

## CHAPTER III



## EXPERIMENTAL

### 3.1 Chemicals

All chemicals (analytical grade) used were obtained as follows:

**Table 3.1** Chemicals and suppliers

Chemicals	Suppliers
Aluminium nitrate nonahydrate	Fluka Chemies A.G., Switzerland
Ammonium carbonate	Aldrich Chemical Company, Inc., USA
Ammonium hydroxide	Fluka Chemies A.G., Switzerland
Benzoic acid	Fluka Chemies A.G., Switzerland
Bromothymol blue	Fluka Chemies A.G., Switzerland
Calcium acetate	Fluka Chemies A.G., Switzerland
Citric acid	Merck
Decane	Fluka Chemies A.G., Switzerland
Ethylene glycol monoethyl ether	Fluka Chemies A.G., Switzerland
Gallium nitrate nonahydrate	Fluka Chemies A.G., Switzerland
Glyceryl tributyrinate (tributylin)	Merck
Hexane	Merck
Magnesium nitrate hexahydrate	Fluka Chemies A.G., Switzerland
Methanol	Merck
Methyl laurate	Merck
Potassium acetate	Fluka Chemies A.G., Switzerland
Potassium bromide	Fluka Chemies A.G., Switzerland
Potassium chloride	Fluka Chemies A.G.
Potassium hydroxide	Aldrich Chemical Company, Inc., USA
Potassium nitrate	Aldrich Chemical Company, Inc., USA
Potassium- tert- butoxide	Fluka Chemies A.G., Switzerland
Sodium acetate	Fluka Chemies A.G., Switzerland

**Table 3.1** Chemicals and suppliers (continued)

<b>Chemicals</b>	<b>Suppliers</b>
Sodium azide	Fluka Chemies A.G., Switzerland
Sodium chloride	Fluka Chemies A.G., Switzerland
Sodium hydroxide	Aldrich Chemical Company, Inc., USA

### 3.2 Equipments

All equipments, used in the catalyst preparation and transesterification reaction, were listed as follows:

- Round bottom flask
- Magnetic stirrer
- Reflux condenser
- Desiccator

### 3.3 Characterization methods

#### 3.3.1 Fourier-transform infrared spectroscopy (FT-IR)

Fourier-transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The samples were made into a KBr pellet. Infrared spectra were recorded between 400 to 4000  $\text{cm}^{-1}$  in transmittance mode.

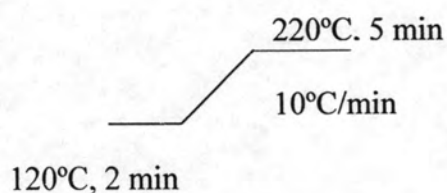
#### 3.3.2 Gas-liquid chromatography (GC)

Capillary column gas chromatograph GC16A (Shimadzu) was used for determination of tributyrin and methyl ester product from palm oil.

The GC conditions for the determination of conversion of tributyrin

Column	: DB-1
Detector	: Flame ionization (FID)
Detector temperature	: 250°C
Injector temperature	: 250°C
Carrier gas	: N <sub>2</sub>
Flow rate	: 70 kPa.

Programmed temperature:

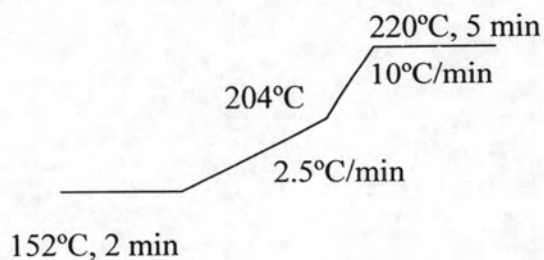


The GC conditions for the determination of conversion of palm oil:

The oven temperature program are set as follows:

Column	: DB-1
Detector	: Flame ionization (FID)
Detector temperature	: 220°C
Injector temperature	: 220°C
Carrier gas	: N <sub>2</sub>
Flow rate	: 100 kPa.

Programmed temperature:



### **3.3.3 Inductively Coupled Plasma (ICP)**

ICP was performed with Perkin Elmer model PLASMA-1000 at Scientific and Technology Research Equipment Centre, Chulalongkorn University.

### **3.3.4 X-ray diffraction spectrometer (XRD)**

The XRD analysis was performed with Rigaku, DMAX 2002/Ultima Plus. X-ray diffraction.

### **3.3.5 Nitrogen adsorption (Brunauer-Emmett-Teller method (BET))**

BET specific surface area of the catalysts was carried out using a BELSORP-mini. The principle of this method is by adsorption of a particular molecular species from a gas or liquid onto the surface. Based upon one adsorbed layer, the quantity of adsorbed material gave directly the total surface area of the sample. The pore size distributions were obtained according to the Barret–Joyner–Halenda (BJH) method from the adsorption branch data.

### **3.3.6 Basicity measurement [5]**

Catalyst (0.4 g) was stirred in 25 ml of distilled water at room temperature for 2 h and then filtered. The filtrate was titrated with 0.02 M benzoic acid solution (in methanol). The indicator used was bromothymol blue (pH range 6-9). The basicity was calculated by mmol of benzoic acid used in the titration of 1 g catalyst.

### 3.4 Catalyst preparation

#### 3.4.1 MgAl Hydrotalcite, alkali free coprecipitation method [20]

An aqueous mixture (60 ml) of 18.46 g (72 mmol)  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 6.75 g (18 mmol)  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (molar ratio of  $\text{Mg}/\text{Al} = 4$ ) was added slowly to 90 ml of an aqueous solution of 11.52 g (0.11 mol)  $(\text{NH}_4)_2\text{CO}_3$ . The pH of the mixture was held at pH 8 by the dropwise addition of  $\text{NH}_4\text{OH}$ . The resulting mixture was heated to  $65^\circ\text{C}$  while stirred vigorously for 3 h. Then it was filtered and washed with distilled water until the filtrate was neutral. The precipitate was dried in an oven at  $100^\circ\text{C}$  for 18 h and calcined at  $450^\circ\text{C}$  for 35 h (in the literature [20], calcination time is 3 h).

The rehydrated hydrotalcite was prepared from the above calcined hydrotalcite by placing it in a desiccator which was saturated with water for 48 h.

#### 3.4.2 MgGa Hydrotalcite

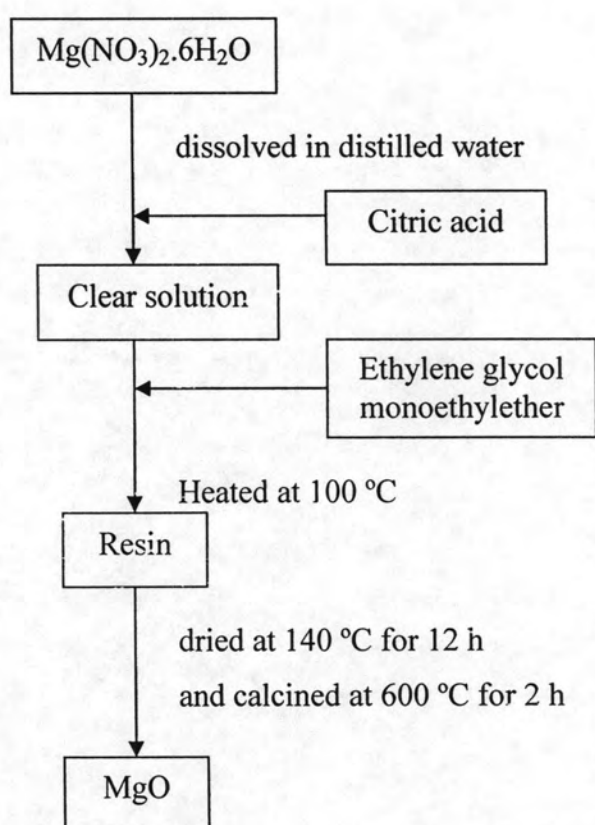
The same procedure as A was performed but  $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was used in place of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , with molar ratio of  $\text{Mg}/\text{Ga} = 4$ .

#### 3.4.3) Metal-loaded catalysts

The calcined MgAl or MgGa hydrotalcites prepared above were loaded with Na, K or Ca salt by using impregnation method. The K or Ca salt which dissolved in a minimum volume of distilled water was added into the calcined hydrotalcite powder and the mixture was stirred at room temperature for 1 h. Then it was dried at  $100^\circ\text{C}$  for 12 h and calcined at  $600^\circ\text{C}$  for 2 h.

### 3.4.4) MgO [22]

This oxide was synthesized using modified citrate precursor method. Magnesium nitrate hexahydrate  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2.04 g, 7.96 mmol), was dissolved in 50 ml distilled water. Then citric acid (5.17 g, 26.91 mmol) was added. After 10 minutes stirring, the solution became clear. Then ethylene glycol monoethyl ether (7.76 g, 86.10 mmol) was added. Then the contents were heat at  $100^\circ\text{C}$  to evaporate water. The gel was dried at  $200^\circ\text{C}$  to get a brown fluffy. The brown fluffy was grinded and calcined at  $600^\circ\text{C}$  2 h.





### 3.4.5) Exchanged hydrotalcite with *tert*-butoxide

The rehydrated hydrotalcite was ion-exchanged with 0.1 M solution of potassium *tert*-butoxide in 100 ml THF under stirring at room temperature for 24 h. The precipitate was filtered and washed with distilled water and dried at 100°C 12 h.

### 3.4.6) Regeneration of catalyst

At the end of reaction the catalyst was separated by filtration and was washed with methanol to remove glycerol (by product) from the reaction. The catalyst was dried at 100°C 12 h before calcined at 600°C 2 h. The regenerated catalyst was prepared by reloading potassium metal and calcined again at the same condition.

## 3.5 Transesterification

### 3.5.1. Transesterification of tributyrin (model compound)

In a 100 ml round bottom flask equipped with a stirrer and a reflux condenser, 12.5 ml (0.30 mol) of methanol and 0.05 g (1.5% w/w tributyrin) catalyst were added. Then 3 ml (0.01 mol) of tributyrin was added. The temperature is set to 60°C. After 3 h, the sample was analyzed by gas chromatography (GC) using decane as an internal standard.

### 3.5.2 Test of metal leaching from the catalyst

Catalyst (0.05 g) was stirred in 12.5 ml methanol at 60°C for 1 h and then was filtered by filter paper. The filtrate was used for transesterification to observe any leaching of metal from the catalyst.

### 3.5.3. Transesterification of refined palm oil

Transesterification of refined palm oil was taken place in either 100 ml round bottom flask equipped with magnetic stirrer and reflux condenser or a Parr reactor. After the reaction, the catalyst was filtered by filter paper. The mixture was put into a separating funnel. The upper layer was methyl ester and the lower layer was glycerol. The methyl ester was separated. The excess methanol was evaporated using rotary evaporator. The methyl ester was washed with saturated NaCl solution and distilled water to separate glycerol and soap. Sodium sulfate anhydrous was used to remove water in the methyl ester product.

### 3.5.4 Analysis of products from refined palm oil transesterification

The analysis of methyl ester was carried out by GC using methyl laurate as reference.

Methyl esters content (%) [23]

$$= \frac{(\text{Weight of reference} \times \text{Area of methyl esters}) \times 100}{\text{Area of reference} \times \text{Weight of methyl esters}}$$

Product yield (%)

$$= \frac{(\text{Weight of upper layer} \times \% \text{Methyl esters content})}{\text{Weight of palm oil used}}$$

The transesterification reaction was studied by varying various parameters as follows:

- Reaction temperature
- Reaction time
- Molar ratio of methanol/oil
- Catalyst amount