

CHAPTER IV

EXPERIMENT

This work is divided into 4 parts: the preparation of catalysts; the determination of the composition of the catalysts; the hydrogenation; and the determination of the properties of the hydrogenated castor oil (castor wax). In each part, the procedure will be clearly described. Also, included are the chemicals and reagents, instruments and apparatus used.

4.1 Preparation of Catalysts.4.1.1 Chemicals and Reagents.

Chemicals used were of analar grade except where specified; $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was manufactured by Fluka Chemie AG, CH-9470 Buchs, Switzerland; Ni-Al alloy was obtained from Wako Pure Chemical Industries, Ltd.

4.1.2 Instruments and Apparatus.

(1) Unit for Digestion (see Fig.4.1). Inasmuch as the reaction between NaOH and Ni-Al alloy is carried out at rather high temperatures and for a period of time, this unit is necessary to prevent loss of water from the reacting mixture. The unit consists of a 250-ml flask and a reflux condenser.

(2) Oil Bath. This is simply made up of heater and a bowl filled up with high boiling point oil.

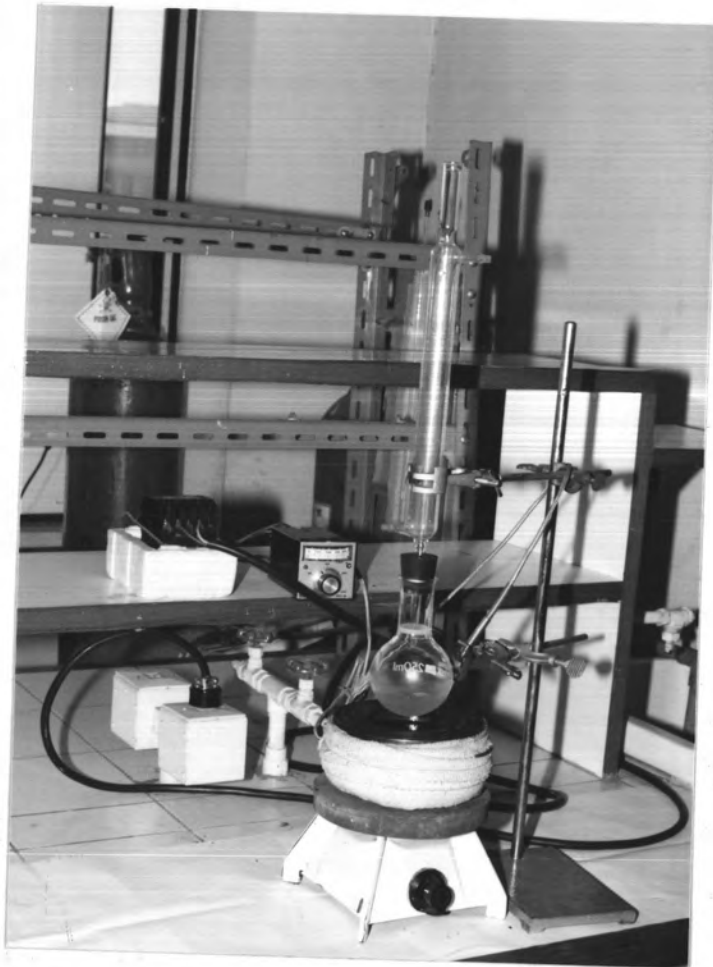


Fig.4.1 Unit for Digestion, Oil Bath with Automatic Controller

(3) Automatic Temperature Controller. It consists of a magnetic contactor, connected to a voltage source on one side, and a RKC model PF-4 temperature controller joined to another side of the contactor. It is used with a thermocouple. A dial setting of the controller establishes a set point at any temperature within the range of 0-200 °C.

(4) Hotplate with magnetic stirrer. This is manufactured by A. Gallenkamp & Co., Ltd., England.

4.1.3 Experimental Procedures.

Two types of catalysts were prepared in the experiment; Raney nickel catalysts and nickel catalysts incorporated with a palladium compound, $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. A Ni-Pd catalyst was obtained with the Ni-catalyst as the base. The preparation procedures of the two catalysts will be separately presented.

4.1.3.1 Preparation of the Raney Nickel Catalyst.

In this study the objective was to know whether the nickel catalysts might be affected by incorporation of a small amount of palladium compounds. Therefore, a simple preparation procedure was selected. However, there were still many conflicting statements concerning the digestion conditions, the ratio of the alloy to NaOH (anhydrous) and the concentration of aqueous sodium hydroxide solution. So it was necessary to find out the most appropriate digestion conditions.

The preparation procedure selected is described, in steps, as follows:

(1) 5 g of NaOH (anhydrous) was placed into a 250-ml flask and distilled water was added to make a total weight of 20 g. The mixture was stirred until the NaOH was completely dissolved in water. While stirring, the flask was placed in a bowl of water in order that the heat of reaction be dissipated and removed, and the loss of water prevented. (The final concentration of sodium hydroxide solution was 25% by weight.)

(2) The flask containing sodium hydroxide solution was placed in a bowl of iced water. One gram of Ni-Al alloy was then slowly poured into the flask and stirring was continuously done while adding the alloy to the solution. The rate of addition was controlled as to not cause excessive foaming.

(3) Stirring was continued for a while after the alloy was all added. Consequently, a reflux condenser was placed on the top of the flask and in turn the flask was placed into the oil bath, which was set at the required digestion temperature. The reaction was carried out for a period of time.

(4) When the digestion time was due, the flask containing the mixture was removed from the oil bath. The mixture was poured into a 100-ml beaker. The mixture was stirred for a minute and subsequently the liquid portion was poured out of the beaker. A small amount of liquid is left.

(5) The catalyst was washed with cold distilled water. For each washing, water was added to the catalyst, the mixture was stirred for a minute, and the liquid portion was then poured out. Ultimately, only the solid catalyst and trace amounts of water were left in the beaker.

(6) 20 g of castor oil was added to the catalyst and a magnetic bar was laid in the beaker. The beaker was placed onto the hotplate with a magnetic stirrer. The mixture was heated until the temperature reached 130°C and held at this temperature for 1 hour in order that the trace amount of water was completely removed. The catalyst was now ready to be used in the hydrogenation.

In this section various effects of the following parameters were studied :

(a) The Digestion Time Period. The periods studied were 1, 2, and 3 hours. The temperature was fixed at 110°C . The concentration of NaOH solution was set at 25% by weight and the ratio of alloy to NaOH was fixed at 1:5.

(b) The Digestion Temperature. The temperatures used were 110°C , 130°C and 150°C . The proper period of digestion time was obtained from (a). Other parameters were the same as (a).

(c) The NaOH Concentration. The concentrations used were 12.5, 16.7 and 25% by weight. The time and temperature were selected using results from (a) and (b). The others remained the same.

(d) The Ratio of Alloy to NaOH. The ratios were 1:3, 1:5 and 1:7.5 (wt:wt). The others were in accordance with the proper parameters from (a), (b) and (c).

4.1.3.2 Preparation of Nickel Catalyst incorporated with Palladium Compound.

The procedure is as follows: (also in steps)

Step (1) to step (5) are the same as in section 4.1.3.1.

(6) $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was weighed, corresponding to the required percentage of Pd/Ni (metal/metal), and placed in a 100-ml beaker. Distilled water was added to the Pd compound and continued until the total weight of the mixture becomes 30 g. The beaker was shaken to completely dissolve Pd compound in water.

(7) The solution from step (6) was poured into the beaker containing the solid catalyst from step (5). Stir for a minute and permit the mixture to stand for 16 hours.

(8) When the time is reached, the mixture was stirred again for a minute and then the liquid portion was poured out.

(9) The solid in the beaker was washed twice. Ultimately, only the solid catalyst and trace amounts of water were left.

(10) The same as (6) in section 4.1.3.1.

In this section effects were studied only when the percentage of Pd/Ni was varied. The percentages of Pd/Ni were 0.5, 1.0, 1.5 and 2.0%.

4.2 The Determination of the Catalyst Compositions.

An inductively coupled plasma Spectrometer (ICPS) [50, 51, 52] was used to determine the composition of the catalysts. Inasmuch as the samples to be analyzed must be in the form of solution, the catalysts have to be digested and dissolved in distilled water. The procedure to prepare the sample [35] will be described as follows:

4.2.1 Chemicals and Reagents.

Chemicals used were of analar grade except where specified.

4.2.2 Instruments and Apparatus.

- (1) Inductively Coupled Plasma Spectrometer.
- (2) Hotplate.
- (3) Glasswares.

4.2.3 Procedure.

0.3 g of catalyst was weighed and placed into a 250-ml beaker. 75 cm³ of concentrated HNO₃ was added and the beaker was placed onto hotplate. Heating was continued until the solution was completely evaporated. The residue was dissolved in 50 cm³ of distilled water. The solution was warmed for 15 minutes and then filtered through a Whatman filter paper No.42. The paper was washed with distilled water until free from salts. The filtrate was then collected in a 250-ml beaker and set to a total weight of

100 g. Then the liquid sample was analyzed using an inductively coupled plasma spectrometer.

4.3 The Hydrogenation.

4.3.1 Chemicals and Reagents.

Castor oil, I.O.C.S. grade, was supplied by the Thai Castor Oil Industries Co.,Ltd.

4.3.2 Instruments and Apparatus.

(1) Reactor (see Fig. 4.2 and Fig. 4.3). The hydrogenation reactor is a model 4521, bought from Parr Instrument Company. It consists of a 1000-ml stainless steel 316 cylindrical bomb, a bomb head and a bomb heater. The reactor is equipped with a stirrer, which is driven by a motor through a pulley and drive shaft, and spiral cooling coil. It can be operated under pressure up to 2000 psig.

(2) High-speed motor. This is attached to the bomb heater.

(3) Automatic temperature controller (see Fig.4.4). It consists of a magnetic switch which is connected to a variac and a RKC temperature controller of PF-8B1C-M model. It is used in conjunction with a thermocouple installed in a thermowell attached to the bomb head. A dial setting establishes a set point at any temperature within the range between 0 and 400 °C.

(4) Cooling System (see Fig.4.5). It is composed of 2 parts for cooling the reaction and cooling the stirrer. It was



Fig.4.2 Reactor

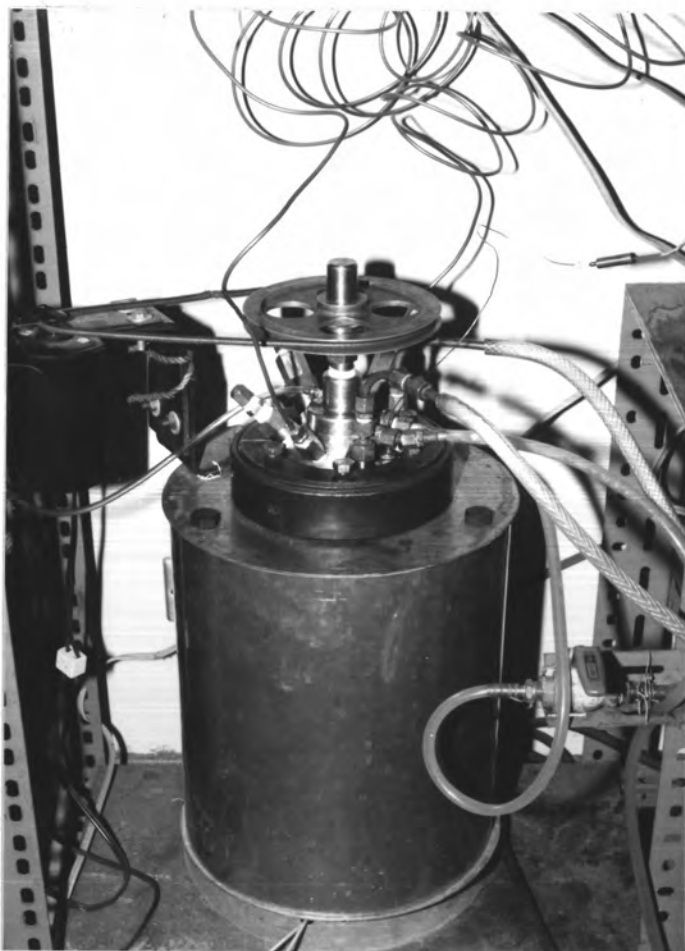


Fig.4.3 Reactor with Bomb Heater and High Speed Motor
while in Operation

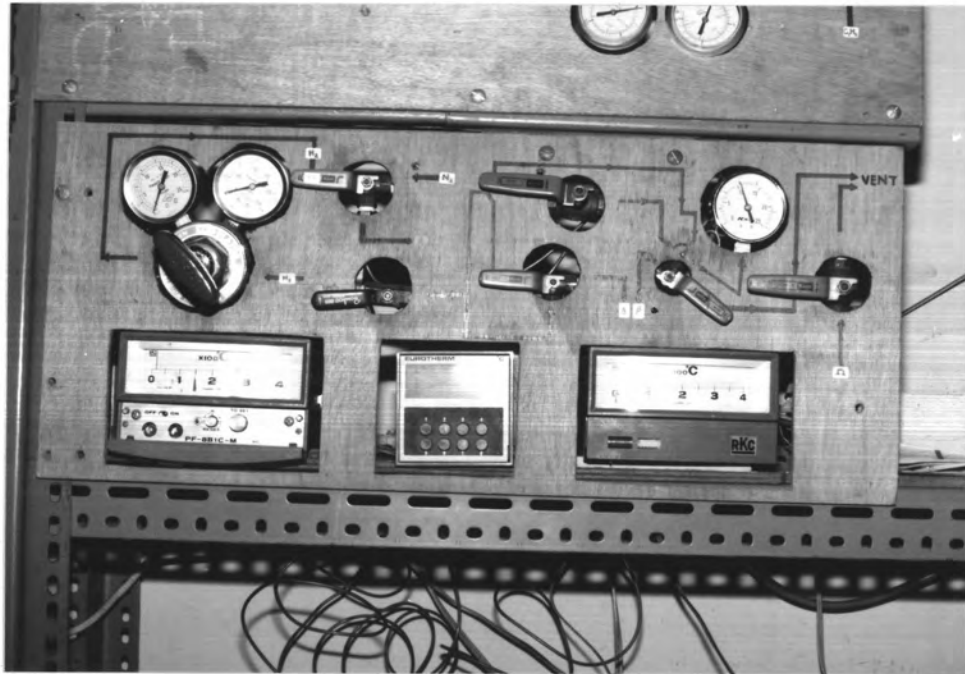


Fig.4.4 Automatic Temperature Controller

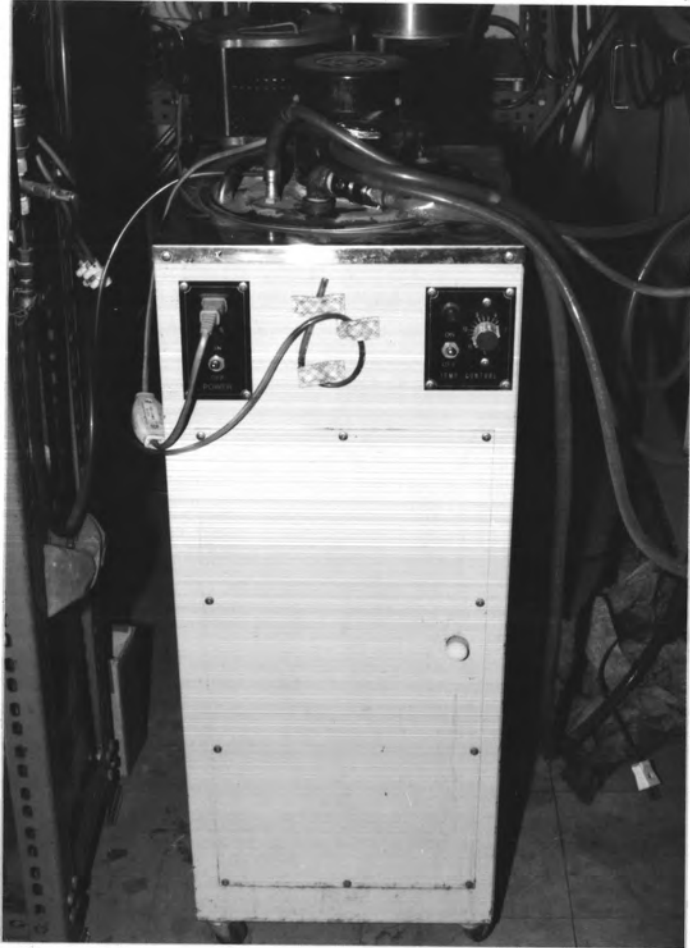


Fig.4.5 Cooling System

found that at the beginning of the reaction, the rate of hydrogenation was so fast that the temperature controller could not keep the temperature at the desired value. Then it must be cooled by the cooling water in the cooling coil. The cooling coil was connected to the water pipe in the laboratory. The cooling system for the stirrer was connected to the Eyela cooling bath.

(5) Gas Controlling System (see Fig.4.6). The system consists of:

- a hydrogen tank 1 equipped with a pressure regulator (0-400 psig) 2 and an on-off valve 3

- a hydrogen tank 4 is used for supplying hydrogen gas to the reactor. This tank is equipped with a pressure gauge 8 and a pressure regulator (0-350 psig) 9.

- an oxygen-free nitrogen tank 5 equipped with a pressure regulator (0-200 psig) 6, a three-way valve 7, pressure gauge 12 and on-off valves 10 and 11.

- an on-off valve 15 and a needle valve 13 were connected to the gas release tube.

4.3.3 Procedure.

200 g of Castor oil and the required quantity of catalyst previously prepared were charged into a high pressure Parr hydrogenator of 1000 cm³ capacity. Before operation, the system was checked for leaks by pressurizing with high-pressure oxygen-free nitrogen gas for half an hour. After being sure that there was no leak in the system, the nitrogen gas was removed and replaced with

- | | | | |
|--------------------------------|----------------------|-------------------|--------------------------------------|
| 1 H ₂ tank | 6 Pressure regulator | 11 On-off valve | 16 Automatic temperature controller |
| 2 Pressure regulator | 7 Three-way valve | 12 Pressure gauge | 17 Thermocouple |
| 3 On-off valve | 8 Pressure gauge | 13 Needle valve | 18 Adjustable speed motor controller |
| 4 Supplied H ₂ tank | 9 Pressure regulator | 14 Reactor | |
| 5 N ₂ tank | 10 On-off valve | 15 On-off valve | |

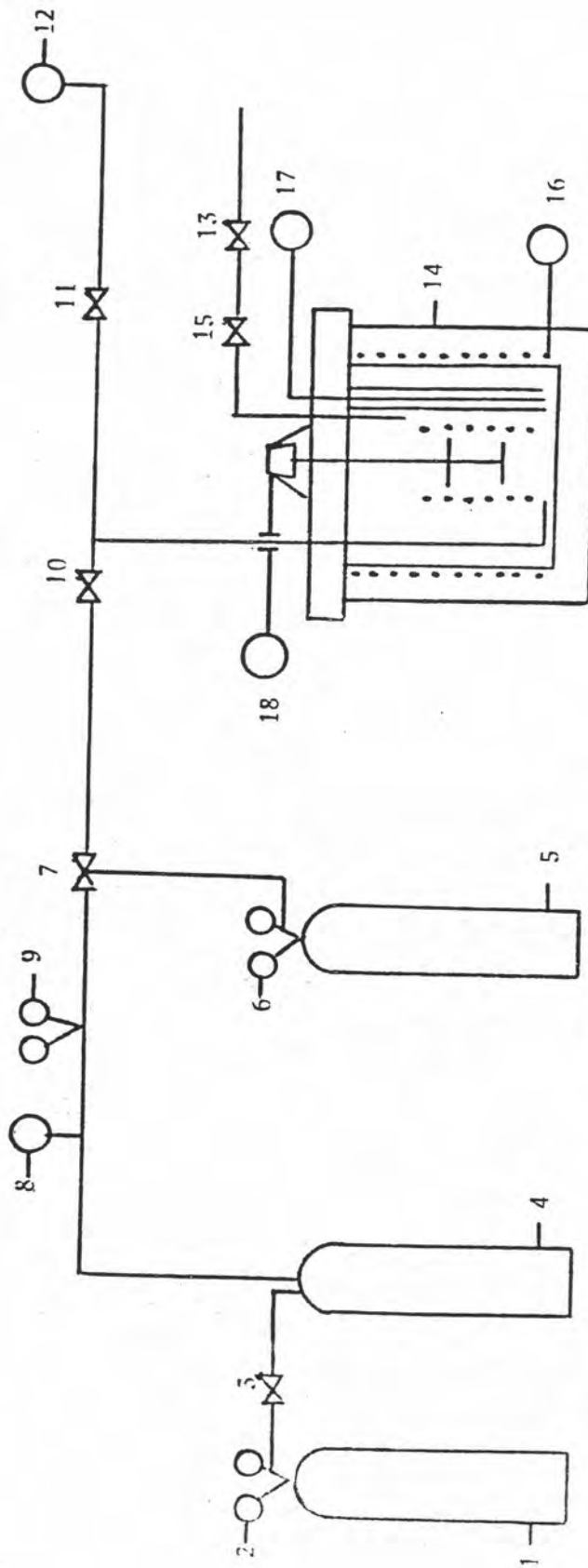


Fig.4.6 Flow Diagram of the Hydrogenation System

hydrogen gas at the required pressure. The reactor was heated up to the desired temperature and kept at this temperature by an automatic temperature controller. The reaction time at the start of heating to the end was 4 hours. The mechanical stirrer was operated after the temperature of 50 °C was reached.

At the end of the reaction, water was fed through cooling coil to reduce the temperature in the reactor until it was about 90 °C. Then the hydrogenated castor oil (castor wax) was poured into a stainless steel bowl. A portion of the wax was separated and filtered through a Whatmann filter paper No.1 to remove the catalyst. The purified wax was kept to be chemically analyzed.

In this section, the reaction conditions were varied and the effects were studied as follows:

(1) Selecting the best conditions of catalyst preparation. In Part 1 section 1.3.1, the conditions for preparing the catalysts were varied and the hydrogenation of castor oil used to test the activity of the catalysts. The reaction conditions were 150 °C, 150 psig and catalyst concentration was 0.1% Ni/oil.

(2) Varying the concentration of catalyst. The concentration varied were 0.1, 0.2, 0.3 and 0.4% Ni/oil. The reaction conditions were 150 °C and 150 psig.

(3) Varying the temperature of reaction. The temperature were varied as 130, 150 and 170 °C. The proper concentration of catalyst was obtained using results from (2). The pressure was set at 150 psig.

(4) Varying the Pressure of Reaction. The pressures studied were 100, 125, 150 and 175 psig. The proper concentration and temperature were derived from (2) and (3).

(5) Varying the percentage of Pd/Ni. Using the proper conditions from (2)-(4), the catalysts prepared in Part 1 section 1.3.2 were tested in the hydrogenation of castor oil to study the effects of palladium on the activity and selectivity of nickel catalyst.

4.4 The Determination of the Properties of Hydrogenated Castor Oil.

As previously mentioned, castor oil is a mixture of triglycerides whose fatty acid components are mainly ricinoleic acid. The acid contains one double, one carbonyl and a hydroxyl group on its molecular structure. To quantitatively determine these functional groups, chemical analyses are used. The values determined are as follows:

- Iodine Value (I.V.): defined as the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed).

- Acid Value (A.V.): defined as the number of milligrams of potassium hydroxide required to neutralize free fatty acids contained in 1 g of the sample.

- Hydroxyl Value (OH.V.): defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid which has been combined with hydroxyl radical when 1 g of the sample is acetylated.

The procedure for determination of each value will be described in Appendix A.