

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemical

Chemicals used in this research work are as follows:

- Vegetable oil (Palm oil) from Naval Engineering Command
- CH₃OH (Anhydrous methanol, 99.9%) supplied by Lab scan
- KOH (Potassium hydroxide) supplied by Lab scan
- NaY zeolite supplied by TOSOH Corporation.
- Na-mordenite zeolite supplied by ZEOLYST Corporation.
- Al₂O₃ supplied by COA World Chemicals
- Bentonite clay supplied by Thai Nippon Company, Thailand
- Na₂SO₄ (Sodium sulfate) supplied by Fisher Scientific.
- n-Heptane (99.5%) supplied by Fisher Scientific
- Methyl heptadecanoate (standard for GC, 99.7%) supplied by Fluka

3.2 Catalyst Preparation

3.2.1 KOH/Al₂O₃ Catalyst

A series of KOH/Al₂O₃ catalysts with varying KOH loadings (10, 15, 20, 25, 30, and 35 wt%) were prepared by the impregnation of an Al₂O₃ support with an aqueous solution of KOH. The prepared catalysts were dried in an oven at 110 °C for 24 h and were calcined at 500 °C for 3 h.

3.2.2 KOH/NaY Zeolite Catalyst

The KOH/NaY was prepared by the method reported by Noiroj *et al.* (2009). The NaY zeolite was dried in an oven at 110 °C for 24 h and was impregnated with an aqueous solution of KOH with various loadings (5, 10, 15, and 20 wt%) for 24 h. Finally, it was dried in air at 110 °C for 24 h.

3.2.3 KOH/Mordenite Zeolite Catalyst

The KOH/mordenite catalyst was prepared by an impregnation method. The pure mordenite zeolite was calcined at 600 °C for 3 h to remove the adsorbed water on the surface. To modify the mordenite zeolite with different amount of K loadings (5, 10, 15, 20, 25, and 30 wt%), the mordenite zeolite was impregnated with an aqueous solution of KOH for 24 h to ensure that KOH solution diffused and dispersed thoroughly on the surface of the support. Then it was dried at 110 °C for 24 h.

3.2.4 KOH/Bentonite Clay Catalyst

The pure bentonite clay was dried at 110 °C for 24 h to remove the adsorbed water on the surface. This support was impregnated with an aqueous solution of KOH with various loadings (5, 10, 15, and 20) wt% and allowed to rest for 24 h. Finally, the modified catalysts were dried in air at 110 °C for 24 h.

3.3 Catalyst Characterization

Both fresh and spent catalysts were used to determine the physical and chemical properties of catalyst in order to understand the catalytic activity of catalysts as follows:

3.3.1 X-ray Diffraction (XRD)

A Bruker X-ray diffractometer system (D8 Advance), equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating CuK_α radiation (1.5405 Å), was used as an X-ray source to obtain the XRD patterns at running conditions for the X-ray tube (40 kV and 40 mA). The sample was prepared and held in the X-ray beam. The detector scans the intensity of diffracted radiation and the peak position from the sample as a function of 2θ by starting at the 10 to 90° (2θ) range with a scan speed of 0.02° (2θ)/ 0.5 second. The XRD patterns were compared to the standards to identify the crystalline phases.

3.3.2 N₂ Adsorption and Desorption

The specific surface area and pore size distribution of the catalysts were determined by N₂ adsorption and desorption, or Brunauer-Emmet-Teller (BET) method, using a Sorptomatic model 1990 instrument (Thermo Finnigan). The catalyst was prepared by outgassing for 24 h at 300 °C. Helium gas was used as an adsorbate for the blank analysis, and nitrogen gas was used as the adsorbate for the analysis. The determination of the surface area of finely-divided and porous materials, in spite of the over simplification of the model on which the theory is based on the BET equation in the linear form as following:

$$\frac{p}{n^a(p^o-p)} = \frac{1}{n_m^a \cdot c} + \frac{(c-1)p}{n_m^a \cdot c \cdot p^o} \quad (3.1)$$

where:

n^a is the amount adsorbed at the relative pressure p/p^o

n_m^a is the monolayer capacity

p is pressure of gas

p^o is saturated vapor pressure of the liquid at the operating temperature

c is related exponentially to the enthalpy (heat) of adsorption in the first adsorbed layer

The specific surface area, pore volume, and pore size distribution were obtained by measuring the volume adsorped at different a P/P_o values. Total pore volume was estimated by measuring the volume adsorped gas at P/P_o of 0.99, and total micropore volume and the micropore size distribution were obtained by applying the Horvath-Kawazoe method, 1983.

The crystallinity of catalyst was calculated from the ratio of the measured micropore volume ($V_{\mu p}$) to the calculated micropore volume (N₂ sorption % crystallinity = $V_{\mu p}/V_{\mu p cal} \times 100$). The calculated micropore volume ($V_{\mu p cal}$) was determined from the potassium loaded on the NaY micropore volume corrected by a loss of volume

3.3.3 Temperature-Programmed Desorption (TPD)

Temperature-programmed Desorption (Micromeritics, 2900) was used for observing desorbed molecules from the surface when the surface temperature was increased. The basic properties of the samples were determined using the temperature-programmed desorption of CO₂ (CO₂-TPD), which was used as the probe molecule. A fresh 0.1 g sample was degassed by heating in a flow of helium gas at a rate of 10°C/min from room temperature to 300°C, and was kept at 300 °C for 2 h. The adsorption of CO₂ gas occurred at 50°C for 1 h and the physically adsorbed CO₂ gas was purged by a He flow at 30°C for 2 h. CO₂-TPD was performed at a heating rate of 10°C/ min up to 600 °C. Finally, the basic site was calculated as shown in Appendix A.

3.3.4 Hammett Indicator

The base strength of the samples (H_-) was determined by using Hammett indicators in a manner similar to that described previously (Xie *et al.*, 2006). The following Hammett indicators were used: bromthymol blue, phenolphthalein, 2,4-dinitroaniline, and 4-nitroaniline.

Table 3.1 Hammett indicators

Indicator	pK_B	Color	
		Neutral (BH)	Basic (B^-)
Bromthymol blue	$H_- = 7.2$	Blue	Green-blue
Phenolphthalein	$H_- = 9.8$	Colorless	Pink
2,4-dinitroaniline	$H_- = 15.0$	Yellow	Purple
4-nitroaniline	$H_- = 18.4$	Yellow	Yellowish orange

3.3.5 Acid Titration Method

The titration method was used to measure the total basicity of the samples. A 20 mg of catalyst samples was shaken in the 5 ml (0.02 M aqueous HCl) for 1 h, and the remaining acid was then titrated with standard base (0.02 M aqueous

KOH) (Wang *et al.*, 2001). The standard solutions were prepared and calculated to estimate the basic site of each catalyst as shown in Appendix B.

3.3.6 Scanning Electron Microscopy equipped with Energy Dispersive Spectrometer (SEM-EDS)

A Scanning Electron Microscope (SEM), Hitachi/S-4800, was utilized to identify the microstructure and capture the micrograph of the catalyst morphology. Most common imaging mode collects at low-energy (<10 kV). An Energy Dispersive Spectrometer (EDS), Oxford Model 6111, was utilized to identify the presence of elements in the catalyst region being examined at high-energy (<20 kV). The catalyst sample was placed on a stub and coated with platinum in a sputtering device before being placed in the sample holder of the SEM.

3.3.7 X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) spectrometry (Oxford, model ED2000) was used to determine the bulk composition of the catalysts. All XRF analysis was performed using an accelerating voltage of 15 kV and a current of 30 μA . The silicon (Si), aluminum (Al), and the potassium content of the fresh and spent catalysts were measured by XRF. Leached potassium refers to the total amount of potassium of the fresh catalyst withdrawn from the amount of potassium of the spent catalyst.

3.3.8 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR was applied especially for the determination of functional group of a support and biodiesel which covered on the spent catalyst. The potassium bromide (KBr) pellet was dried at 110 °C for 24 h and kept it in the desiccator. The samples were prepared by mixing a small amount of sample powder with dried KBr and pressing into 13 mm diameter circular wafers using 3 metric tons of force for 1 min. The spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1} .

3.3.9 Nuclear Magnetic Resonance (NMR)

NMR spectroscopy is used to determine distinction of physical, chemical, electronic and structural materials in term of molecules due to their chemical shift. The Nuclear magnetic resonance (NMR) spectra were obtained by a Varian Inova Model 400 spectrometer. ^1H , ^{27}Al , and ^{29}Si solid-state NMR were operated at frequencies of 400, 130.32, and 99.36 MHz, respectively and were performed at room temperature with a spin rate of 10 kHz. About 2000 scans were accumulated for each spectrum. The Bruker program, WINNMR, was used for data processing.

3.4 Experimental Procedure

3.4.1 Catalytic Reaction in a Batch Reactor

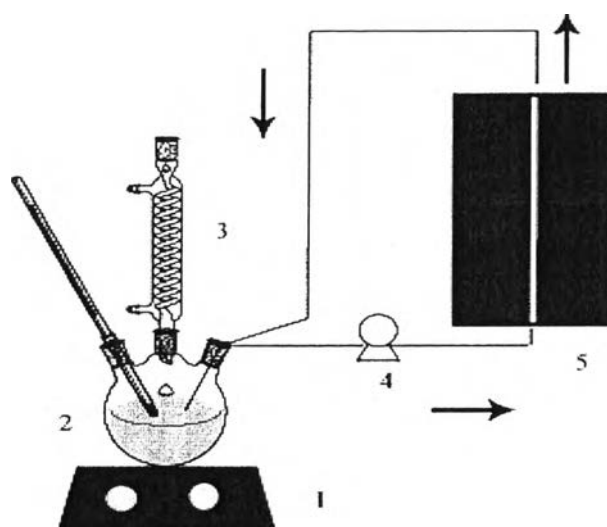
One hundred grams of palm oil was weighed and placed in a 500 ml three-necked flask. The vegetable oil was heated to 60 °C by heater. The desired amount of methanol and catalyst was weighed and added into the oil reactor. A magnetic stirrer was used for mixing the oil, methanol, and catalyst at the desired speed. The reaction was carried out until it reached the desired reaction time. After that, the reaction was stopped by cooling the reactor to room temperature and the catalyst was immediately separated from the product mixture by using a suction flask. The mixture was placed in the separatory funnel and allowed to stand overnight to ensure that the separation of the methyl esters and the glycerol phase occurred completely. The glycerol phase (bottom phase) was removed and left in a separate container. Finally, the methyl esters (biodiesel) were dried by adding 25 wt% Na_2SO_4 base on weight of oil

3.4.2 Catalytic Reaction in a Packed-bed Reactor (with recirculation)

Refined palm oil and methanol were weighed and placed into a three-necked flask and heated to 60 °C. The mixture was stirred until it reached the desired temperature and was driven by a peristaltic pump at a constant rate to the bottom of the packed-bed reactor. The mixtures were circulated back to the system until they

reached the desired reaction time. The products were pumped back into the flask to separate and purify as described in the batch reactor procedure.

The peristaltic pump can deliver flow rates from 0.07 to 1140 mL/min. Head gear speed can be adjusted manually or automatically through external control interface from 1 to 300 rpm, and uses the power supply of AC 90-260V, and 50/60 Hz. The Tygon® Fuel Tubing No. 13 was used with the pump because it resists the swelling and hardening caused by hydrocarbon-based fluids. This significantly reduces the risk of adulteration and leakage.



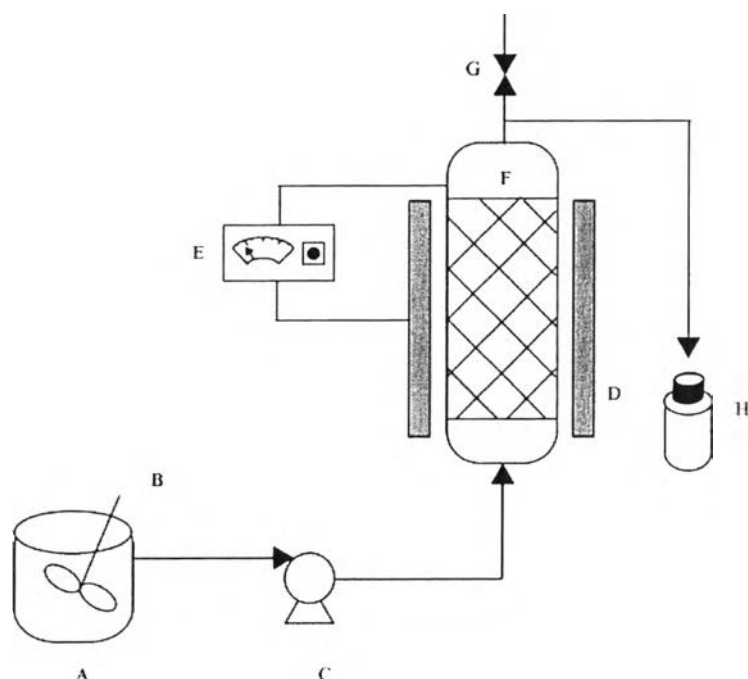
1 Hot plate, 2 Round bottom flask, 3 Condenser, 4 Peristaltic pump, 5 Reactor

Figure 3.1 Schematic of packed-bed reactor (recirculation).

3.4.3 Catalytic Reaction in a Packed-bed Reactor

The transesterification reaction was performed in a packed-bed reactor system operating at atmospheric pressure as shown in Figure 3.2. Palm oil and methanol (1:15 molar ratio) were weighed and placed in a stirrer tank. The reactor system consisted of stainless steel column (dimension of 2.5 cm i.d. x 15 cm length), and furnace (dimension of 3 cm i.d. x 25 cm length) equipped with a temperature controller (Shimax) employing a K-type thermocouple (measuring temperature within the range of 0-650 °C) thereby providing reactor stages. Sixty grams of catalyst (10-20 mesh) were packed into stainless steel column and heated to

60 °C for 2 h before reactant mixtures were fed into a column at a preferred flow rate. The methyl esters product was separated from glycerol phase.



A= tank, B =mechanical stirrer, C = Peristaltic pump, D= Furnace, E = Temperature controller and thermocouple, F = Reactor, G = Pressure relief valve, and H = sample collector

Figure 3.2 Schematic of packed-bed reactor.

3.5 Catalytic Activity Measurement

3.5.1 Methyl Ester Measurement

The FAMES of the biodiesel were analyzed by an HP 5890 gas chromatograph equipped with a flame ionization detector and a capillary column DB-WAX (30 m x 0.25 mm). The injection and detector temperatures were 200 and 230 °C, respectively. The oven temperature was held at 130 °C for 2 min and increased to 220 °C at a heating rate of 2 °C/min, and then held for 5 min. Methyl heptadecanoate was used as an internal standard to determine the amount of FAME.

The methyl ester content was determined by using Equation 3.2, and its chromatogram was shown in Appendix C.

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} * \frac{C_{EI} * V_{EI}}{m} * 100 \quad (3.2)$$

Where	C	Fatty acid methyl ester content (FAME)
	$\sum A$	The overall area of methyl ester from C_{12} to $C_{24:1}$
	A_{EI}	The peak area of that which is aligned with methyl heptadecanoate solution
	C_{EI}	Concentration in mg/ml of methyl hepta decanoate solution
	V_{EI}	Volume of methyl hepyta decanoate solution
	m	Weight in mg of sample

3.5.2 Mono-, Di-, Tri-glyceride Measurement

The composition of the reaction mixture samples was determined by the somewhat modified High Performance Liquid Chromatography (HPLC) method of Holčapek *et al.*, (1999) using a Perkin Elmer High Performance Liquid Chromatography, equipped with a degasser, a binary pump, a Zorbax Eclipse XDB-C18 capillary column (4.6 m x 150 mm x 5 μ m) and an UV/VIS detector. The flow rate of a binary solvent mixture methanol, (solvent A), and 2-propanol/n-hexane, 5:4 by volume, (solvent B) was 1 ml/min with a linear gradient (from 100% A to 40% A + 60% B in 15 min) and held for 15 min. The components were detected at 205 nm. The fatty acids were identified by comparison of retention times of the oil components with those of standards. The samples of the reaction mixture were dissolved into a mixture of 2-propanol/n-hexane, 5:4 v/v. All samples and solvents were filtered through 0.45 μ m Millipore filters. The methyl ester content, and mono-, di-, and tri-glyceride were determined and their chromatogram was shown in Appendix D.