CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Methyl ester (white grade), Thai Oleochemicals Co., Ltd., Thailand
2. Alpha methyl ester sulfonate C16 and C18, Lion Corporation, Japan
3. n-Hexane (AR grade)
4. n-Butanol (AR grade)
5. propan-2-ol (HPLC grade)
6. Acetonitrile (HPLC grade)
7. Methanol (HPLC grade)
8. Methanol (AR grade)
9. Water (HPLC grade)
10. Deionized water
11. Soduim hydroxide
12. Oxygen
13. Nitrogen
14. Sulfur dioxide

3.2 Equipment

1. Photochemical reactor with 16 lamps (UVC, 35 watt, 253.7 nm)
2. Thermo Nicolet, Nexus 670, Fourier Transform Infrared Spectrometer (FT-IR)
3. Agilent© 7890, Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)
4. Shimadzu Scientific Instrument, High performance liquid chromatography with UV detector (HPLC-UV)
5. Bruker Daltonics, Micromass Q-TOF Mass Spectrometer (ESI-MS)
6. Buchi Rotavapor®R-III, Rotary Evaporator
7. Ozone generator
8. Liquid Extractor (solvents lighter than water)
9. Separatory funnel

3.3 Methodology

3.3.1 Analysis of Methyl Ester and Alpha Methyl Ester Sulfonate

The main functional groups and compositions of methyl ester and commercial α-MES were identified by using a Fourier transform infrared spectrometer (FT-IR), a gas chromatography-mass spectrometer (GC-MS), and Electrospray Ionization Mass Spectrometer (ESI-MS).

3.3.2 MES Synthesis

To synthesize Φ-MES, 200 mL of methyl ester (density ≈ 0.86 g/cm^3) was added into a photochemical reactor as shown in Figure 3.1, which consisted of 16 lamps at the wavelength of 253.7 nm. All experiments were performed in a batch reactor at 40 °C in anhydrous medium. After that, SO_2 and O_2 were flowed into a reactor continuously for certain time. After reaction was done, N_2 was used to purge into the reactor for an hour so as to remove residual SO_2 in the system. Procedure flow diagrams of synthesis, separation, and purification steps are shown in Figure 3.2

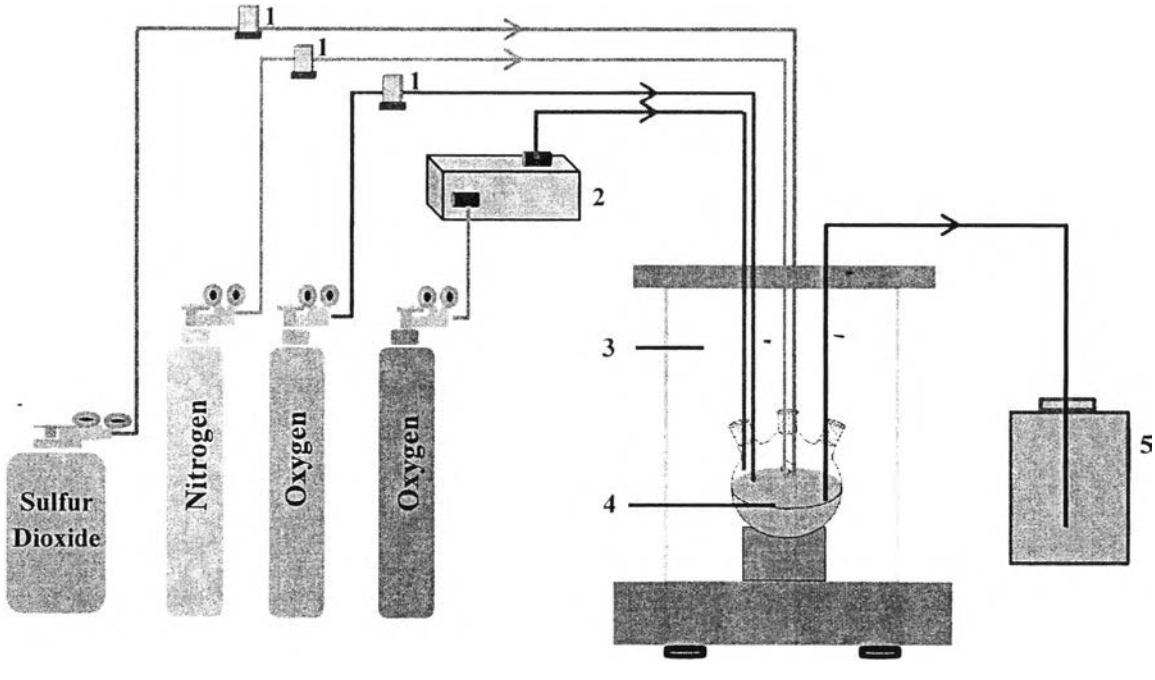

Figure 3.1 Schematic of experimental set-up: 1 = Flow meter, 2 = Ozone generator, 3 = 16 UVC lamps (253.7 nm), 4 = Reactor 5 = Water container.

3.3.3 Separation Technique

In this step, undesired products were separated from reactor outlet by liquid extraction techniques. Reactor outlet was mixed with hot water in a separatory funnel. Water (150 ml) was heated to 70 °C before shaking with product outlet. Mixture solution was left over night in the oven set 60 °C. There were two phases in the funnel: an upper layer (or organic phase) and a lower layer (or aqueous phase). After the water phase was separated out, 150 ml of hot water was mixed again with the organic phase and left in the oven. All aqueous phase was then blended with 300 ml of methanol.

For the organic phase which contained unreacted methyl ester, a small amount of fatty acid and water, it was transferred to a rotary evaporator (80 to 100 °C for 2 h) in order to remove a small amount of water in methyl ester and the left unreacted methyl ester was weighed to calculate conversion.

For water-methanol solution, it contained methyl ester sulfonic acid, sulfuric acids, and a small amount of fatty acid. Fatty acids were extracted out by using n-hexane as a solvent in a liquid-liquid extractor (for solvents lighter than water) as shown in Figure 3.3. The bottom flask filled with 500 ml of n-hexane was heated to reflux for 8 h at 100 °C. The free fatty acid solution remained in the extractor, while unreacted methyl ester, fatty acids, and n-hexane were recovered in the bottom flask. Free fatty acid solution was continuously transferred to a rotary evaporator. Methanol was evaporated out by slightly reducing pressure from 280 to 160 mbar at 50°C for 2 hours.

3.3.4 Purification Technique

To acquire the MES product, n-butanol was used as a solvent to extract desirable products from the water phase. In this step, solution was sent to the liquid-liquid extractor with 500 ml of n-butanol. The extraction condition was set at 150 to 160 °C and heated to reflux for 10 hours. The MES was recovered with n-butanol in the bottom flask, while the impurities were left in the aqueous phase. The n-butanol phase was distilled under vacuum in a rotary evaporator set at 100 °C for 2 hours. Finally, the acid solution was neutralized with a 30 %w/w sodium hydroxide solution until pH was equal to 7.

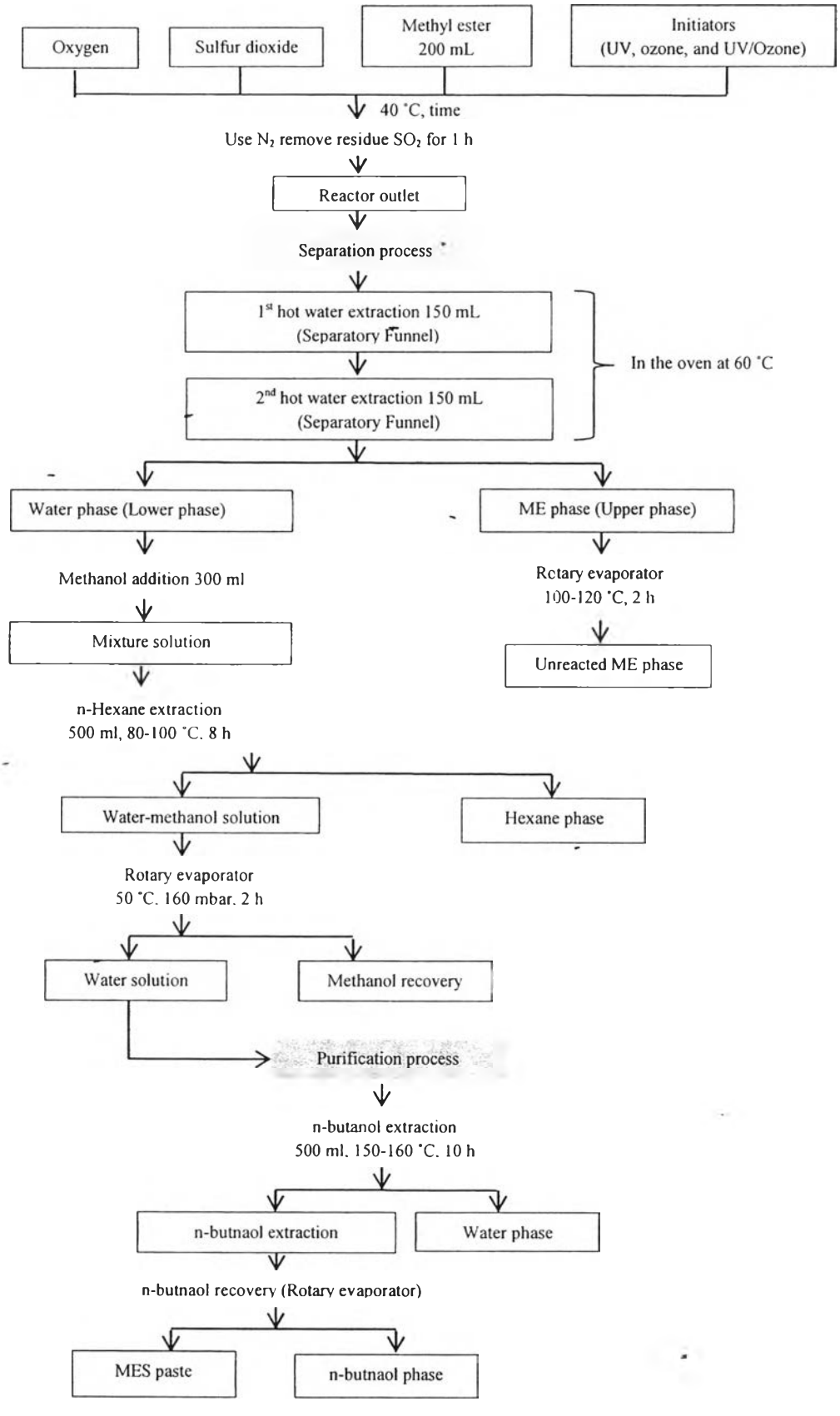

Figure 3.2 Synthesis, separation, and purification procedure flow diagrams.

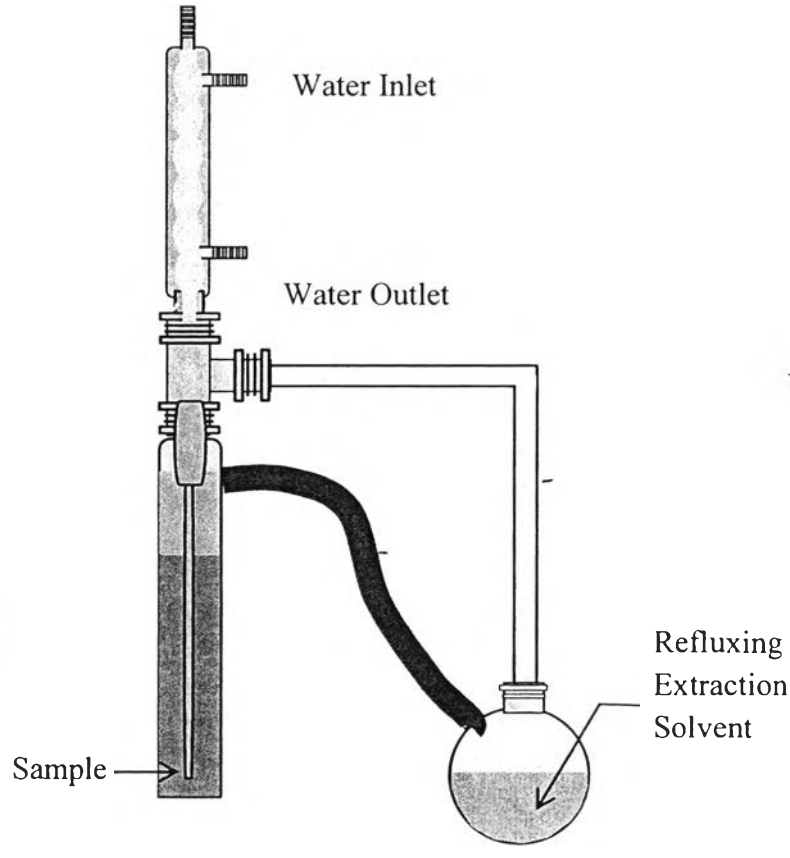

Figure 3.3 Schematic of liquid-liquid extractor for solvents lighter than water.

3.3.5 Product Analysis

3.3.5.1 Conversion Calculation

Conversion calculation was based on mass balance of methyl ester, which are the amount of starting methyl ester (200 ml) minus the recovered unreacted methyl ester and divided by the starting amount of methyl ester.

3.3.5.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared Spectroscopy (FT-IR) was performed to confirm the presence of sulfonic acid functional group of products. A Thermo Nicolet (Nexus 670) was operated in the transmittance mode with 128 scans, a resolution of 8 cm^{-1}, and wave number ranges of 4,000-650 cm^{-1}. A ZnSe disc was used as a background material of a liquid sample.

3.3.5.3 Gas Chromatography-Mass Spectrometry (GC-MS)

A Gas Chromatography equipped with a Mass Spectrometry of Time of Flight type (GC-TOF), Agilent©7890, was used to identify carbon distribution of methyl ester and unreacted methyl ester. Samples were injected to the GC-MS after dilution with carbon disulfide (CS_2) at a ratio of 1:100. Helium and nitrogen were used as a carried gas and a cooling gas, respectively. GC conditions were set as follows: Initial temperature of 120 °C, time at initial temperature of 1 minute, 2 °C/min heating rate to 200 °C, held 3 minutes at 200 °C, 3 °C/min to 280 °C, final temperature of 280 °C, held for 10 minutes, and split ratio at 1:20.

3.3.5.4 High Performance Liquid Chromatography (HPLC-UV)

In order to calculate a ratio between mono- and disulfonates, aqueous solutions were analyzed by using a high performance liquid chromatography (HPLC). HPLC consisted of a pump (LC-20AD, Shimadzu Scientific Instrument), a column oven (CTO-10AS VP, Shimadzu Scientific Instrument), and a UV detector (SPD-20A, Shimadzu Scientific Instrument). A HPLC column was Inertsil®ODS-3 (Octadecyl column; length = 250 mm; diameter = 4.6 mm; particle sizes = 5um). Propan-2-ol and methanol at the ratio of 20:80 was used as a mobile phase to perform the chromatography separation at the wavelength of 220 nm and at temperature of 30 °C.

3.3.5.5 Electrospray Ionization Mass Spectrometry (ESI-MS)

Samples were analyzed by direct infusion ESI at the flow rate of 180 µl/hour. ESI-MS fingerprints were obtained in the negative ion modes in a Q-TOF mass spectrometer (micrOTOP II, Bruker Daltonics). Typical ESI-MS conditions were set as follows: source temperature 100 °C, desolvation temperature 100°C, capillary voltage 3.8 kV, and cone voltage 40 V. Fingerprint mass spectra were acquired in the range between m/z 50 and 1000. Sodium formate, which was prepared by 40 µL of formic acid, 10 mL of isopropyl alcohol, and 10 mL of sodium hydroxide (1 M), was used as a standard. All samples were diluted to 10 µL/1 mL of acetonitrile.