

CHAPTER 3

RESEARCH METHODOLOGY

This thesis focused on the creating a two-stage process model. The procedure followed the thesis consisted of six steps as shown in Figure 3.1. Firstly, the apparatus was set for producing biodiesel from MCPO by the two-stage process. Subsequently, experimental conditions of the two-stage process were set. Next, the experiment was carried out and data collected. After that, rate coefficients and reaction orders of the two-stage process were calculated. In addition, activated energies were investigated. After that, experimental data, rate laws, and rate coefficients of the two-stage process were used to study the kinetics and to create the model. Finally, predicted data of the model was verified with experimented data.

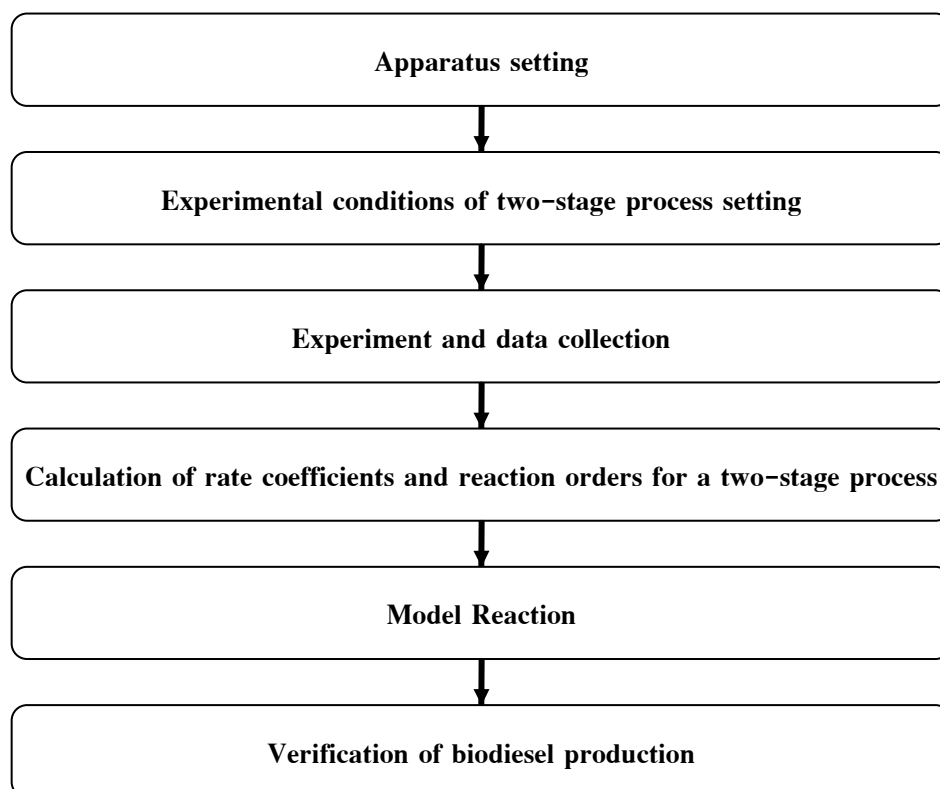


Figure 3.1 Diagram of research methodology

3.1 Materials

Mixed crude palm oil (FFA \approx 8–14 %wt) (un-degummed and un-deacidified), commercial methanol (95%) (MeOH), commercial sodium hydroxide (98%) (NaOH), phenolphthalein, iso-propanol, and commercial sulfuric acid (H_2SO_4) were used in this experiment.

Analytical grade sodium hydroxide, isopropanol, and phenolphthalein were used to analyse FFA contents and acid values.

Hexane, diethyl ether, formic acid, and benzene, also of analytical grade, were used in TLC/FID (Thin Layer Chromatography/ Flame Ionization Detector) analysis.

The analytical grade hydranal-coulomat CG and the analytical grade hydranol-coulomat AG were used for Karl Fischer determination of water.

Analytical grade potassium hydrogen phthalate, sodium periodate, ethanediol, carbonate free sodium hydroxide, H_2SO_4 , and bromothymol blue were used to analyse the glycerol content.

3.2 Apparatus

A 2000 ml. round bottom flask equipped with a mechanical stirrer, thermocouple, a fixed condensing coil and a sampling port were used in all experiments as shown in Figure 3.2. The reactor was immersed in a constant-temperature water bath. Samples were withdrawn with a pipette from the top of the reactor during the experiment (Thaweensinsoha, 2006, and Jansri, 2007).

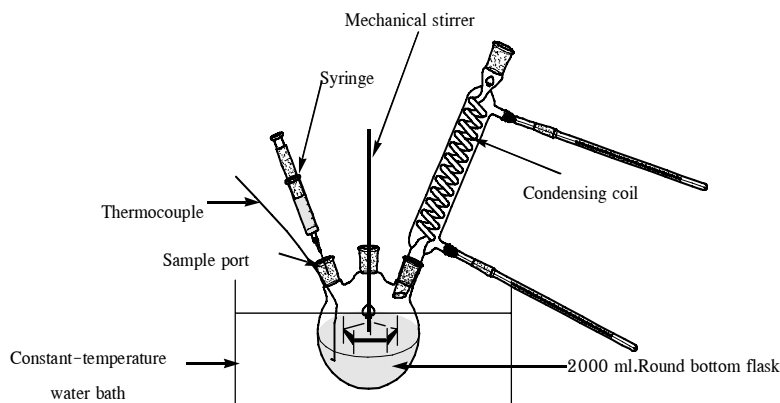


Figure 3.2 Equipment used in this study

3.3 Two-Stage Process

The objective of this work was to use the two-stage process producing biodiesel from MCPO in a batch reactor. Esterification was the first reaction used to reduce FFA in MCPO in the presence of an acid catalyst (H_2SO_4) and this was followed by a base-catalyzed transesterification reaction, which converted the first stage solution to be biodiesel.

3.3.1 The Two-Stage Process Experiments

Procedures used of the two-stage process in this work consisted of 8 steps as followed:

1. MCPO (which was already analyzed for the FFA content) was weighed and heated in the round bottom flask until its temperature in the round bottom flask rose to the required temperature.
2. Methanol was added slowly into the flask and mixing was performed for blending oil and methanol. Then H_2SO_4 was added slowly into the solution as catalyst of esterification. After that, mixing was performed until the reaction time of the first-stage achieved.
3. The stirring was stopped to separate the product into 2 phases (oily phase and black phase: water, unreacted methanol, and H_2SO_4).

4. Oily solution was titrated to check the acid value and calculate the amount of NaOH, which was required to neutralize the oily solution.
5. Oily solution was heated until the solution temperature rose to that required point.
6. Sodium methoxide solution, which consisted of methanol, NaOH (catalyst), and NaOH (neutralization), was added slowly into heated solution, and then the reaction continued to the required time.
7. The agitation was stopped for separating liquid into 2 phases (red phase: biodiesel and black phase: glycerol).
8. Red solution was washed and quantitatively and qualitatively verified for biodiesel content.

3.3.2 Reaction Conditions

This study focused on reducing FFA, which contained in MCPO, to less than 1 %wt with the acid-catalyzed esterification and converting initial triglycerides of MCPO to better than 96.5%wt of biodiesel by using the two-stage process. Therefore, some conditions of the pre-experiment were investigated before starting the production of biodiesel from MCPO with the two-stage process as shown in Table 3.1. In addition, variations of the molar ratio of methanol to FFA, of the molar ratio of methanol to TG, and of the reaction temperature were investigated as shown in Figure 3.3.

3.3.3 Sampling

2 ml. samples were collected from the reactor at the retention time as shown in Table 3.1 and Figure 3.3 (May, 2004 and Jansri, 2007). Reactions of samples were stopped immediately by immersing in cold water (5 degree Celsius) until the temperature of the sample reached the ambient temperature (24 degree Celsius). Subsequently, purified samples were analyzed with other analytical techniques.

3.3.4 Monitoring Analysis

3 methods were used to analyze the substances in each sample such as TLC/FID, Karl Fischer, and titration. Substance contents in each sample such as methyl

ester, tri-, di-, mono-glyceride, and FFA were determined by TLC/FID (Thaweensinsoha, 2006). Karl Fischer, the procedure shown in APPENDIX B, was used to analyse water contained in each sample. Acid values (the amount of NaOH to neutralize acid in the solution), the FFA content (Thaweensinsoha, 2006), and glycerol (BS 2621-5:1964 Specification for glycerol (glycerine) in Thailand) were analyzed by titration techniques.

3.4 Kinetics of Two-Stage Process

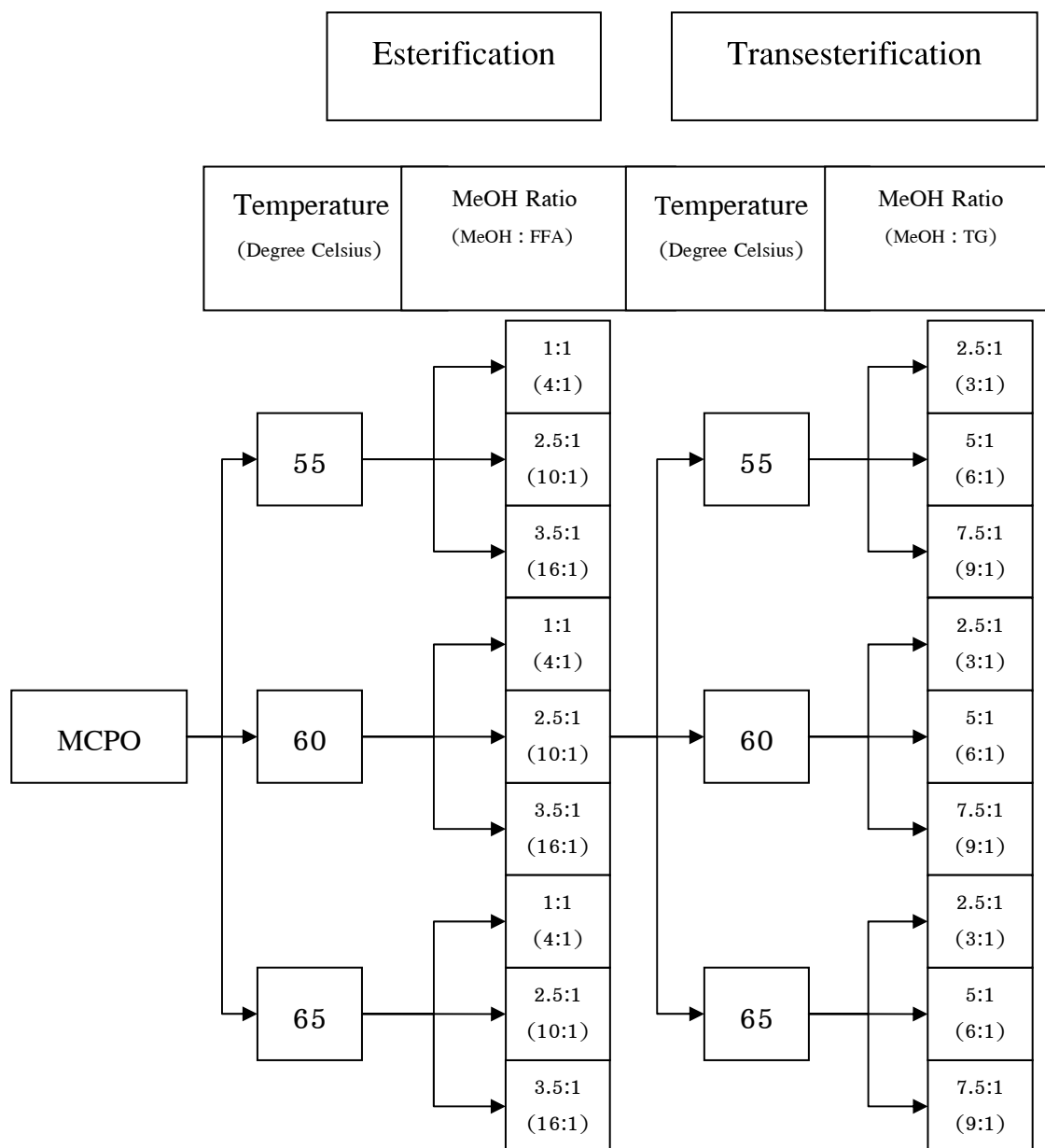
The kinetics of the two stage process including rate laws of the two-stage process (esterification and transesterification), rate coefficients and reaction order of the two-stage process, and activation energies were investigated. Firstly, experimental data and rate laws (Equation 2.12 and 2.14) were used to compute rate coefficients of the two-stage process (esterification and transesterification) and reaction orders of the first-stage process (esterification), which was varied the overall order in the rang of the first to fourth order, by using the curve-fitting tool of MATLAB7 (Noureddini, *et al.*, 1997), which determined the final outputs from curve-fitting (rate coefficients and reaction orders) with a goodness-of-fit such as the determination coefficient (R^2). Secondly, predicted outputs, which used the Runge-Kutta method, rate laws of the two stage process, rate coefficients and reaction orders obtained from MATLAB7, were compared with the experimental data by determining the % data error mean (μ) and the standard deviation (σ) in categories. Finally, activation energies of the two-stage process were calculated by using rate coefficients of the two-stage process, the natural logarithm of Arrhenius equation as shown in equation 2.16 and the curve-fitting tool of MATLAB7 (Darnoko, *et al.*, 2000, Fogler, 1999, and Noureddini, *et al.*, 1997).

3.5 Two-Stage Process Modeling

The mechanism of esterification and transesterification reactions (Equation 2.12 and 2.14), rate coefficient and reaction order values of the two-stage process as shown in the methodology in Topic 3.4, and ODE (Runge-Kutta method) were used to create a two-stage process model within MATLAB7 (Jansri, *et al.*, 2007) as shown the diagram in Figure 3.4.

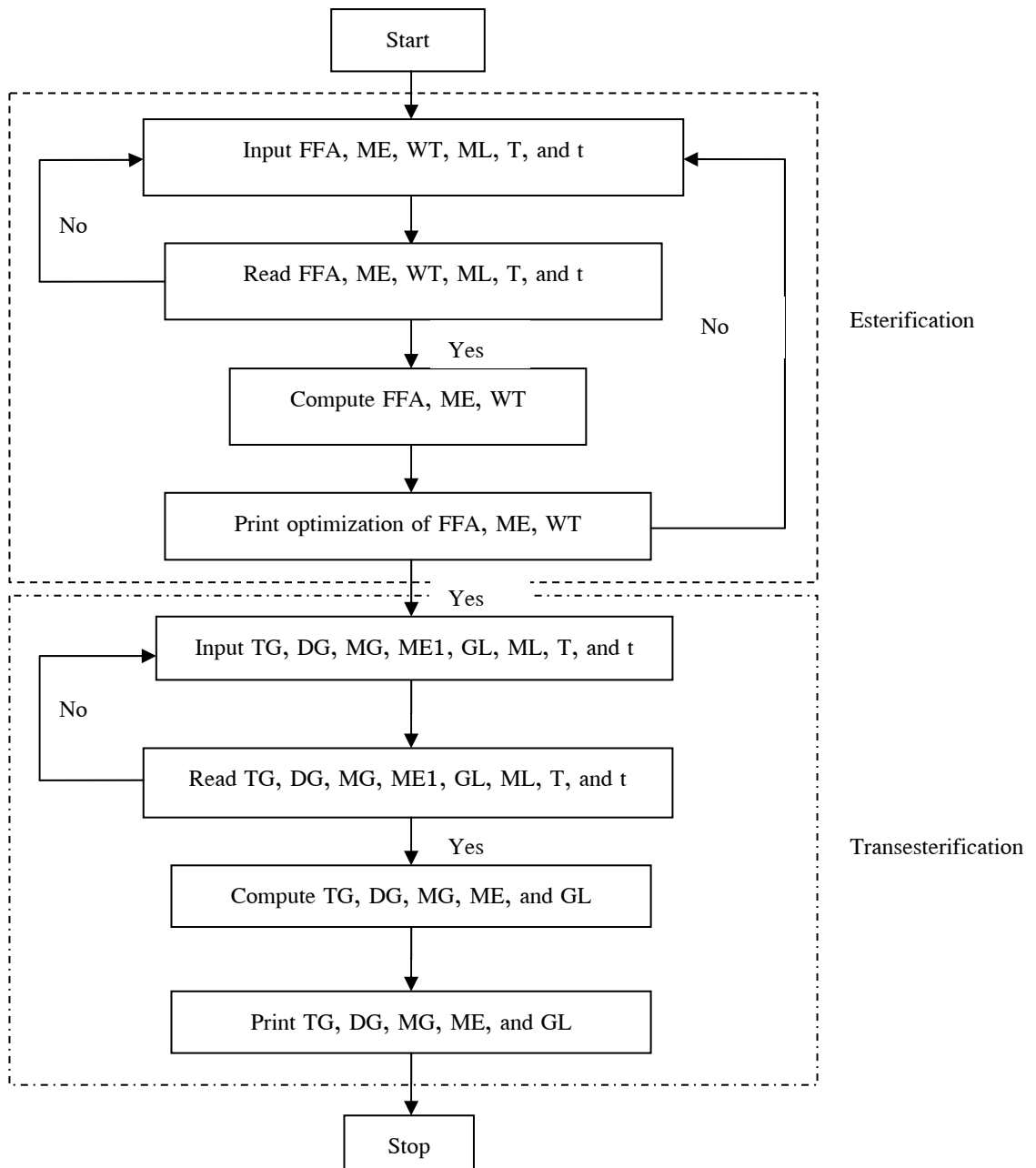
Table 3.1 Pre-experiment conditions for the two-stage production

Experiment	Methanol Molar Ratio	Catalyst (%wt of oil)	Reaction Temperature (degree Celsius)	Speed of Stirrer (rpm)	Reaction Time (min)	Sampling Time (min)	Purification Method	Analysis Method
The Amount of Alcohol	5:1 (MeOH :oil) or 20:1(MeOH :FFA)	0.8 (H ₂ SO ₄)	60	-	60	-	Unwashed	GC/FID
The Speed of the Stirrer	5:1 (MeOH :oil) or 20:1 (MeOH :FFA)	0.8 (H ₂ SO ₄)	55, 60, & 65	200,300, & 400	60	0, 0.5, 1, 3, 5, 7, 9, 12, 15, 18, 21, 25, 30, 35, 40, 45, 50, & 60	Hot Water	TLC/FID
The Amount of H ₂ SO ₄ Used	2.5:1 (MeOH :oil) or 10:1(MeOH :FFA)	0.4, 0.8, & 1.2	60	300	120	0, 0.5, 1, 3, 5, 7, 9, 12, 15, 18, 21, 25, 30, 35, 40, 45, 50, 60, 75, 90, & 120	Hot Water	TLC/FID
The Amount of NaOH Used	5:1 (MeOH :oil) or 6:1(MeOH :TG)	0.25, 0.50, & 0.75	60	300	60	0, 1, 3, 5, 7, 9, 12, 15, 18, 21, 25, 30, 35, 40, 45, 50, & 60	Hot Water	TLC/FID
Water and H ₂ SO ₄ Separation	2.5:1 (MeOH :oil) or 10:1(MeOH :FFA)	0.8 (H ₂ SO ₄)	60	300	15	-	-	-
Purification Methods	2.5:1 (MeOH :oil) or 10:1(MeOH :FFA)	0.4 (H ₂ SO ₄)	60	300	60	0, 0.5, 1, 3, 5, 7, 9, 12, 15, 18, 21, 25, 30, 35, 40, 45, 50, & 60	Hot Water, Hot Water with NaOH, & Unwashed	TLC/FID



The experiments fixed the amount of H_2SO_4 and NaOH at 10 and 0.6 %wt of FFA and TG (0.8 and 0.5 %wt base on MCPO), respectively, washed the solution with hot water, sampled esterification solution at 0, 0.5, 1, 3, 5, 7, 9, 12, 15, and 20 min, sampled transesterification solution at 0, 1, 3, 5, 7, 9, 12, 15, 18, and 20 min, and analyzed with TLC/FID & Karl Fisher.

Figure 3.3 Two-stage process



Where DG = Diglyceride FFA = Free fatty acid GL = Glycerol ME = Methyl ester ME1= Methyl ester from stage 1

MG = Monoglyceride ML = Methanol T= Temperature t = time TG = Triglyceride WT = Water

Figure 3.4 Diagram of the two-stage process modeling