CHAPTER V

EFFECT OF ADDITIONAL PARAMETERS AND SCALE-UP REACTOR OPTIMIZATION

5.1. Effect of reaction time on ME content in 250-mL batch reactor

Refer to Tables 4.1 and 4.2, the highest ME content obtained was found to be not over 88 % in 250-mL batch reactor at 10 min reaction time, which is lower than that reported in the literature employing co-solvents [8, 47]. According to the relevant literature, the conditions were: reaction temperature 350 to 400 °C; methanol to oil molar ratio of 40:1 to 42:1; reaction time of 2.4 to 40 min; and, reactor volume of 5 to 250-mL [6, 8, 39, 47]. To confirm that the reaction reached equilibrium under the present conditions, we ran another set of experiments for 5 to 60 min and the result is illustrated in Figure 5.1.

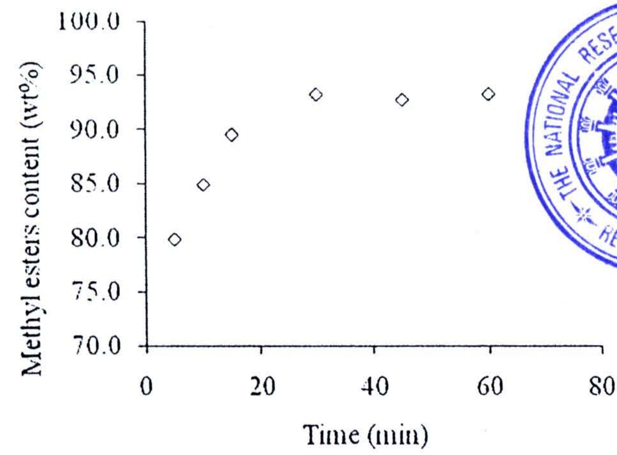

Figure 5.1 Changes in ME content with time of co-solvent free process from transesterification of crude PKO in 250-mL reactor at 350 °C and the methanol to oil molar ratio of 42:1.

From Figure 5.1, maximum ME content was reached after reaction time of 30 min and a ME content of 92.0 ±1% was observed. Due to slightly lower ME content, we further established two possible hypotheses and verified them as follows:

5.2. Effect of temperature gradient between reactor wall and bulk fluid

In the 250-mL reactor, the reaction vessel employed was heated externally and the contents in the vessel were mixed by a stirrer. As the temperature near the wall of the vessel is somewhat higher than in the center, it may cause an in situ thermal cracking reaction, resulting in slightly lower ME content. To verify this hypothesis, the experiments were performed at high temperature, i.e. 350 and 400 °C, in both 5.5 and 250-mL reactors at 30 min of reaction time, and the biodiesel samples were analyzed. The chromatograms obtained were then compared with that obtained from the conventional method at 60 °C, 30 min reaction time, 1% NaOH, and methanol to oil molar ratio of 6:1.

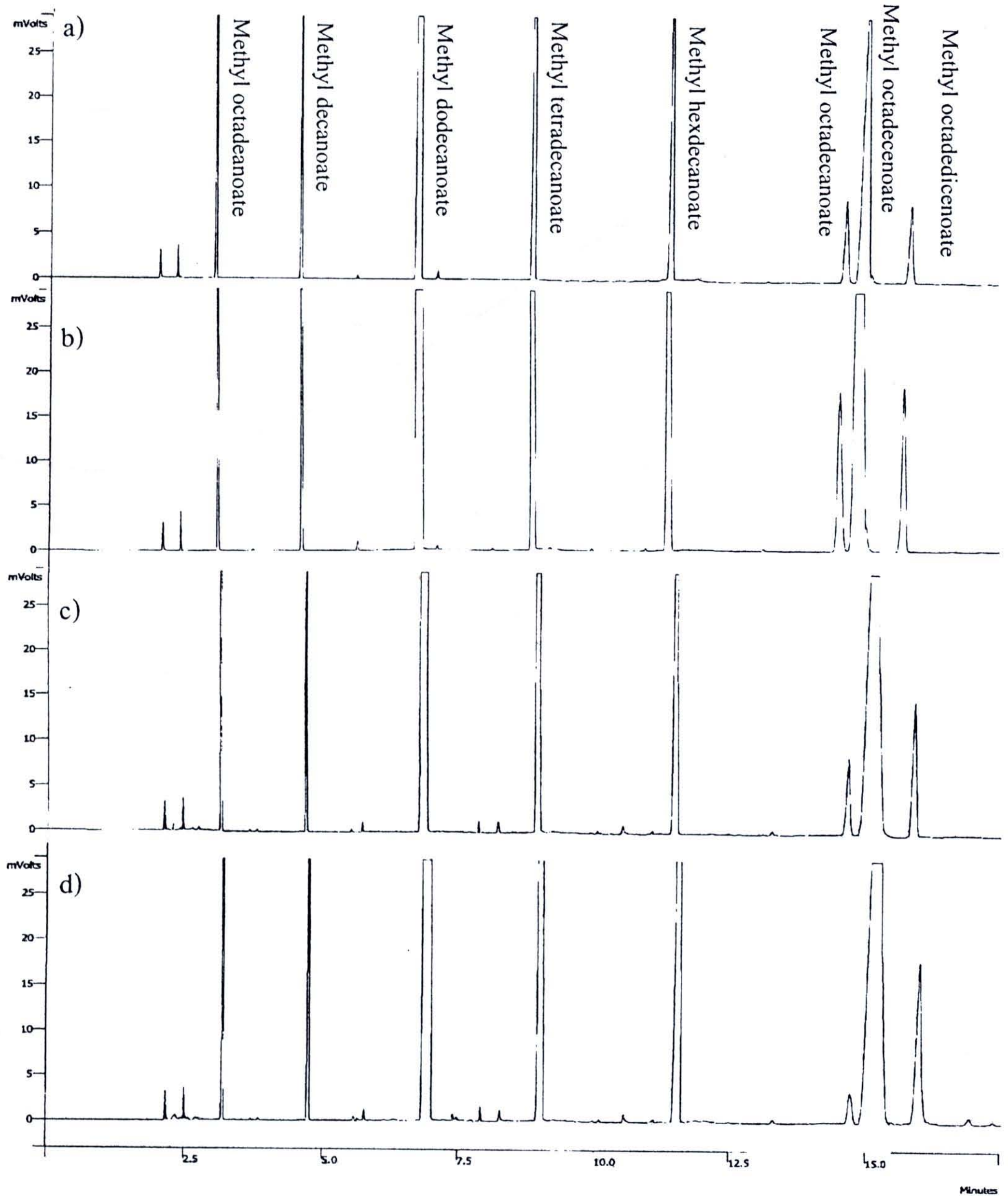

Figure 5.2 Comparison of GC chromatogram of biodiesel product from crude PKO at various temperatures, indicating some small peaks observed as in c) and d).

a) conventional method (60 °C)
b) 350 °C in 5.5-mL reactor
c) 400 °C in 5.5-mL reactor
d) 350 °C in 250-mL reactor

From Figure 5.2, sample (a), no thermal cracking occurred. In the chromatogram of this sample, no noise was detected, same as in sample (b). Therefore, it was concluded that thermal cracking did not take place in the 5.5-mL reactor at 350°C. Comparing samples (c) and (d) with the sample (a) and (b), it was found that the chromatograms of both samples (c) and (d) had higher small peaks, and their retention times were nearly the same. These small peaks, for instance, at retention time of 6 and 8 min, were probably from the same compounds derived from the thermal cracking reaction at temperature over 350°C.

According to the ME content obtained from the 5.5-mL reactor, it was assumed that there was no temperature gradient between reactor wall and bulk fluid, at 350 °C, methanol to oil molar ratio of 42:1, co-solvent to oil molar ratio of 0 to 5 and reaction time of 10 min. The experimental data are illustrated in Table 5.1. The ME content of the biodiesel products was slightly higher than those obtained from the 250-mL reactor at the same conditions (see Tables 4.1 and 4.2). Therefore, the hypothesis that thermal cracking occurred in the 250-mL reactor could be valid. However, the ME content was still slightly lower than the literature value, especially for the employed co-solvent process. Therefore, we established a second hypothesis, which is discussed in next section.

Table 5.1 Experimental data from 5.5-mL reactor for 10 min with crude PKO as reactant, temperature controlled by fluidized sand bath

Process	Temperature (°C)	Co-solvent to oil molar ratio	Methanol to oil molar ratio	ME content (%wt)
Unemployed co-solvent	350	0.0	42.0	95.5
	350	0.0	42.1	96.3
THF	350	5.1	41.1	94.7
	350	6.8	45.1	93.8
Hexane	350	5.2	40.3	93.9
	350	5.8	42.3	94.5

5.3. Effect of contaminants in crude palm kernel oil

The crude PKO contained 95 to 98% of triglycerides and 2 to 5% complex minor compounds such as wax ester, hydrocarbons, pigments and alcoholic compounds [88]. Thus, the slightly lower ME content obtained from crude PKO than that from refined PKO was probably due to the percentage of triglycerides. This hypothesis was verified in the 5.5-mL reactor, to ensure that thermal cracking did not take place, by using refined PKO as the reactant. The effect of co-solvent by using the experimental design as mentioned earlier was also reinvestigated and the results were illustrated in next section.

5.4. Effect of co-solvents on ME content in biodiesel production in a 5.5-mL reactor

The experimental data, as shown in Tables 5.2 and 5.3, were treated by the factorial design procedure and the ANOVA tables, as shown in Tables 5.4 and 5.5, respectively.

Table 5.2 Experimental data from employed THF process in 5.5-mL reactor for 10 min with refined PKO as reactant

Run order	Temperature (°C)	THF to oil molar ratio	MeOH to oil molar ratio	ME content (%wt)
1	350	0.0	44.5	99.3
2	320	3.7	24.3	83.2
3	350	5.2	12.0	83.3
4	320	2.1	20.2	81.3
5	290	0.0	12.0	53.6
6	350	5.0	43.0	97.5
7	350	0.0	12.0	81.1
8	350	0.0	40.8	99.4
9	290	8.3	20.1	56.5
10	290	4.8	40.7	78.3
11	290	5.0	12.0	54.2
12	320	2.3	21.7	82.5
13	350	5.1	41.9	98.7
14	350	5.3	12.2	84.6
15	290	0.0	41.9	78.2
16	320	2.5	22.9	84.6
17	350	0.0	12.0	82.6
18	290	0.0	41.8	76.8
19	290	5.2	42.4	77.5
20	290	0.0	12.0	57.0

From Table 5.2 and 5.3, the maximum ME content obtained from both THF and hexane co-solvents was 99.4 % compared to 94.7 and 94.5 % obtained from crude PKO (Table 5.1). It was clear that the maximum ME content from refined PKO was higher than that from crude PKO, which was 96.3 % (Table 5.1). Therefore, the slightly lower ME content obtained from crude PKO than that from refined PKO was due to the lower percentage of triglyceride in crude PKO.

Table 5.3 Experimental data from employed hexane process in a 5.5-mL reactor for 10 min with refined PKO as reactant

Run order	**Temperature (°C)**	**Hexane to oil molar ratio**	**MeOH to oil molar ratio**	**ME content (%wt)**
1	320	2.6	23.9	80.5
2	290	5.4	42.0	79.5
3	320	2.5	23.9	81.2
4	290	5.4	12.0	52.2
5	350	5.1	11.9	76.0
6	290	5.0	11.9	54.4
7	350	6.8	43.5	97.1
8	320	2.6	23.7	80.2
9	290	5.0	41.1	80.1
10	320	2.5	23.0	80.2
11	350	4.9	37.9	86.7
12	350	5.0	12.2	78.1
13	290	0.0	12.0	57.0
14	290	0.0	12.0	53.6
15	290	0.0	41.8	76.8
16	290	0.0	41.9	78.2
17	350	0.0	12.0	81.1
18	350	0.0	12.0	82.6
19	350	0.0	44.5	99.4
20	350	0.0	40.8	99.3

Table 5.4 Analysis of variance from employed THF process in a 5.5-mL reactor for 10 min with refined PKO as reactant

Source	**Sum of Squares**	**Degree of Freedom**	**Mean Square**	**F Value**	**Prob. > F**
A (Temperature)	2400.84	1	2400.84	138.81	< 0.0001
B (THF to oil)	2.00	1	2.00	0.12	0.7399
C (MeOH to oil)	1340.93	1	1340.93	77.53	< 0.0001
AB	6.11	1	6.11	0.35	0.5634
AC	58.91	1	58.91	3.41	0.0898
BC	0.02	1	0.02	0.00	0.9756
ABC	8.39	1	8.39	0.49	0.4994
Residual	207.55	12	17.30		
Total	3950.57	19			

Table 5.5 Analysis of variance from employed hexane process in 5.5-mL reactor for 10 min with refined PKO as reactant

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob. > F
A (Temperature)	1783.85	1	1783.85	136.94	< 0.0001
B (Hexane to oil)	22.61	1	22.61	1.74	0.2123
C (MeOH to oil)	1640.57	1	1640.57	125.94	< 0.0001
AB	27.62	1	27.62	2.12	0.171
AC	53.23	1	53.23	4.09	0.0661
BC	9.30	1	9.30	0.71	0.4146
ABC	2.88	1	2.88	0.22	0.6466
Residual	156.31	12	13.03		
Total	3673.21	19			

From Tables 5.4 and 5.5, it is clear that the co-solvents did not affect the ME content. Also, the interaction term between temperature and methanol to oil molar ratio (Factor AC) had no significant effect. The regression model in terms of coded unit for 5.5-mL reactor for the employed THF and hexane process are given in Equations 5.1 and 5.2, respectively.

$$\%ME = 79.79 + 12.32A + 9.08C \quad (5.1)$$

$$\%ME = 78.24 + 10.51A + 10.11C \quad (5.2)$$

where $\%ME$ is ME content in biodiesel product (%wt)

A is temperature in terms of coded unit, derived by Equation (4.3)

C is methanol to oil molar ratio in terms of coded unit, derived by Equation (4.4).

For the 5.5-mL reactor, the regression model indicated that the effect of temperature and methanol to oil molar ratio had a similar magnitude and also had positive effect. In comparison with the regression model for a 250-mL reactor (Eq. 4.1 and 4.2), the overall mean (the first term on the right hand side) was higher. This indicates that the ME content in the biodiesel product, which is obtained from the same temperature and methanol to oil molar ratio in the 5.5-mL reactor, is always higher than that obtained from the 250-mL reactor. Additionally, the interaction term between temperature ant methanol to oil molar ratio (AC) has no significant effect in 5.5-mL which was mentioned that the amount of methanol affects the transition temperature.

5.5. Effect of delayed quenching time

5.5.1. Effect of delayed quenching time in a 5.5-mL batch reactor

In this section, we hypothesized that the ME content from scale-up reactor was lower than the lab-scale reactor due to the delayed and deficient quenching of the product as it leaves the reactor outlet. Since the transesterification reaction is reversible, it should be stopped immediately by quenching to ambient temperature as quickly and sufficiently as possible. The outlet tube of scale-up reactor, approximately 2 m. long, was exposed to air before immersing into the cooling bath as the effect of delayed quenching did not come to full attention in our previous study [20]. This hypothesis was tested in 5.5-mL reactor before modification of our cooling system of the scale-up reactor. Preliminary results from 5.5-mL reactor are shown Figure 5.3.

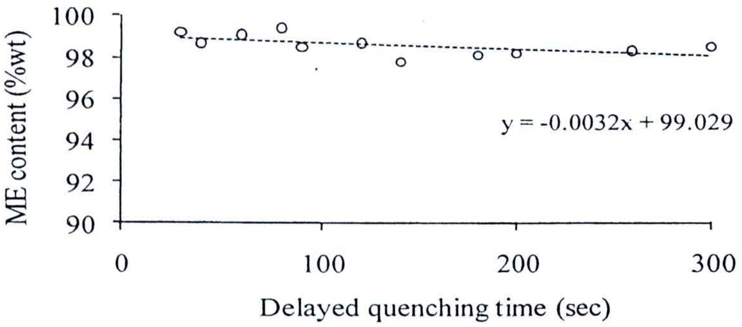

Figure 5.3 The ME content versus the delayed quenching time in 5.5-mL tube reactor.

According to Figure 5.3, the ME content slightly reduced with delayed quenching time. However, the effect of delayed quenching time in batch system was probably different from continuous flow system. Therefore, this hypothesis was tested consequently in a scale-up reactor by replacing of the cooling bath with a heat exchanger.

5.5.2. Effect of delay quenching time in scale-up reactor

Refer to Figure 3.1, the cooling bath was replaced with double-pipe heat exchanger using tap water as cooling medium as shown in Figure 5.4.

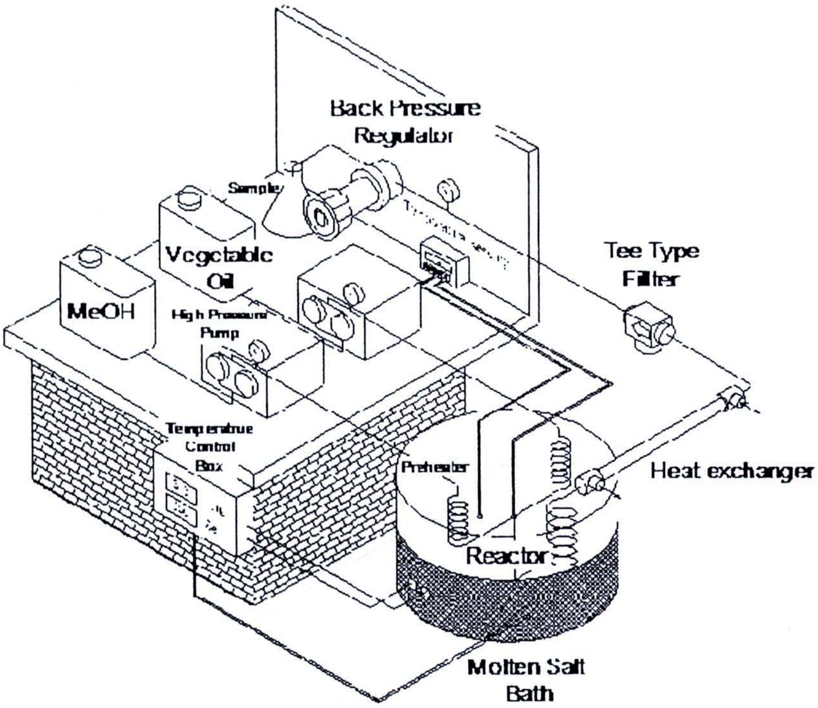

Figure 5.4 The scale-up reactor after replaced cooling bath with heat exchanger.

After the cooling system was modified, the scale-up reactor was tested on the conditions in our previous study [20] to investigate the effect of delay quenching time in continuous flow reactor and the results are illustrated in Table 5.6.

Table 5.6 The ME content in products from scale-up reactor with different cooling systems

	Pressure (MPa)	Temperature (°C)	MeOH to oil molar ratio	%ME content
Cooling bath	13.1	300	22.1	69.24
	13.1	300	22.1	71.12
	11.9	350	30.3	79.36
Heat exchanger	13.0	300	21.1	70.12
	13.2	300	22.2	70.59
	12.1	350	30.1	80.11

According to Table 5.1, the ME content only increased slightly after upgrading the cooling system, thus it could be concluded that the delayed and deficient quenching of product had no significant effect on the ME content in the scale-up reactor.

5.6. Effect of pressure and process optimization

The effect of pressure was reinvestigated because the investigation range in our previous study (10.0 to 15.0 MPa) shows that pressure had no significant effect on ME content [20], but some studies reported that pressure has strong effect at pressure over 15.0 MPa [11, 61].

The effect of pressure was studied by Central Composite Design (CCD) within the pressure range of 15.0 to 20.0 MPa, temperature range of 270 to 330 °C and methanol to oil molar ratio range of 35:1 to 20:1. In addition, the effect of co-solvent was neglected by adding 20% v/v of hexane in all experiments. The experimental design and results from CCD are illustrated in Table 5.7 and the ANOVA table in Table 5.8.

Table 5.7 The experimental conditions and results from CCD to reinvestigate the effect of pressure, temperature and methanol to oil molar ratio in scale-up reactor

Run	Temperature (°C)	Pressure (MPa)	MeOH to Oil molar ratio	%ME content
1	299.0	16.5	27.0	76.3
2	270.0	18.1	36.6	32.7
3	300.0	19.1	26.7	83.2
4	300.0	16.6	27.0	78.3
5	300.0	13.9	27.0	39.0
6	330.0	14.9	37.5	73.0
7	270.0	15.0	38.3	29.5
8	330.0	15.0	18.9	45.5
9	270.0	15.0	18.3	22.2
10	330.0	18.0	37.8	91.5
11	300.0	16.6	27.1	80.6
12	270.0	18.0	18.3	24.6
13	300.0	16.7	13.7	35.9
14	351.0	16.5	27.4	60.4
15	330.0	18.0	19.5	65.8
16	255.0	16.4	27.1	12.1
17	300.0	16.5	45.9	82.4
18	300.0	16.5	26.7	78.3

Table 5.8 Analysis of variance of results in Table 5.7

Source	Sum of square	Degree of freedom	Mean square	F-Value	p-Value
A (Temperature)	4898.2	1	4898.2	90.92	< 0.0001
B (Pressure)	941.4	1	941.4	17.47	0.0031
C (MeOH:Oil)	2059.7	1	2059.7	38.23	0.0003
A^2	3312.1	1	471.0	8.74	0.0182
B^2	471.0	1	3312.1	61.48	< 0.0001
C^2	724.9	1	724.9	13.46	0.0063
AB	126.1	1	126.1	2.34	0.1646
AC	239.5	1	239.5	4.45	0.0680
BC	1.1	1	1.1	0.02	0.8888
Residual	431.0	8	53.9		
Total	11213.2	17			

From Table 5.8, the second order regression model for scale-up reactor can be written as Equation 5.3. The interaction terms (AB, AC and BC) were not included to the regression model because their p-value were less than 0.05, and indicated they had no significant effect on the ME content. The coefficient of determination of this regression model (R^2) was calculated and found to be 0.9732. Additionally, all statistical analysis of the regression model for scale-up reactor is given in Appendix A. The predicted and observed values were plotted in Figure 5.5.

$$\%ME = 75.90 + 21.02A + 9.60B + 13.78C - 16.89A^2 - 3.72B^2 - 4.57C^2 \qquad (5.3)$$

$\%ME$ is ME content in biodiesel product (%wt)

A is temperature in terms of coded unit, derived by the Equation (5.4)

$$A = \frac{\text{Temperature } (^\circ\text{C}) - 330}{30} \qquad (5.4)$$

C is the methanol to oil molar ratio in terms of coded unit, derived by the Equation (5.5)

$$B = \frac{\text{Pressure (MPa)} - 16.5}{1.5} \qquad (5.5)$$

C is the methanol to oil molar ratio in terms of coded unit, derived by the Equation (5.6)

$$C = \frac{\text{Mole of MeOH (mol)} - 27.5}{7.5} \qquad (5.6)$$

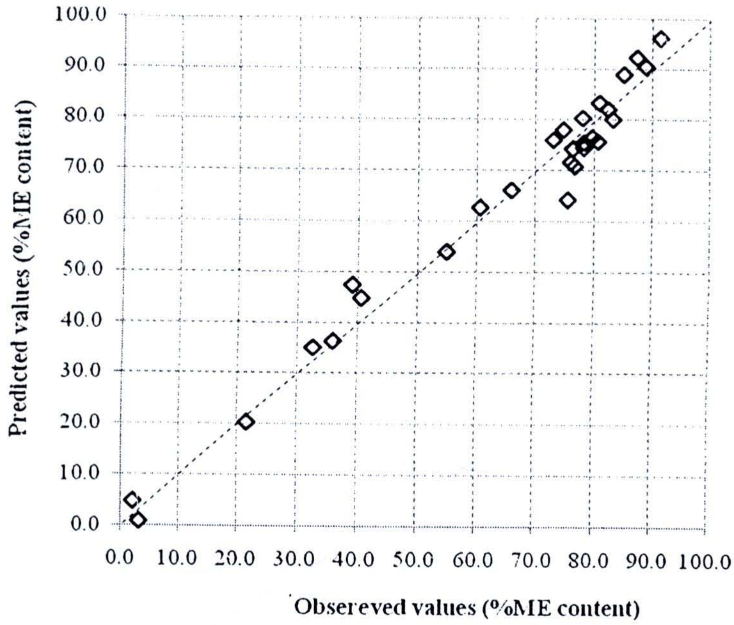

Figure 5.5 The plot of experimented and calculated value by Equation 5.3.

From the coefficient of Equation (5.3), it can be concluded that the effect of pressure was smaller than the effect of temperature and methanol to oil molar ratio. The response surface can be created by regression model as shown in Figure 5.6.

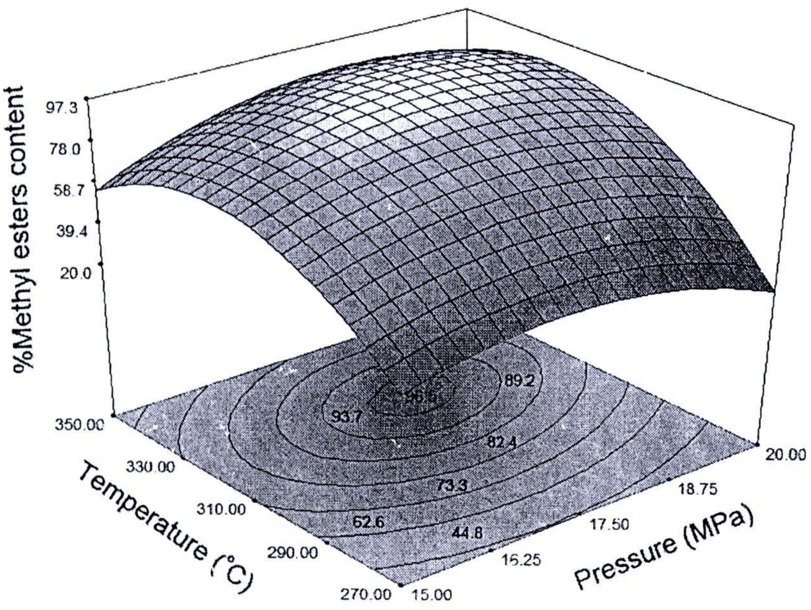

Figure 5.6 The response surface of ME content versus temperature and pressure at the methanol to oil of 35:1.

The optimization process was conducted by Design Expert ® 6.0 software with a maximum ME content as objective function. From the response surface in Figure 5.6, the ME content over 96.5 % could be found at temperature range of 310 to 330 °C, pressure range of 17.5 to 18.5 MPa and methanol to oil molar ratio of 35:1 to 40:1. The maximum ME content in Table 5.7 was 91.5 % at 330 °C, 18.0 MPa and 38:1 methanol to oil molar ratio which was also located within the optimal range.

Even though some repetition experiments were conducted within the optimal range, but the highest ME content to be only approximately 93 % was found from the scale-up reactor. This was lower than the target value of 96.5 %, probably because the optimal range from the regression model was narrower than the controllable range of the operating parameters, especially for pressure and methanol to oil molar ratio. For instance, the observed pressure slightly fluctuated at the vegetable oil pump. In addition, the methanol and vegetable oil flow rate can deviate from the initial value during the run as the real-time flow rate measurement was not available.