CHAPTER 3

Results and Discussion

Results of all experiments were composed of three main parts i.e. batch ultrasonic, continuous ultrasonic and CSTR esterifications. They were stepwise demonstrated by using tabulated and graphical methods as following.

3.1 Studies of batch acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation

3.1.1 Preliminary experiments.

Results of the preliminary experiments are shown below.

Table 3.1 Factors of the preliminary experiments

Level	Factors				
	Cat	Amp	MR	Temp	Time
1	1	35	5	50	0.5
2	2	55	10	60	1
3	5	75	20	70	2
4	20	100	40	80	4

Table 3.2 Results of the preliminary experiments

Run No.	Factors					y
	Cat	Amp	MR	Temp	Time	(% FFA)
1	1	35	5	50	0.5	5.34
2	1	55	10	60	1	4.78
3	1	75	20	70	2	3.27
4	1	100	40	80	4	1.77
5	2	35	10	70	4	2.59
6	2	55	5	80	2	3.58
7	2	75	40	50	1	4.54
8	2	100	20	60	0.5	4.46

Table 3.2 Results of the preliminary experiments (Cont.)

Run No.	Factors					y
	Cat	Amp	MR	Temp	Time	(% FFA)
9	5	35	20	80	1	1.72
10	5	55	40	70	0.5	3.06
11	5	75	5	60	4	3.47
12	5	100	10	50	2	3.66
13	20	35	40	60	2	0.74
14	20	55	20	50	4	1.03
15	20	75	10	80	0.5	2.27
16	20	100	5	70	1	2.89
Average, T						**3.07**
Conf. run	20	35	40	80	2	**1.15**

Table 3.3 The response table of the preliminary experiments

Level	Cat	Amp	MR	Temp	Time
1	3.79	2.60	3.82	3.65	3.79
2	3.79	3.11	3.32	3.36	3.48
3	2.98	3.39	2.62	2.95	2.81
4	1.73	3.20	2.53	2.34	2.22
Delta	2.06	0.79	1.29	1.31	1.57
Order	1	5	4	3	2
Select	Cat4	Amp1	MR4	Temp4	Temp4

$\mu = T + (Cat4-T) + (Time4-T) + (Temp4-T) + (MR4-T) + (Amp1-T)$

$\mu = Cat4+Time4+Temp4+MR4+ Amp1-4T$

$\mu = 1.73+2.22+2.34+2.53+2.60-4(3.07) = -0.86$

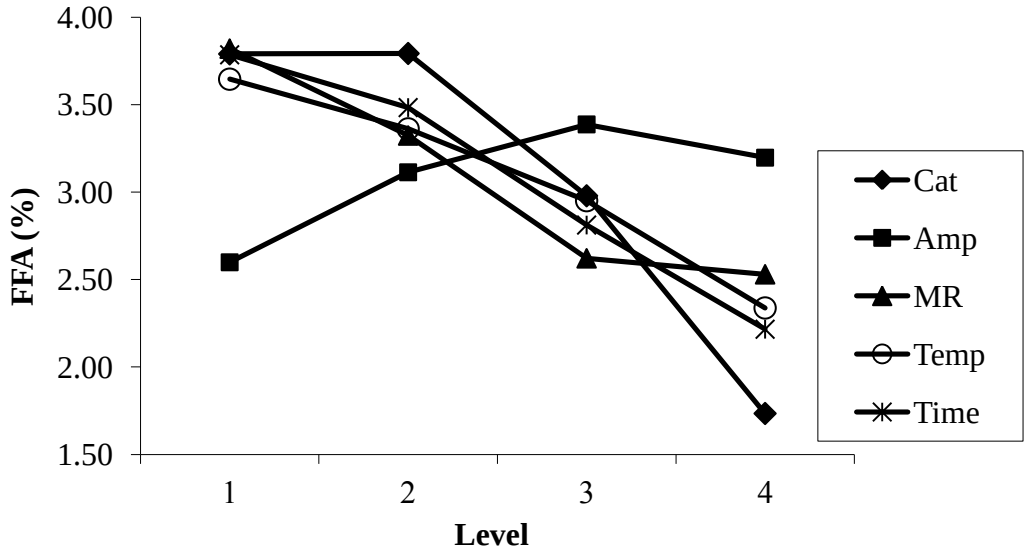

Figure 3.1 The response graph of the preliminary experiments

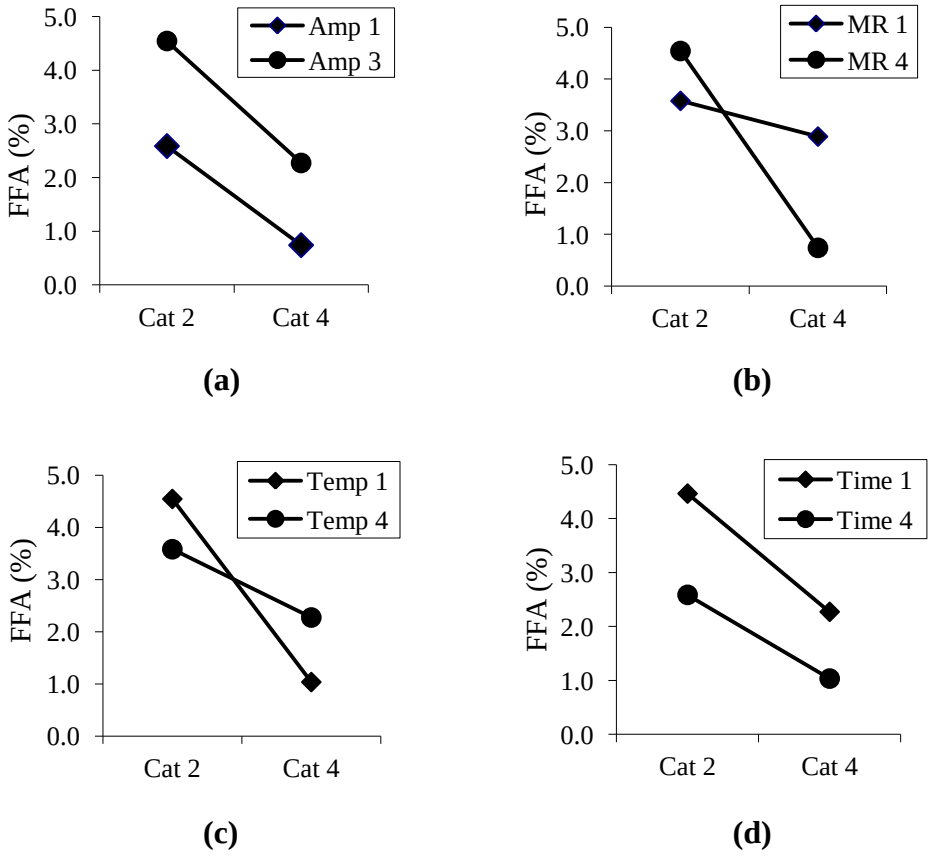

Figure 3.2 Interaction graphs between Cat-Amp (a), Cat-MR (b), Cat-Temp (c) and Cat-Time (d) of the preliminary experiments

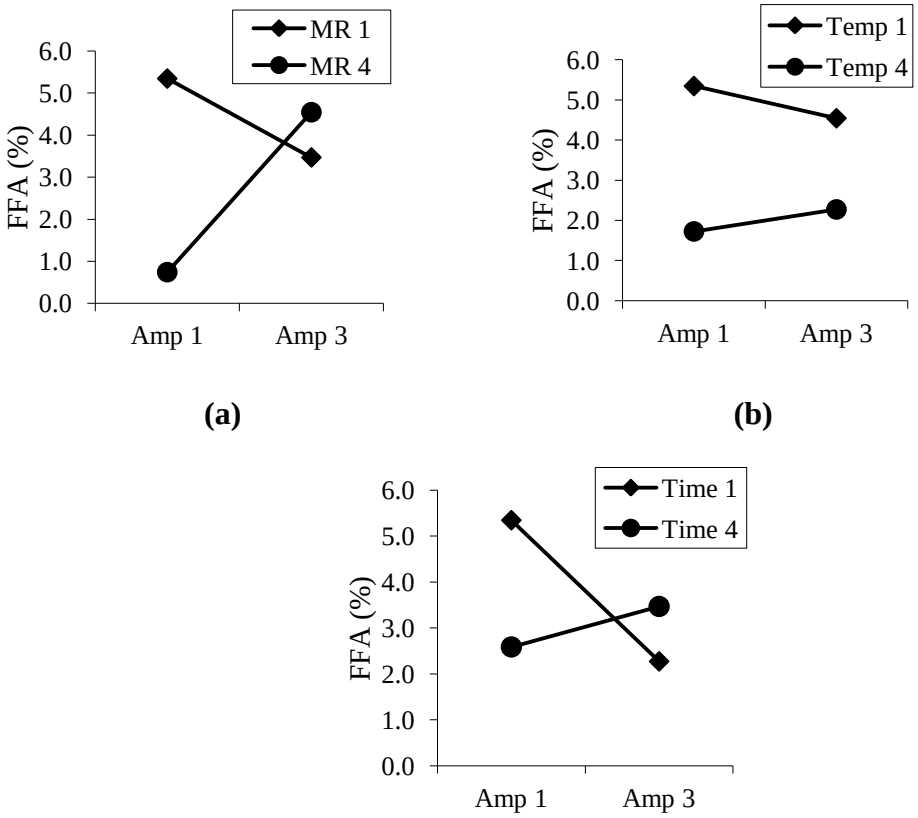

Figure 3.3 Interaction graphs between Amp-MR (a), Amp-Temp (b) and Amp-Time (c) of the preliminary experiments

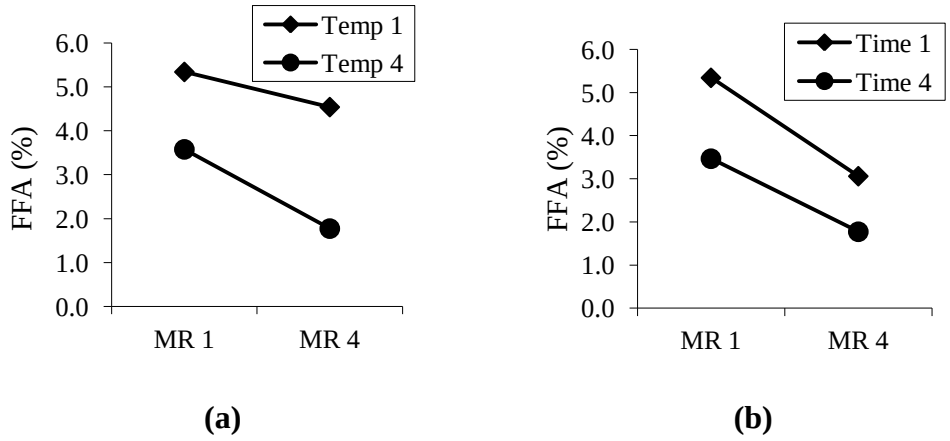

Figure 3.4 Interaction graphs between MR-Temp (a) and MR-Time (b) of the preliminary experiments

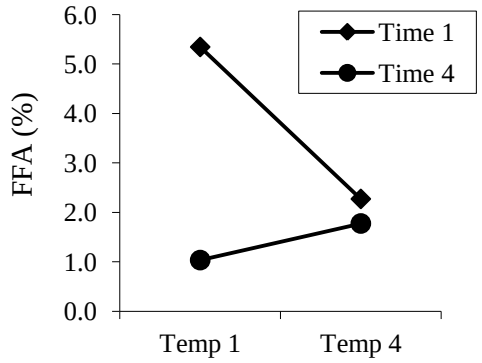

Figure 3.5 An interaction graph between Temp-Time of the preliminary experiments

The response table and graph of the preliminary experiments are shown by Table 3.3 and Figure 3.1, respectively. The analysis of the Delta values was been shown that the significant factors in descending order were amount of catalyst, reaction time, reaction temperature, molar ratio of ethanol to FFA and amplitude of acoustic power. All the factors were used to calculate the predicted FFA (μ value), but the calculation resulted in a negative value (-0.86). According selected target level of each factor using to conduct a confirmation run which obtained FFA content of 1.15 wt% that did not correspond with the predicted FFA. As regards the interactions from Figure 3.2-3.5, those CatxMR (catalyst interacted with molar ratio of ethanol) and CatxTemp (catalyst interacted with temperature) were significant, but amplitude was a less significant factor that AmpxMR and AmpxTime could be disregarded. Hence those significant interactions should be involved the experiments and they were taken into consideration in seeking to achieve the optimum result for the secondary experiments. The response graph illustrated that all the effective factors except the amplitude of acoustic power reduced the FFA content in the same way. Therefore, a second set of experiments was conducted based on the preliminary results by re-ordering the significant factors, taking into account the interactions and assigning new levels as shown in Table 3.4.

3.1.2 Secondary experiments

The secondary experiments exploited results of the previous one and its results are shown below.

Table 3.4 Factors of the secondary experiments

	Factors						
Level	Cat	Time	Temp	CatxTemp	MR	CatxMR	Amp
1	30	1	60	30x60	20	30x20	35
2	60	2	80	60x80	30	60x30	75

Table 3.5 Results of the secondary experiments

Run No.	Factors							y
	Cat	Time	Temp	CatxTemp	MR	CatxMR	Amp	(% FFA)
1	30	1	60	30x60	20	30x20	35	1.41
2	30	1	60	60x80	30	60x30	75	0.96
3	30	2	80	30x60	20	60x30	75	1.41
4	30	2	80	60x80	30	30x20	35	1.21
5	60	1	80	30x60	30	30x20	75	0.66
6	60	1	80	60x80	20	60x30	35	1.10
7	60	2	60	30x60	30	60x30	35	0.46
8	60	2	60	60x80	20	30x20	75	0.61
Average, T								**0.98**
Conf. run								**0.47**

Table 3.6 The response table of the secondary experiments

Level	Cat	Time	Temp	CatxTemp	MR	CatxMR	Amp
1	1.25	1.03	**0.86**	0.98	1.13	**0.97**	1.04
2	**0.70**	**0.92**	1.09	**0.97**	**0.82**	0.98	**0.91**
Delta	**0.54**	0.11	**0.23**	0.02	**0.31**	0.01	**0.13**
Order	**1**	5	**3**	6	**2**	7	**4**
Select	Cat2	Time2	Temp1		MR2		Amp2

μ = T+ (Cat2-T) + (MR2-T) + (Temp1-T)

μ = Cat2+ MR2+Temp1 -2T

μ = 0.70+0.82+0.86-2(0.98) = 0.42

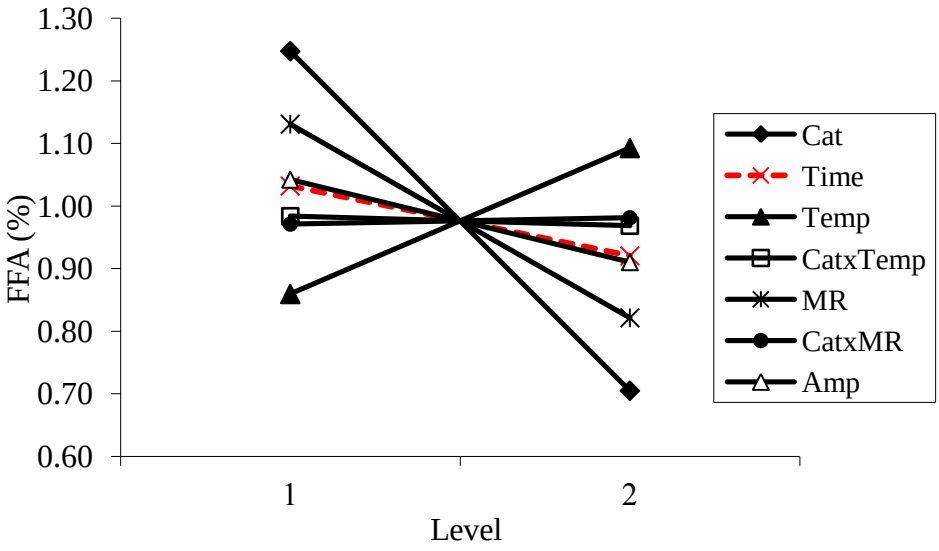

Figure 3.6 The response graph of the secondary experiments

The results of the secondary experiments are shown in Table 3.5. The response table and graph are shown in Table 3.6 and Figure 3.6, respectively. Data analysis was performed in the same fashion as for the preliminary results. The factors and interactions were considered by comparing each effect to the next strongest effect (Peace, 1993). The significant factors in descending order are amount of catalyst, molar ratio of ethanol: FFA and reaction temperature. Based on the Delta values, the amplitude of acoustic power, reaction time, and the CatxTemp and CatxMR interactions were disregarded in accordance with the one-half rule of thumb; that is, they were less than half of the next strongest effect. The predicted FFA was a positive value of 0.42 wt% corresponding to 0.47 wt% of the confirmation run result. Figure 3.6 shows the effect of the five factors: amount of catalyst, molar ratio of ethanol: FFA and amplitude had a positive effect at a higher level, but reaction temperature had a negative effect. The secondary experiments showed the optimum conditions to be: catalyst amount at 60 wt% of FFA, molar ratio of ethanol to FFA at 30:1, temperature at 60ºC, reaction time of two hours, and amplitude of acoustic power at 75%. It was apparent that reaction time was a less significant factor and the results obtained differed only slightly between different periods. Therefore further

experiments were conducted using the optimum conditions with different reaction times to fine-tune this parameter.

3.1.3 Further experiments

The further experiments were performed with the same fashion of the confirmation run of the secondary experiments with different reaction times. Results are showed in Table 3.7 and Figure 3.7. There were 3 repeatable runs compared with the confirmation run of the secondary experiments. The results showed that the FFA content was reduced over different reaction times between 30 and 120 minutes. All three runs of this part produced less than 0.5 wt% of FFA within one hour by using the optimum conditions (catalyst at 60 wt% of FFA, molar ratio of ethanol to FFA at 30:1, temperature at 60ºC, reaction time of one hour, and amplitude of acoustic power at 75%) Therefore new optimal conditions were derived from the repeated experiments and the results were not significantly varied by changing the reaction time between one and two hours suggesting that a point of reaction equilibrium was reached at one hour. By considering the esterification reaction shown in Eq 3.1 below, it can be seen that the reaction is reversible with undesired water being produced. In the presence of triglycerides and water especially under acidic condition, hydrolysis can easily take place producing FFA (Eq 3.2-3.4 below). However, if the water is removed, the reaction will shifts to the product side.

$$\mathbf{R_1COOH + CH_3CH_2OH \xrightleftharpoons{H_2SO_4} R_1COCH_2CH_3 + H_2O} \quad \text{(Eq 3.1)}$$

$$\mathbf{TG + H_2O \xrightleftharpoons{H_2SO_4} DG + R_1COOH} \quad \text{(Eq 3.2)}$$

$$\mathbf{DG + H_2O \xrightleftharpoons{H_2SO_4} MG + R_1COOH} \quad \text{(Eq 3.3)}$$

$$\mathbf{MG + H_2O \xrightleftharpoons{H_2SO_4} C_3H_8O_3 + R_1COOH} \quad \text{(Eq 3.4)}$$

3.1.4 Additional experiments

Results of the additional experiment are shown in Table 3.7 below.

Table 3.7 The FFA content obtained from further and additional experiments

Time (min)	Secondary expt. Conf. run	Further experiments Run #1	Run #2	Run #3	Additional expt. 2 Steps
0	5.06	5.96	5.96	5.96	5.96
30	0.69	0.97			
60		0.5	0.45	0.48	0.475
120	0.47				0.22

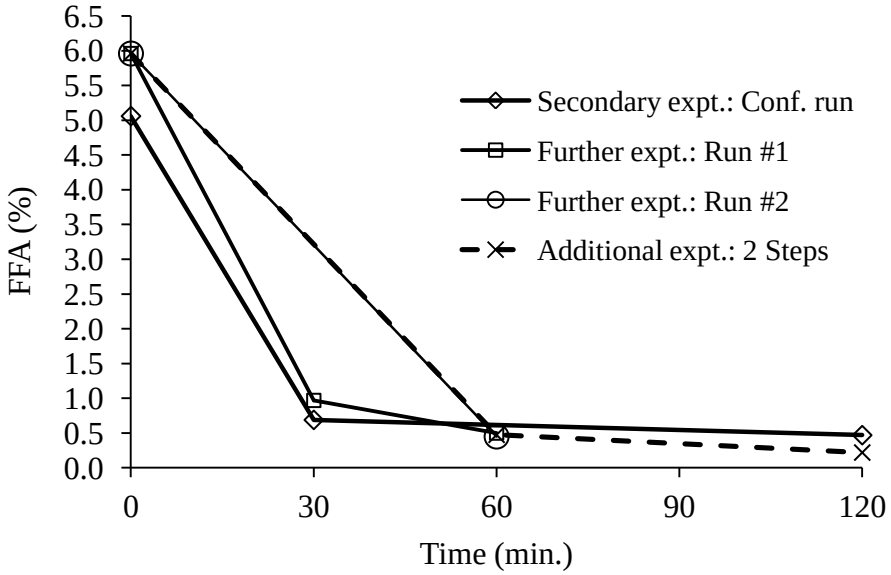

Figure 3.7 The FFA content obtained from further and additional experiments

The additional experiment involving two stages esterification was conducted and the result was detailed in Table 3.7 and Figure 3.7 (2 steps line). The conditions employed in both steps of the esterification were: catalyst at 60 wt% of FFA, molar ratio of ethanol to FFA at 30:1, temperature at 60ºC, reaction time of one hour, and amplitude of acoustic power at 75%. The result was revealed the FFA content was finally reduced to 0.22 wt%. Therefore it can be concluded that after one hour of reaction the equilibrium was attained due to a reversible of esterification reaction (Eq 3.1) including hydrolysis reactions (Eq 3.1-3.4). Therefore after water

abolishment and the performance of the second step esterification under the same conditions for a further hour, the FFA content was able to be reduced further indicating that a new equilibrium had been reached and the water had acted to interrupt the process of esterification.

3.1.5 The energy consumption of the batch experiments

Table 3.8 Theoretical and actual energy consumptions

No	CPO (g)	EtOH (g)	ΔT (°C)	Q (kJ)	Q′ (Wh)	Consumed Power (Wh)
1	235.58	64.42	30.0	18.35	5.10	64
2	235.58	64.42	30.0	18.35	5.10	61
3	238.36	61.64	30.0	18.31	5.08	61
4	255.88	44.12	30.0	18.04	5.01	61
5	238.36	61.64	30.0	18.31	5.08	59
6	255.88	44.12	30.0	18.04	5.01	59
7	238.36	61.64	30.0	18.31	5.08	70
8	238.36	61.64	30.0	18.31	5.08	58
9	255.88	44.12	30.0	18.04	5.01	62
10	238.36	61.64	30.0	18.31	5.08	62
11	255.88	44.12	30.0	18.04	5.01	59
Average	244.23				5.06	61.45
	1 kg				21	252

Remark: Cp of CPO and ethanol are 1.929 and 2.440 kJ/(kg C), respectively.

The experimental and theoretical energy consumption was 252 and 21 Wh/kg of CPO, respectively. The energy efficiency was 8.23%, it was quite low. However this experimental consumption was corresponding to 250 Wh/kg oil for the transesterification of soybean oil using the ultrasonic method (Ji, 2006). The most advantage of the ultrasonic esterification method is no requiring an external heating source of which saving a heating unit.

3.1.6 Phosphorus content analysis of some samples

The initial and final (after conducting the reaction) phosphorus contents of CPO were 11.24 and 1.46 mg/kg, respectively. This values shows that a lower phosphorus content can be achieved concomitantly under the acid catalyzed esterification assisted by ultrasonic irradiation and the final phosphorus content meets the methyl ester standard (EN 14214: 2008 in Appendix A). Thus, the esterification process can reduces the phosphorus content to an acceptant level without performing a separated degumming step.

3.2 Studies of continuous acid catalyzed esterification of CPO with ethanol assisted by ultrasonic irradiation

3.2.1 The 1st continuous experiments; continuous acid catalyzed esterification at 80ºC with stainless steel reactor having volume of 4.6 L, inner diameter of 97 mm and height of 700 mm. The flow pattern was a vertical up flow.

Table 3.9 Factors of the 1st continuous experiments

Level	Factors		
	Cat	MR	RT
1	30	20	0.5
2	60	30	1

Table 3.10 Orthogonal array of the 1st continuous experiments

Run No.	Factors		
	Cat	MR	RT
1	30	20	0.5
2	30	30	1
3	60	20	1
4	60	30	0.5

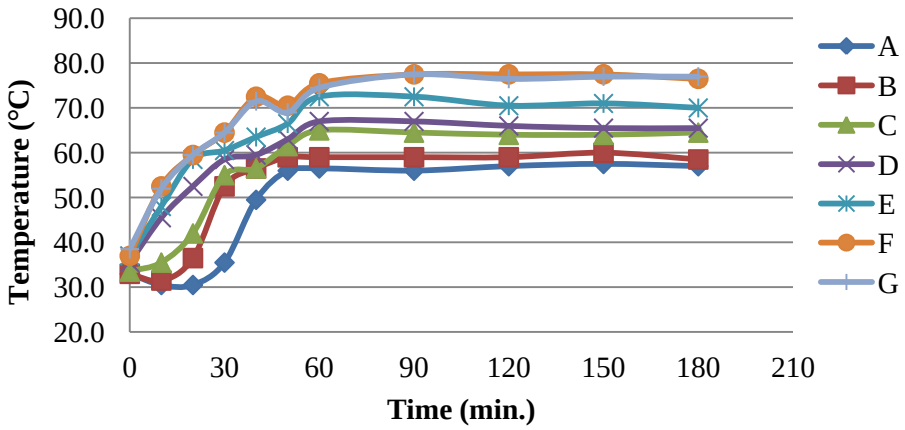

Figure 3.8 Reactor temperature profile: Run # 1 of the 1st continuous experiments

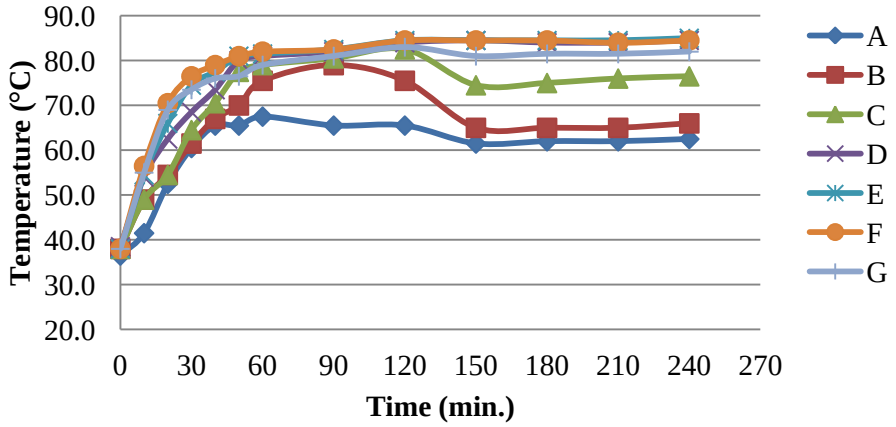

Figure 3.9 Reactor temperature profile: Run # 2 of the 1st continuous experiments

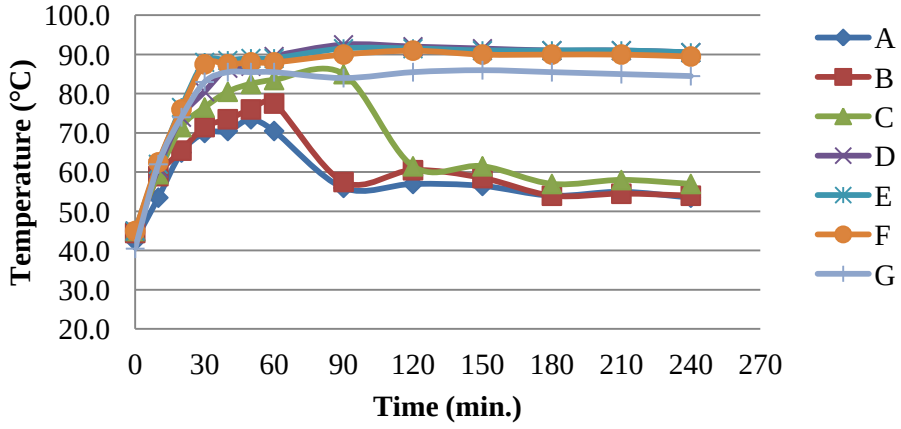

Figure 3.10 Reactor temperature profile: Run # 3 of the 1st continuous experiments

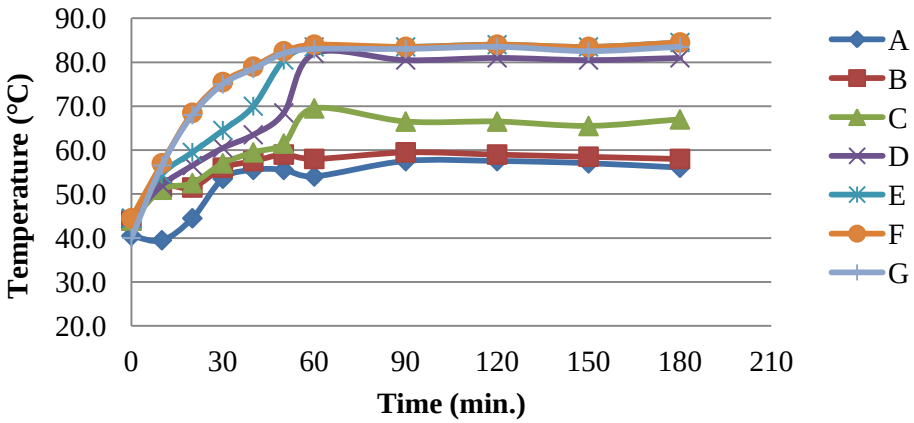

Figure 3.11 Reactor temperature profile: Run # 4 of the 1st continuous experiments

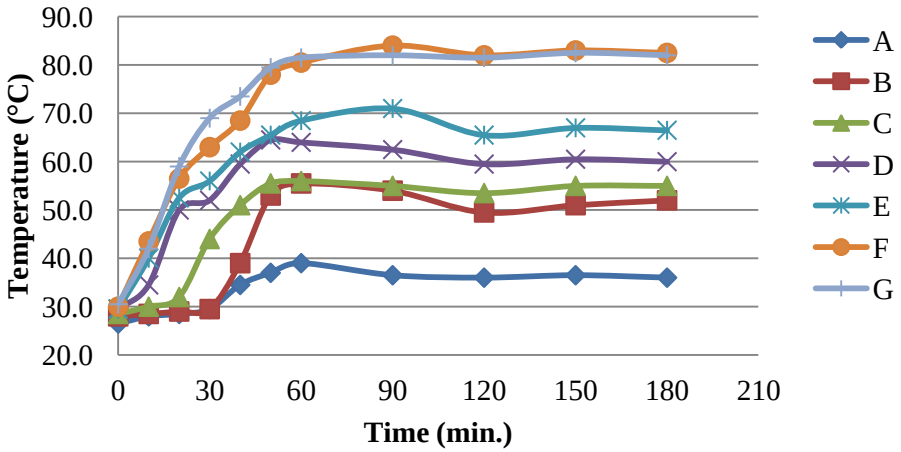

Figure 3.12 Reactor temperature profile: Run # 5 of the 1st continuous experiments

Table 3.11 Results of FFA analysis of the 1st continuous experiments

Time	Average FFA (%)				
(min)	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5
0	4.88	4.88	4.88	4.88	5.76
30	3.72			1.59	2.99
60	2.56	1.44	1.81	1.46	2.18
90	**2.06**	1.47	2.21	**1.39**	**1.84**
120	**1.89**	1.54	2.33	**1.51**	**2.02**
150	1.84	1.67	2.19	1.43	1.98
180	1.90	**1.63**	**2.22**	1.56	1.90
210		1.90	2.00		
240		**2.06**	**2.09**		
Average					**1.93**
Cal FFA					**1.50**

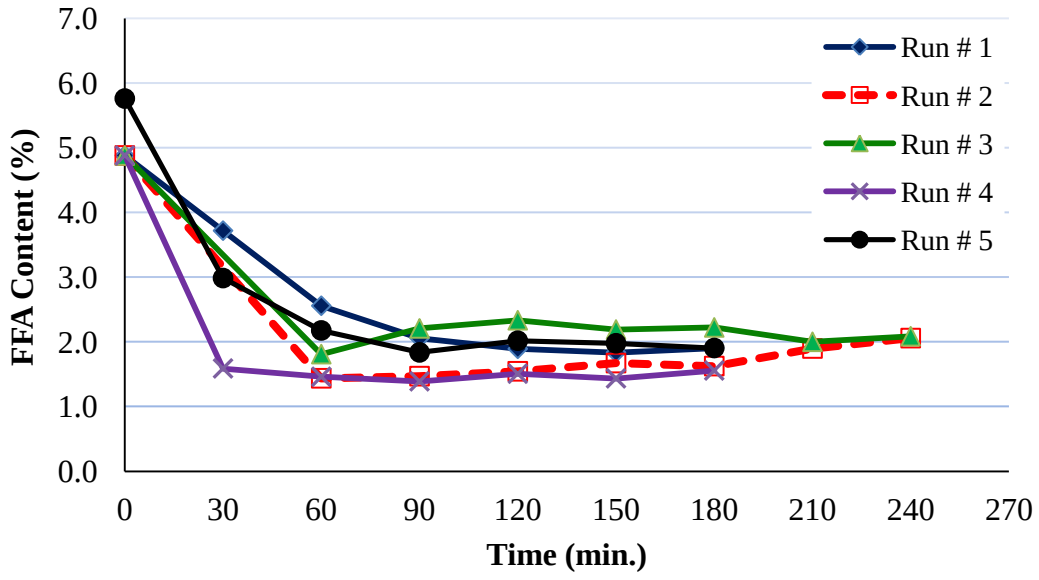

Figure 3.13 The FFA reduction of the 1st continuous experiments

Table 3.12 Response characteristics of the 1st continuous experiments

Run No.	Factors					Response Characteristic (y)
	Cat	MR	RT	y1	y2	
1	30	20	0.5	2.06	1.89	**1.97**
2	30	30	1	1.63	2.06	**1.84**
3	60	20	1	2.22	2.09	**2.15**
4	60	30	0.5	1.39	1.51	**1.45**
T						**1.85**

Table 3.13 The response table of the 1st continuous experiments

Level	Cat	MR	RT
1	1.91	2.06	**1.71**
2	**1.80**	**1.64**	2.00
Delta	0.11	0.42	0.29
Order		1	2
Select	Cat2	MR2	RT1
μ	= T+(MR2-T)+(RT1-T)		
μ	= 1.50		

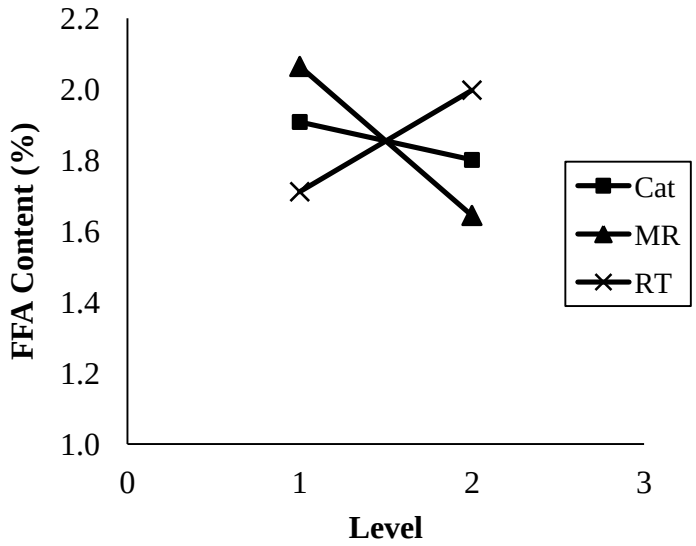

Figure 3.14 The response graph of the 1st continuous experiments

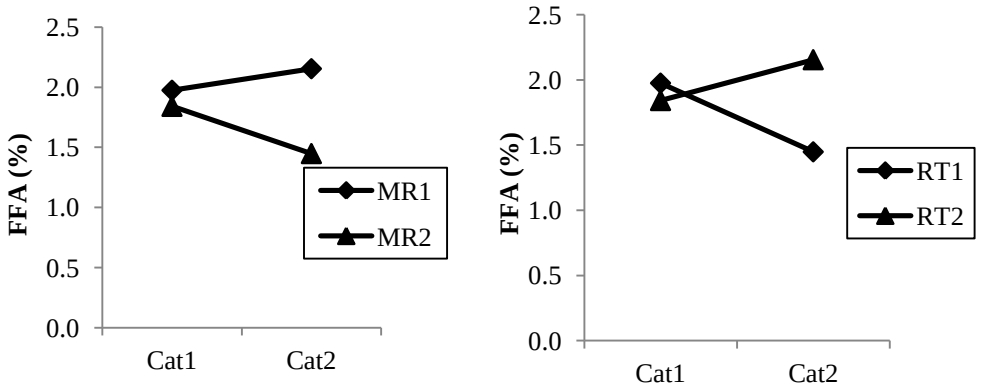

Figure 3.15 The interaction graphs between Cat-MR (a) and Cat-RT (b) of the 1st continuous experiments

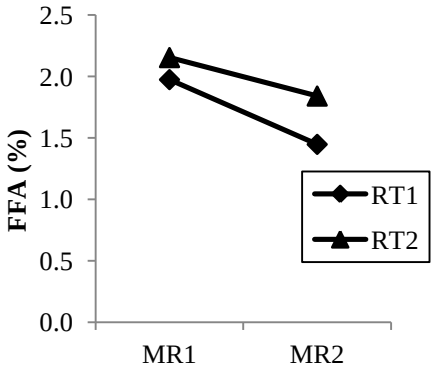

Figure 3.16 The interaction graph between MR-RT of the 1st continuous experiments

Temperature profiles of 5 runs obtaining from the 1st continuous experiments showed steady state after 1 hour running (Figure 3.8-3.12). At steady state, run number 1-4 had temperature between 60 to 80ºC because the reaction temperature had no controlling and at the input side had lower temperature than the output side. Run number 5 had more distribution in temperature over the height of reactor (Figure 3.12). According the FFA reduction graph (Figure 3.13), it is found that FFA was reduced when reaction time increased and it was ongoing to steady state after 90 minutes (3RT for the shortest retention time). It was suitable to select the results at 3RT and 4RT for data analysis. The response table showed that the most significant factor was a molar ratio followed by retention time, but catalyst content

could be neglect corresponding to the response graph showing less steepness. Selected factors for a confirmation run were Cat2, MR2 and RT1, consequently obtained average FFA content of 1.93 wt% but the predicted FFA was 1.5 wt%. There was no interaction between MR and RT.

3.2.2 The 2nd continuous experiments; continuous acid catalyzed esterification at 80ºC with stainless steel reactor having volume of 1.47 L, inner diameter of 61 mm and height of 700 mm. The flow pattern was a vertical up flow.

Table 3.14 Factors of the 2nd continuous experiments

Level	Factors		
	Cat	MR	RT
1	30	20	0.5
2	60	30	1

Table 3.15 Results of FFA analysis of the 2nd continuous experiments

Time	Average FFA (%)				
(min)	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5
0	5.49	5.49	5.49	5.49	5.49
60	1.92			1.70	1.53
90	**2.15**			**1.30**	**1.44**
120	**2.18**	2.24	1.75	**1.37**	**1.52**
150	2.15	2.21	1.64	1.65	1.44
180	2.19	**2.20**	**1.66**	1.57	1.46
210		1.98	1.45		
240		**1.90**	**1.52**		
Average					**1.48**
Cal FFA					**1.37**

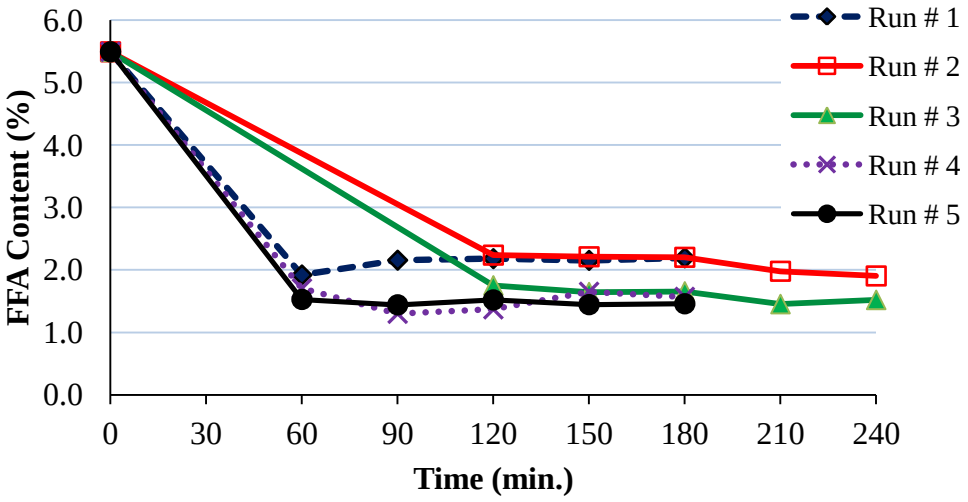

Figure 3.17 The FFA reduction of the 2nd continuous experiments

Table 3.16 Response characteristics of the 2nd continuous experiments

Run No.	Factors					Response Characteristic (y)
	Cat	MR	RT	y1	y2	
1	30	20	0.5	2.15	2.18	2.17
2	30	30	1	2.20	1.90	2.05
3	60	20	1	1.66	1.52	1.59
4	60	30	0.5	1.30	1.37	1.33
T						**1.79**

Table 3.17 The response table of the 2nd continuous experiments

Level	Cat	MR	RT
1	2.11	1.88	**1.75**
2	**1.46**	**1.69**	1.82
Delta	0.65	0.18	0.07
Order	1	2	
Select	Cat 2	MR 2	RT 1

μ = T+(Cat2-T)+(MR2-T)

μ = 1.37

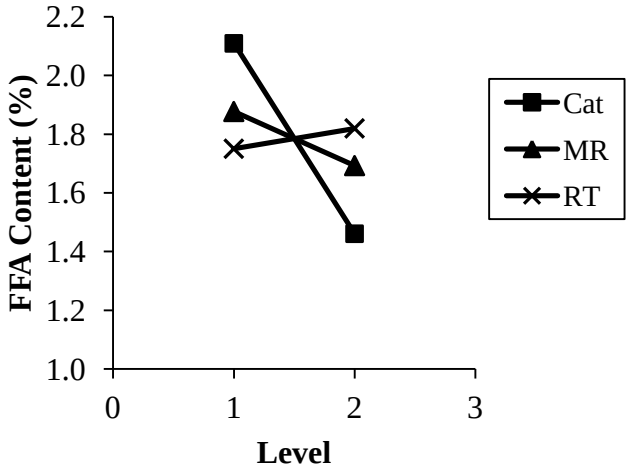

Figure 3.18 The response graph of the 2nd continuous experiments

Temperature profiles of 5 runs obtaining from the 2nd continuous experiments showed steady state after 0.5 hour running (Figure C11-C15, Appendix C). At steady state, all points except feed point (point A) of all runs had temperature nearly 80ºC. Clearly, temperature distribution of a narrow reactor was better than a wide one, it meant that cavitation took place thoroughly in a suitable narrow reactor which corresponding to the sonotrode diameter. According the FFA reduction graph (Figure 3.17), it was found that FFA was reduced when reaction time increased and it was ongoing to steady state after 60 and 120 minutes for the runs of RT 0.5 and 1 hour, respectively. Therefore, results at 3RT and 4RT were suitable for data analysis. The response table showed that the most significant factor was a catalyst content followed by molar ratio, but retention time could be neglect corresponding to its steepness and negative effect in the response graph in which showing positive effect of catalyst content and molar ratio. Selected factors for a confirmation run are Cat2, MR2 and RT1; consequently obtained average FFA content of 1.48 wt% corresponding to the predicted FFA of 1.37 wt%. There was no interaction of the both significant factors.

3.2.3 The 3rd continuous experiments; continuous acid catalyzed esterification at 80ºC with stainless steel reactor having volume of 1.47 L, inner diameter of 61 mm and height of 700 mm. The flow pattern was a vertical down flow.

Table 3.18 Factors of the 3rd continuous experiments

Level	Factors		
	Cat	MR	RT
1	30	20	0.5
2	60	30	1

Table 3.19 Results of FFA analysis of the 3rd continuous experiments

Time	Average FFA (%)				
(min)	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5
0	5.49	5.49	5.49	5.49	5.49
60	1.75			0.94	
90	**1.68**			**1.10**	
120	**1.65**	1.10	1.35	**1.09**	1.11
150	1.59	1.06	1.29	1.09	0.99
180	1.62	**1.17**	**1.39**	1.12	**1.11**
210		1.09	1.32		1.12
240		**1.21**	**1.35**		**1.10**
Average					**1.11**
Cal FFA					**1.04**

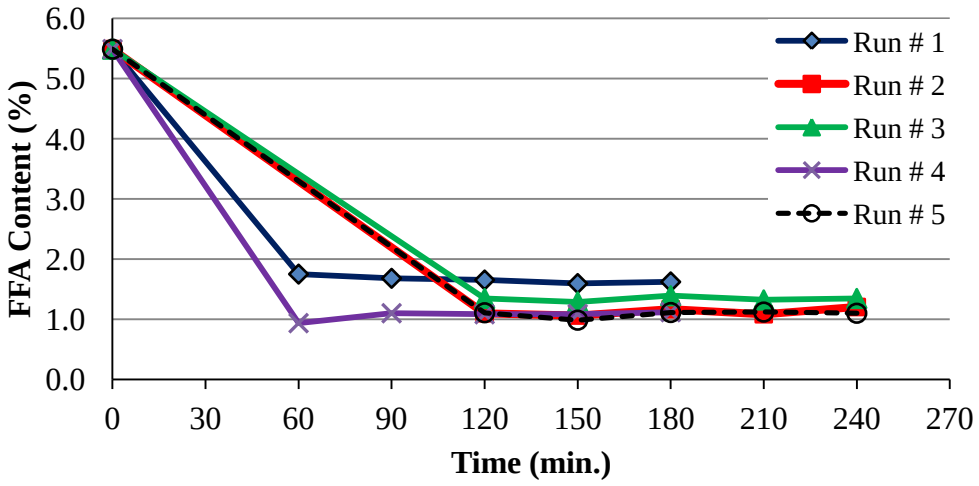

Figure 3.19 The FFA reduction of the 3rd continuous experiments

Table 3.20 Response characteristics of the 3rd continuous experiments

Run No.	Factors					Response Characteristic (y)
	Cat	MR	RT	y1	y2	
1	30	20	0.5	1.68	1.65	1.67
2	30	30	1	1.17	1.21	1.19
3	60	20	1	1.39	1.35	1.37
4	60	30	0.5	1.10	1.09	1.09
T						**1.33**

Table 3.21 The response table of the 3rd continuous experiments

Level	Cat	MR	RT
1	1.43	1.52	1.38
2	**1.23**	**1.14**	**1.28**
Delta	0.20	0.38	0.10
Order	2	1	3
Select	Cat2	MR2	RT2
μ	= T+(Cat2-T)+(MR2-T)+(RT2-T)		
μ	= 1.04		

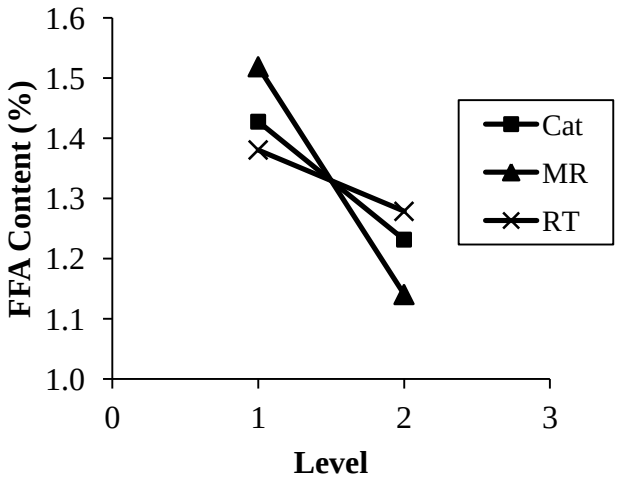

Figure 3.20 The response graph of the 3rd continuous experiments

Temperature profiles of 5 runs obtaining from the 3rd continuous experiments showed steady state after 0.5 hour running (Figure C16-C20, Appendix C). At steady state, all runs had average temperature nearly 80ºC. It was shown that temperature distribution was better than the up flow experiments (the 2nd experiments) According the FFA reduction graph (Figure 3.19), it was found that FFA was reduced when reaction time increased and it was ongoing to steady state after 60 and 120 minutes for the runs of RT 0.5 and 1 hour, respectively. The response table showed that the most significant factor was a molar ratio followed by catalyst content, but retention time can be neglect corresponding to its steepness in the response graph in which showing positive effect of all three factors. Selected factors for a confirmation run are Cat2, MR2 and RT2; consequently obtained average FFA content of 1.11 wt% corresponding to the predicted FFA of 1.04 wt%. There is no interaction of the both significant factors.

3.2.4 The 4th continuous experiments; continuous acid catalyzed esterification at 60ºC with stainless steel reactor having volume of 1.47 L, inner diameter of 61 mm and height of 700 mm. The flow pattern was a horizontal flow.

Table 3.22 Factors of the 4th continuous experiments

	Factors		
Level	Cat	MR	RT
1	30	20	0.5
2	60	30	1

Table 3.23 Results of FFA analysis of the 4th continuous experiments

Time	Average FFA (%)				
(min)	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5
0	6.26	6.26	6.26	6.26	6.26
60	2.08			1.02	
90	**2.13**			**0.96**	
120	**2.15**	0.97	0.96	0.91	0.32
150	2.16	1.00	0.91	**0.94**	0.37
180	2.14	**0.97**	**0.96**	0.96	**0.35**
210		0.97	0.90		0.37
240		**0.98**	**0.92**		**0.36**
Average					**0.35**
Cal FFA					**0.36**

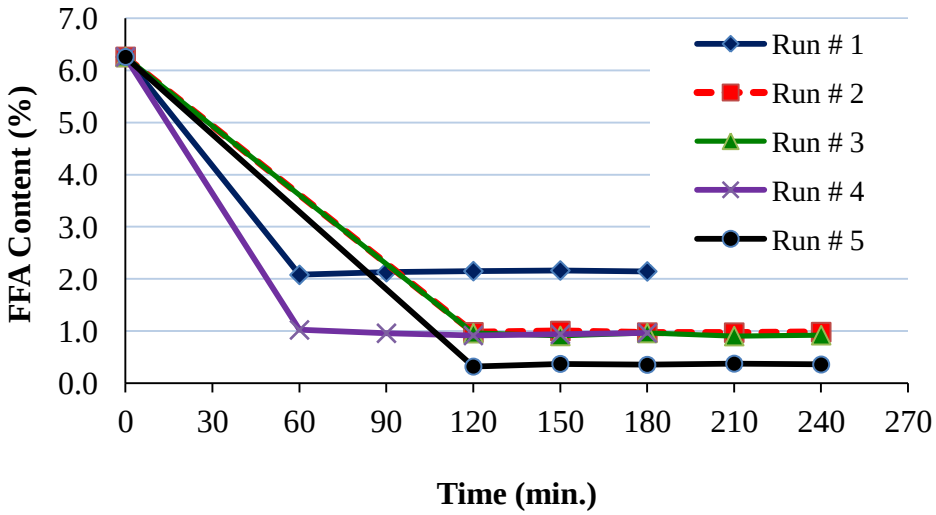

Figure 3.21 The FFA reduction of the 4th continuous experiments

Table 3.24 Response characteristics of the 4th continuous experiments

Run No.	Factors					Response Characteristic (y)
	Cat	MR	RT	y1	y2	
1	30	20	0.5	2.13	2.15	2.14
2	30	30	1	0.97	0.98	0.97
3	60	20	1	0.96	0.92	0.94
4	60	30	0.5	0.96	0.94	0.95
T						**1.25**

Table 3.25 The response table of the 4th continuous experiments

Level	Cat	MR	RT
1	1.56	1.54	1.54
2	**0.94**	**0.96**	**0.96**
Delta	0.61	0.58	0.58
Order	1	2	3
Select	Cat2	MR2	RT2
μ	= T+(Cat2-T)+(MR2-T)+(RT2-T)		
μ	= 0.36		

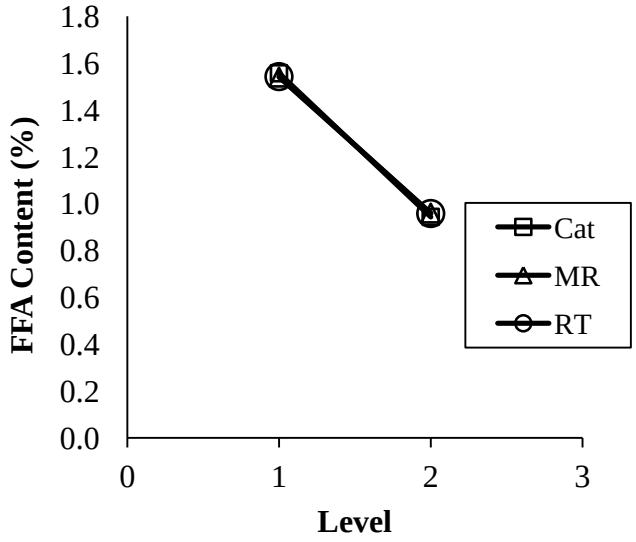

Figure 3.22 The response graph of the 4th continuous experiments

Temperature profiles of 5 runs obtaining from the 4th continuous experiments showed steady state after 0.5 to 1 hour running (Figure C21-C25, Appendix C). At steady state, all points of all runs had temperature nearly 60ºC because of temperature controlling. According the FFA reduction graph (Figure 3.21), it was found that FFA was reduced when reaction time increased and it was ongoing to steady state after 60 and 120 minutes for the runs of RT 0.5 and 1 hour, respectively. The response table showed that all three factors were the same level significant factors, in descending order as catalyst content, molar ratio and retention time corresponding to the response graph showing positive effect of them. Selected factors for a confirmation run were Cat2, MR2 and RT2; consequently obtained average FFA content of 0.35 wt% corresponding to the predicted FFA of 0.36 wt%. There was no interaction of the significant factors.

3.2.5 The energy efficiency of continuous experiments

Table 3.26 Energy efficiency of the continuous experiments

Experiments	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5
1st	32.09%	25.46%	30.34%	39.94%	37.89%
2nd	20.47%	11.12%	12.21%	20.42%	21.39%
3rd	24.25%	15.74%	15.65%	22.48%	16.04%
4th	12.17%	7.03%	6.77%	14.66%	6.85%

When considering each run of each experiment, it is found that run number 1 and 4 had closely efficiency of energy consumption and run number 2 and 3 had closely of those. That might be caused by a retention time; the longer RT had lower energy efficiency. Possibly, input electrical power was excessively high in order to generate ultrasound, too much if comparing with heating by a conventional method, and also because of heat loss at surface of the reactors without insulation. All four experiments showed the energy efficiency in same fashion. The horizontal flow represents the least energy efficiency that caused by more heat loss with cooling water used for controlling temperature.

3.2.6 Comparing between reactor sizes

In the continuous experiment, there were two sizes of reactors, 97 and 61 mm of inner diameter corresponding to 4.60 and 1.47 L belonging to the 1st and 2nd continuous experiments (item 3.2.1 and 3.2.2), respectively. The sonotrode diameter is 50 mm. The average FFA obtained from the 1st and 2nd continuous experiments were 1.85 and 1.79 wt%, respectively, but the response of factors of the 2nd continuous experiments is more obvious than those the 1st one and the order of significant factors are different. This may be caused by mismatching between diameter of sonotrode and reactor. In the narrow diameter reactor matching to the sonotrode diameter, ultrasound can irradiate more thoroughly that make better mixing and cavitation corresponding to a lower FFA content and a higher temperature profile. Therefore, the matching of reactor and sonotrode in size should be considered when the ultrasonic method is preceded. Consequently, the 61 mm ID reactor was be used for the next experiments.

3.2.7 Comparing between flow patterns

In the continuous experiment, there were two flow patterns, up and down flow in the 2nd and 3rd experiments, respectively. The up flow was a bottom feeding and product flowed out at the top valve, the feed stream was a counter current to ultrasound irradiation. The down flow was opposite to the up flow. The results are found that the average FFA content of down flow (1.33 wt%) is significantly better than that of up flow pattern (1.79 wt%) and also the confirmation run of the down flow experiment obtained the better result of 1.11 wt% FFA compared to 1.48 wt% of the up flow experiment. Moreover the energy efficiency of the down flow is apparently higher than the up flow (see Table 3.26). This may be in sense of generated heat is naturally dissipated upward and concurrent with the up flow pattern of the mixture so it is easy to take the heat off. This phenomenon is happened opposite to the down flow pattern which uses the heat with more efficiency.

3.2.8 Comparing between reactor configurations

The first three continuous experiments are all vertical flow and the reaction took place at 80ºC, but their results cannot obtain 0.5 wt% FFA, this might be

affected by hydrolysis of CPO which highly occur with high temperature under acid condition as same as results of the batch experiments. Thus the author performed the additional continuous experiments using 61 mm inner diameter reactor under the confirmation run condition of the 3rd ultrasonic experiment at 60ºC and also did the same of batch experiment to prove the influence of the hydrolysis, the results were shown in Figure 3.48.

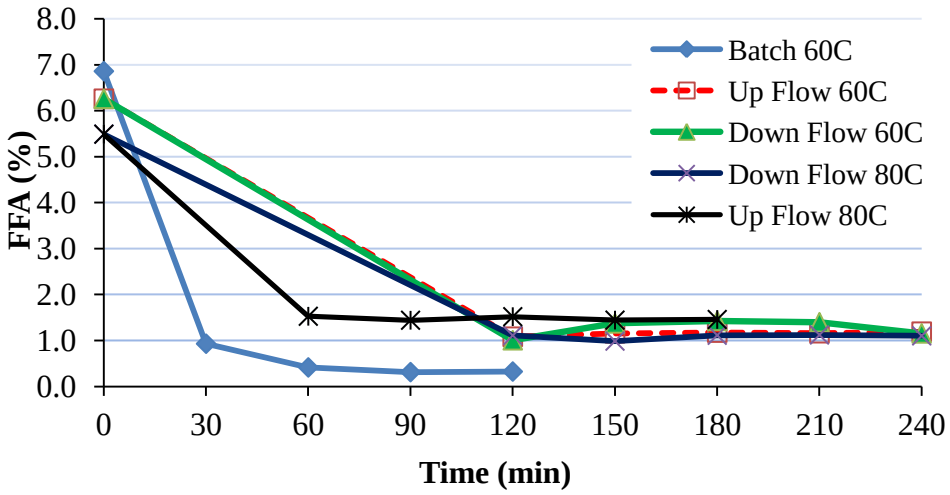

Figure 3.23 Additional experiments of the continuous experiments

The results were shown that the batch experiment (60ºC) could extremely reduce FFA content to 0.4 wt% after 60 minutes compared to other experiments especially performing at 80ºC. For up flow experiments with the different reaction temperatures, at 60ºC obtained a lower FFA content at 1.18 wt% compared to 1.48 wt% of performing at 80ºC. For the down flow experiments, they are no significant of FFA content. Anyhow it can be concluded that the reaction temperature at 60ºC is obviously optimized than at 80ºC because of hydrolysis effect, but why the batch experiment obtained better results than continuous one at the same 60ºC. The hypothesis for this reason is mixing effect. Normally, the dissolution of ethanol in CPO at 60°C looks well when it has a good agitation in the batch, but in the vertical ultrasonic reactor, the mixing takes place with micro jet generated after implosion of cavities and it does not provide an appropriate mixing condition because the ethanol in feed stream tends to flow upward in a shorter time (short cut flowing) including high viscosity of the mixture, especially at a lower temperature. Therefore the good

mixing in the reactor is probably difficult. The reaction system likes a quasi-homogeneous more that an ideal homogeneous system. At a lower reaction temperature, the quasi-homogeneous of ethanol-CPO solution is much in evidence but it is necessary to react at a lower temperature by reason of avoiding the hydrolysis reactions. The possible way to obtain a good mixing at 60ºC under ultrasound is to arrange the reactor in a horizontal configuration due to keep ethanol as long as the specific retention time. Hence, the 4th continuous experiments were conducted to prove the mixing assumption and the results were proved in 3.2.4. The FFA content obtained by a confirmation run of the experiments was 0.35 lower than 1.11 wt% of a vertical down flow. Consequently, it can be summarized that the mixing has more influence for the viscous esterification of CPO with ethanol assisted by ultrasound irradiation. The best conditions for continuous esterification of CPO with ethanol assisted by ultrasound irradiation are catalyst content of 60 wt% of FFA, molar ratio of ethanol: CPO at 30: 1, retention time at 1 hour and horizontal reactor configuration.

3.3 Studies of acid catalyzed esterification of CPO with ethanol using continuous stirred-tank reactor

The factors and orthogonal array of the experiments were same as the continuous ultrasonic experiments shown in Table 3.9 and 3.10, respectively. This CSTR experiments were conducted at 60ºC under turbulence mixing condition, N_{Re} > 20,000. Results of the CSTR were followed.

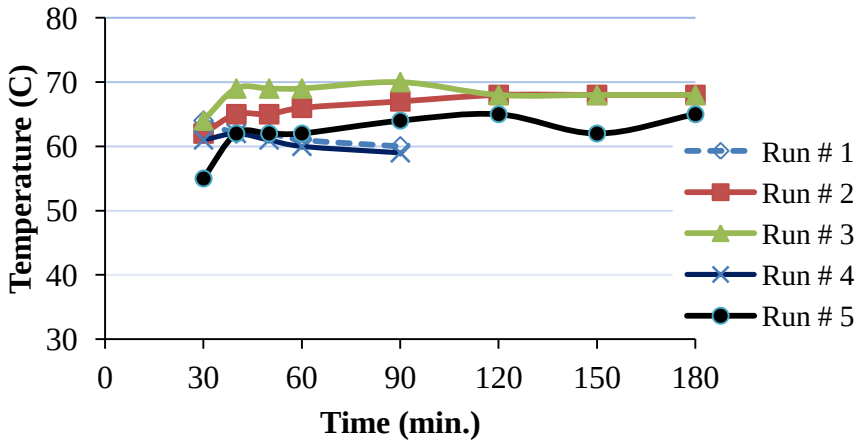

Figure 3.24 Reactor temperature profiles of the CSTR experiments

Table 3.27 Results of FFA analysis of the CSTR experiments

Time	Average FFA (%)				
(min)	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5
0	7.07	8.32	6.11	6.24	7.50
30	2.01			1.69	
45	2.07			1.63	
60	2.37	1.00	1.36	1.60	0.85
75	2.51			1.72	
90	2.52	0.95	1.27	1.74	0.81
120		0.99	1.33		0.74
150		0.99	1.47		0.80
180		0.98	1.53		0.88
Average					**0.81**
Cal FFA					**0.90**

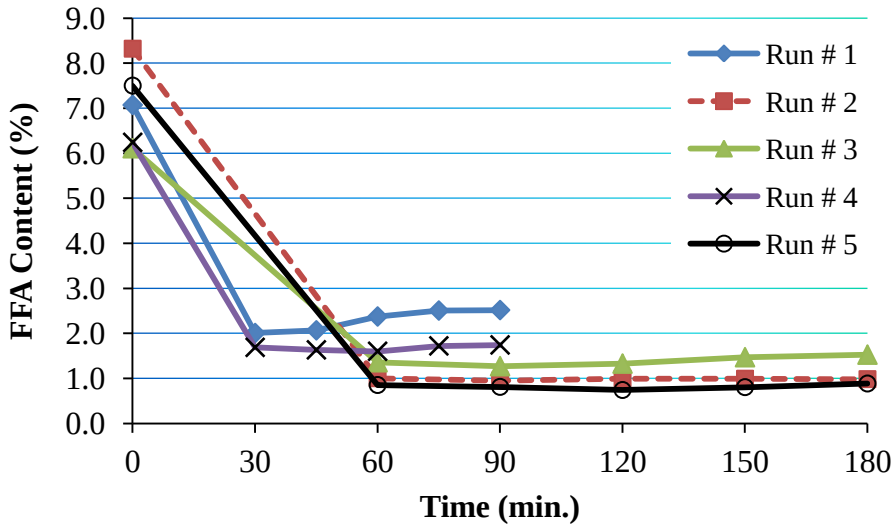

Figure 3.25 The FFA reduction of the CSTR experiments

Table 3.28 Response characteristics of the CSTR experiments

Run No.	Factors					Response Characteristic (y)
	Cat	MR	Time	y1	y2	
1	1	1	1	2.37	2.52	2.44
2	1	2	2	0.99	0.98	0.99
3	2	1	2	1.33	1.53	1.43
4	2	2	1	1.60	1.74	1.67
T						**1.63**

Table 3.29 The response table of the CSTR experiments

Level	Cat	MR	Time
1	1.72	1.94	2.06
2	**1.55**	**1.33**	**1.21**
Delta	0.17	0.61	0.85
Order		2	1
Select	Cat 2	MR 2	Time 2

μ = T+(MR2-T)+(Time2-T)

μ = 0.90

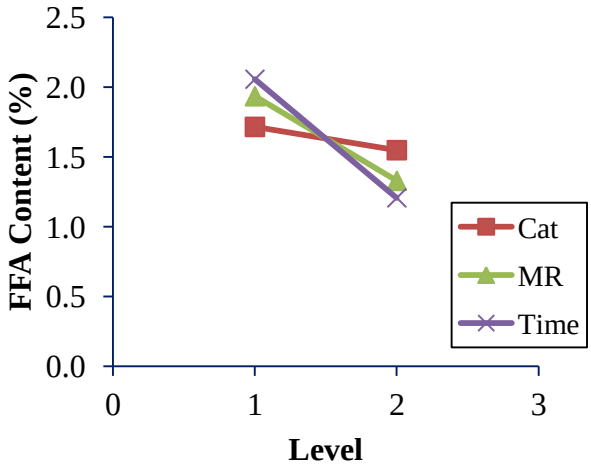

Figure 3.26 The response graph of the CSTR experiments

The interaction graphs of the CSTR experiments were shown in Figure C11 and C12 in an appendix C.

Table 3.30 Energy efficiency of the CSTR experiments

	Energy (Wh/kg CPO)				
	Run # 1	Run # 2	Run # 3	Run # 4	Run # 5
CSTR	28.24	41.28	34.92	29.44	33.94
Theory	21.67	31.31	25.72	22.56	27.05
Efficiency	76.74%	75.86%	73.67%	76.62%	79.70%

The CSTR experiments were run at 60ºC for 3 RT long and their temperature profiles were shown in figure 3.24. Their results were shown in Table 3.27 and Figure 3.25. The response characteristics showed the average FFA at 1.63 wt%. After analysis by response table in Table 3.29, it showed the significant factors in descending order as retention time, molar ratio and catalyst content corresponding to the response graph in Figure 3.26 and calculated FFA was 0.90 wt% closing to 0.81 wt% of the confirmation run. Therefore, the optimum conditions for esterification of CPO with ethanol using CSTR were retention time at 1 hour, molar ratio of ethanol: FFA is 30: 1 and catalyst content is 60 wt% of FFA, it could reduce the FFA content from 7.50 to 0.81 wt%.

However the final FFA content still higher than 0.5 wt% that means the effectiveness of CSTR method is lower than the ultrasonic irradiation method. The researcher had ever run this reactor as a batch type and found that it could reduce FFA to 0.5 wt%, but why a continuous run could not be. It may describe by considering the study of Leevijit et al. (2006) on transesterification of palm oil in series of continuous stirred tank reactors. Leevijit et al. (2006) performed 6 stages CSTRs that it could obtain the same results of the batch or plug flow reactors. The author described that single CSTR could not show the ideal mixing performance as the plug flow reactor because it probably has short cut flow and stagnant zone. So if fully mixing performance is needed, it has to use more than one CSTR. His study used six CSTRs to obtain fully mixing performance as same as a plug flow reactor showing in the Figure 3.27.

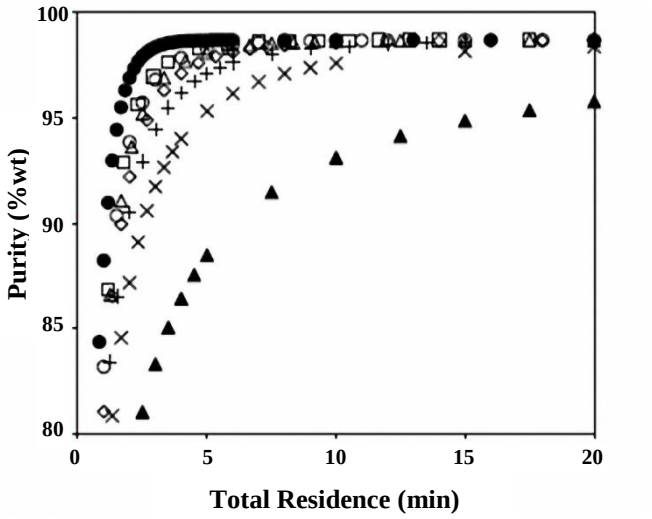

Figure 3.27 Predicted purity for the transesterification of palm oil in series of CSTRs at molar ratio 6:1, temperature 60°C, NaOH concentration 1 wt % of oil; (▲) 1-CSTR; (×) 2-CSTRs; (+) 3-CSTRs; (◊) 4-CSTRs; (Δ) 5-CSTRs; (o) 6-CSTRs; (□) 7-CSTRs; (●) PFR. (Leevijit et al., 2006)

For the CSTR experiments of this research, the reactor contains 3 stages of blades (N_{Re} = 20,249) that can be imagined to 3 series of CSTRs, so mixing condition of the viscous mixture of CPO and ethanol is hardly to be homogeneous mixture. If the complete mixing is needed, it should have many stages of blade. It can be concluded that FFA reduction capacity of ultrasonic esterification of CPO with ethanol is superior to that of esterification by CSTR system. Therefore, to reduce FFA content lower than 0.5 wt% in CSTR should be study further.

For the energy efficiency of the CSTR experiments are 72-78% in range which enormously better than the ultrasonic ones, it is probably caused by a large size of the reactor and good insulation system which can efficiently consume energy.