CHAPTER III

EXPERIMENTAL

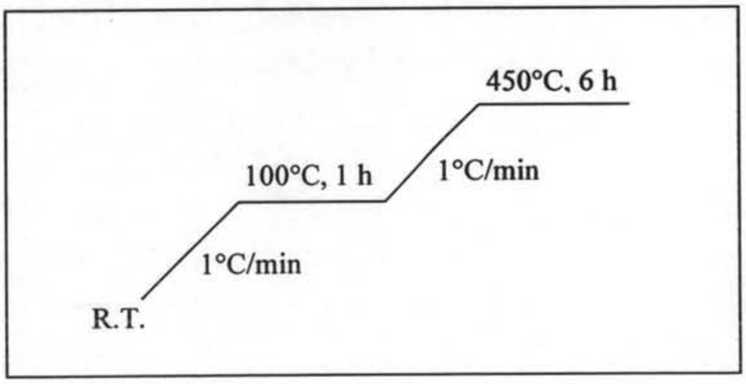
3.1 Instruments, apparatus and analytical techniques

3.1.1 Centrifuge

The separation and collection of the ETS-10 solid after hydrothermal crystallization were processed by a Sanyo Centaur 2 centrifuge at speed of 6,000 rpm. In addition, this equipment was used in recovering the catalyst after transesterification reaction.

3.1.2 Oven and furnace

ETS-10 catalysts were hydrothermally synthesized in a Memmert UM-500 oven at 200°C and 220°C for 45 and 24 h, respectively. Moreover, the catalysts were dried at 100°C in the oven. The calcination was performed on a Carbolite RHF 1600 muffle furnace in air. Calcination of ETS-10 catalyst was conducted in order to remove moisture and some impurities from the catalyst. The temperature program used for the calcination of ETS-10 catalyst is shown in Scheme 3.1.



Scheme 3.1 The temperature program for the calcination of ETS-10 catalyst.

3.1.3 Powder X-ray diffraction (XRD)

The XRD pattern and d-spacing of ETS-10 catalyst were determined by a Rigaku, Dmax 2200/Ultima$^+$ diffractometer equipped with a monochromator and Cu Kα radiation. The tube voltage and current were set at 40 kV and 30 mA, respectively. The diffraction pattern was recorded in the 2-theta ranged from 1 to 45 degree with scan speed of 3 degree/min and scan step of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree and 0.15 mm, respectively.

3.1.4 Scanning electron microscopy (SEM)

The morphology and size of ETS-10 particles were identified by a JSM-5410 LV scanning electron microscope. In SEM analysis, the samples were coated with gold. The coupled EDX mode was used in determination of the germanium content in ETGeS-10 catalysts.

3.1.5 Nitrogen adsorption-desorption technique

Microporous surface area and porosity properties of ETS-10 catalysts were determined by a BEL Japan BELSORP-mini 28SP adsorptometer in t-plot and MP (microporous) mode, respectively. The ETS-10 samples were degassed at 400°C for 2 h and nitrogen gas was used as an adsorbate at 77 K in measurement step.

3.1.6 Diffuse-reflectance UV-Visible technique (DR-UV)

Titanium coordination in ETS-10 catalyst was measured by a Shimadzu UV-2550 UV-Visible spectrophotometer in the reflectance mode equipped with an integrating sphere of 60° and $BaSO_4$ as reference. The measurement was in the range of 200 to 400 nm, the sampling interval and slit width were 0.1 nm and 2.0 nm, respectively.

3.1.7 Inductive couple plasma-atomic emission spectroscopy (ICP-AES)

Titanium contents in the catalysts were analyzed using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES). The sample prepared for ICP-AES and AAS analysis was as in general procedure of HF digestion of insoluble samples as follows:

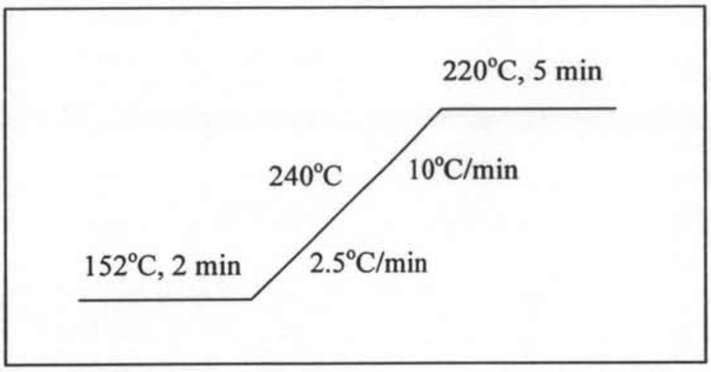
In a 100-cm^3 Teflon beaker 0.0400 g of a calcined catalyst was soaking with 10 cm^3 of conc. HCl and subsequently 10 cm^3 of 48% hydrofluoric acid (Merck) was added dropwise to get rid off silica in the form of volatile SiF_4. The sample was heated but not boiled until dryness on a hot plate and the fluoride treatment was repeated twice more. An amount of 10 cm^3 of a mixture of 6 M HCl : 6 M HNO_3 at a ratio of 1:3 was added slowly and warmed until dryness again. An amount of 10 cm^3 deionized water was added to and warmed about 5 min to complete dissolution. The solution was transferred to a 50-cm^3 polypropylene volumetric flask and made to the volume with deionized water. The flask was capped and shaken thoroughly. The solution was transferred into a plastic bottle with a treaded cap lined under with a polyethylene seal.

3.1.8 Atomic absorption spectroscopy (AAS)

Varian, 280FS atomic absorption spectroscopy was used in determination of the sodium and potassium contents in the catalysts. The method of preparing sample for AAS analysis was as same as ICP-AES technique described above.

3.1.9 Gas chromatography analysis (GC)

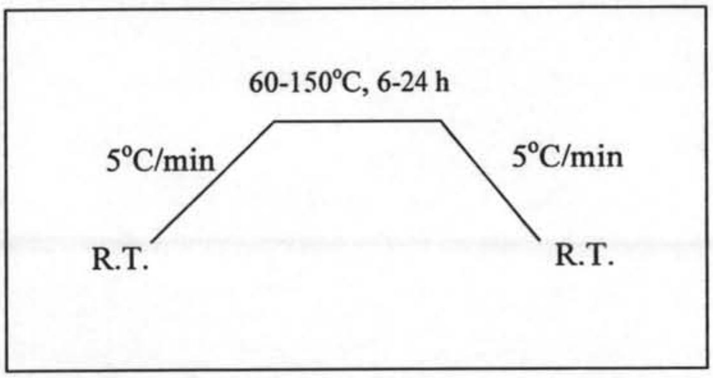
The methyl ester yield can be analyzed by Gas Chromatography which was carried out on a VARIAN CP-3800 chromatography equipped with split ratio 1:100, flame ionization detector (FID, N_2 as a carrier gas and a 30 m long CP-sil-8 column equivalent to HP-5 (0.25-mm outer diameter, 0.25 μm film thickness). Eicosane was used as an internal standard. A stock solution of *n*-hexane with a known amount of eicosane was prepared and used for analysis. Samples were prepared for analysis by adding exactly 1.0000 g of oil phase to about 5.000 g of *n*-hexane and 1 μL of sample was injected into the column. The GC temperature program for product analysis was shown in Scheme 3.2.



Scheme 3.2 The temperature program used for GC analysis of methyl ester compounds.

3.1.10 PARR reactor

The transesterification reaction of palm oil was performed in 100 ml PARR reactor. The temperature program for the reaction was shown in Scheme 3.3.



Scheme 3.3 The temperature program for transesterification reaction.

3.2 Starting materials

3.2.1 Water glass solution

Water glass solution ($Na_2SiO_3.xH_2O$), used as silica source in ETS-10 synthesis was CN-38 commercial grade obtained from C. Thai Chemicals Sodium Silicate Manufacture. The composition of sodium silicate was analyzed by following method and the value was shown in Table 3.1.

Table 3.1 The composition of water glass solution

Component	% wt
SiO_2	27.94
Na_2O	9.52
H_2O	62.54

Investigation of water glass compositions [59]

(a) Determination of % Na_2O

The empty 250 ml Erlenmeyer flask (W_1) was weighed. A 0.5 g of sodium silicate solution was added to the flask and weighed (W_2). A 50 ml of DI water was added into the flask, the solution was stirred until the homogeneous solution was The yellow solution was titrated with a 0.5 N HCl standard solution until the end point was observed (orange solution) and HCl volume (V_{HCl}) was recorded. The %Na_2O was calculated from the following formula:

$$\%Na_2O = \frac{(3.1 \times V_{HCl} \times \text{HCl conc.})}{(W_2 - W_1)} \tag{2.7}$$

(b) Determination of % SiO_2

A 2.5 g of NaF was added into the solution in step 1.4, the solution with yellow color and then stirred until homogeneous. The solution was titrated with 0.5 N HCl standard solution until the end point (pink solution) and the HCl volume (V_{HCl}) was record. The solution was then back titrated with a 0.5 N KOH standard solution until the end point was observed (yellow solution) and the KOH volume (V_{KOH}) was recorded. The %SiO_2 was calculated from the following formula:

$$\%SiO_2 = \frac{1.5022 \times (\text{HCl conc.} \times V_{HCl}) - \text{KOH conc.} \times V_{KOH})}{(W_2 - W_1)} \tag{2.8}$$

3.2.2 Palm oil

Palm oil used as triglyceride source in transesterification reaction was the commercial grade from OLEEN, Co., Ltd. The fatty acid compositions of palm oil were summarized in Table 3.2.

Table 3.2 The fatty acid composition of palm oil (OLEEN, Co., Ltd.)

Fatty acid	C No.: db	% wt
Lauric acid	C12:0	0.67
Myristic acid	C14:0	1.19
Palmitic acid	C16:0	37.94
Stearic acid	C18:0	3.84
Oleic acid	C18:1	45.22
Linoleic acid	C18:2	10.89
Linolenic acid	C18:3	0.27

3.3 Chemicals

1. Titanium (II) dioxide, TiO_2 (Riedel-deHaën, 99-100.5%)
2. Colloidal silica, SiO_2 (Aldrich, 40%)
3. Water glass solution, $Na_2SiO_3.xH_2O$ (CTC Sodium Silicate Manufacture)
4. Sodium hydroxide, NaOH (Merck, 99%)
5. Sodium chloride, NaCl (CARLO ERBA, 99.5-100.5%)
6. Potassium fluoride dihydrate, $KF.2H_2O$ (CARLO ERBA, 98%)
7. Potassium chloride, KCl (Univar, 99.8%)
8. Germanium (II) dioxide, GeO_2 (Aldrich, 99%)
9. Refined palm oil (OLEEN, Co. Ltd., commercial grade)
10. Methanol, CH_3OH (Merck, 99.9%)
11. *n*-Hexane, C_6H_{14} (Lab-Scan, reagent grade)
12. Eicosane, $C_{20}H_{42}$ (Fluka, ≥97%)
13. Dichloromethane, CH_2Cl_2 (Lab-Scan, reagent grade)
14. Methyl palmitate, $C_{17}H_{34}O_2$ (Fluka, ≥97.0%)
15. Methyl oleate, $C_{19}H_{36}O_2$ (Aldrich, 99%)
16. Acetone, C_3H_6O (Merck, 99.5%)

17. Hydrofluoric acid, HF (Merck, 48%)
18. Hydrochloric acid, HCl (CARLO ERBA, 37%)
19. Nitric acid, HNO_3 (Lab Scan, 65%)
20. Fatty cid methyl esters standard (Aldrich, 99%)

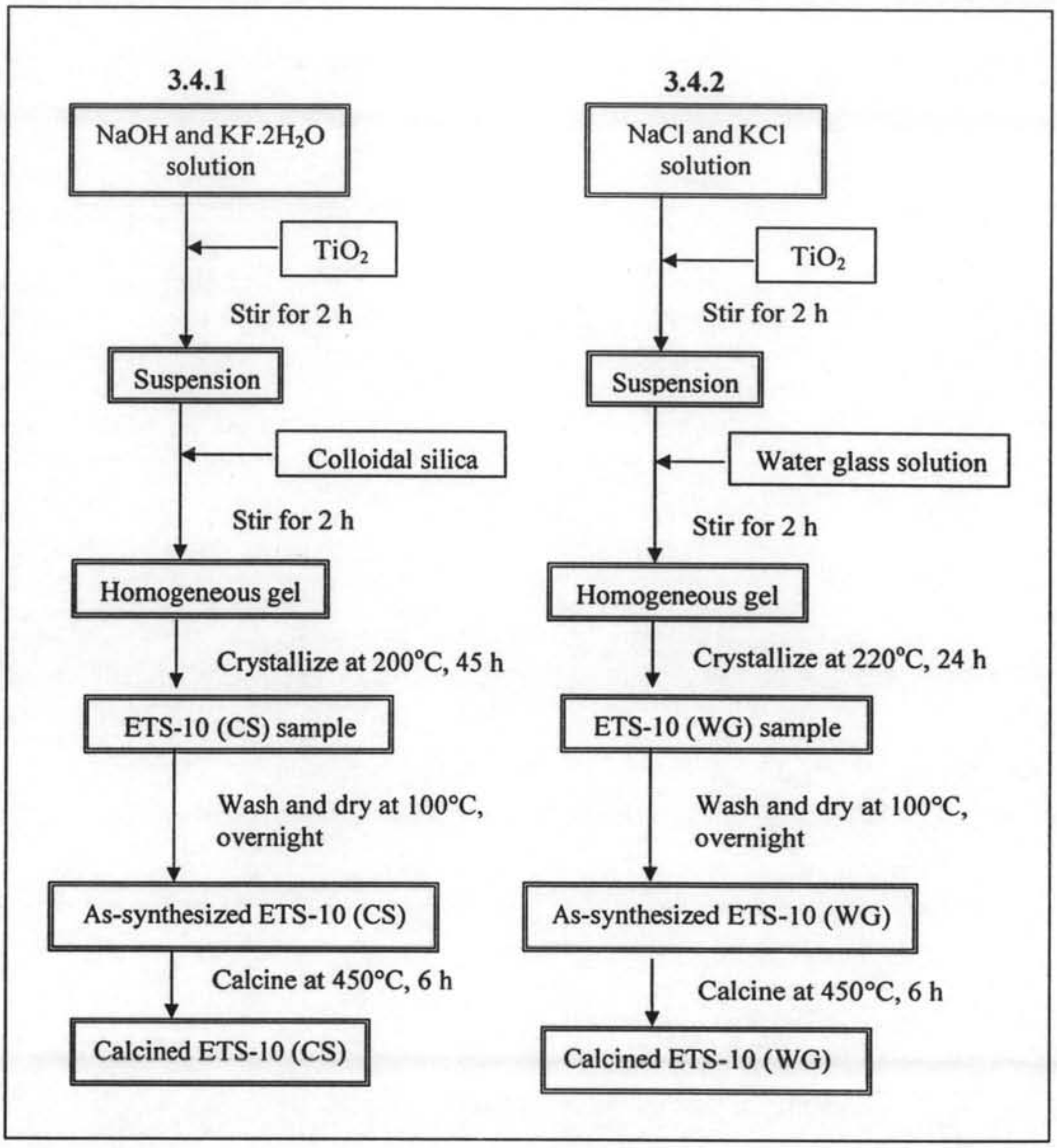
3.4 Synthesis of ETS-10 catalysts

3.4.1 Using colloidal silica as silica source

The ETS-10 catalysts were prepared following the gel composition $5SiO_2$: TiO_2: 3NaOH: KF: $75H_2O$ applied by T. Tatsumi et al. [16]. The synthesis was prepared in a 500 cm^3 4-necked round bottom flask by gradual addition of titanium dioxide in an aqueous solution of sodium hydroxide and potassium fluoride dihydrate. The milky suspension was stirred about 2 h and then the colloidal silica was added dropwise into the suspension and continuous stirred for another 2 h. The resulting gel was transferred to a PARR autoclave and crystallized at 200°C for 45 h. After hydrothermal crystallization, the ETS-10 solid was washed with deionized water and dried overnight at 100°C. The product was calcined to remove the moisture and some volatile impurities at 450°C for 6 h. The ETS-10 synthesis procedure was illustrated in Scheme 3.4.1.

3.4.2 Using water glass solution as silica source

The ETS-10 catalysts were modified from the method of Anderson et al. [10] with the gel composition $5.2Na_2O$: $0.5K_2O$: TiO_2: $5.5SiO_2$: $113H_2O$. In a 500 cm^3 4-necked round bottom flask, TiO_2 was slowly dispersed in a sodium chloride and potassium chloride solution, and then a water glass solution was added dropwise into the suspension, followed by crystallization at 220°C for 24 h. The ETS-10 solid product was washed with deionized water and dried overnight at 100°C. The calcination step was performed at 450°C for 6 h. The ETS-10 synthesis procedure was illustrated in Scheme 3.4.2.



Scheme 3.4 Diagram of ETS-10 synthesis using different silica sources.

3.5 Synthesis of ETGeS-10

The ETGeS-10 catalyst was prepared following the gel composition $5SiO_2$: TiO_2: M_2O_3: 3NaOH: KF: $75H_2O$ applied by Tatsumi et al. [60]. M represents germanium metal, whereas was varied in the range of 0.15-1.5 mol, respectively. The synthesis was performed in a 500 cm^3 4-necked round bottom flask by slowly gradual dispersion of titanium dioxide in an aqueous solution of sodium hydroxide and potassium fluoride dihydrate. GeO_2 was slowly added, and then the colloidal silica was added dropwise into the suspension and crystallized at 200°C for 45 h. After hydrothermal crystallization, the ETGeS-10 product was washed with DI water and dried at 100°C overnight. The calcination step was performed at 450°C for 6 h to remove the moisture from the ETGeS-10 powder.

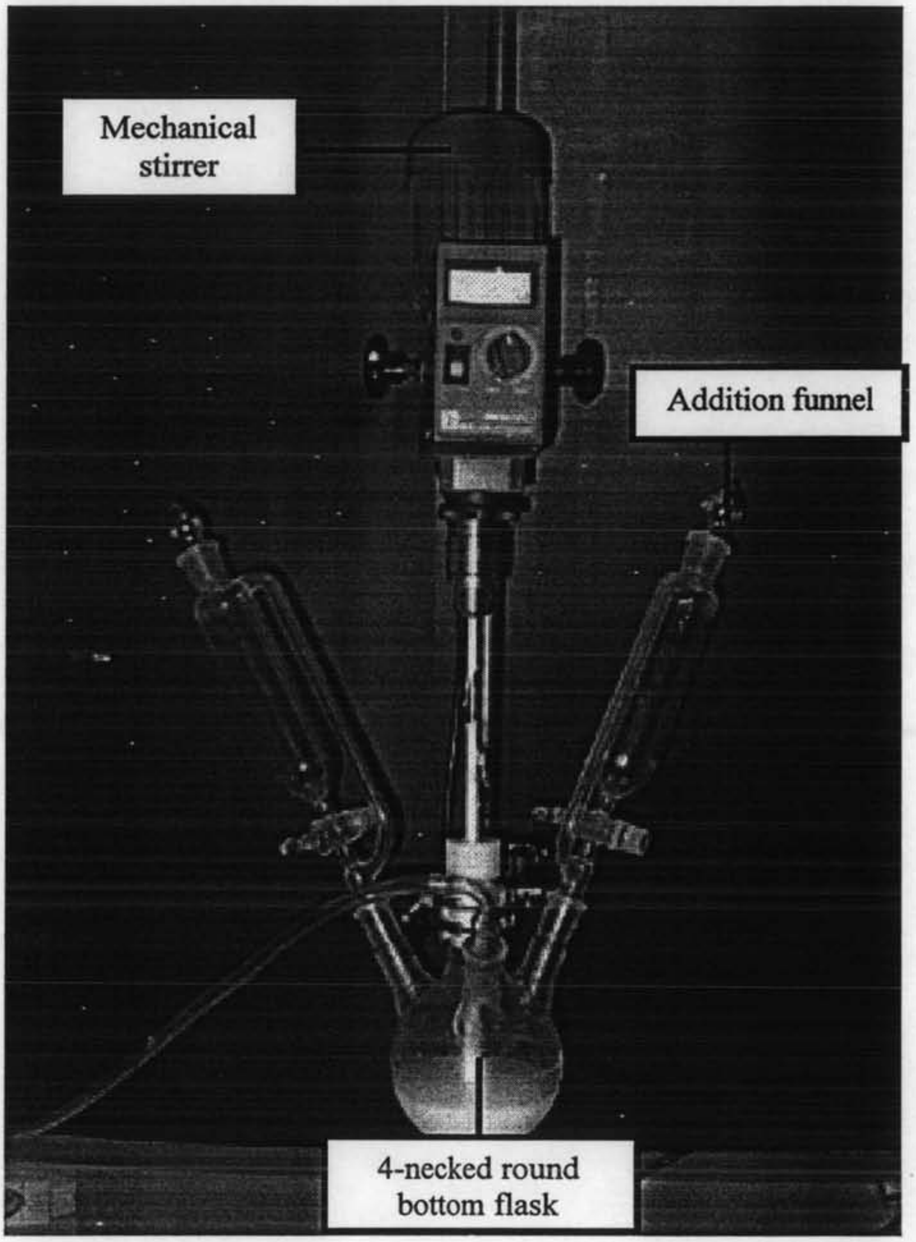


Figure 3.1 Apparatus for ETS-10 synthesis.

3.6 Alkali modification of ETS-10

3.6.1 Ion-exchange [16]

The sodium ion exchanged ETS-10 was prepared by treatment of 1 g of as-synthesized ETS-10 with 30 ml of 0.5 M sodium hydroxide at 60°C under reflux for 3 h. The resulting solid was collected by centrifuge and dried overnight at 100°C, followed by calcination at 450°C for 6 h. This sample was denoted as NaETS-10.

3.6.2 Impregnation [61]

The incipient wetness impregnation of ETS-10 was prepared using two different sodium sources, sodium acetate (NaOAc) and sodium hydroxide (NaOH) (0.5mmol/1g of calcined ETS-10). The aqueous solution of NaOAc or NaOH was added dropwise to calcined ETS-10 sample (0.5ml/1 g of ETS-10). The mixture was heated and stirred at 100°C for 1 h. Finally, the Na-loaded ETS-10 catalysts were dried at 100°C overnight and calcined at 450°C for 6 h. The alkali impregnated samples were denoted as NaOAc/ETS-10 and NaOH/ETS-10.

3.7 Catalytic activity of ETS-10, ETGeS-10 and Na-loaded ETS-10 catalysts in transesterification reaction of palm oil

3.7.1 General procedure

The transesterification reaction was performed in a PARR reactor using palm oil and methanol as starting materials. The reaction was conducted in the presence of ETS-10, ETGeS-10 or Na-modified ETS-10 catalysts. The starting solution was comprises of palm oil 7.54 g and methanol 2.46 g and then it was continuously stirred to desired reaction temperature and reaction time. After the reaction, the sample chamber was allowed to cool to room temperature and the used catalyst was separated from the liquid phase by centrifuge. The liquid fraction was evaporated to remove methanol and then diluted with 5 g of *n*-hexane. After that, 1 g of internal standard solution (estimated 0.03 M eicosane in *n*-hexane) was added before gas chromatography analysis. The used catalyst was washed with acetone, dried and calcined for regeneration.

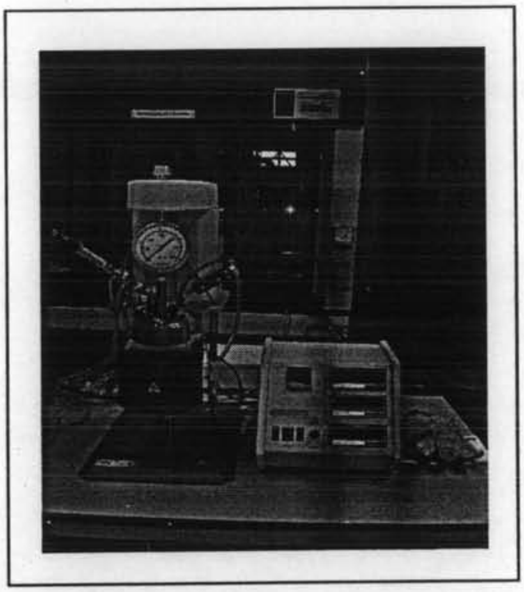
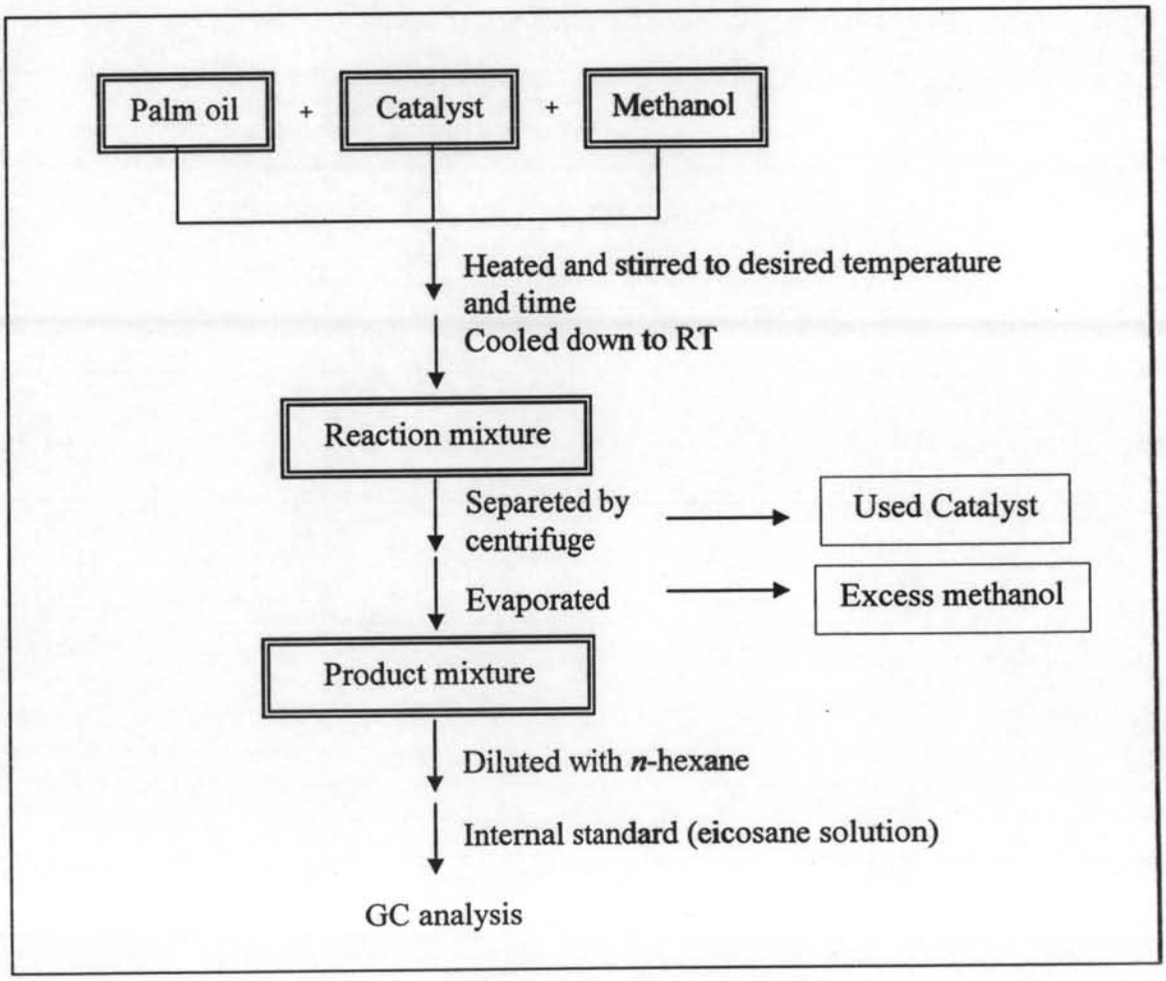


Figure 3.2 Apparatus for transesterification reaction.



Scheme 3.5 Diagram of transesterification reaction of palm oil.

3.7.2 Parameters affecting transesterification reaction

3.7.2.1 Effect of catalyst modification method

Transesterification reaction of palm oil was performed according to the general procedure mentioned above. The effect of catalyst type was studied using the ETS-10, ETGeS-10 and Na-modified catalysts. The calcined catalysts (450°C for 6 h) were introduced to the reaction mixture at MeOH to palm oil mole ratio of 9:1. The reaction was performed at 120°C for 24 h.

3.7.2.2 Effect of catalyst amount

The effect of catalyst loading was also studied in transesterification reaction. The catalyst amounts to reaction mixture were varied to 1 wt%, 5 wt% and 10 wt% at triglycerides to methanol mole ratio of 9:1, and at 120°C for 24 h.

3.7.2.3 Effect of methanol to palm oil mol ratio

The transesterification reaction was performed at various methanol to palm oil mole ratios according to the general procedure mentioned above. The effect of methanol to palm oil mole ratios were investigated at the value of 6:1, 9:1 and 12:1, respectively.

3.7.2.4 Effect of reaction time

The reaction was performed at 120°C for different reaction time of 6, 12, 24, and 36 h. Other parameters are kept the same as in the general procedure.

3.7.2.5 Effect of reaction temperature

To investigate the effect of temperature and time in transesterification reaction, the reaction was also performed at various temperatures as the general procedure above. The reaction temperature was varied to 90°C, 120°C and 150°C and the reaction time was kept for 24 h.

3.7.2.6 Activity of regenerated catalysts

The used Na-modified ETS-10 catalysts were tested for their activity again without any treatment except washing with acetone and calcination.

3.7.2.7 Activity of Na-reloaded catalysts

After reaction, the catalysts were washed with acetone to remove some impurities. Then it was dried overnight at 100°C and regenerated by the calcination at 450°C for 6 h. The regenerated catalysts were reloaded with Na sources the by ion exchange and impregnation prior to use. The catalytic activities of Na-reloaded catalysts were also studied in transesterification reaction at palm oil to methanol mole ratio of 9:1, at 120°C, and for 24 h. Moreover, the retained structure of catalyst was confirmed by XRD technique.