CHAPTER 5
EXPERIMENT

Palm oil, like other edible oils, is an organic compound which is called a glyceryl ester because each molecule is comprised of a glycerol molecule bonded to a maximum of three fatty acid (carboxylic acid) residues. Each of the three fatty acid groups in palm oil is long chains comprising several carbon atoms (normally 11-19 atoms in length). In the production of palm-oil, there are two crude oil products extracted: one is crude oil from palm fruit fibre and the other is oil from palm fruit kernel. Free fatty acids from these two kinds of oil are normally controlled at 5 wt% but for small palm oil extracting industries, palm oil from the whole fruit is extracted (kernel and fibre). Because palm fruit in this process has to be toasted before extraction takes place, the FFA of the oil produced is usually quite high (typically greater than 10 wt%).

It is difficult to utilize MCPO for making biodiesel by the alkaline transesterification process because the FFA content is too high. In countries where there are large numbers of small oil palm plantations, especially where commercial fuel (petroleum products) is imported, it is essential that farmers should be able to produce their own energy from their own product. For economic reasons, they would prefer to extract palm oil for themselves using the processes generally used in small oil-producing industries. As a consequence, the oil produced by farmers always contains high levels of FFA. There are other potential sources of biodiesel that contain high concentrations of FFA which make them unsuitable for a one-stage transesterification process. These sources include badly stored vegetable oils and waste cooking oils. It follows that there is a need for a simple process for the production of biodiesel from high FFA mixed crude palm oil by a two- stage esterification-transesterification process.

Esterification (the first process) was selected to reduce FFA by converting it into biodiesel or methyl ester (ME). Then glycerides: triglyceride (TG), diglyceride (DG) and monoglyceride (MG) were also converted into ME by transesterification (the second process). For obtaining a large amount of biodiesel in batch process, large size reactor, high energy consumption and high labor cost were required. In addition, the quality of the product in each batch was difficult to control. In order to reduce the

batch process problem; therefore, the continuous process in form of CSTR was investigated because of low investment cost, suitability for liquid-liquid reaction and simply design.

In a brief procedure, estimation of the number and volume of tanks is the first procedure of the continuous reactor. Then the estimation was confirmed by numerical and analytical technique. After that other apparatuses such as decanters, methanol recovery system and washing system were designed. Prior to the fabrication of the system, it was simulated for verifying the competence of system and for investigating the tendency of final product (such as retention time, product components and flow rate). While the system was simulating, it was sketched followed by fabrication. Finally, after acquiring the continuous system for producing biodiesel from MCPO, the performance of this system was tested as followed:

5.1 Materials

Mixed crude palm oil (MCPO) (un-degummed and containing FFA around 16-18 wt%) is used as the feed stock for biodiesel production. It is obtained from a local palm oil mill in Had Yai, Songkhla, Thailand. Sulfuric acid, potassium hydroxide and methanol of 98% purity commercial grade are purchased from a local chemical store in Had Yai, Songkhla, Thailand. Moreover, commercial grades of potassium hydroxide (pelleted), HYDRANAL-coulomat AG No. 34836, and Lewtit® GF202 macroporous cation exchange resin were used.

5.2 Apparatus

The two-stage continuous technology of this study (Figure 5.1 and Appendix D) was used to producing biodiesel from high free fatty acid MCPO (feeding flow rate 50 L/hr). Like the work of Lastella (2005) and of Teall *et al.* (2005), production unit, separator unit, distillation unit were installed in the part of transesterification of this system as shown in Figure 5.2. However, this process proposed to produce biodiesel from high FFA oil though the part of esterification was an adjunct to the aid of generating biodiesel (Figure 5.3). In addition, this thesis focused on cleansing of

biodiesel with dry process. Due to high investment cost, only laboratory scale at 0.6 L/hr of crude biodiesel feeding flow rate as shown in Figure 5.4 was used.

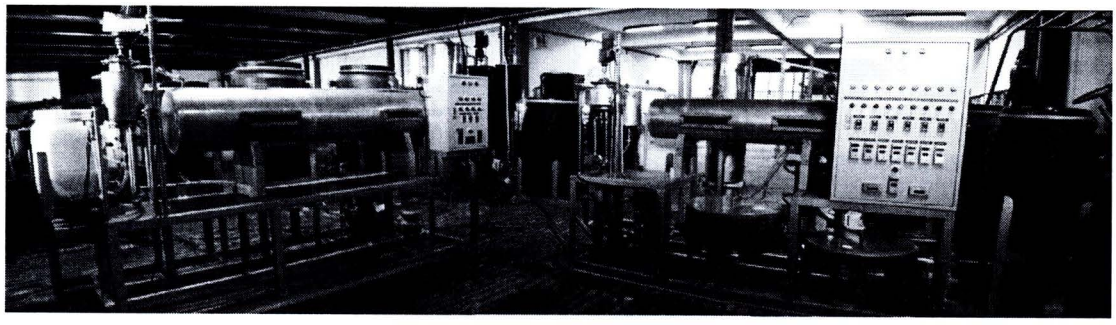
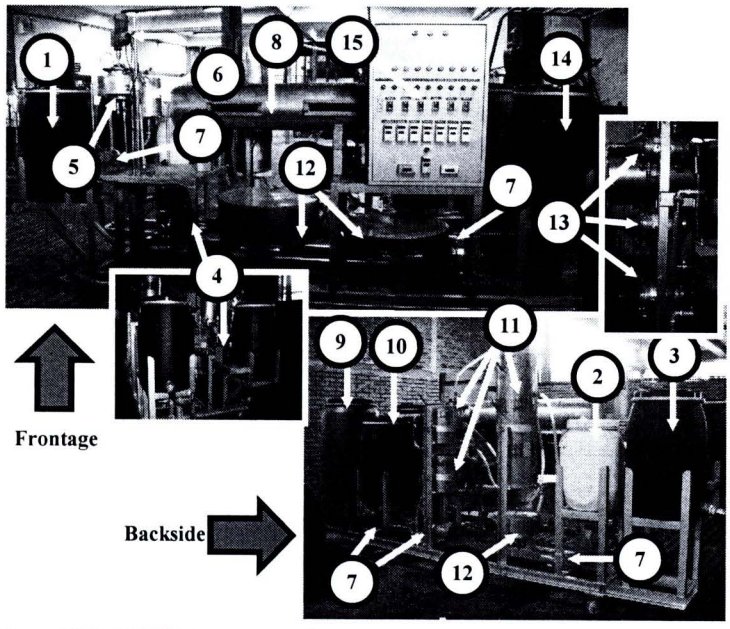
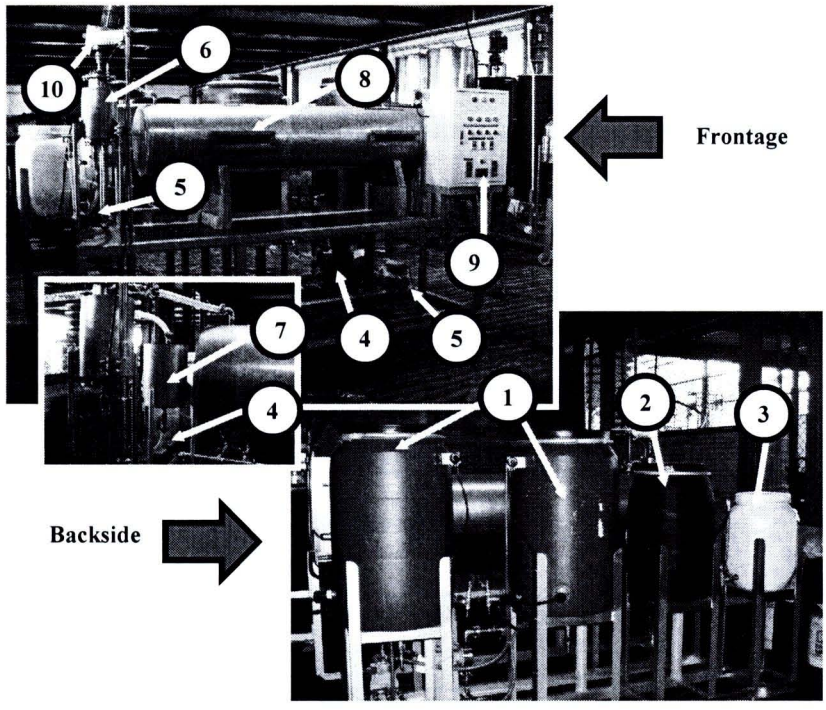


Figure 5.1 Continuous pilot plant for producing biodiesel from MCPO



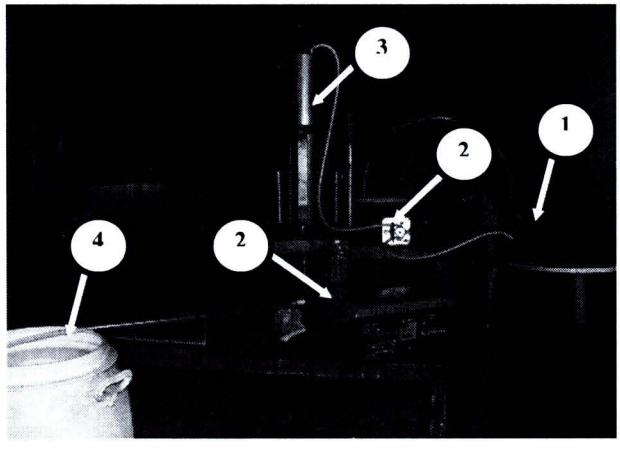
1. De-acidified MCPO storage tank
2. 1st-stage waste solution storage tank
3. Potassium methoxide solution storage tank
4. Metering pump
5. CSTR
6. Hot paraffin oil tank
7. Pump
8. Separate tank
9. Crude biodiesel storage tank
10. Crude glycerol storage tank
11. Distillation tower
12. Re-boiler
13. Condenser
14. Water tank
15. Controller
16. Stirrer motor

Figure 5.2 Transesterification System



1. MCPO storage tank
2. Methanol storage tank
3. Sulfuric acid storage tank
4. Metering pump
5. Pump
6. CSTR
7. Hot paraffin oil tank
8. Separate tank
9. Controller
10. Stirrer motor

Figure 5.3 Esterification system



1. Crude biodiesel storage tank
2. Peristaltic pump
3. Resin column
4. Clean biodiesel storage tank

Figure 5.4 Biodiesel washing system

5.3 Methodology

According the diagram in Figure 5.5, before starting experiments, the oxidation reaction of MCPO was stopped by heating until it reached 60 °C and then adding 0.02 wt% of butylated hydroxytoluene (BHT) as an antioxidant (Food and Drug Administration, 1981).

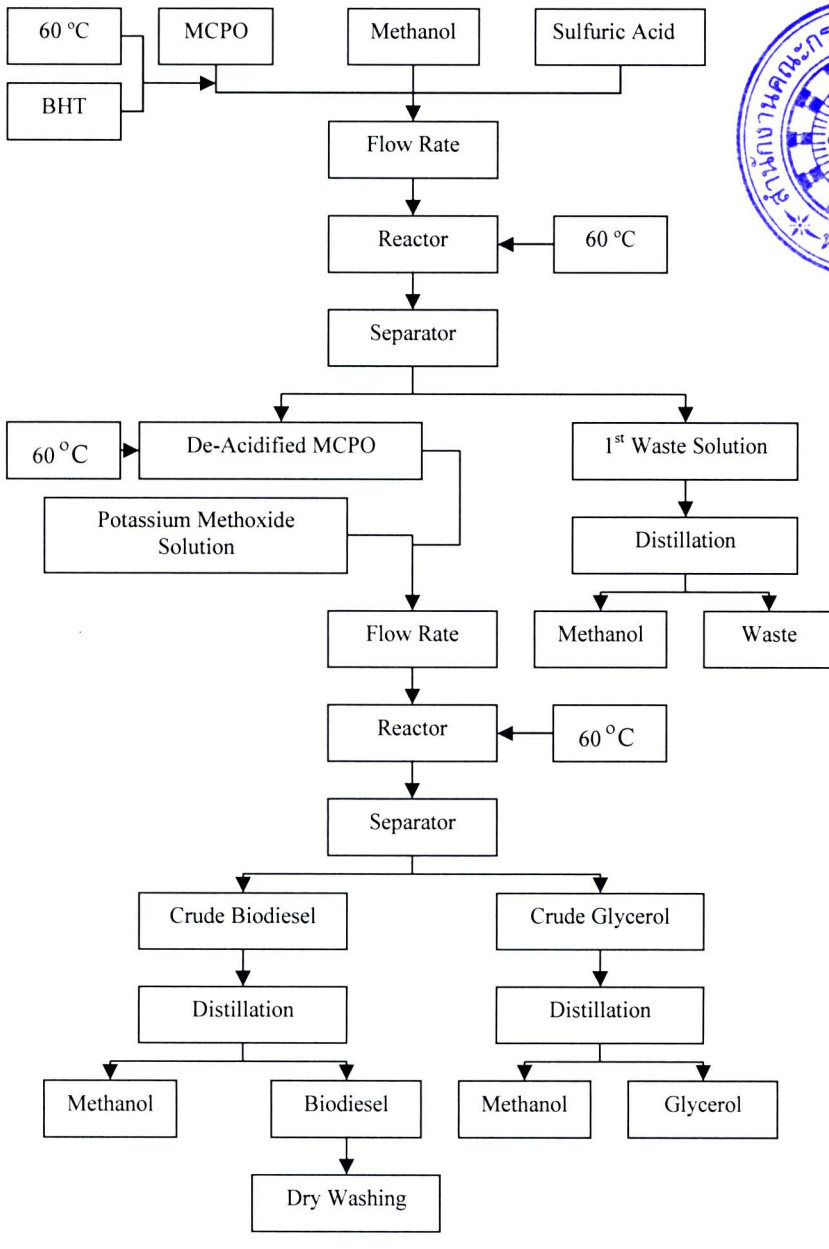


Figure 5.5 Methodology

After that, the flow rate of MCPO, methanol and sulfuric acid was checked and fed into the reactor, which was warmed up by hot paraffin oil (Somnuk, 2008 and Prateepchaikul, 2009). During mixing reactants in the esterification reactor, the temperature of reagent was controlled at 60 °C. After reaching the reaction time, the solution flew to the separated tank. The solution separated into 2 phases: oily phase (top phase) and black phase (bottom phase). Oily phase flew to a de-acidified MCPO storage tank and its temperature at 60 °C was controlled by immerse heater. Simultaneously, the waste solution (black phase) was kept for recovering methanol. Next, acid value content of de-acidified MCPO (oily phase) was checked and then the potassium methoxide solution was prepared. Afterward, the flow rate of de-acidified MCPO and the potassium methoxide solution was checked. Then both solutions were fed into the transesterification reactor which was warmed up and controlled the reaction temperature at 60 °C with hot paraffin oil. Then the solution was released in the separated tank for separating solution into crude biodiesel (top phase) and glycerol (bottom phase) and kept in their storage tank. Methanol in crude biodiesel, glycerol and the first waste solution was recovered. Finally, the recovered crude biodiesel in this process was purified with dry washing process.

5.4 Monitoring

Previous, the composition of the solution was monitoring periodically the two-stage process by Thin Layer Chromatography/ Flame Ionization Detector (TLC/FID), Karl Fischer titration technique, and titration technique. Now, since TLC/FID was broken, only titration techniques were used to progress the reaction. Make certain that the acid-base titration could be used instead of TLC/FID; therefore, the accuracy of them was compared. Figure 5.6 showed that there was no significant difference in FFA analysis. Therefore, only acid-base titration was used to analyze FFA in this investigated. Additionally, the analysis of ME concentration in biodiesel by TLC/FID was replaced with ^{1}H-NMR (in house method refer to WI-RES-NMR and REF-RES-NMR-023 of the Science Equipment Cetre, Prince of Songkla University, Had Yai, Thailand).

When the reaction time reached the requirement, the sample of 50 ml was withdrawn (Somnuk, 2008 and Prateepchaikul, 2009). The sample reaction was stopped

immediately by chilling with 5 °C of cold water (Jansri, 2007) and then freezing in refrigerator. Un-purified samples of the first stage were analyzed the water content by Karl Fischer titration technique. After that, the impurities of samples was removed by washing with 250 ml of hot water (80 °C) in three times (Jansri, 2007) or cleaning until the wasted water reached pH = 7 for protecting the interference of the contaminations in solution during analysis. Finally, cleansed samples were analyzing the concentration of FFA with titration in esterification and the concentration of ME with ^{1}H-NMR in transesterification. The disadvantage of both analysis methods was that the concentration of DG, MG and TG of each sample was not shown. Therefore, the progression of reaction was difficult to monitor. It caused unknown something might have happened during the reaction.

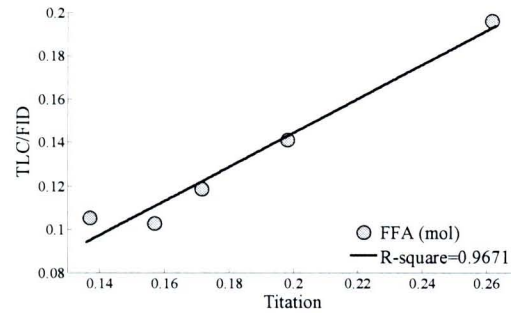


Figure 5.6 Accuracy of analytical method

5.5 Analytical Methods

5.5.1 Acid Value

The acid value of the initial oil and the final product of the first stage were determined by the acid-base titration technique. The sample of 5.6 ml was withdrawn from un-cleaned solution with pipette and then the sample was diluted with 15-20 ml. iso-propanol by using 5 % wt/v of phenolphthalein as an indicator. The solution was titrated with a 0.1 mol/L of KOH solution until the solution reached the end point. The acid value of the sample ratio in gram of potassium hydroxide to litre of oil was determined (applying from Link (1989)).

5.5.2 FFA Content

Although the process for preparing the titrand (analyst) and the titrant (titrator) of FFA analysis was similar to the analysis of acid value, the samples in this method must be weighed. After reaching the end point the mass ratio of FFA were calculated by Equation 5.1.

$$\%FFA = \frac{\text{ml of KOH} \times N \times 27.3}{\text{weight of sample}} \tag{5.1}$$

Where N is concentration of KOH solution (N)

5.5.2 Karl Fischer Titration Technique

Karl Fisher titration technique was used to analyze the water content in each sample. Analysis was performed via Metter Toledo DL39 Karl Fisher coulometer. The external solution was prepared by mixing the weighed sample with the weighed commercial methanol and then the solution was released for separating the solution into two phases: the top phase (the clear solution or the external solution) and the bottom phase (the oily phase). Commercial methanol and the external solution are also determined the water content by titrating with hydranal - coulomat AG No. 34836: Karl Fischer reagent. The mass ratio of water in commercial methanol and the external solution was determined. After that, the mass ratio of water in each sample was calculated with the water content value of both commercial methanol and the external solution.

5.5.3 Physical-Chemical Properties of Biodiesel Production from High Free Fatty Acid MCPO

The final biodiesel production from the suitable condition and some sample, in which physical and chemical properties were determined according to the standard procedures such as ASTM, and EN analyzing by the Science Equipment Cetre, Prince of Songkla University, Had Yai, Thailand.

5.6 Experimental Design

The suitable condition for reducing FFA that contained in MCPO was obtained by using response surface modeling (RSM) in term of central composite design (CCD). Generally, CCD in 2^k factorial term (Equation 5.2) was used for designing the experiment for finding an axle point or star point. For example, if 2 independent variables was used in this experiment, it was found that 2^k factorial factors in normal term consists of (-1, -1), (+1, -1), (-1, +1), (+1, +1) in contrast to in an axle point. 2^k factorial factors in an axle point consist of (-α, 0), (+α, 0), (0, -α), (0, +α) and replicate 4-6 runs in the centre point (Steppan, 1998).

$$\alpha = \sqrt[4]{2^{k_y}} \tag{5.2}$$

5.6.1 Experimental Design for Esterification

The main factors for reducing FFA to less than 1 wt% in esterification process was alcohol (M), catalyst (S), stirrer speed (P) and retention time (T). Therefore, they were used as factors for designing the experiment. CCD is used to design experiment under 4 independent variable 5 parameter levels (-2, -1, 0, 1, 2) and a response as shown the setting in Figure 5.7.

After setting the experiment, the ranks of independent variables in Table 5.1 are assigned by essential experimental design and essential regression as shown the method in Figure 5.8 and the results in Table 5.2 [4 independent variable 5 parameter levels (-2, -1, 0, 1, 2)]. The results indicated that there were 28 runs of each process were experimented as shown in Table 5.3.

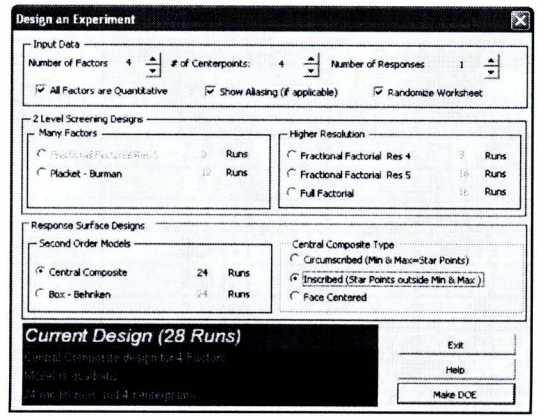


Figure 5.7 Experiment design

Table 5.1 Ranks of independent variables

Independent variables	Ranks of experimental parameters
Esterification	
Methanol (v%)	[10-20]
Sulfuric acid (v%)	[1.0-2.5]
Retention time (min)	[1.5-2.5]
Speed of Stirrer (rpm)	[600-1000]

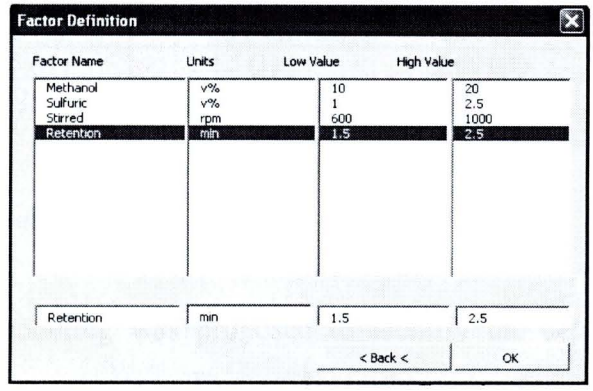


Figure 5.8 Variable assignment

Table 5.2 Independent variables and parameter levels of esterification

Independent variables	Parameter levels				
	-2	-1	0	1	2
Methanol (M) (vol%)	10	15	20	25	30
Sulfuric acid (S) (vol%)	1.0	1.5	2.0	2.5	3.0
Retention time (T) (min)	1.75	2.00	2.25	2.50	2.75
Speed of Stirrer (P) (RPM)	400	600	800	1000	1200

Table 5.3 Esterification experimental design

Experiments	Methanol (vol %)	Sulfuric acid (vol %)	Retention time (min)	Speed of stirrer (RPM)
1	20 (0)	1.0 (-2)	2.25 (0)	800 (0)
2	20 (0)	2.0 (0)	1.75 (-2)	800 (0)
3	25 (1)	1.5 (-1)	2.00 (-1)	600 (-1)
4	15 (-1)	2.5 (1)	2.50 (1)	600 (-1)
5	25 (1)	2.5 (1)	2.50 (1)	600 (-1)
6	20 (0)	2.0 (0)	2.25 (0)	800 (0)
7	20 (0)	2.0 (0)	2.25 (0)	400 (-2)
8	30 (2)	2.0 (0)	2.25 (0)	800 (0)
9	20 (0)	2.0 (0)	2.75 (2)	800 (0)
10	25 (1)	1.5 (-1)	2.00 (0)	1000 (1)
11	15 (-1)	1.5 (-1)	2.00 (0)	600 (-1)
12	20 (0)	2.0 (0)	2.25 (0)	800 (0)
13	15 (-1)	1.5 (-1)	2.50 (1)	1000 (1)
14	25 (1)	1.5 (-1)	2.50 (1)	600 (-1)
15	15 (-1)	1.5 (-1)	2.50 (1)	600 (-1)
16	20 (0)	2.0 (0)	2.25 (0)	1200 (2)
17	25 (1)	2.5 (1)	2.50 (1)	1000 (1)
18	25 (1)	2.5 (1)	2.00 (-1)	600 (-1)
19	15 (-1)	2.5 (1)	2.00 (-1)	1000 (1)
20	25 (1)	2.5 (1)	2.00 (-1)	1000 (1)
21	15 (-1)	2.5 (1)	2.50 (1)	1000 (1)
22	15 (-1)	1.5 (-1)	2.00 (-1)	1000 (1)
23	10 (-2)	2.0 (0)	2.25 (0)	800 (0)
24	20 (0)	2.0 (0)	2.25 (0)	800 (0)
25	25 (1)	1.5 (-1)	2.50 (1)	1000 (1)
26	15 (-1)	2.5 (1)	2.00 (-1)	600 (-1)
27	20 (0)	2.0 (0)	2.25 (0)	800 (0)
28	20 (0)	3.0 (2)	2.25 (0)	800 (0)

5.7 Regression Model

Response surface modeling was proposed to identify the detailed dependence of different factors on a response. This study fairly convinced that all factors were important and the response regression model was indicated in the term of a full quadratic model which was computed by the multiple regression technique under 95 % of coefficient confidence intervals as shown in Equation 5.3 (Steppen, 1998).

$$y = \beta_0 + \sum_{i=1}^{k_y} \beta_i x_i + \sum_{i<j=1}^{k_y} \beta_{ij} x_i x_j + \sum_{i=1}^{k_y} \beta_{ii} x_i^2 \qquad (5.3)$$

After getting the regression model, P-value and F-test was be used for getting rid of no significant parameter. Finally, the complete regression model was used for plotting

response surface graph and presenting the relation between response and independent variables by contour graph (Somnuk, 2008).

5.8 Results and Discussion

5.8.1 Testing the Distribution of Reaction Time within the Reactor

Somnuk (2008) and Ruangying (2002) suggested that before testing the performance of continuous reactor, the distribution of reaction time should be investigated. Hence, this experiment was investigated the reaction time distribution for confirming the results of Somnuk (2008), and Ruangying (2002). There were 6 conditions set by RSM [experiment number (condition number) 11 (1), 13 (4), 15 (3), 19 (6), 22 (2) and 26 (5)] were selected as a case study of the retention time distribution in esterification reactor as shown condition in Table 5.3.

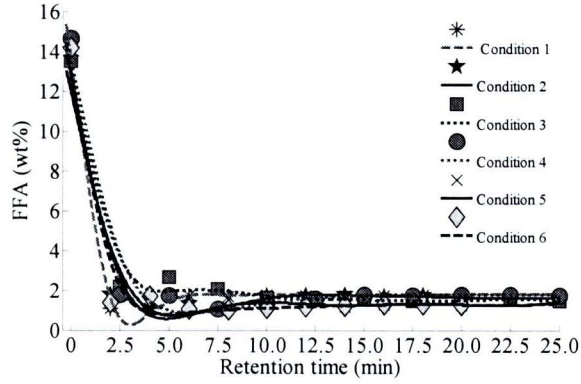


Figure 5.9 The distribution of reaction time within the esterification continuous reactor

The results as shown in Figure 5.9 indicated that FFA of all condition was reduced rapidly around 2.5-6.0 min. Due to effecting of mixing intensity, the concentration of FFA, then, decreased and formed steadily. All reactions had been a steady state about 10 min which were similar to the distribution of retention time of Somnuk (2008) and Ruangying (2002) experiment. Moreover, like FFA reduction, ME concentration was speedy increased in first 5 min and then go to equilibrium as shown in Figure 5.10.

Reactants should be allowed to react in process around 20 min for making sure that the reactants in transesterification r

eactor were mixed well. Therefore, the sample of FFA reduction and ME production should be start keeping around 12 and 24 min until the reaction reached the requirement time.

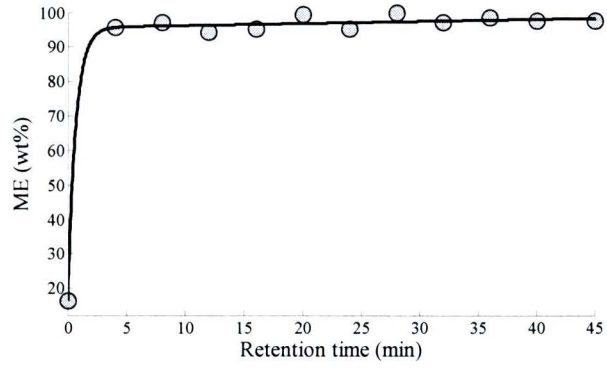


Figure 5.10 The distribution of reaction time within the transesterification continuous reactor

5.8.2 Multiple Regression Analysis Model of Esterification

The results (Table 5.4) were used for estimating the optimization of 50 L/hr continuous esterification reactor for reducing FFA in MCPO by multiple regression analysis model (Appendix F). After computation, the equation in term of full quadratic polynomial was obtained as shown in Equation 5.4 and Table 5.5 was shown theirs statistic. Under the coefficients confidence intervals at 95 %, statistic of Equation 5.4 indicated that $R^2 = 0.986$ and $R^2_{adjusted} = 0.971$. Although the value of R^2 was rather similar to $R^2_{adjusted}$, some factor had P-vale more than 0.05. Therefore, P-value was considered the significant factors again. According the statistic, the significant factors must be had P-value to less than 0.05, so some factor in Equation 5.4 was eliminated.

$$FFA = \beta_0 + \beta_1(M) + \beta_2(S) + \beta_3(T) + \beta_4(P) + \beta_5(M^2) + \beta_6(S^2) + \beta_7(T^2) + \beta_8(P^2) + \beta_9(MS) + \beta_{10}(MT) + \beta_{11}(MP) + \beta_{12}(ST) + \beta_{13}(SP) + \beta_{14}(TP) \quad (5.4)$$

Table 5.4 Esterification results

Experiments	Methanol (%vol/vol)	Sulfuric acid (%vol/vol)	Retention time (min)	Stirrer speed (RPM)	FFA (%wt/wt)
1	20 (0)	1.0 (-2)	2.25 (0)	800 (0)	1.413
2	20 (0)	2.0 (0)	1.75 (-2)	800 (0)	1.074
3	25 (1)	1.5 (-1)	2.00 (-1)	600 (-1)	0.969
4	15 (-1)	2.5 (1)	2.50 (1)	600 (-1)	1.349
5	25 (1)	2.5 (1)	2.50 (1)	600 (-1)	1.032
6	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
7	20 (0)	2.0 (0)	2.25 (0)	400 (-2)	1.154
8	30 (2)	2.0 (0)	2.25 (0)	800 (0)	1.155
9	20 (0)	2.0 (0)	2.75 (2)	800 (0)	1.154
10	25 (1)	1.5 (-1)	2.00 (0)	1000 (1)	1.028
11	15 (-1)	1.5 (-1)	2.00 (0)	600 (-1)	1.761
12	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
13	15 (-1)	1.5 (-1)	2.50 (1)	1000 (1)	1.773
14	25 (1)	1.5 (-1)	2.50 (1)	600 (-1)	0.991
15	15 (-1)	1.5 (-1)	2.50 (1)	600 (-1)	1.507
16	20 (0)	2.0 (0)	2.25 (0)	1200 (2)	1.151
17	25 (1)	2.5 (1)	2.50 (1)	1000 (1)	1.066
18	25 (1)	2.5 (1)	2.00 (-1)	600 (-1)	1.058
19	15 (-1)	2.5 (1)	2.00 (-1)	1000 (1)	1.252
20	25 (1)	2.5 (1)	2.00 (-1)	1000 (1)	0.943
21	15 (-1)	2.5 (1)	2.50 (1)	1000 (1)	1.331
22	15 (-1)	1.5 (-1)	2.00 (-1)	1000 (1)	1.709
23	10 (-2)	2.0 (0)	2.25 (0)	800 (0)	2.159
24	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
25	25 (1)	1.5 (-1)	2.50 (1)	1000 (1)	0.952
26	15 (-1)	2.5 (1)	2.00 (-1)	600 (-1)	1.277
27	20 (0)	2.0 (0)	2.25 (0)	800 (0)	0.870
28	20 (0)	3.0 (2)	2.25 (0)	800 (0)	1.061

Table 5.5 Regression coefficients and statistics of Equation 5.4

Terms	Regression coefficients	P-value	Std Error
Intercept			
B_0	15.190	9.406×10^{-8}	1.437
Linear			
B_1	-0.436	1.071×10^{-8}	3.437×10^{-2}
B_2	-2.757	2.171×10^{-6}	0.344
B_3	-4.827	1.220×10^{-4}	0.894
B_4	-2.85×10^{-3}	5.540×10^{-3}	8.590×10^{-4}
Quadratic			
B_5	7.600×10^{-3}	3.081×10^{-10}	4.490×10^{-4}
B_6	0.340	4.093×10^{-6}	4.489×10^{-2}
B_7	0.867	3.290×10^{-4}	0.180
B_8	1.594×10^{-6}	7.513×10^{-5}	2.806×10^{-7}
Interaction			
B_9	4.250×10^{-2}	3.247×10^{-6}	5.500×10^{-3}
β_{10}	4.110×10^{-3}	0.714	1.100×10^{-2}
β_{11}	-1.452×10^{-5}	0.310	1.374×10^{-5}
β_{12}	0.246	4.333×10^{-2}	0.110
β_{13}	-2.240×10^{-4}	0.127	1.370×10^{-4}
β_{14}	4.710×10^{-4}	0.110	2.750×10^{-4}

$R^2 = 0.986$, $R^2_{adjusted} = 0.971$

After removal the insignificant factors, the new equation as shown in Equation 5.5 and shown it's statistic in Table 5.7 (R^2 = 0.979, $R^2_{adjusted}$ = 0.966, P-value < 0.05 under the coefficients confidence intervals at 95 %).

$$FFA = \beta_0 + \beta_1(M) + \beta_2(S) + \beta_3(T) + \beta_4(P) + \beta_5(M^2) + \beta_6(S^2) + \beta_7(T^2) + \beta_8(P^2) + \beta_9(MS) + \beta_{10}(MT) \quad (5.5)$$

After that, Equation 5.5 was considered with F-test again. The results indicated that Equation 5.5 had F-value at 77.84 (Appendix F), which was greater than F-critical as shown in Appendix G. Hence, Equation 5.5 could be used for calculating the optimization of this reactor. Finally, equation 5.5 and independents variables (the amount of methanol and sulfuric acid, speed of stirrer and retention time) were used for creating contours as shown in Figure 5.11 -5.16. The investigation indicated that the amount of methanol and sulfuric acid, speed of stirrer and retention time were also impact on FFA reduction (considering for P-value in Table 5.6). The amount of methanol had strong influence on the FFA reduction because it had the lowest P-value.

Table 5.6 Regression coefficients and statistics of Equation 5.5

Terms	Regression coefficients	P-value	Std Error
Intercept			
B_0	14.740	2.775×10^{-9}	1.314
Linear			
B_1	-0.438	6.037×10^{-13}	2.288×10^{-2}
B_2	-2.936	2.048×10^{-7}	0.352
B_3	-4.368	1.600×10^{-4}	0.906
B_4	-2.530×10^{-3}	7.622×10^{-5}	4.890×10^{-4}
Quadratic			
B_5	7.600×10^{-3}	1.553×10^{-11}	4.850×10^{-4}
B_6	0.340	2.130×10^{-6}	4.851×10^{-2}
B_7	0.867	3.370×10^{-4}	0.194
B_8	1.594×10^{-6}	6.405×10^{-5}	3.032×10^{-7}
Interaction			
B_9	4.250×10^{-2}	1.615×10^{-6}	5.940×10^{-3}
B_{10}	0.246	5.385×10^{-2}	0.119

R^2 = 0.979, $R^2_{adjusted}$ = 0.966, P-value < 0.05

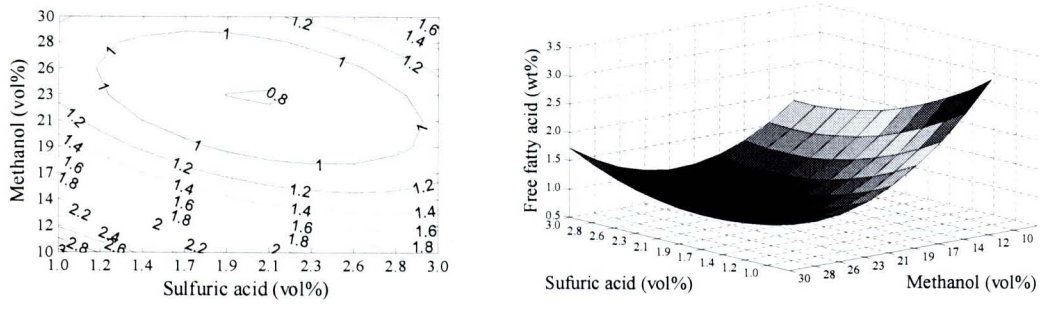


Figure 5.11 The FFA reduction contour and surface are of the relationship between the amount of methanol and the amount of sulfuric acid in unit of wt%

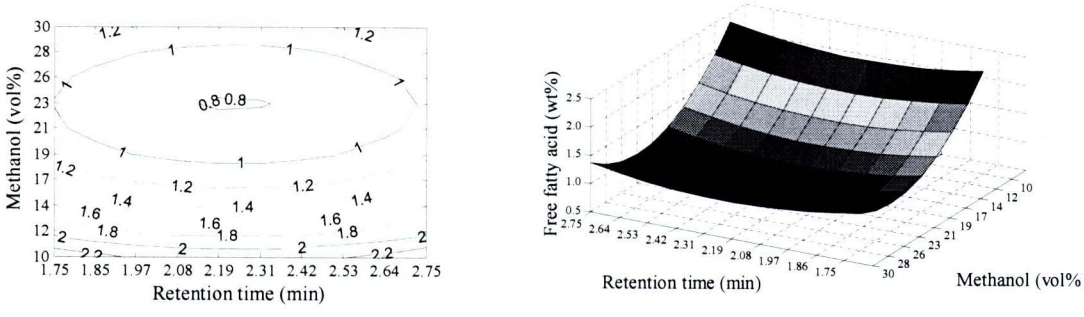


Figure 5.12 The FFA reduction contour and surface are of the relationship between the amount of methanol and retention time in unit of wt%

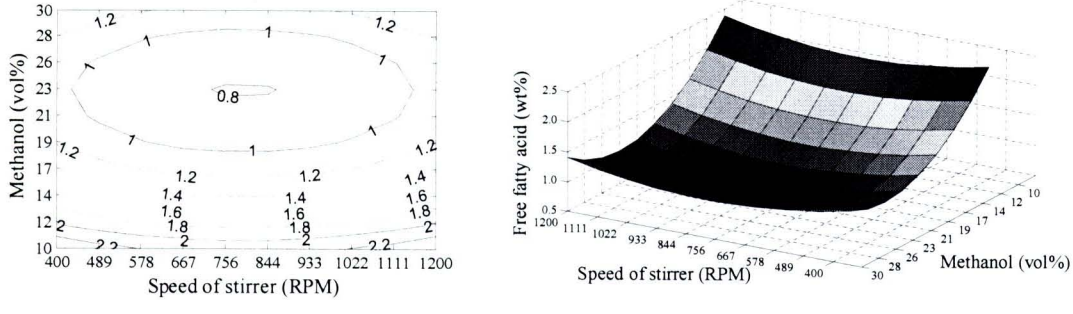


Figure 5.13 The FFA reduction contour and surface area of the relationship between the amount of methanol and speed of stirrer in unit of wt%

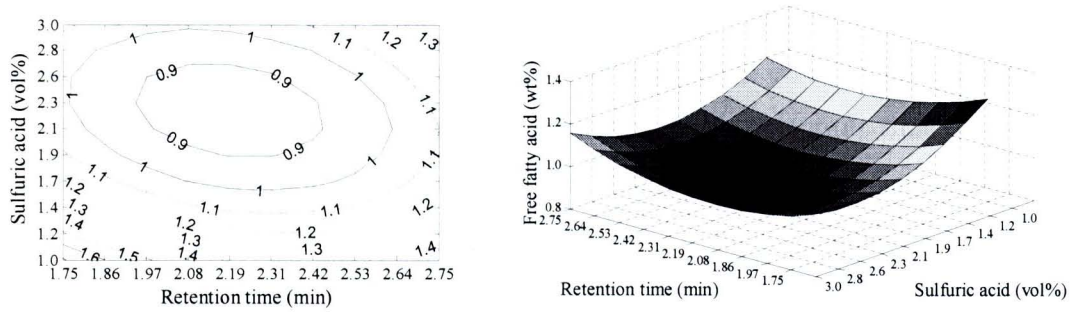


Figure 5.14 The FFA reduction contour and surface area of the relationship between the amount of sulfuric acid and retention time in unit of wt%

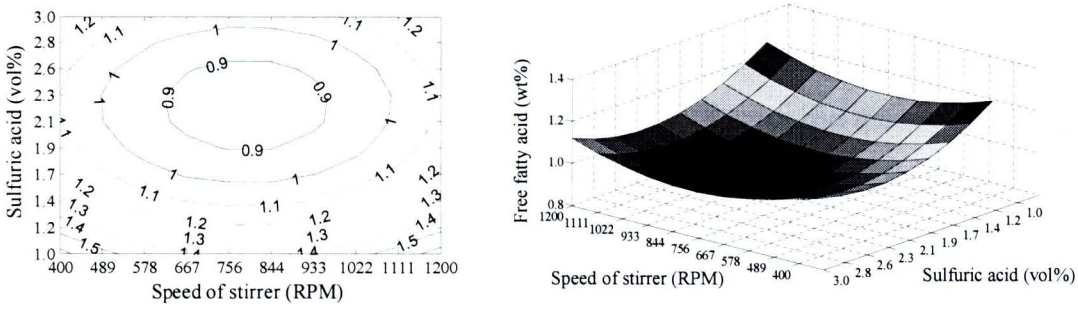


Figure 5.15 The FFA reduction contour and surface are of the relationship between the amount of sulfuric acid and speed of stirrer in unit of wt%

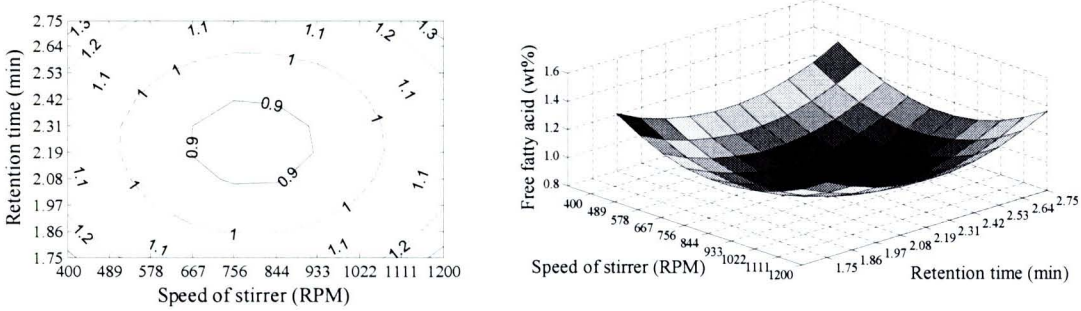


Figure 5.16 The FFA reduction contour and surface are of the relationship between retention time and speed of stirrer in unit of wt%

In addition, methanol was main reagent which was necessary for driving the forward reaction to obtain the highest yield of the product according to Le Châtelier's Principle (Brown et al., 2003). Moreover, P-value of retention time indicated that it

had a little effect on the FFA treatment due to using high volume of methanol, volume of sulfuric and speed of stirrer which caused the reaction to go to equilibrium rapidly. On the other hand, if low speed of stirrer was used, retention time had strong influence on the reduction of FFA as could see the result in thesis of Somnuk (2008).

5.8.3 Optimization for Reducing FFA in MCPO with Esterification Continuous Reactor

The results, which was predicted from the Multiple Regression Analysis Model as shown the contour Figure 5.11-5.16, indicated that the continuous reactor of esterification could be reduced FFA from 16-18 wt% to 0.870 wt%. The optimum condition for reducing FFA to less than 1 wt% was used methanol of 23.04 v% and sulfuric acid of 2.07 v% under the retention time of 2.22 min and the speed of stirrer of 793 rpm. Actually, the efficiency of the reactor was lower than the design around 10 %. The reason was that MCPO of this work was contained FFA higher than the design about more than 30%. Moreover, the analytical method of two works was different. The results of FFA reduction from TLC/FID were used in design but from acid-base were used in RSM. That might cause to be predicted the optimal condition in error. However, it was found that a little bit error occurred when TLC/FID and titration analyzed results as shown in 5.6 were compared. Thus, the analytical method was not the main reason to make an error in design and actual work. In fact, the concentration of FFA in MCPO was the main problem in calculation. Therefore, the flow rate of MCPO at 45 L/hr was offered to use for operating the optimization of FFA reduction in full system.

5.8.4 Operation of the Two-Stage Process in Full System

Beginning, the esterification continuous system was verified under the optimal condition as shown in an above discussion. The results in Figure 5.17 indicated that FFA could be reduced from 18 wt% to less than 0.908 wt% and water was appeared around 1 wt% on average. That was the reduction of FFA reached the requirement which was assigned in the objective of thesis.

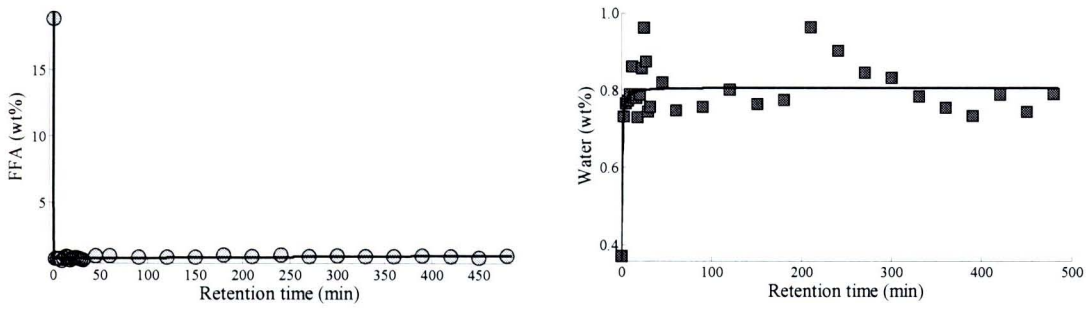


Figure 5.17 Verification the optimization for reducing FFA (Appendix H)

After reaching the reaction, its product was then continuous transferred to the decanter in order to separate waste from oily solution which caused to protect the high consumption of alkali catalyst and the soap formation in the next process. During transferring the product to the decanter, the sample was withdrawn for analyzing acid value and water content of it. The results in Figure 5.18 indicated that the acid value more than 20 g KOH/ L of oil was contained in the product owing to including the acid value of H_2SO_4. Moreover, approximately 1.482 wt% of water was obtained in sample. After the product was reached the separation by gravity, final product found that the acid value and water contained lower than the initial one around 88 and 75 % respectively. Moreover, 40 L/hr of oily solution yield and 15 L/hr of waste solution yield were obtained approximately.

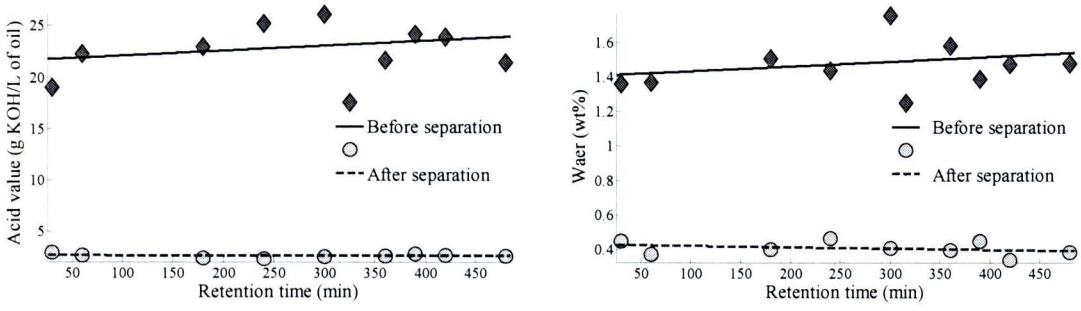
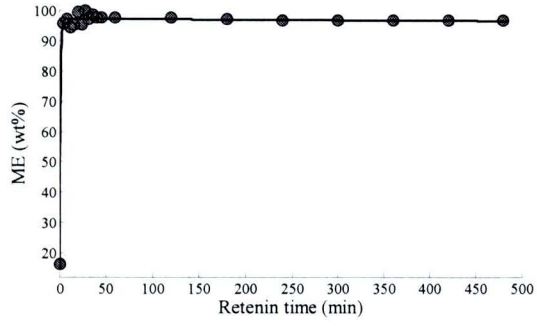


Figure 5.18 Acid value before and after separation by esterification decanter (Appendix H)

In addition, 4.17 hr was spent on the separation time of this work which was higher than the separation time in design around 10 wt% because of the change of the flow rate of MCPO.

After obtaining the treated oil from the first-stage, the continuous system of transesterification was starting to produce biodiesel. However, this work proposed to check on the system operation, so only one condition was offered. The oily solution (de-acidified MCPO) obtained from the esterification was analyzed acid value and then heated until it reached 60°C. While oil was warming up, potassium methoxide solution was prepared by using 12.60 g/L of oil of potassium hydroxide (acid value and catalyst (1.0 wt% of potassium hydroxide)) and 24 vol % of methanol. For reducing the space of the retention time of esterification system to combine with transesterification system, the flow rate of oily solution in transesterification should be equal to esterification. Therefore, oily solution at the feeding flow rate of 45 L/hr was used to operate the biodiesel production. In addition, 10.72 L/hr of potassium methoxide solution feeding flow rate was used under similar in the speed of stirrer to esterification condition.



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ห้องสมุดงานวิจัย

Figure 5.19 Methyl ester production under the condition of 45 L/hr of oily solution, 10.72 L/hr of potassium methoxide solution, 793 rpm of stirrer speed and 60 °C of reaction temperature

The results that were analyzed by ^{1}H-NMR as shown in Figure 5.19 indicated that the reactor can be produce biodiesel to more than 97.68 wt% on average. Make certain that the biodiesel production reached the requirement, final produce was verified according to the standard procedures of ASTM, and EN by the Science Equipment

Cetre, Prince of Songkla University, Had Yai, Thailand, again as show the results and discussion later.

Then the product was continuous transferred to transesterification decanter. It was found that the product was gravitational separation completed in 60 min. In addition, the yield of crude biodiesel around 43 L/hr and of glycerin around 12 L/hr was obtained. Afterward, the separated biodiesel was sent to the Science Equipment Cetre for analyzing ME and GL concentration. The results shown that 96.62 wt% of ME and 0.56 wt% of free glycerin was obtained in crude biodiesel. It meant that the decanter could be separated glycerin out of product quite achievement. Next, both products were transferred to their storage tanks.

The 1st-stage waste solution, crude biodiesel and crude glycerin which were kept in their storage tank were used as a feed stock in methanol recovery. Since full system was operated in only two times; therefore, the amount of product and by-product was not enough to operate all conditions that had been arranged by RSM. For that reason, only one condition was used to test for recovering methanol from them.

Before starting to recover methanol, the initial methanol that contained in each sample was analyzed. The results indicated that a large amount of methanol was contained in 1st-stage waste solution, crude glycerin and crude biodiesel, respectively. Beginning, the feeding flow rate of initial feed stocks was set on 1.20 L/hr of 1st- stage waste solution, 40 L/hr of crude biodiesel and 10 L/hr of crude glycerin. Next, 65°C, 70°C and 65°C were set according to simulation in distillation tower of 1st-stage waste solution, crude biodiesel and crude glycerol, respectively. Finally, the re-boiler of 1st-stage waste solution, crude biodiesel and crude glycerol was set on 105°C, 165°C and 165°C, respectively.

The results in Figure 5.20 indicated that small amount of methanol remained in crude biodiesel and crude glycerin when they were throughout the process around 3 hr. Due to large amount of methanol contained in 1st-stage waste solution that caused more time was spent to recover methanol. Recovery methanol system indicated that 4.5 L/hr of methanol in total (10 % of total methanol using in system) could be recovered under the purity of 85 %.

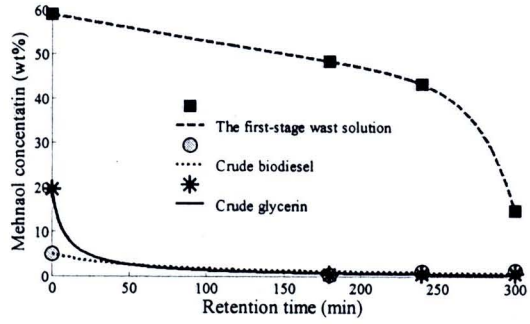

Figure 5.20 Methanol content during distillation

Finally, distilled crude biodiesel was cleansed with Lewtit resin under crude biodiesel feeding flow rate of 0.6 L/hr and analyzed its properties. The results in Table 5.7 were indicated that the properties of biodiesel were not succeeded in the requirement of both biodiesel standard that enacted in the Royal Gazette of Department of Energy Business (2006 and 2009). The reason was that the properties crude biodiesel (Table 5.7) before passing through the Lewtit GF202 column was not achieved in the requirement of Bayer Thai Co., Ltd. (Ion Exchange Resins Group) (GL < 0.15 wt%, soap < 0.05 wt%, water < 0.05 wt%, MeOH < 0.10 wt% and salt < 0.10 wt%).

Therefore, the purification of biodiesel under Suwanmanee technique (2006) was took the place of dry washing technique. The results showed that its properties reached only adequate qualities of biodiesel standard for agriculture engine. As a result of lower ME concentration, high water remainder, high acid number and high DG concentration containing in biodiesel, that caused the biodiesel was not succeeded in the requirement of commercial biodiesel standard. The reason was that the optimization of transesterification (the amount of reagent, the reaction time and the speed of stirrer) was not investigated casing could not be promoted the completed reaction. Therefore, the concentration of ME and of DG was not reached the biodiesel standard. For solving this problem, the optimization of transesterification should be study again.

Table 5.7 Properties of biodiesel production

Parameters	Corresponding Value				
	Commercial Biodiesel	Biodiesel for Agricultural Engine	Crude Biodiesel	Cleaned Biodiesel (Resin)	Cleaned Biodiesel (Water)
Methyl Ester (%wt)	≥ 96.5		92.08	91.18	95.70
Density at 15°C (kg/m^3)	≥ 860 and ≤ 900	≥ 860 and ≤ 900	879.8	878.7	877.2
Viscosity at 40°C (cSt)	≥ 3.5 and ≤ 5	≥ 1.9 and ≤ 8	4.92	4.78	4.59
Flash point (°C)	≥120	≥ 120	71	55	162
Sulphur (%wt)	≤ 0.0010	≤ 0.0015	-	-	-
Carbon Residue, on 10 % distillation residue (%wt)	≤ 0.30	-	0.27	0.15	0.047
Cetane Number	≥ 51	≥ 47	-	-	-
Sulfated Ash (%wt)	≤ 0.02	≤ 0.02	0.27	0.04	0.0093
Water (%wt)	≤ 0.050	-	0.146	0.135	0.118
Total Contaminate (%wt)	≤ 0.0024	-	0.0066	0.0005	0.0002
Water and Sediment (%vol)	-	≤ 0.2	-	-	-
Copper Strip Corrosion	≤ Number 1	≤ Number 3	Number 1	Number 1	Number 1
Oxidation Stability at 110°C (hours)	≥ 10	-	4.47	1.08	10.28
Acid Value (mg KOH/g)	≤ 0.50	≤ 0.80	0.34	0.37	0.61
Iodine Value (g iodine /100g)	≤ 120	-	47.93	51.85	47.2
Linolenic Acid Methyl Ester (%wt)	≤ 12.0	-	0.33	0.32	0.1
Methanol (%wt)	≤ 0.20	-	0.41	0.11	< 0.20
Monoglyceride (%wt)	≤ 0.80	-	0.96	0.83	0.56
Diglyceride (%wt)	≤ 0.20	-	0.68	0.67	0.61
Triglyceride (%wt)	≤ 0.20	-	0.19	0.23	0.13
Free Glycerin (%wt)	≤ 0.02	≤ 0.02	0.46	0.02	0.00047
Total Glycerin (%wt)	≤ 0.25	≤ 1.50	0.86	0.35	0.24
Group I metals (Na+K) mg/kg	≤ 5.0	-	-	-	-
Group II metals (Ca+Mg) mg/kg	≤ 5.0	-	-	-	-
Phosphorus (%wt)	≤ 0.0010	-	-	-	-
Colour	-	Purple	-	-	-
Additive	-	According to Department of Energy Business	-	-	-

Moreover, large amount of KOH was used in this condition as a result of being in difficulty to eradicate alkali by cleaning according to the step of Suwanmanee purifiction. Thus, in the first step, acidic water was spray on the surface of crude biodiesel and then cleansing biodiesel following the second step of Suwanmanee technique. Although KOH was eliminated from biodiesel, some acid was still remained in it that meant 4 times of biodiesel washing were not enough to eliminate acid from biodiesel. For preventing the raising of acid number, the consumption of alkali catalyst in biodiesel production should be reduced and/or the step of purification should be increased.

Finally, after cleaning biodiesel, it was found that some water was suspended in it. Therefore, prior to consumption biodiesel, remained waster must be removed from biodiesel. Beginning, cleansed biodiesel was heated until the temperature of biodiesel was reached 80°C around 30 min in order to get rid of water contamination. Then, biodiesel was released overnight in un-cover vessel for cooling down until it reached the ambient temperature. After that water which was deposited at the bottom was drained. The analyzed result indicated that high water still remained in biodiesel. The reason was that during to be bottled biodiesel into container as an analyzed sample, some water may be mixed in the biodiesel.

The yield of biodiesel after washing with water was found that 75.06% of biodiesel based on initial MCPO (84.44% of biodiesel based on acidified MCPO) was obtained. Although during treatment FFA and producing ME, some oil was lost during separation, it was lost lower than during purification. The reason was that large amount of KOH was used in transesterification; therefore, some biodiesel could be promoted the emulsion. When the waste water was drained some biodiesel in the form of emulsion was also drained that may cause this process obtain lower yield of biodiesel.

5.8.5 Estimation the Biodiesel Production Cost

Cost of raw material, chemical reagents and public utility, except for fabricated cost and labor cost were used for estimating the biodiesel cost in this investigated. All of unit variable costs as shown in Table 5.8 were obtained from experiments. The result

showed that the price of biodiesel depended on the price of MCPO and MeOH. At this time, the price of MCPO and petroleum was increased that caused its price was higher than petro-diesel. For reducing the price of biodiesel, producers should be extract palm oil for themselves using the processes generally used in small oil-producing industries. Moreover, for reducing the biodiesel investment cost, recovered methanol should be as an initial reagent in esterification.

Table 5.8 Unit variation cost and the estimation cost of biodiesel production based on initial MCPO

Variable cost	Unit cost (THB)	Amount	Cost/hr (THB)	Cost/yield (THB/L)
Raw material*				
- MCPO (L)	32	45.00	1440.00	42.67
Chemical reagents*				
- MeOH (L)	20.00	16.14***	322.80	9.56
- H_2SO_4 (L)	38.15	0.93	35.48	1.05
- KOH (kg)	99.30	0.013	1.29	0.04
Public utility**				
- Electricity (kwh)	3.107	38.40	119.31	3.53
- Water (L)	0.00163	75.00	0.12	0.01
Total (THB)			**1919.00**	**56.86**

Note:

* Price including VAT 7% and transportation cost

** The rate of household used of Thailand

*** Excluding recovered MeOH

5.9 Conclusions

- The optimum condition for reducing FFA (16-18 wt%) to less than 1 wt% was used methanol of 23.04 v% and sulfuric acid of 2.07 v% under the retention time of 2.22 min and the speed of stirrer of 793 rpm. After separating solution, the yield oily solution and waste solution were obtained approximately at 40 and 15 L/hr, respectively.

- The concentration of biodiesel at 97.68 wt% (analyzed by ^{1}H-NMR) having yield around 43 L/hr and of glycerin around 12 L/hr was obtained under the test operated condition of 45 L/hr of oily solution, 10.72 L/hr of potassium methoxide solution under the retention time of 4 min, 793 rpm of stirrer speed and 60 °C of reaction temperature.

- The yield of recovered methanol in the purity of 85% was obtained around 4.5 L/hr of methanol in total (10 % of total methanol using in system).

- Due to crude biodiesel having initial concentration such as MeOH, GL and water higher than the limitation of the requirement of Bayer Thai Co., Ltd. (Ion Exchange Resins Group), the cleansed biodiesel was not achieved in Thailand biodiesel standard. Therefore, washing biodiesel with Suwanmanee technique was used instead of resin ion-exchange technique.

- The final yield of biodiesel was found that 75.06% of biodiesel based on initial MCPO (84.44% of biodiesel based on acidified MCPO) was obtained when 45 L of MCPO, 16.14 L of MeOH, 0.93 L of H_2SO_4. 0.013 kg of KOH were used in an hour. In addition, 38.40 kwh of electricity and 75 L of water were also used.

- The price of biodiesel that generate by this step was higher than petro-diesel because its price was depended on the price of MCPO and petroleum. Therefore, producers should be extract palm oil for themselves and the methanol distillation system should be investigated again.

- The efficiency of the two-stage continuous process in full system was lower than the design around 10 %.