CHAPTER 4
SIMULATION FOR VERIFICATION THE DESIGN OF TWO-STAGE CONTINUOUS SYSTEM

Normally, simulation is used (prior to start the chemical laboratory) to study the competence of system and the tendency of final product (such as retention time, product components and flow rate) for verifying the settle of experiments, which can reduce the experimental failure, and help to cut down the laboratory experiments and the operating of pilot plant (Fogler, 2002). In addition, the comparison between experimental data and simulation data is required for increasing the high quality of published paper. The ASPEN PLUS Simulation Engine, a commercial program, is used for estimating the biodiesel production from MCPO having high FFA by using the two-stage continuous process because it is suitable for using to simulate the chemical reaction and easy to input, and verify the information.

4.1 Physical Properties of ASPEN PLUS Simulation Engine

4.1.1 ASPEN PLUS Main Window

In the main window, title bar, menu bar, toolbar, process flow sheet window, selection bottom of the steam type, and model library are showed. The process flow sheet window is used to create, and to display simulation flow sheets and drawings. The model library at the bottom of the main window employs in selecting unit operation models and icons by placing on the flow sheet.

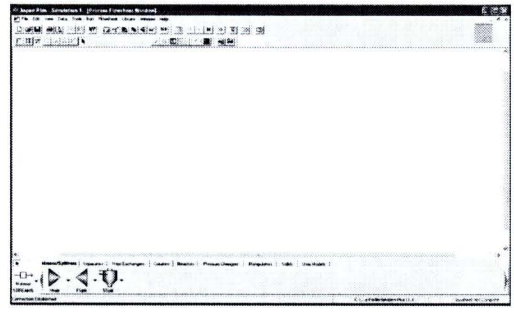

Figure 4.1 ASPEN PLUS Main Window

4.1.2 Setup

The required input specifications are entered in order of setting up the global simulation and of accounting options for running the flow sheet as shown in Figure 4.2 and 4.3.

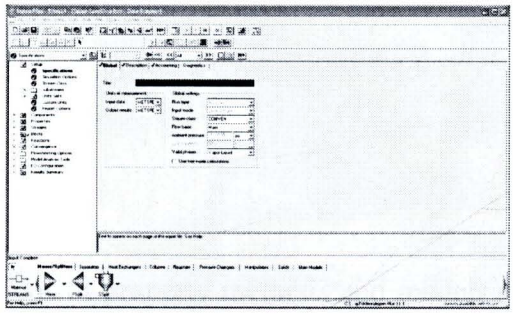

Figure 4.2 Global simulation options

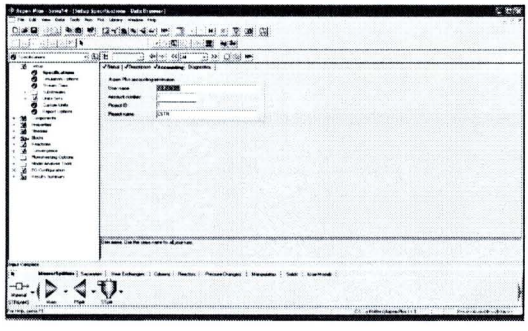

Figure 4.3 Accounting options

4.1.3 Component

After entering the required input specification in setup, the conventional chemical components of each reaction, which is used in simulation, are adding from databank list by normally searching with component name or formula. In addition, molecular weight, boiling point, and component identification are also used to search the component from databank list as shown in Figure 4.4.

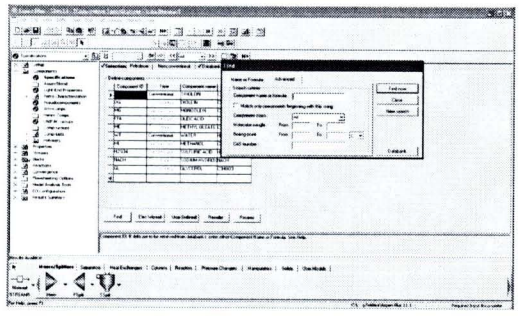

Figure4.4 Component folder

4.1.4 Properties

The required specifications of property methods and models options in properties are input into property specification folder as shown in Figure 4.5. Then the molecular structures, which are written by ChemDraw, are imported to the conventional chemical components as shown Figure 4.6. After that, the molecular structure bond is calculated as shown in Figure 4.7.

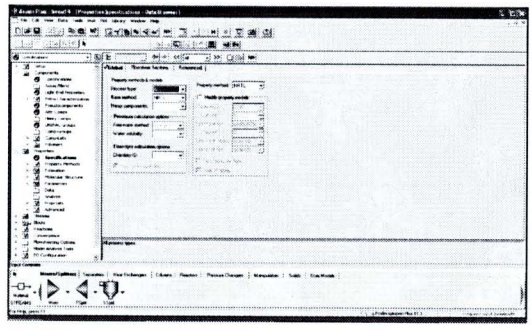

Figure 4.5 Property methods and models options

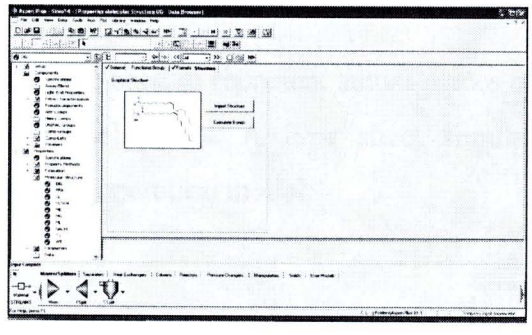

Figure 4.6 Graphical structure

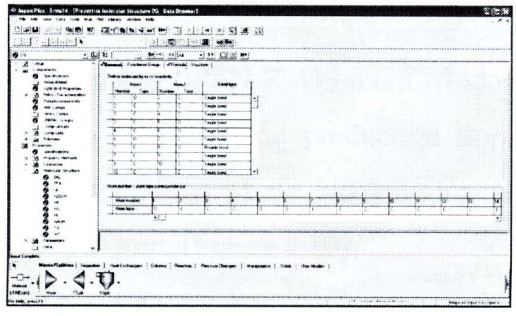

Figure 4.7 Molecule definitions by its connectivity

4.1.5 Streams

The required input specifications and flash options of composition, flows and thermodynamic condition are entered for initial material process feed streams as shown in Figure 4.8.

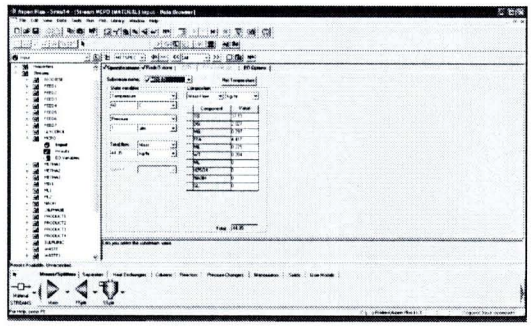

Figure 4.8 Steam properties and phase conditions determination

4.1.6 Blocks

The unit operation models are used to represent actual pieces of equipment, which are found in processing biodiesel plants. A flow sheet simulation is run under the specification at least one unit operation model.

4.1.6.1 Heater

The block of heater is installed in ASPEN PLUS main window, and then the material stream block is connected to feed line and production line of heater as shown in Figure 4.9. The specification options of its block (temperature and pressure) are required before running the program (Figure 4.10).

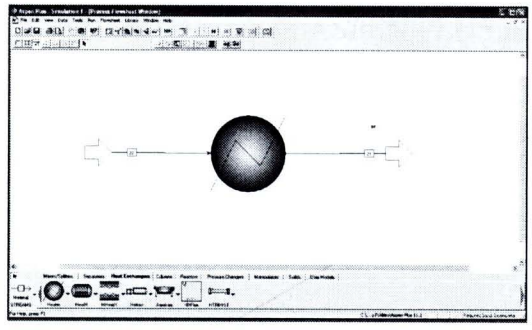

Figure 4.9 The block of heater in ASPEN PLUS main window

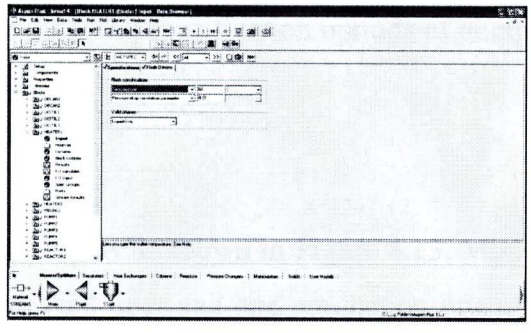

Figure 4.10 The specification options of heater block

4.1.6.2 Pump

The block of pump (connecting feed line and production line with material stream block) is installed in ASPEN PLUS main window as shown in Figure 4.11. The condition of its block (pressure and pump efficiency) are input in specification options as shown in Figure 4.12.

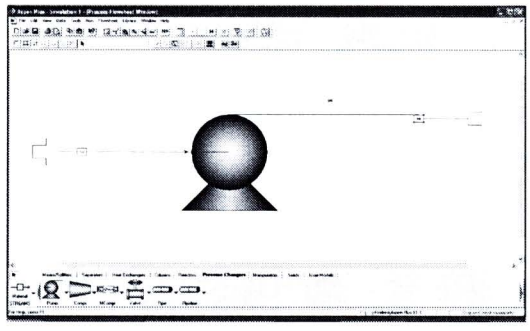

Figure 4.11 The block of pump in ASPEN PLUS main window

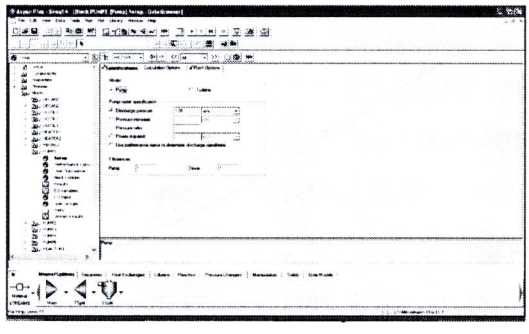

Figure 4.12 The specification options of pump block

4.1.6.3 Mixer

In ASPEN PLUS main window as shown in Figure 4.13, Mixer block is installed and then connected with two feed lines and one production line of material stream block. After that, in Figure 4.14, the requirements of flash options (pressure and temperature) are input.

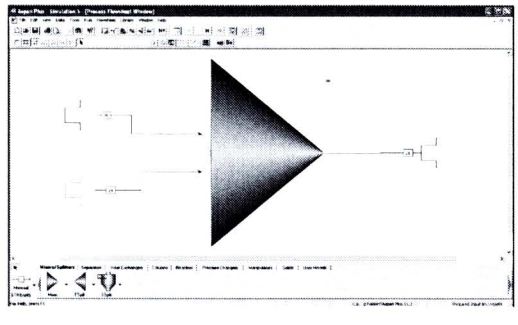

Figure 4.13 The block of mixer in ASPEN PLUS main window

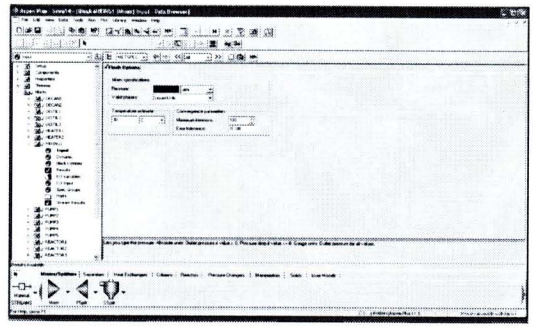

Figure 4.14 The flash options of mixer block

4.1.6.4 Reactor

Two blocks of CSTR are selected from reactor unit operation models and connected with three feed lines and a line of each production as shown in Figure 4.15. After that, the requirements (temperature, pressure and volume of reactor) of CSTR block are input in specification options as shown in Figure 4.16. After that, the reaction is added into reaction options (Figure 4.17) before simulating the model.

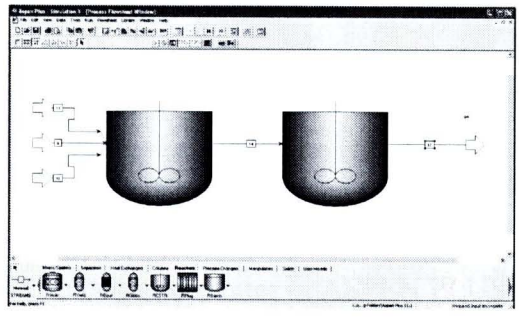

Figure 4.15 The block of reactor in ASPEN PLUS main window

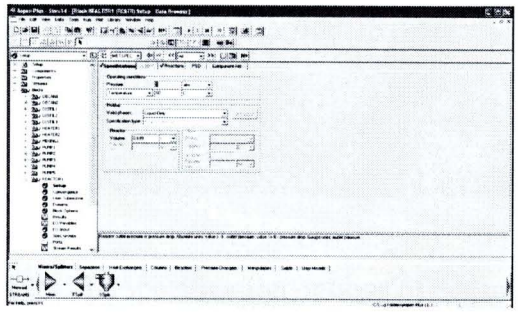

Figure 4.16 The specification options of CSTR block

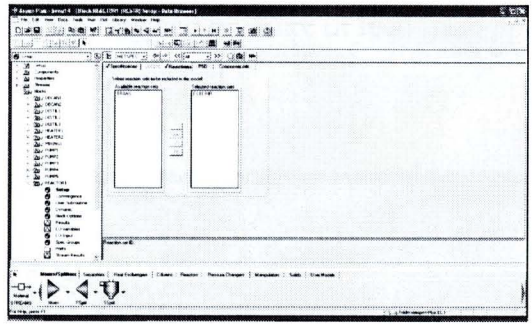

Figure 4.17 The reaction option of CSTR block

4.1.6.5 Decanter

In ASPEN PLUS main window, decanter is installed and connected with one feed line and two production lines of material stream block as shown in Figure 4.18.

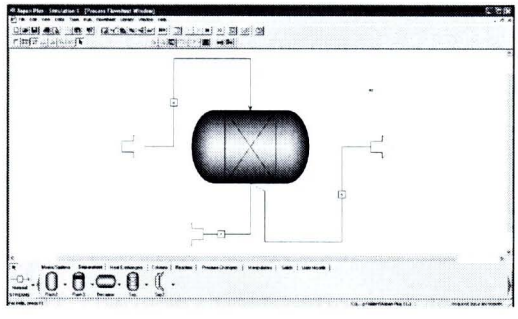

Figure 4.18 The block of decanter in ASPEN PLUS main window

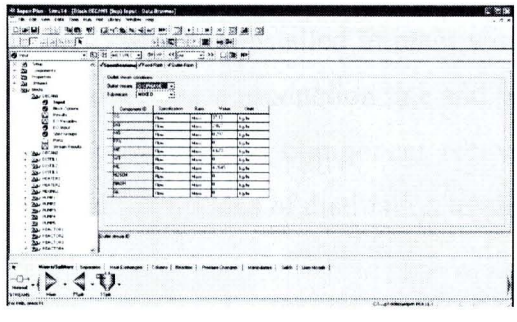

Figure 4.19 The specification options of decanter block

Then the outlet steam conditions in specification options are set are shown in Figure 4.19. Finally, both of temperature and pressure in feed flash options and outlet options are set as shown in Figure 4.20 and 4.21.

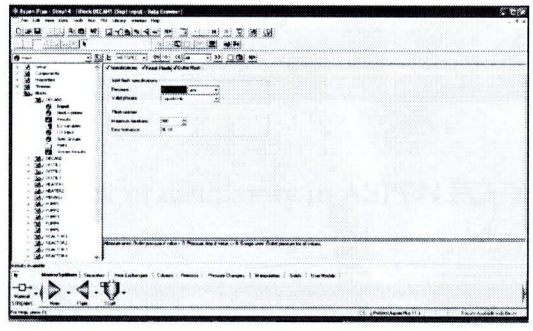

Figure 4.20 The feed flash options of decanter block

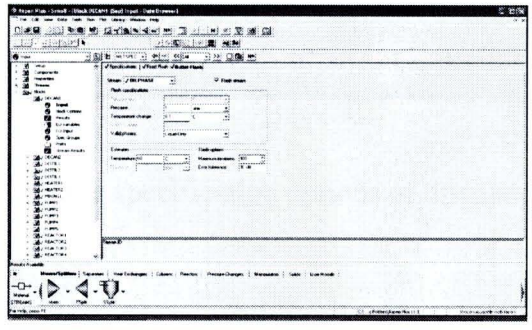

Figure 4.21 The outlet flash options of decanter block

4.1.6.6 Distillatory

The distillatory in Figure 4.22, which is installed in main window of ASPEN PLUS, is connected with a feed line, over phase production line and bottom phase production line. The number of stages, pressure, and component recovery of light phase and heavy phase are set in specification options of distillation as shown in Figure 4.23.

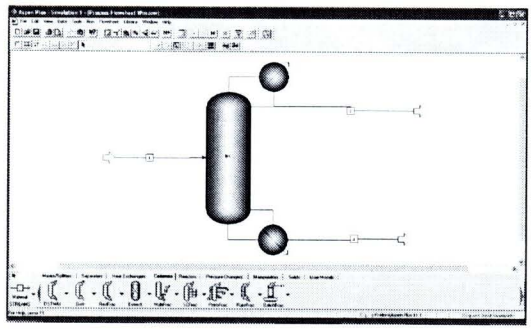

Figure 4.22 The block of distillatory in ASPEN PLUS main window

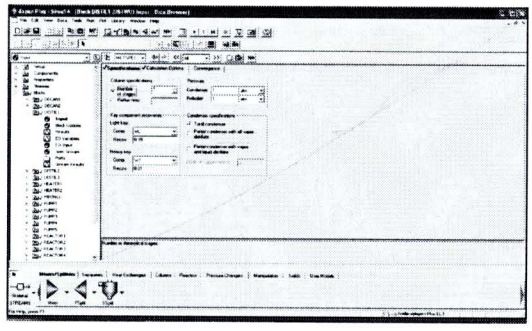

Figure 4.23 The specification options of distillatory block

4.1.7 Reactions

First, rate lows of reactions (Equation 3.13-3.20) are added into stoichiometry options as shown in Figure 4.24. Then rate coefficient and exponent of reactants and products are also added in stoichiometry options as shown in Figure 4.25. Finally, the required kinetics of each reaction as shown in Equation 3.13-3.20 is input in kinetic options as shown in Figure 4.26.

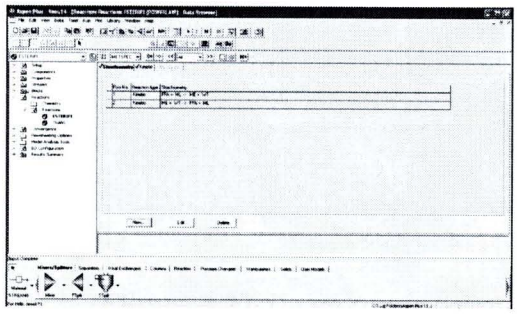

Figure 4.24 The stoichiometry options of reactions

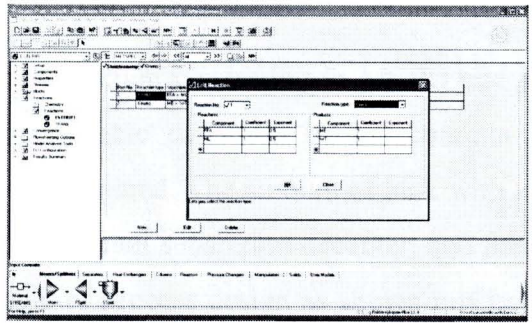

Figure 4.25 Addition of rate coefficient and exponent of reactants and products

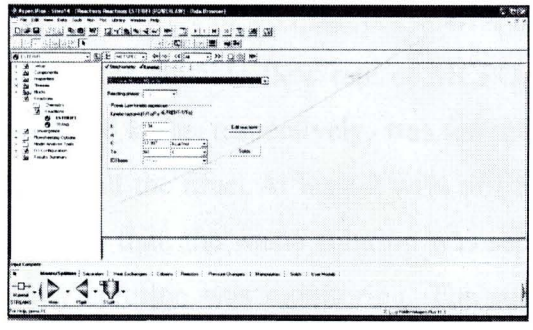

Figure 4.26 The kinetic options of reactions

4.1.8 Steam Result

After achieving simulation, the results in stream result are shown according to the requirement, which is set in Topic 4.1.2 as shown in Figure 4.27.

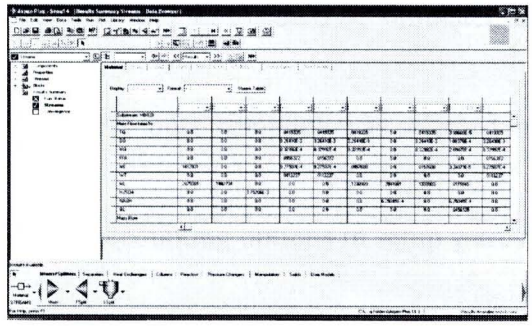

Figure 4.27 Steam result

4.2 Methodology

The continuous of FFA reduction containing in MCPO and of biodiesel production from MCPO under the suitable condition by the continuous stirred tank reactor (CSTR) in series were investigated. The amount of tank with kinetics of esterification and transesterification, horizontal separation decanter, and methanol distillatory were estimated by the principle of process design as shown in Chapter 3 and by condition as followed:

First, MCPO, which consisted of 9.966 wt% of FFA, 0.618 wt% of ME, 83.718 wt% of TG, 4.566 wt% of DG, 0.676 wt% of MG and 0.458 wt% of WT, was heated until it reached 60 °C. After that, the suitable flow rate of MCPO, methanol and sulfuric acid at 44.35, 4.751, and 0.368 kg/hr, respectively, was fed into reactor which will be heated by hot oil and stirred all the time. At least 2 wt% of FFA must be resulted the periodically monitoring. After that, the waste solution was separated by decanter and then the acid value in oily solution was monitoring. The suitable flow rate of oily solution and sodium methoxide solution at 43.25 and 9.182 kg/hr were fed into reactor heating at 60 °C by hot oil and stirred all the time. The result of the periodically monitoring must be indicated biodiesel at least 96.5 wt%. Finally, before cleaning biodiesel, methanol in the final production and waste solution were distilled and verified its purity.

The ASPEN PLUS Simulation Engine was used to verify the design in Chapter 3 and to investigate a tendency of biodiesel production before stating the experiment. The methodology (Figure 4.28, 4.29 and 4.30) could be simulated as followed:

1. Specific chemical with metric units' template was selected in this study.

2. The global simulation and accounting options in setup were set.

3. The first block of CSTR and material steam block of feed (MCPO, Methanol and H_2SO_4) and product was installed in the ASPEN PLUS main window.

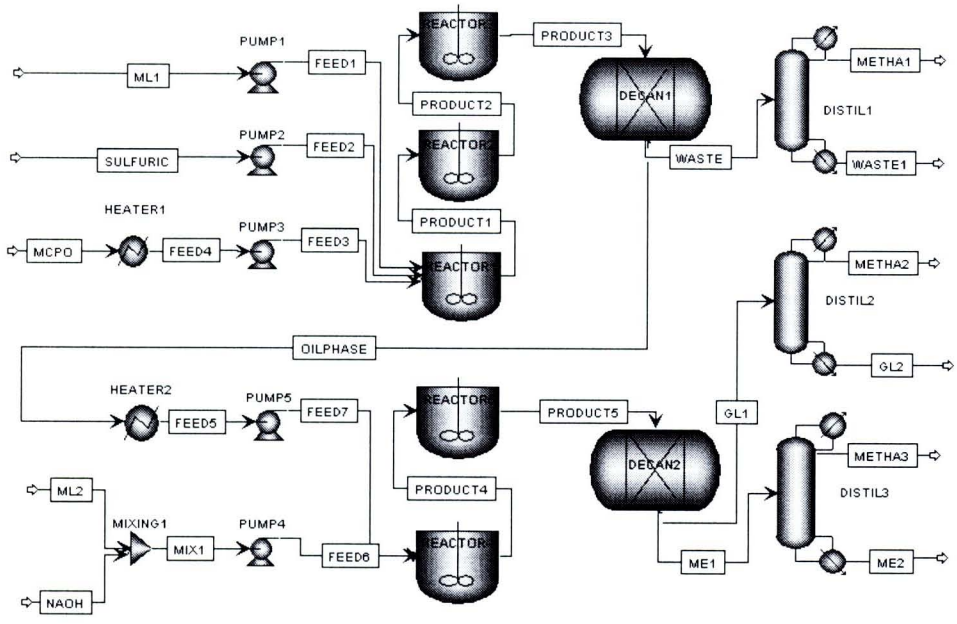

Figure 4.28 ASPEN PLUS Simulation Engine model for analysis full system of biodiesel production from MCPO

4. The chemical structures of MCPO, Methanol and H_2SO_4 in esterification reaction, which was used in simulation, were adding from databank list in components.

5. The methods option and the structures of MCPO, Methanol and H_2SO_4 were set in properties.

6. Mass flow rates of MCPO, Methanol and H_2SO_4 in term of kg/hr were input in steams according to condition of design.

7. Esterification reaction and reaction kinetics in Equation 3.8, 3.15 and 3.16 were set in reactions. Then CSTR in blocks was set.

8. The simulation was run. If it failed, the initial conditions of mass flow rate, reaction and block of CSTR were verified again until the simulation succeeded.

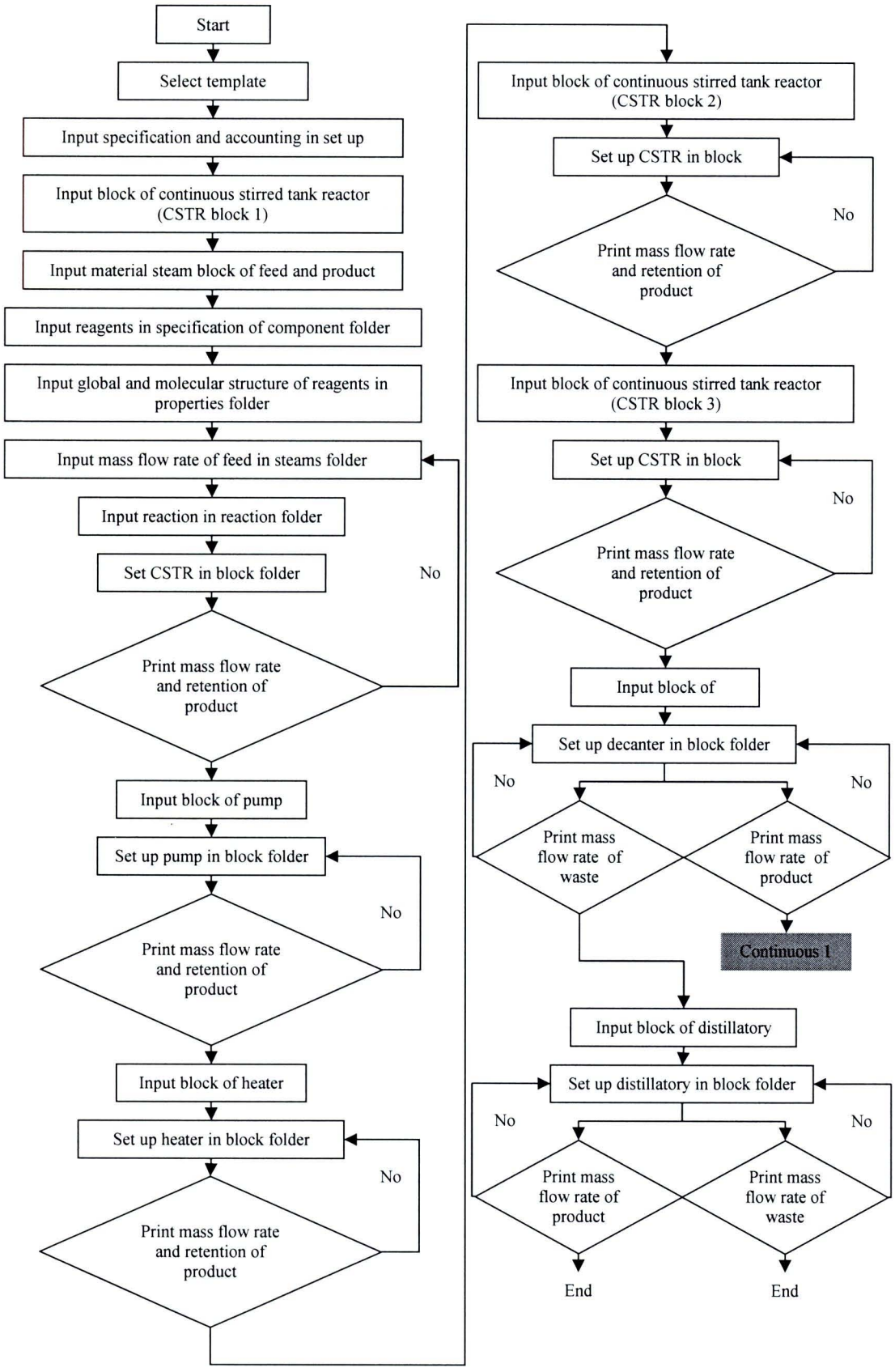

Figure 4.29 Diagram for simulation the process of biodiesel production from MCPO with ASPEN PLUS Simulation Engine

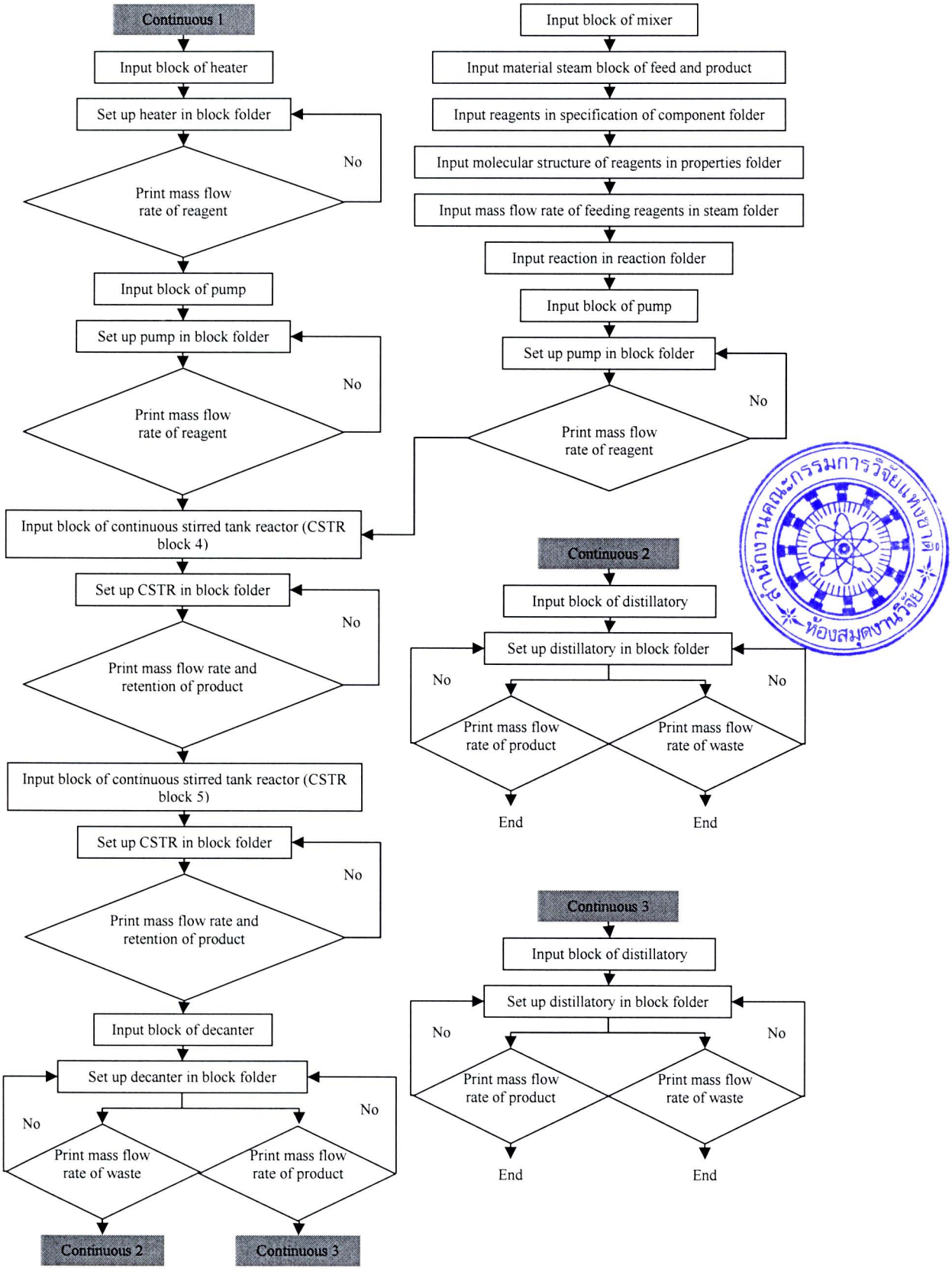

Figure 4.30 Diagram for simulation the process of biodiesel production from MCPO with ASPEN PLUS Simulation Engine (Cont')

9. The blocks of MCPO, methanol and sulfuric acid pump were installed and reconnected destination. After that the conditions of pumps were set and the simulation was run. If it could not print the results, the conditions of pump were verified until the simulation was achieved.

10. The block of heater was installed and reconnected destination to the block of pump. After installing and setting the heater for heating MCPO in main window, the simulations was run again until it succeeded.

11. The second block of CSTR was installed and reconnected destination, respectively. The conditions of each block such as initial conditions of reactor and the reaction were set. Subsequently, the simulation was run until it was successful.

12. After succeeding simulation the second block of CSTR, the third one was similarly simulated in the step for the second block of CSTR.

13. The block of decanter was installed and reconnected destination. The solution was separated into 2 phases: oily solution and waste by setting in the decanter condition. If the results could not print, the conditions of decanter were verified until the simulation was achieved.

14. Process line of oily solution was added the block of heater and pump, respectively. Both conditions were set and simulation until the simulation was reached.

15. During setting the block of heater and pump, the sodium methoxide solution was started to install the block of mixer and material steam block of methanol, sodium hydroxide and production.

16. The chemical structure of sodium hydroxide, which was used in the simulation of transesterification reaction, was adding from databank list in components.

17. The methods option and the structures of sodium hydroxide were set in properties.

18. According to condition of design, mass flow rates of methanol and sodium hydroxide in term of kg/hr were input in steams.

19. Transesterification reaction and reaction kinetics in Equation 3.13 and 3.17-3.20 were set in reactions. Then CSTR in blocks for transesterification process was connected to the line of sodium methodixe solution.

20. After setting the conditions in CSTR, the simulation was run. If it failed, the initial conditions of mass flow rate, reaction and block of CSTR were verified again until the simulation achieved.

21. After succeeding simulation the first block of CSTR for transesterification, the second one was similarly simulated in the step for the first block of CSTR.

21. The block of decanter was installed and reconnected destination to the end line of second CSTR block. Before printing the results, the condition of decanter was set for separating final product into crude biodiesel and glycerin. If the results could not print, the conditions of decanter were verified until the simulation was achieved.

22. The final product of each end line was connected to the distillatory block for studying the conditions of methanol recovery. The conditions of distillatory were verified until the simulation was succeeded.

4.3 Results and Discussion

After finishing the simulation, the results of final product was printed for verifying the design. The results were shown in term of mass flow rate, retention time, the concentration of product and some conditions, which was usefully for future work.

4.3.1. Esterification

After already setting the conditions of esterification reaction according to the reactor design, the simulation was run. It was found that the total retention time of each tank CSTR in series was around 18 seconds. The concentration of FFA at 9.96 wt% (the

ratio between FFA mass flow rate and total flow rate) could be reduced to less than 1 wt% from the first tank as shown the results in Table 4.1. On the other hand, it was found that the retention time for reducing the concentration of FFA to less than 1 wt% of each tank in process design (around 32 seconds) was more than the time in simulation. The reason was that only oleic acid might be used in simulation but three fatty acids (palmitic acid, oleic acid and linoleic acid) were used to calculate in process design. After achieving the simulation of esterification, the production was fed into decanter for separating the solution into oily solution and the first process waste. Oily solution consisted of TG, DG, MG, ME, and ML. For the first process waste, it consisted of FFA, ML, WT, and H_2SO_4 as shown in Table 4.2.

Table 4.1 The simulation conditions and results of esterification

Results	MCPO	MeOH	H_2SO_4	Reactor 1	Reactor 2	Reactor 3
Volume (L)	-	-	-	0.5	0.5	0.5
Retention time (sec)	-	-	-	18	18	18
Mass fraction						
TG	0.8372	0.0000	0.0000	0.7506	0.7506	0.7506
DG	0.0457	0.0000	0.0000	0.0410	0.0410	0.0410
MG	0.0067	0.0000	0.0000	0.0060	0.0060	0.0060
FFA	0.0996	0.0000	0.0000	0.0010	0.0009	0.0009
ME	0.0062	0.0000	0.0000	0.0983	0.0983	0.0983
WT	0.0046	0.0000	0.0000	0.0097	0.0098	0.0098
ML	0.0000	1.0000	0.0000	0.0860	0.0860	0.0860
H_2SO_4	0.0000	0.0000	1.0000	0.0074	0.0074	0.0074
Total Mass flow rate (kg/hr)	44.3500	4.7510	0.3680	49.4690	49.4690	49.4690

Table 4.2 The simulation results of the first decanter

Results	Reactor 3	Oily Solution	The 1st waste
Volume (L)	0.5	-	-
Retention time (sec)	18	-	-
Mass fraction			
TG	0.7506	0.7703	0.0000
DG	0.0410	0.0421	0.0000
MG	0.0060	0.0062	0.0000
FFA	0.0009	0.0000	0.0347
ME	0.0983	0.1009	0.0000
WT	0.0098	0.0000	0.3809
ML	0.0860	0.0805	0.2942
H_2SO_4	0.0074	0.0000	0.2902
Total Mass flow rate (kg/hr)	49.4690	48.2010	1.2680

Because, in experiment, FFA in oil was neutralized, the remained concentration of FFA in this step of simulation was eradicated from the esterification solution. In addition, the oily solution and the first stage waste were verification the remained methanol as shown in Appendix E. Therefore, theirs values were used to estimated the remained methanol values in both solution that was leaving the decanter.

4.3.2 Transesterification

The oily solution, methanol and sodium hydroxide (a raw material of transesterification) were fed into reactor in which the required condition was already set. After that the simulation was run until it reached the retention time. It was found that the concentration of TG, DG and MG were reduced to less than 1 wt%. Besides, the concentration of ME and GL were increased from 10.97 and 0.00 wt% to 90.24 and 8.41 wt%, respectively as shown in Table 4.3. In addition, the results indicated that the retention time for produce biodiesel of simulation was less than the retention time of process design, which the reason was similarly to Topic 4.3.1.

After that the production was fed into the second decanter. The product was separate into crude biodiesel phase and glycerol phase as shown in Table 4.4. The reason for grouping TG, DG, MG and ME in biodiesel phase because their concentrations were detected when biodiesel was analyzed with TLC/FID in previous work.

Table 4.3 The simulation conditions and results of transesterification

Results	Oily solution	MeOH	NaOH	Reactor 4	Reactor 5
Volume (L)	-	-	-	1.5	1.5
Retention time (min)	-	-	-	1.34	1.34
Mass fraction					
TG	0.7703	0.0000	0.0000	0.0008	0.0000
DG	0.0421	0.0000	0.0000	0.0036	0.0019
MG	0.0062	0.0000	0.0000	0.0098	0.0094
ME	0.1009	0.0000	0.0000	0.7612	0.7639
GL	0.0000	0.0000	0.0000	0.0708	0.0712
ML	0.0805	1.0000	0.0000	0.1534	0.1532
NaOH	0.0000	0.0000	1.0000	0.0004	0.0004
Total Mass flow rate (kg/hr)	48.2010	9.1060	0.0250	57.3320	57.3320

44.32082 43.7902 44.4438 4.082 48.5258

Due to the molecule of methanol consisted of polar function (hydroxyl group) and non-polar function (alkyl group); therefore, methanol (could be dissolved in both phases) are shown the analyzed results in Appendix E. Although, small amount of methanol in crude biodiesel was detected, because of no analyzing of methanol in vapor phase, it was assumed that a lot of methanol was remained in crude biodiesel. After separating glycerol out of the final product, the concentration of TG, DG, MG and ME at 0.00, 0.22, 0.68 and 99.09 wt% was obtained, respectively.

Table 4.4 The simulation results of the second decanter

Results	Reactor 5	Crude biodiesel	Glycerol
Volume (L)	1.5	-	-
Retention time (min)	1.34	-	-
Mass fraction			
TG	0.0001	0.0000	0.0000
DG	0.0019	0.0021	0.0010
MG	0.0094	0.0064	0.0229
ME	0.7638	0.9352	0.0000
GL	0.0712	0.0000	0.3887
ML	0.1532	0.0563	0.5850
NaOH	0.0004	0.0000	0.0024
Total Mass flow rate (kg/hr)	57.3320	46.826	10.5000

4.3.3 Distillation

Methanol in the 1st stage waste, crude biodiesel and glycerol were recovered by distillation. Due to absence of the equilibrium curve of a pair of solution (methanol-water, methanol-crude biodiesel and of methanol-glycerol), only the number of plates in methanol distillatory tower was estimation. Therefore, reflux ratio, feed stage, and temperature was simulated by ASPEN PLUS Simulation Engine which results are shown in Table 4.5. The simulation of methanol distillatory of methanol-crude biodiesel and of methanol-glycerol had some errors because the number of plate in the design work was lower than the limit of plate number, which could added in the simulation. However, the simulation results were the guideline for fabricating the distillatory in actual work.

In experiment, excess methanol was used to produce biodiesel so the un-reacted methanol in each solution should be recovered for using to reduce the concentration

of FFA in esterification. From the simulation results shown in Table 4.5, it was found that 63.65 % of excess methanol could be recovered from all final products.

Table 4.5 The simulation results of distillation

Results	Distillatory 1			Distillatory 2			Distillatory 3		
Reflux ratio	1.22			0.74			0.27		
Number of stages	7			2			2		
Feed stage	4.70			1.81			1.82		
Distillate temperature (°C)	64.9			64.6			69.2		
Bottom temperature (°C)	103.2			160.3			160.0		
Mass fraction	The 1st waste	Methanol	The final waste	Glycerol 1	Methanol	Glycerol 2	Crude biodiesel	Methanol	Biodiesel
TG	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DG	0.0000	0.0000	0.0000	0.0010	0.0000	0.0024	0.0021	0.0000	0.0025
MG	0.0000	0.0000	0.0000	0.0229	0.0000	0.0548	0.0064	0.0008	0.0074
FFA	0.0347	0.0000	0.0492	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ME	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.9352	0.6482	0.9836
WT	0.3809	0.0134	0.5347	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
GL	0.0000	0.0000	0.0000	0.3887	0.0067	0.9228	0.0000	0.0000	0.0000
ML	0.2942	0.9866	0.0045	0.5850	0.9933	0.0140	0.0563	0.3510	0.0066
H_2SO_4	0.2902	0.0000	0.4116	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
NaOH	0.0000	0.0000	0.0000	0.0024	0.0000	0.0057	0.0000	0.0000	0.0000
Total flow rate (kg/hr)	1.2680	0.3740	0.8940	10.5000	6.1200	4.3800	46.826	6.7561	40.0699

Its concentration that estimated by simulation was around 96.37 wt%. The tendency estimated concentration of methanol was lower the requirement of methanol concentration in actual work because high temperature was used to re-boiling solution. Therefore, some impurities such as water, triglyceride and methyl ester, was blended in methanol. Therefore, this concentration of methanol should be verified again by experiment.

4.4 Conclusions

The results of simulation (closing to the process design) were summarized as followed:

- The total retention time of 3 tanks CSTR in series within 1 minute could be reduced the concentration of FFA at 9.96 wt% to less than 0.50 wt%.

- The concentration of ME more than 96.5 wt% was detected when the reaction was performed in a tank of CSTR within 3 minutes.

- 63 % of excess methanol could be recovered from all final products, which 96 wt% concentration was detected.