

CHAPTER III

EXPERIMENTAL

3.1 Apparatus and Instruments

Hotplate magnetic stirrer from Snijders model 34532 was used for preparation of methyl ricinoleate by transesterification of castor oil with methanol. The calcinator from carbolite furnace model GSM was used to calcine catalysts. The prepared catalysts were packed in Annealed 316 stainless steel tubular reactors with $\frac{1}{4}$ in. O.D. x 0.035 in. wall thickness x 6 feet length. Furnaces for reaction unit was adapted from old gas chromatograph instrument from Pye Unicame GC model Pye series 104 chromatograph. The temperature of the reaction unit was controlled by Union model PZ-6 temperature controller. To adapt the electronic power for heating coil (3000 W), the system used Mitsubishi magnetic contractor model S-N10 for temperature support. The Gas chromatograph – mass spectrometer (GC-MS) from Fisons Instruments, GC 8000 Series; MS VG TRIO 2000 was used to identify and quantitatively determination of the methyl ester components of product. The structure of product was identify by nuclear magnetic resonance spectrometer (NMR) from Bruker, model AC-F 200. The prepared catalysts were characterized by Wavelength Dispersive X-ray fluorescence Spectrometer (XRF) from Phillips model PW 2400.

3.2 Materials

Castor oil was obtained from Thai Kawaken Co., Ltd. Pure hydrogen gas and oxygen-free nitrogen gas were bought from Praxair (Thailand) Co., Ltd. and T.I.G Co., Ltd., respectively. Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) analytical grade, sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) analytical grade, iodine (I_2) chemical grade were purchased from Fluka. Methyl alcohol, glacial acetic acid, absolute ethanol, iodine trichloride (ICl_3), potassium iodide (KI), potassium hydroxide (KOH), and sodium sulfate anhydrous (Na_2SO_4) all analytical grade were purchased from Merck. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$ chemical grade) was obtained from May & Baker Co.Ltd. Alumina support (Al_2O_3) and Sulfuric acid (98% w/w, analytical grade) were purchased from J.T. Baker Chemical Company.

3.3 Experimental Procedures

1. Preparation, Activation, Regeneration and Characterization of Catalysts

1.1 Preparation of catalyst

1.1.1 Catalyst containing 10% Ni on alumina support by impregnation

The nickel salt stock solution was prepared by dissolving 33.56 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50.0 cm^3 distilled water. A 40.0-g of alumina support was poured into 500- cm^3 flask equipped with 50 cm^3 burette. The amount of 26.0 cm^3 of the nickel stock solution was gradually dropped on the support, which was left at room temperature for 1 hour and stirred occasionally. Then the mixture was first dried at 120 °C for 16 hours. Finally, it was calcined at 600 °C for 3 hours to convert the nickel salt to

nickel oxide and the color of catalyst was changed from green ($\text{Ni}(\text{NO}_3)_2$) to black (NiO).

1.1.2 Catalyst containing 15% Ni on alumina support by impregnation

The preparation procedure was carried out as in 1.1.1 but the amount of nickel was increased to 57.48 g.

1.1.3 Catalyst containing 20% Ni on alumina support by impregnation

The preparation procedure was carried out as in 1.1.1 but the amount of nickel was increased to 77.12 g.

1.2 Activation of catalysts

The catalysts were activated under hydrogen pressure before used. Each calcined catalyst in this research was packed in a tubular reactor, which was installed in a furnace and was heated at $450\text{ }^\circ\text{C}$ while maintained the flow of hydrogen at 20 psi for 6 hours to obtain the activated catalyst.

1.3 Regeneration of catalysts

The used catalysts were taken out of the tubular reactor and decoked in a furnace at $650\text{ }^\circ\text{C}$ for minimum of 10 hours, and then was activated following activation procedure that mentioned before reused.

1.4 Characterization of catalysts

The percentages of nickel in the catalysts were characterized by X-ray fluorescence spectrometer (XRF), calculated the composition and percentages with the library search program.

2. Transesterification of castor oil

Castor oil (100 g) were placed into a 1000 ml round bottom flask. Methanol (200 g) and concentrated sulfuric acid (3.2 ml, 5% by weight by alcohol) were added. Then, the reaction flask was fitted with a condenser, stirred by a magnetic bar. The mixture was heated to 70 °C for 12 hours. Then, it was poured into the separatory funnel and added distilled water in order to separate methyl ester from methanol. The excess acid was washed out from the oil by 5% sodium hydrogen carbonate solution. Finally, it was dried with sodium sulfate anhydrous to give the product that called castor oil methyl ester, which contained about 90 percent of methyl ricinoleate.

3. Continuous hydrogenation reaction procedure

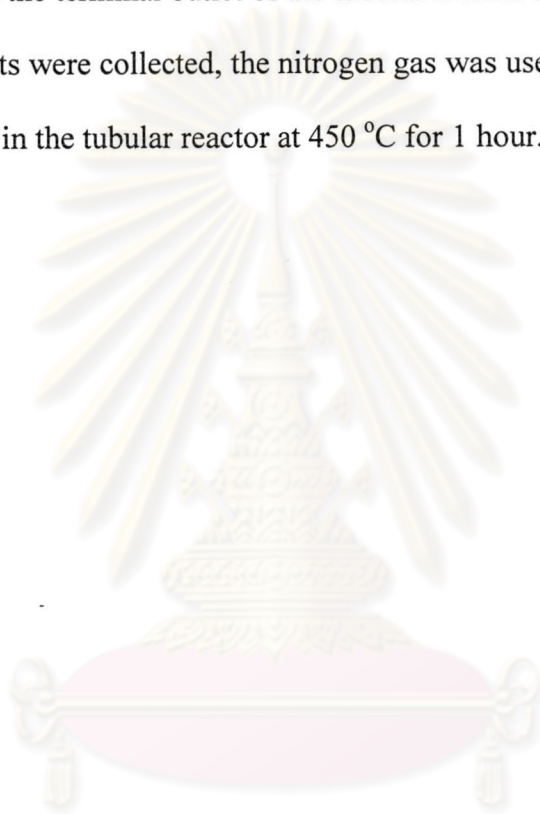
3.1 Reaction unit

Using the reaction unit as shown in Figure 3.1 performed all studies in this research. The hydrogenation reaction was operated in a tubular reactor (B) containing packed catalyst. This tubular reactor was installed in a furnace (D) that the temperature could be controlled for desired reaction temperature by the temperature control unit (E) equipped with a thermocouple (C) in the furnace for checking the accuracy of reaction temperatures.

Hydrogen and nitrogen tanks were connected together by three-way valves before connected to the inlet side of the tubular reactor before an injection unit (A) in order to supply mixed hydrogen/nitrogen into the tubular reactor during reaction operation. Furthermore, the nitrogen gas was used to flush the rest of products which remaining in the tubular reactor after the reaction was stop.

3.2 Reaction Procedure

Methyl ricinoleate was injected into the heated tubular reactor, which packed with the catalysts during the flow of mixed hydrogen/nitrogen. The product in liquid phase was collected at the terminal outlet of the tubular reactor into a storage unit (F). After all of the products were collected, the nitrogen gas was used to flush out the rest of products remaining in the tubular reactor at 450 °C for 1 hour.



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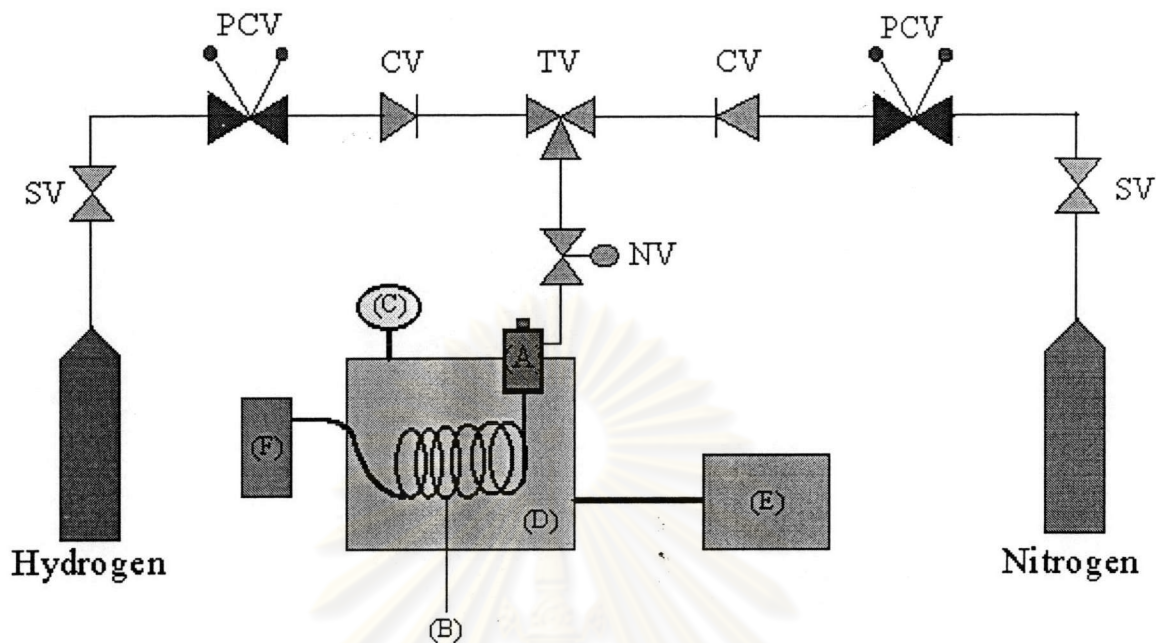


Figure 3.1 Schematic drawing of the reaction unit

CV = CHECK VALVE

NV = NEEDLE VALVE

PCV = PRESSURE CONTROL VALVE (REGULATOR)

SV = STOP VALVE

TV = THREE WAY VALVE

A = INJECTION UNIT

B = TUBULAR REACTOR

C = TEMPERATURE GAUGE

D = FURNACE

E = TEMPERATURE CONTROL UNIT

F = STORAGE UNIT

4. Various effects on continuous hydrogenation reactions

4.1 Effect of reaction temperature

The effect of temperature on continuous hydrogenation of methyl ricinoleate was studied by varying the reaction temperatures at 90, 120, 150, 180, and 200 °C using 10, 15 and 20% Ni/Al₂O₃ catalysts under 20 psig hydrogen/nitrogen pressure to find the optimum reaction temperature.

4.2 Effect of hydrogen pressure

The effect of hydrogen pressure on continuous hydrogenation of methyl ricinoleate was studied under hydrogen/nitrogen pressure at 20, 40, and 60 psig and the reaction temperature at 90 and 200 °C using 15% Ni/Al₂O₃ catalyst.

4.3 Effect of catalyst concentration

The effect of catalyst concentration on continuous hydrogenation of methyl ricinoleate was studied using 10, 15 and 20 % Ni/Al₂O₃ at 120 °C, which was the optimum reaction temperatures, and under 20 psig hydrogen/nitrogen pressure.

4.4 Activities of regenerated catalyst and reproducibility of used catalyst

The reproducibility and activity of used catalyst were studied on 15 % Ni/Al₂O₃ catalyst under 20 psig hydrogen/nitrogen pressure at 90,120, 150, 180, and 200 °C reaction temperature.

5. Analysis of hydrogenated methyl ricinoleate

5.1 Gas chromatograph – Mass spectrometer(GC-MS)

Gas chromatograph – mass spectrometer was used to identify and quantitative determination of the methyl ester components. The general conditions could be summarized as follows,

Column	: 25 m, 0.2 mm I.D. DB wax
Column packing	: PEG (polyethyleneglycol); 0.25 microns
Temperature of injection port	: 320 °C, split 1:100
Temperature program of oven	: 150 °C for 1 min. 150 to 300 °C at 150°C/min. 300 °C for 5 min
Carrier gas	: He pressure 28 cm/sec
MS source temperature	: 200 °C

5.2 Determination of iodine value

The iodine value is defined as the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed). The iodine value of the product were determined by the Japanese Industrial Standard JIS K 0070-1966 (see Appendix A). Weigh accurately about 3.0 g of the sample into a 250-ml Iodine flask and add 10 ml of Wijs' solution and tightly stopper with a glass stopper wet with potassium iodide solution (10 %) in order to prevent volatilization of iodine and chlorine and gently swirl the flask. Place the flask in the dark place kept at a temperature of 20 to 30 °C for 30 minutes and swirl the flask occasionally. Add 50 to 70 ml of potassium iodide solution (10 %), swirl the flask and titrate with N/10 sodium thiosulfate solution until the color of solution turns pale yellow. Add 1 ml of starch solution and continue the

titration, with swirling, until the blue color of iodine-starch disappears. Run the blank titration.

Calculate the iodine value, I.V., by the following formula:

$$\text{I.V.} = \frac{(B - C) \times f \times 1.269}{S}$$

Where B : volume of N/10 sodium thiosulfate solution consumed in blank titration (ml)

C : volume of N/10 sodium thiosulfate solution consumed in actual titration (ml)

f : factor of N/10 sodium thiosulfate solution

S : weight of sample (g)

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