

CHAPTER III

MATERIALS AND METHODS

3.1 Materials and equipments

In this research, materials and equipments were divided into 2 groups for transesterification process and purification of the synthetic biodiesel. As the first step, biodiesel was synthesized from crude palm oil. Then, the biodiesel was cleaned up with adsorbent materials such as alumina, activated carbon, bentonite clay and molecular sieve.

3.1.1. Chemicals and equipments for transesterification process

- 1.1 Crude palm oil; Thai Eastern Group CO., Ltd.
- 1.2 Sodium hydroxide (NaOH) or Potassium hydroxide (KOH); Carlo Erba
- 1.3 Methanol (CH₃OH); Merck KGaA Darmstadt, Germany
- 1.4 Anhydrous sodium sulfate (Na₂SO₄): Analytical grade; Carlo Erba
- 1.5 Hexane; commercial grade
- 1.6 Ethyl acetate; analytical grade
- 1.7 Acetic acid (CH₃COOH); analytical grade
- 1.8 Sulfuric acid (H₂SO₄); analytical grade
- 1.9 Chloroform-D: NMR spectroscopy grade; Merck KGaA Darmstadt, Germany
- 1.10 Hot plate with magnetic stirrer set
- 1.11 Reflux condenser set
- 1.12 Separation funnel stand and clamps
- 1.13 Thermometer
- 1.14 Volumetric flask or round bottom flask
- 1.15 Beaker
- 1.16 Filter paper, funnel

3.1.2. Materials and equipments for purification of methyl ester

- 2.1 Methyl ester from crude palm oil which is transesterified
- 2.2 Alumina oxide (powder)
- 2.3 Activated carbon; Gigantic CO., Ltd.
- 2.4 Molecular sieve 4 Å; Merck KGaA Darmstadt, Germany
- 2.5 Magnesol; Dallas group of America, Inc.
- 2.6 Beaker
- 2.7 Filter paper, funnel and suction flask
- 2.8 Fourier-Transform NMR Spectrometer: Mercury (400 MHz); Varian
- 2.9 Karl Fischer Coulometer (Ω Metrohm)
- 2.10 BET Surface Area Analyzer: SA 3100 Coulter
- 2.11 Inductively Coupled Plasma Emission Spectrometer (ICP-AES): Perkin Elmer OPTIMA-3000
- 2.12 Micro Carbon Residue Tester: MCRT-160

3.2 Synthesis of methyl ester

3.2.1 Synthesis of methyl ester via base-catalyzed process

Crude palm oil 400 g (476.70 mmol) was added into the two neck round bottom flask equipped with condenser (The apparatus set for transesterification is shown in Figure 3.1). After preheating the palm oil to the desired temperature for transesterification, a solution of sodium hydroxide 5.60 g (140 mmol or 1.4% wt of oil) in methanol 300 ml was added and then refluxed at the temperature 50°C for 1.5 h. The reaction was monitored by TLC developed by hexane:ethylacetate:acetic acid (90:10:1 v/v) and visualized by iodine's vapor and vanillin solution. After cooling down to room temperature the reaction mixture was transferred to separatory funnel and left overnight. The methyl ester layer and the glycerol layer were separated. The glycerol (bottom phase) was partitioned with hexane (200 ml) two times. The hexane layer was added to the methyl ester layer. A mixture of hexane and the methyl ester was partitioned with warm water (50 ml) 7-8 times, dried (anhydrous Na_2SO_4) and filtered through filter paper using suction. The filtrate

was evaporated using rotary evaporator to give a palm oil methyl ester as an orange-red liquid. The methyl ester (5 mg) was subjected to $^1\text{H-NMR}$ analysis.

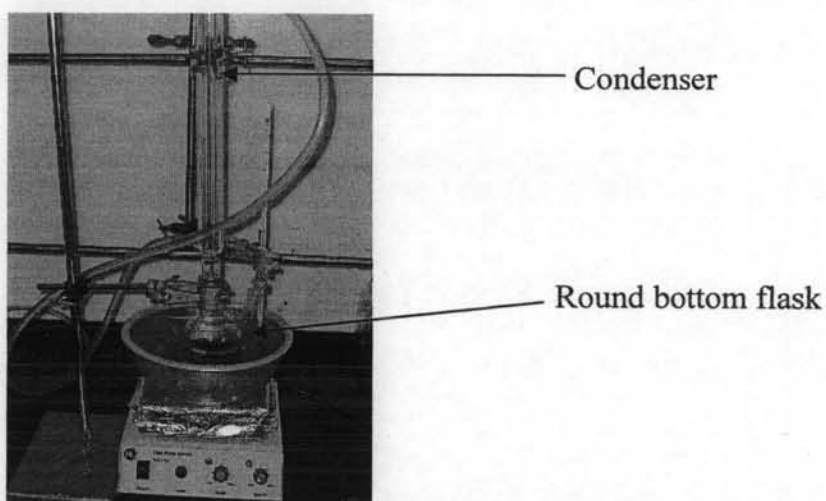


Figure 3.1 The apparatus set for transesterification.

The flow diagram for base-catalyzed process on the laboratory scale was showed in Figure 3.2.

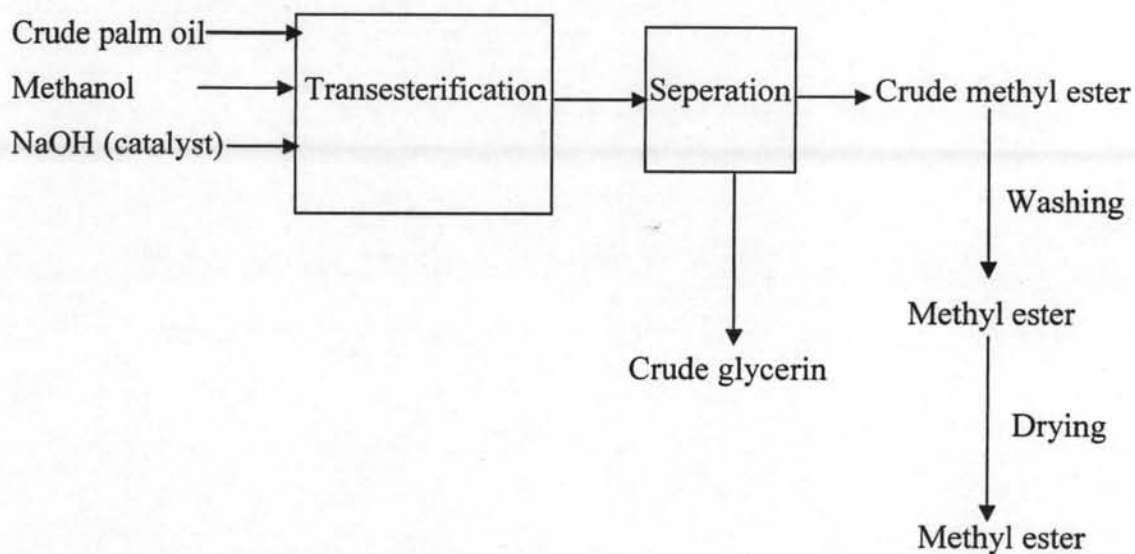


Figure 3.2 Base-catalyzed transesterification on the laboratory scale

3.2.2 Synthesis of methyl ester via 2-step catalyzed process

This is a two-stage procedure involving acid esterification as first-stage and transesterification using KOH as second-stage. At first, crude palm oil 400 g (476.70 mmol) was added into the two neck round bottom flask equipped with condenser. After preheating the palm oil to the desired temperature for esterification, a solution of sulfuric acid (H_2SO_4) 4.35 ml (81.67 mmol or 2% wt of oil) in methanol 190 ml was added and then refluxed at the temperature 80°C for esterification for 4 h. The reaction was monitored by TLC developed by hexane:ethylacetate:acetic acid (90:10:1 v/v) and visualized by iodine's vapor and vanillin solution. After cooling down to room temperature the reaction mixture was transferred to separatory funnel and left overnight. The mixture was left to settle to separate into two layers. The upper oil layer was the methyl ester and unreacted triglyceride that was subjected to the second stage, transesterification, and the lower layer was a mixture of water and catalyst. The second, the collected oil layer (upper) was transferred to the two neck round bottom flask equipped with condenser. After preheating oil to the desired temperature for transesterification, a solution of potassium hydroxide (KOH) 4.0 g (71.42 mmol or 1% wt of oil) in methanol 113 ml was added and then refluxed at 50°C for 1 h. The reaction was monitored by TLC developed by hexane:ethylacetate:acetic acid (90:10:1 v/v) and visualized by iodine's vapor and vanillin solution. After cooling down to room temperature the reaction mixture was transferred to separatory funnel and left overnight. The methyl ester layer and the glycerol layer were separated. The glycerol (bottom phase) was partitioned with hexane (200 ml) for two times. The hexane layer was added to the methyl ester layer. A mixture of hexane and the methyl ester was partitioned with warm water (50 ml) 7-8 times, dried (anhydrous Na_2SO_4) and filtered through filter paper using suction. The filtrate was evaporated using rotary evaporator to give a palm oil methyl ester as an orange-red liquid. The methyl ester (5 mg) was subjected to $^1\text{H-NMR}$ analysis.

The flow diagram for 2-step catalyzed process on the laboratory scale was showed in Figure 3.3.

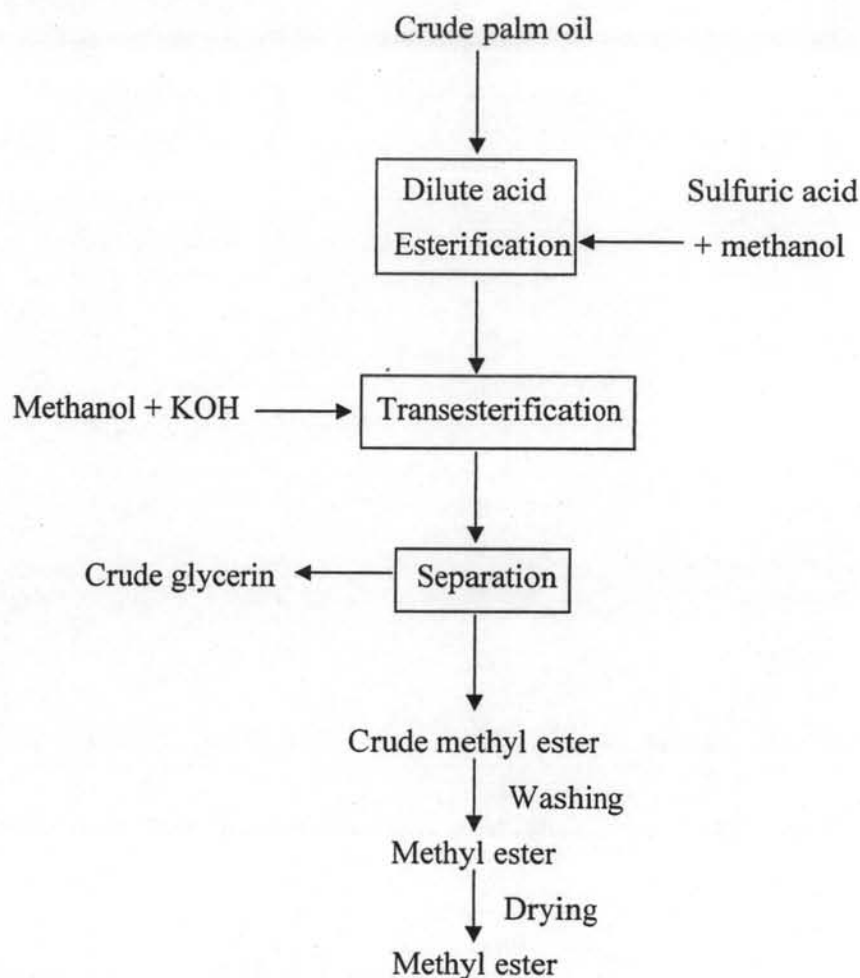


Figure 3.3 Two-step catalyzed process on the laboratory scale

3.3 Procedure for purification of methyl ester with adsorbents

The methyl ester (70 g) was heated to the desired temperatures (30, 40, 50 and 60°C) then was added the desired amount of the adsorbents (1.0, 2.0, 3.0 and 4.0% wt of methyl ester) and stirred. After the desired adsorption times (10, 20 and 30 min), the mixture was filtered through filter paper using suction and then the filtrate was weighed and determined for %FFAs, total moisture and metal contents according to ASTM standard as shown in Table 3.1.

Table 3.1 Tested method of purified methyl ester

Properties	Method
Free fatty acids (FFAs)	ASTM D 5555
Total moisture	ASTM D 5530
Metal content	ASTM D 5185

3.4 Procedure for recovering the adsorbents

The used adsorbent was washed with hexane or methanol to remove oil and FFAs at room temperature. Then, the solvent was evaporated at 80°C and the adsorbent was kept in desiccator containing silica gel under reduced pressure at least for 30 min before it was used for adsorption.