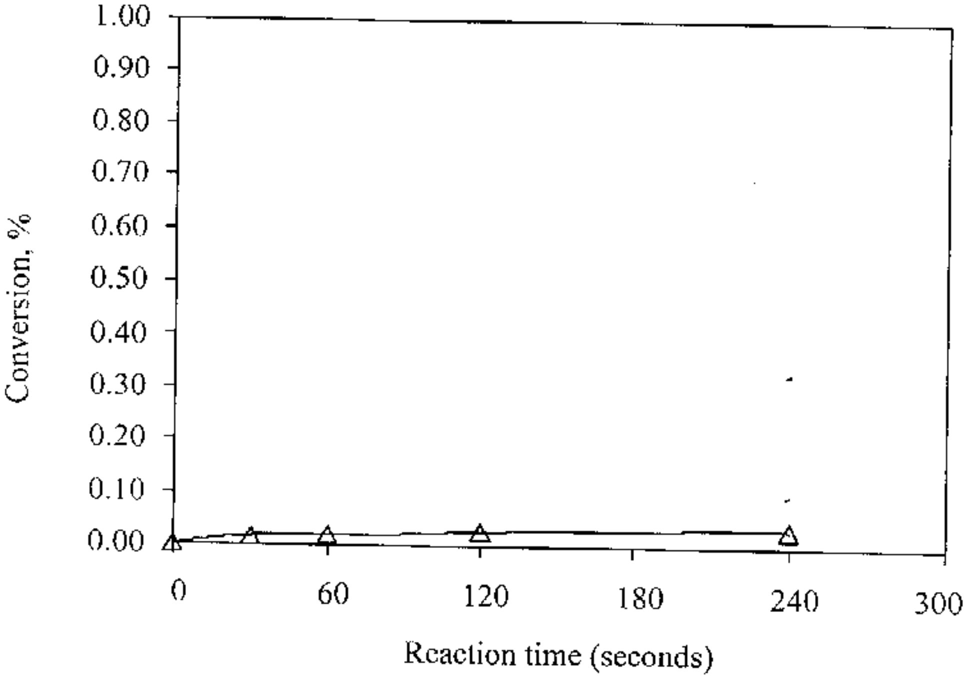

Figure 5.3 Effect of the reaction temperature on the ethyl esters formation at 250°C and molar ratio of 1:50 (rice bran oil:ethanol).

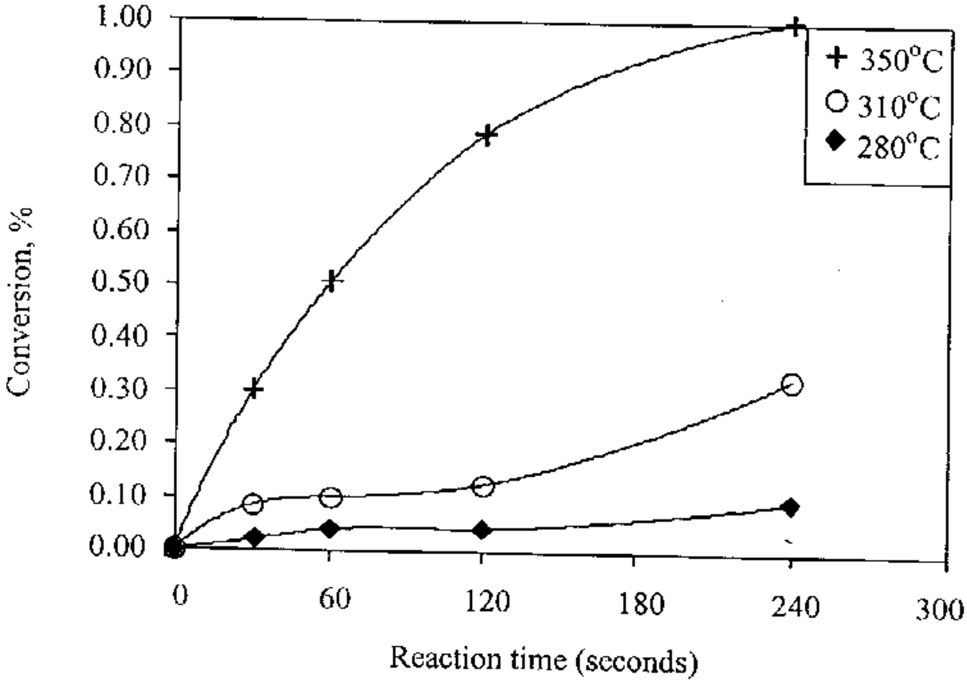

Figure 5.4 Effect of the reaction temperature on the ethyl esters formation at 280, 310, 350°C and molar ratio of 1:50 (rice bran oil:ethanol).

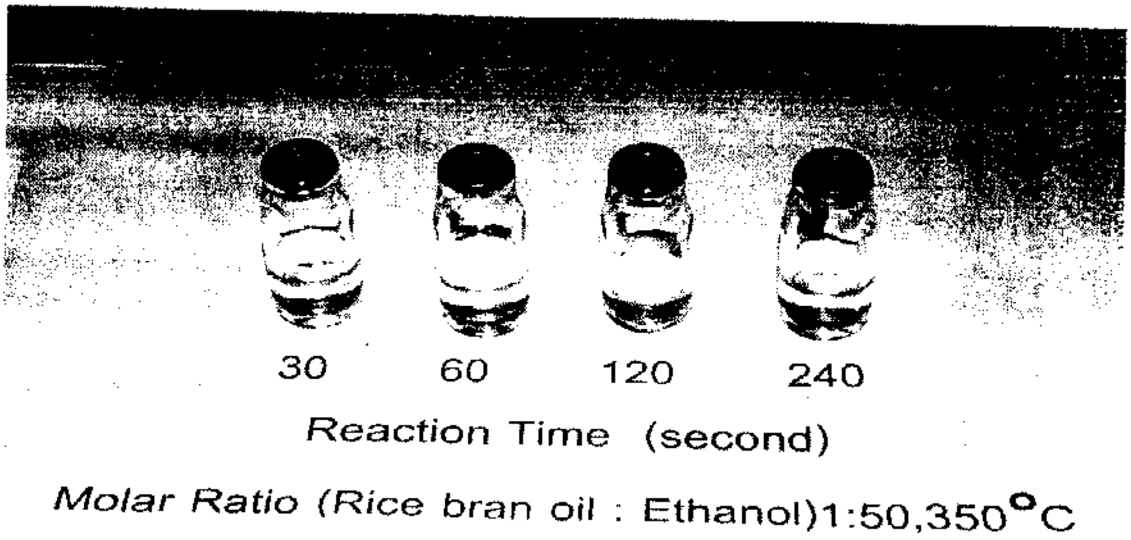

Figure 5.5 Products derived from rice bran oil after setting for 24 hours.

5.4 Power rate laws

The kinetics of transesterification reaction in rice bran oil to its ethyl esters as treated in supercritical ethanol can be considered in the following way.

$$rate = -\frac{d[TG]}{dt} \tag{5.1}$$

$$\frac{-d[TG]}{dt} = k'[TG]^n \tag{5.2}$$

$$[TG] = [TG]_0(1-X) \tag{5.3}$$

$$\frac{[TG]_0 dX}{dt} = k'[TG]_0^n(1-X)^n \tag{5.4}$$

$$\frac{dX}{dt} = k''(1-X)^n \tag{5.5}$$

where $n = 0,\ X = kt$ (5.6)

$n = 1,\ \ln(1-X) = kt$ (5.7)

$n = 2,\quad \frac{X}{1-X} = kt$ (5.8)

$[TG]$ refers to the content of rice bran oil used in this study.

Figure 5.6 to 5.8 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 5.6. 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. All temperatures were fit straightly. It was shown a good agreement of first order as shown in Figure 5.7.

In contrast, a proving of second order did not agree with the experimental data, as shown in Figure 5.8.

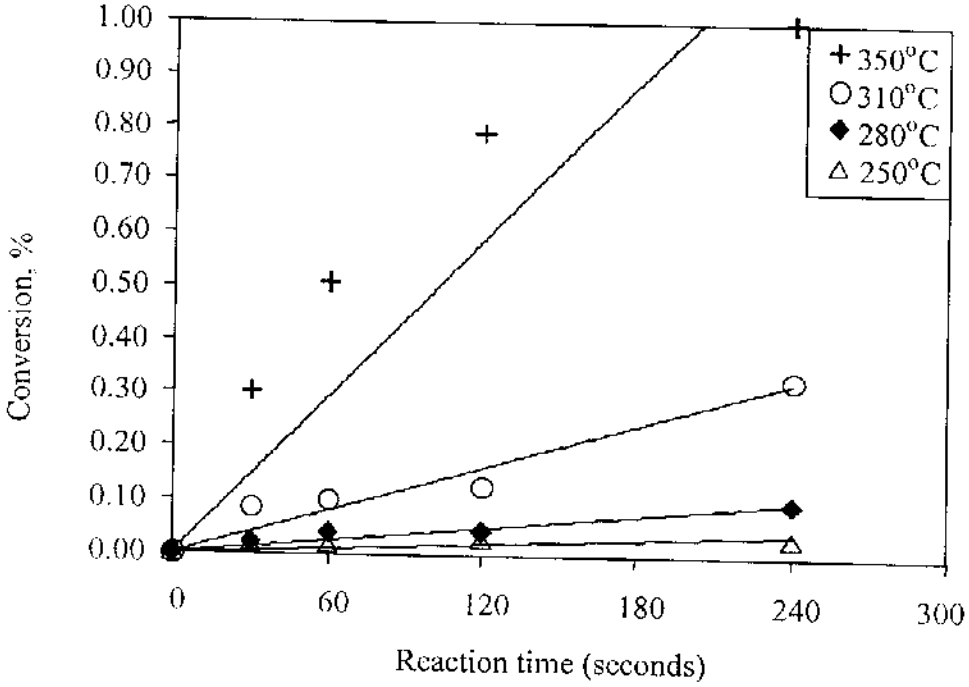

Figure 5.6 Proof of zero order (rice bran oil:ethanol ratio of 1:50).

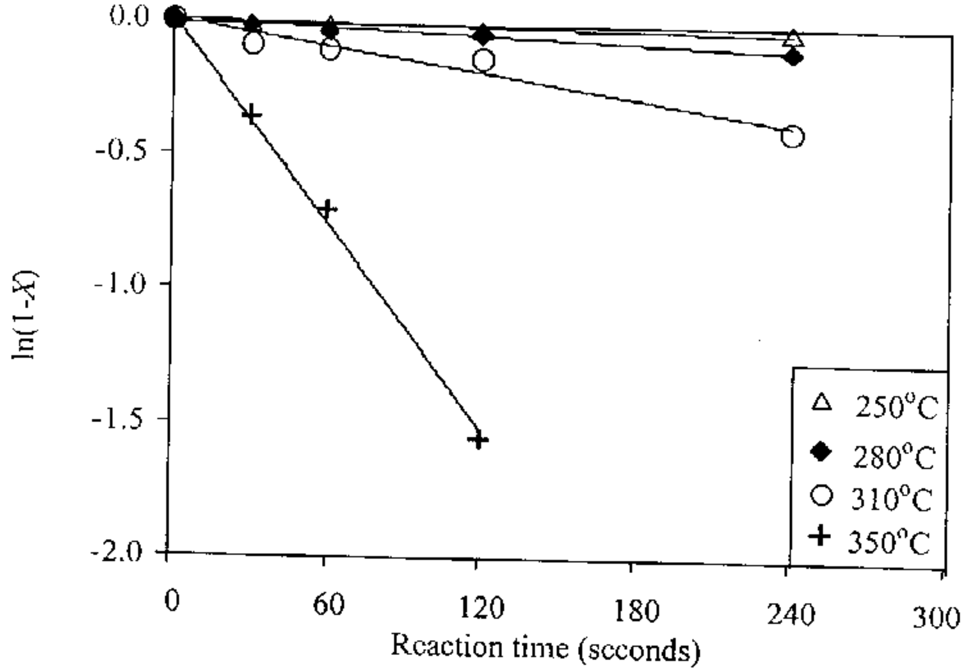

Figure 5.7 Proof of first order (rice bran oil:ethanol ratio of 1:50).

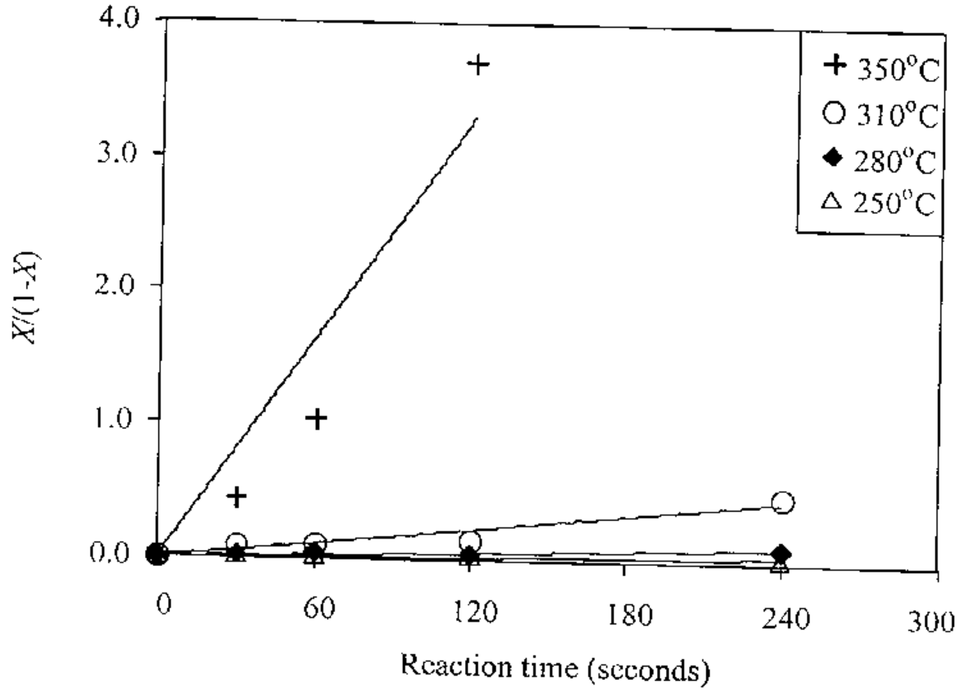

Figure 5.8 Proof of second order (rice bran oil:ethanol ratio of 1:50).

As shown, this reaction behaved kinetically somewhat to first order reaction (Equation 5.7). Only one parameter of rate constant for each temperature should be evaluate. According to Equation 5.7, k rate constant could be determined by the slope of each line in Figure 5.7, and its value of k was tabulated in Table 5.1. These k data would further be used for evaluating an activation energy of this reaction.

The k values were plotted as shown in Figure 5.9. From this line the apparent activation energy for transesterification of rice bran oil under supercritical ethanol condition was estimated to be 117.16 kJ/mol. The kinetic constant k for this reaction can hence be expressed as:

$$k = (6.4540274 \times 10^{7}) \exp\left(\frac{-117156.731}{RT}\right) \qquad (5.9)$$

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

A parity plot for this model is presented in Figure 5.10, which indicates that the expression provides an adequate representation to the observed data.

Table 5.1 The rate constant of transesterification reaction of rice bran oil with respect to temperature.

Reaction temperature (°C)	k (s^{-1})
250	0.0001690
280	0.0004311
310	0.0015745
350	0.0126601

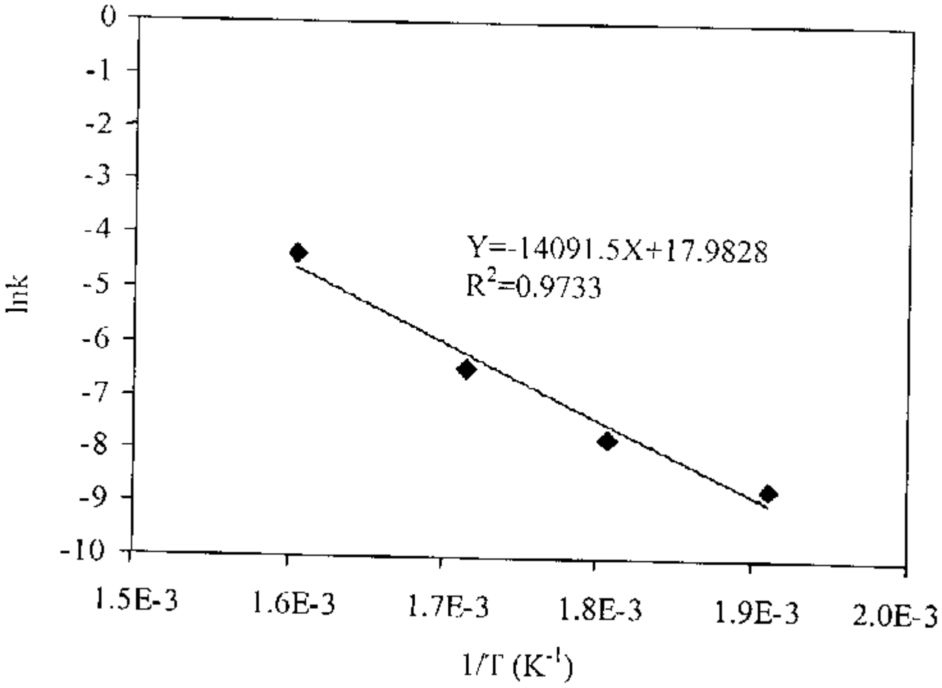

Figure 5.9 First order reaction rate constant in Arrhenius plot of rice bran oil in ethanol during transesterification reaction.

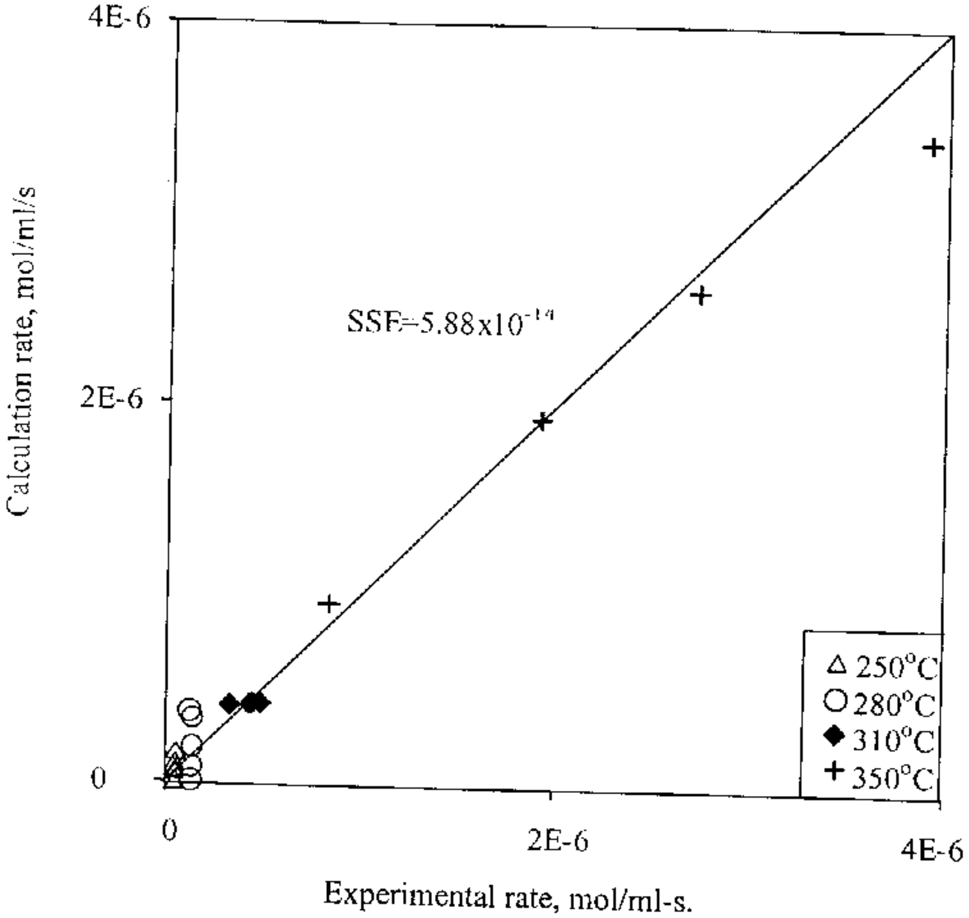

Figure 5.10 Parity plot for Equation 5.7 and experimental rate at different temperatures.

From the results in Figure 5.10 the sum square error was obtained to be 5.88×10^{-14}, which is very low.