

CHAPTER V

EXPERIMENT

In the present study of the hydrogenation of methyl ricinoleate, the experiments were divided into two parts : hydrogenation and analysis of hydrogenated product. The detail of the experiments were discussed in the followings.

5.1 Catalysts and Materials.

Chemicals used were of Analar grade except where specified. Methyl ricinoleate was no.1 grade (I.V. 84.0, OH.V. 170) from Thai Kawaken Co.,Ltd. Pure hydrogen gas and oxygen-free nitrogen were bought from T. I. G. Co.,Ltd. The commercial hydrogenation catalysts in our laboratory were shown in the Table 5.1.

5.2 Apparatus

All experiments for the hydrogenation study of methyl ricinoleate were carried out in the hydrogenation apparatus which consisted of five parts as the followings :

Table 5.1 The commercial hydrogenation catalysts

Type of Catalyst	%Ni	Form	BET Surface Area (m ² /gm)	Particle Size (m)
Ni 3712 F*	21.72	powder	-	-
Ni 5132 P*	66.33	powder	170	20
Ni 3609 F*	25.00	flake	-	-
Ni 0104 P*	65.00	flake	125	20
G 53 D**	25.00	flake	-	3
Ni 3742 D*	20.00	pellet	-	-

* from the Harshaw Chemical Company.

** from the United Catalysts Inc.

(1) Reactor (Figure 5.1) The hydrogenation reactor was a batch high pressure stirred autoclave model 4521 from the Parr Instrument Company with consisting of 1000 cm³ stainless steel 316 cylindrical bomb, bomb head, a bomb heater, two stirrers and a cooling coil. The reactor can work at the pressure range of 0-1900 psig and the temperature range 0-350°C.

(2) Adjustable Speed Motor Controller (Figure 5.2) The Controller used was model 64EEN from the Parr Instrument Company. Its stirring speed can be adjusted in the range of 0-1000 rpm.

(3) Automatic Temperature Controller (Figure 5.3)

The controller used was RKC model series RE 96 from the Worthing England and the indicator from the Model No.141-03-451-19-00. They were operated in conjunction with a thermocouple installed in a thermowell attached to the bomb head to provide both time proportioning temperature control and temperature read out.

(4) Cooling System (Figure 5.4). The cooler used

was CA-101 ser. No. 01200370 from Tokyo Rikakikai Co., Ltd. The cooler was connected with bomb head by water tubes for cooling the axial sealing rubber of stirrer rod

(5) Gas Controllers System. The system consisted

of a hydrogen tank 1 equipped with a pressure regulator (0-3000psi.) 2, an oxygen free nitrogen tank 3 equipped with a pressure regulator(0-300psi.) 4, on-off valve 5, 6, 7, 12, 13 and 17 a three way valve 11, a small hydrogen cylindrical tank (6.7lit.) 8, pressure gauges 9 and 14. The flow diagram of the hydrogenation system was shown in Figure 5.5

The melting point of methyl ester wax was determined by using magnetic stirrer-heater (Figure 5.6)

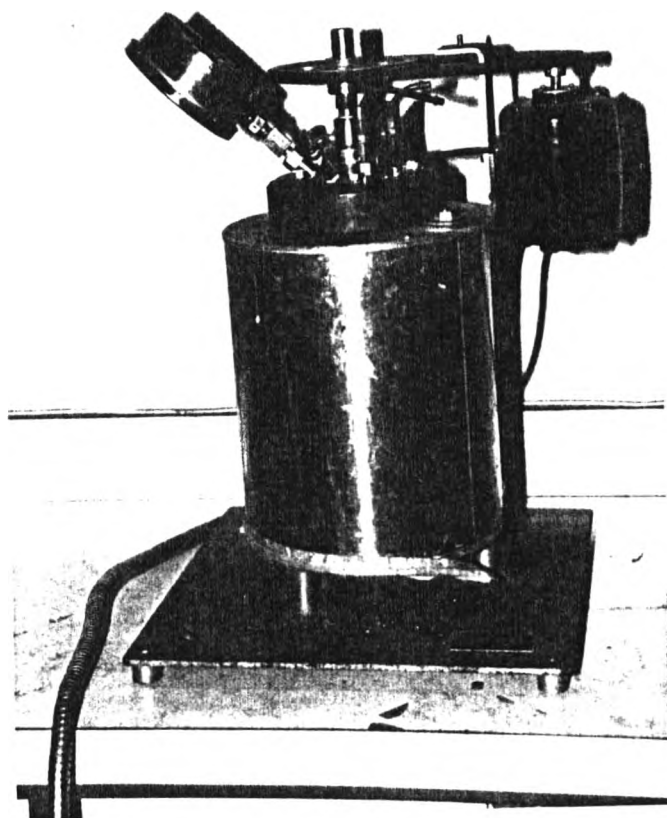


Figure 5.1 High pressure stirred reactor Parr 4521

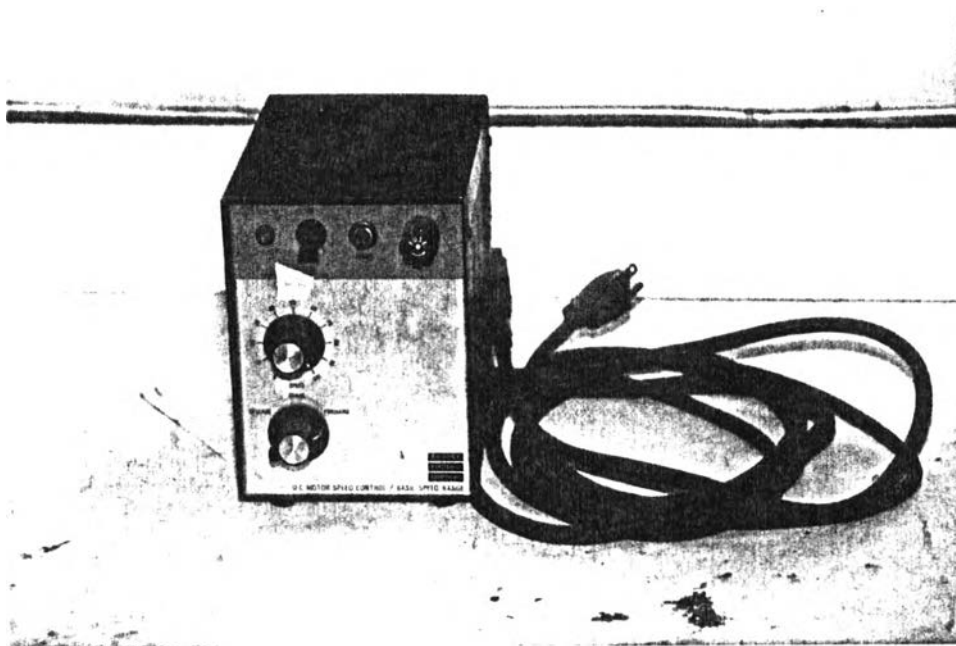


Figure 5.2 Adjustable speed motor controller Parr 64EEN

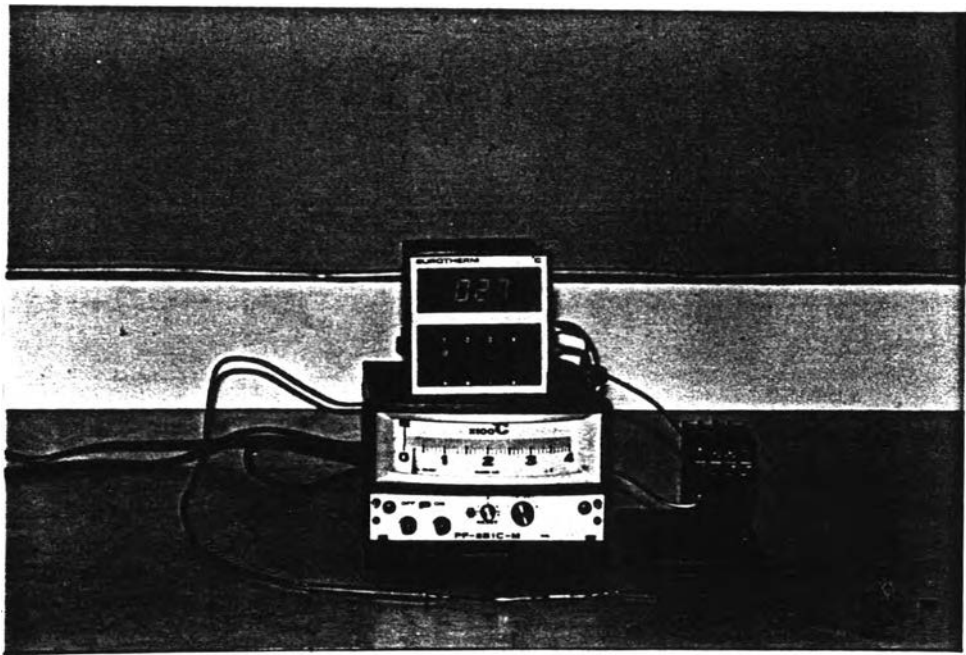


Figure 5.3 Automatic temperature controller and Indicator

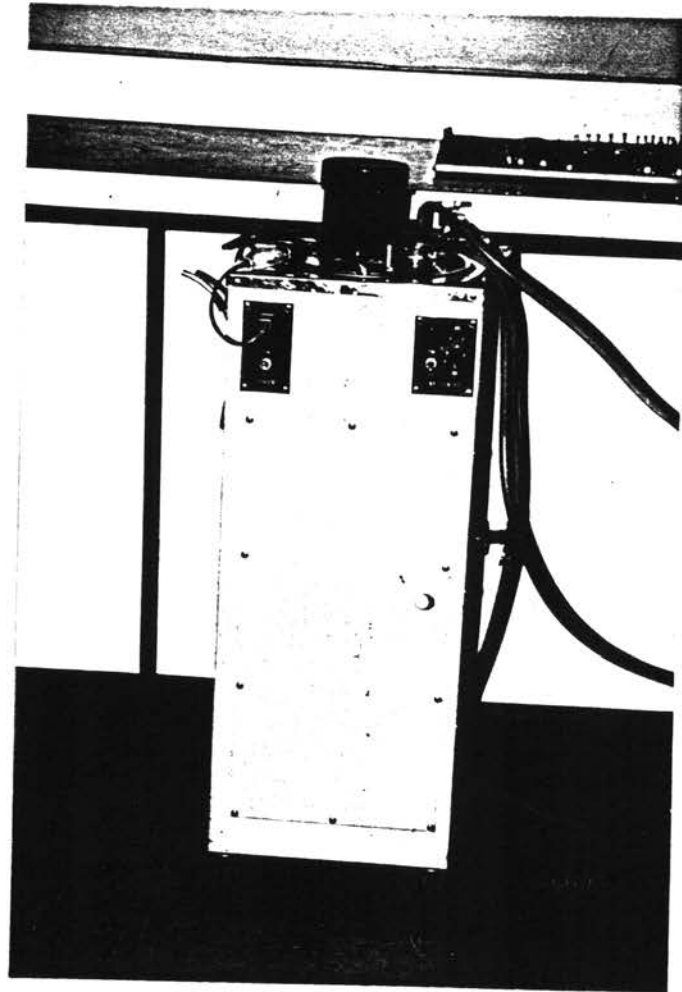
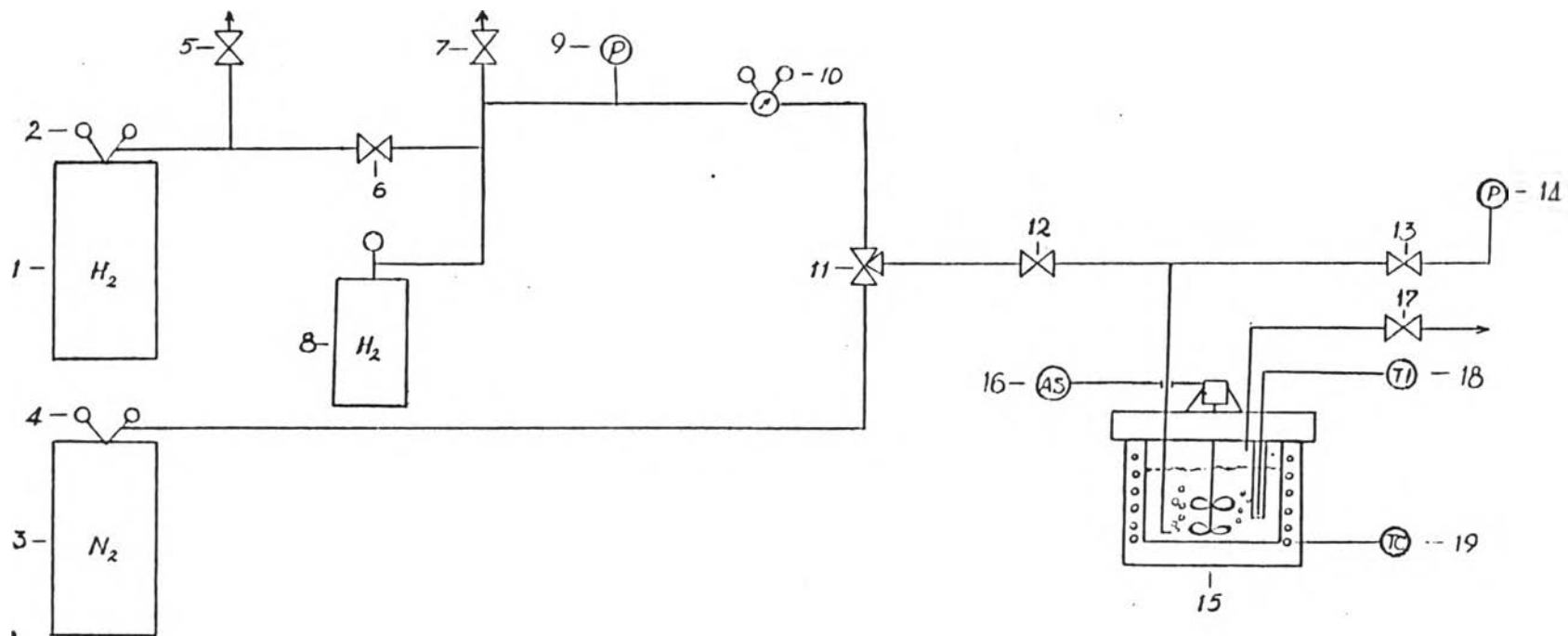


Figure 5.4 Cooling system



- | | | | |
|------------------------|---------------------------------|---------------------|---------------------------------------|
| 1. H ₂ Tank | 8. On-off valve | 11. Three-way valve | 16. Adjustable speed motor controller |
| 2. Regulator | 7. On-off valve | 12. On-off valve | 17. On-off valve |
| 3. N ₂ Tank | 8. H ₂ Supplied tank | 13. On-off valve | 18. Temperature indicator |
| 4. Regulator | 9. Pressure gauge | 14. Pressure gauge | 19. Automatic temperature controller |
| 5. On-off valve | 10. Regulator | 15. Reactor | |

Figure 5.5 Flow diagram of the hydrogenation system

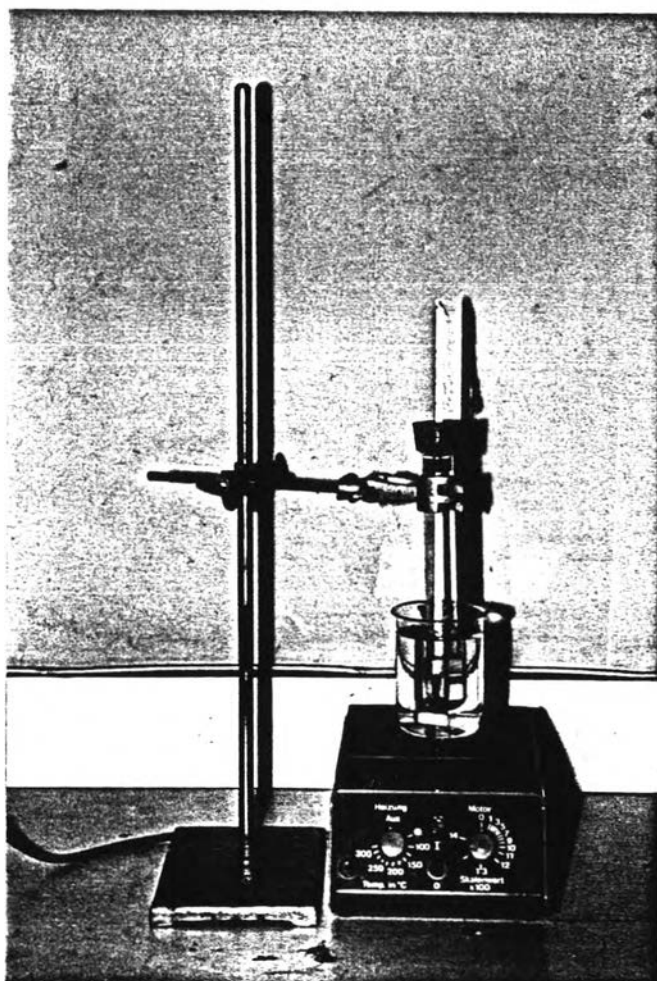


Figure 5.6 Magnetic stirrer-heater for determination of melting point

5.3 Procedure

5.3.1 Hydrogenation

The hydrogenation of methyl ricinoleate was carried out in the Parr hydrogenation reactor. Methyl ricinoleate (200 g.) was charged into the reactor along with a known quantity of catalyst. Before closing the bomb, the head gasket was examined to be sure that it was in good condition and matching surfaces on the bomb and the head was also done to be sure that they were clean and free from burrs, then the head was set on the bomb. The bomb was closed by sliding the two ring sections into place so that the slot between the two sections was about one inch to the right the thermowell and the bomb was raised to encircle them. Position the band so that the cone pointed screw enters the slot between the ring sections and tighten the screw to spread the sections firmly against the inside of the band. The bomb was sealed by tightening each of the cap screws with the wrench furnished with the apparatus. The bomb was allowed to stand for about five minutes after the initial tightening them the cap screws were tightened again. The bomb was set in the heater with the gauge facing forward and positioned so as not to interfere with the driving belt. The vee belt was slipped into the pulleys and the bracket was adjusted so that the belt was only moderately tightened.

The gas controllers system connected to the gas inlet valve of the reactor, the N₂ tank 3, was opened and the regulator 4, was adjusted till the pressure in the system was about 100 psig., the three way valve 11, was switched to allow N₂ to flow to the reactor and then the on-off valve 12, and 13 were opened. All valves were checked carefully by the

snoop leak solution before H_2 was admitted to the system. To remove all of O_2 in the system, the on-off valve 17, was opened and N_2 was purged twice through the system. After this, the vent valves 17, were shut so that the reactor was then flushed with N_2 . The pressure of the system read from the pressure gauge 14, was about 100 psig., then the on-off valves 12, was shut.

A desired temperature was set, the heater switch was turned on and a Variac to control the heat input. To control the desired temperature of the reaction, the thermocouple was connected to the indicator and controller, controlling the Variac. The adjustable speeds controller was connected to the reactor to adjust the stirring speeds. When the reactor temperature reached a value about $50^\circ C$, the stirrer power was turned on. The function switch was set at Forward; the speed control knob was turned clockwise until motor rotation occurred and then it was adjusted to the required speed. When the reactor temperature reached a value about $5^\circ C$ below the operating temperature, the H_2 tank 1 was opened while on-off valve 5, 6 and 7 were closed. The H_2 tank 8 and on-off valve 6 were opened slowly until the pressure gauge 9 indicated at 200 psig. After this, the H_2 tank 1 and on-off valve 6 were closed, and N_2 in the reactor was vented out by opening the vent valve 17 while on-off valve 12 was closed. The reactor was then flushed with N_2 and vented N_2 out twice again so the pressure was reduced to the atmospheric pressure then the N_2 tank 3 was closed and the three way valve 11 was switched to allow H_2 to flow to the reactor. The pressure was maintained constant throughout the run by means of a pressure regulating valve 10 and which was read from the pressure gauge 14. The progress of the reaction was followed by observing the change in H_2

pressure at different times, shown on pressure gauge 9. After the reaction started, the temperature was maintained at the desired value ($\pm 1-2^{\circ}\text{C}$) by the manual operation of the Variac and/or by adjusting water flow into the cooling coil to remove the exothermic heat of the reaction.

To stop the reaction, the H_2 tank 8 was closed and the vent valve 17 was opened, then the three way valve 11 was switched to allow N_2 to displace H_2 in the system. The N_2 tank 3 was closed. The heater was switched off and the water was flowed into the cooling coil. The temperature was decreased until about 60°C , then the stirrer and the cooler were turned off. The bomb head was opened. The catalyst-methyl ester wax mixture was transferred into a 500 cm^3 stainless steel bowl and the catalyst was separated from the wax by filtering on Whatman filter paper No.1 in an oven at temperature $50-55^{\circ}\text{C}$. The properties of the methyl ester wax were determined.

For hydrogenation by initial hydrogen feed at room temperature, there was difference from above procedure. When N_2 had been flushed and vented twice or more again, before the heater was turned on, H_2 was flushed into the system. The temperature was increased to the desired value. After this, it was the same procedure as above.

5.3.1.1 Screening Commercial Catalysts

To select the best commercial hydrogenation catalysts out of six whose characteristics were shown in Table 5.1, the hydrogenation condition was set at Temperature 150°C , hydrogen pressure 150 psig., agitation speed 800 rpm., concentration of catalyst 0.2% N:/oil (weight by weight) and

reaction time 5 hours.

5.3.1.2 Selecting an Suitable Operating Condition

The effect of reaction temperature, hydrogen pressure, reaction time ; agitation speed and catalyst concentration were studied under the conditions which were shown in the Table 5.2.

5.3.1.3 Studying the Effect of the Initial Hydrogen Feeding on Hydrogenation.

In the section 5.3.1, hydrogen gas as reactant was flowed into the system at the desired constant temperature until the reaction time obtained (Procedure 1). On the other hand, the H_2 gas was flowed continuously since the heater was turned on at room temperature (Procedure 2). The temperature was increased till the desired value and took it constant. The latter procedure, the hydrogen consumption might be started at temperature below the desired value so the total operating time was shorter than the first. After this the hydrogenated products were analysed. The hydrogenation condition were set at the suitable operating condition obtained in the section 5.3.1.2

5.3.1.4 Studying the Effect of the Storage Time on Hydrogenation

The effect of the storage time of methyl ricinoleate in drum was studied after four months of finding suitable operating condition in section 5.3.1.2. The hydrogenation condition was set at temperature $150^\circ C$, hydrogen pressure 150 psig., agitation speed 800 rpm.,

Table 5.2 The various operating conditions for this experiment

Studied Parameter	Reaction Temperature (°C)	Hydrogen Pressure (psig.)	Reaction Time (hrs.)	Agitation Speed (rpm.)	Conc. of Catalyst (% Ni/oil)
Reaction Temperature	110	150	2	800	0.03
	130	150	2	800	0.03
	150	150	2	800	0.03
	170	150	2	800	0.03
	180	150	2	800	0.03
	200	150	2	800	0.03
Hydrogen Pressure	150	100	2	800	0.03
	150	125	2	800	0.03
	150	150	2	800	0.03
	150	175	2	800	0.03
Reaction Time	150	150	1	800	0.03
	150	150	2	800	0.03
	150	150	3	800	0.03
	150	150	5	800	0.03
Agitation Speed	150	150	2	200	0.03
	150	150	2	400	0.03
	150	150	2	600	0.03
	150	150	2	800	0.03
Conc. of Catalyst	150	150	2	800	0.01
	150	150	2	800	0.03
	150	150	2	800	0.06
	150	150	2	800	0.10
	150	150	2	800	0.20
	150	150	2	800	0.50

concentration of catalyst 0.03% Ni/oil, reaction time 2 hours.

5.3.2 Analysis of the Hydrogenated Methyl Ricinoleate

5.3.2.1 Determination of Acid Value

The acid value is defined by the number of milligrams of potassium hydroxide required to neutralize free fatty acid in 1 g of the sample. The acid value of the products were determined by the Japanese Industrial standard JIS K 0070-1966 (see Appendix A). A 10-15 g of a sample was weighed accurately into a 100-cm³ conical flask. Add 50 ml of the neutralized ethyl alcohol and heated on a water bath until the sample dissolves completely. Add few drops of phenolphthalein indicator solution and titrate with N/10 ethyl alcoholic potassium hydroxide solution until a pale pink colour persists for 30 seconds.

Calculate the acid value, A.V., by the following formula:

$$A.V. = \frac{A \times f \times 5.611}{S}$$

Where A : volume of N/10 ethyl alcoholic potassium hydroxide solution consumed in titration (cm³)
 f : factor of N/10 ethyl alcoholic potassium hydroxide solution.
 S : weight of sample (g)

5.3.2.2 Determination of Iodine Value

The iodine value is defined by the amount of halogen (calculated by the number of grams of iodine) absorbed by 100 g of the sample under the prescribed conditions. The iodine value of the products were determined by the Japanese Industrial Standard JIS K 0070-1966 (see Appendix A). Weigh accurately about 3 g of the sample into a 250-cm³ iodine flask and add 10 cm³ of Wijs' solution and tightly stopper with a glass stopper wet with potassium iodide solution (5%) in order to prevent volatilization of iodine and chlorine and gently swirl the flask. Place the flask in a dark place kept at a temperature of 20 to 30 °C for 30 minutes and swirl the flask occasionally. Add 50 to 70 cm³ of potassium iodide solution (5%), swirl the flask and titrate with N/10 thiosulfate solution until the solution colours pale yellow. Add 1 cm³ of starch solution and continue the titration, with swirling, until the blue colour of iodine-starch disappears. Run the blank titration.

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

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

Where A : volume of N/10 sodium thiosulfate solution consumed in actual titration (cm³)
 B : volume of N/10 sodium thiosulfate solution consumed in blank titration (cm³)
 f : factor of N/10 sodium thiosulfate solution
 S : weight of sample (g)

5.3.2.3 Determination of Hydroxyl Value

The hydroxyl value is defined by the number of milligrams of potassium hydroxide required to neutralize acetic acid which has been combined with hydroxyl radical when 1 g of the sample is acetylated by specified procedure. The hydroxyl value of the products were determined by The Japanese Industrial Standard JIS K 0070-1966. (see Appendix A). Weigh accurately 1.0 g of the sample into a 200 cm³. Erlenmeyer flask and exactly 5-cm³ of acetylation reagent. Attach an air condenser to the flask and immerse in an glycerine bath kept a temperature of 95 to 100 °C so deep that bottom of the flask is approximately 1 cm. below the bath liquid. After heating for 1 hour, take the flask out of the bath and allow cool. Add 1 cm³ of water through the condenser and swirl the flask to decompose acetic anhydride. Reheat the flask in the oil bath for 10 minutes to complete the decomposition and allow to cool. Wash the condenser and the inside of the flask with 20 to 50 cm³ of neutralized ethyl alcohol and titrate with N/2 ethyl alcoholic potassium hydroxide solution using phenolphthalein solution as the indicator. Run the blank titration.

Calculate the hydroxyl value, OH.V., by the following formula :

$$\text{OH.V.} = \frac{(B-A) \times f \times 28.055}{S} + C$$

Where A : volume of N/2 ethyl alcoholic potassium solution consumed in actual titration (cm³).

B : volume of N/2 ethyl alcoholic potassium solution consumed in blank titration (cm³).

- f : factor of N/2 ethyl alcoholic potassium solution
S : weight of sample (g)
C : acid value

5.3.2.4 Measuring of Melting Point

The melting point of the products were determined by The Method 2 of the Japanese Industrial Standard JIS K 0064-1966 (see Appendix B). This method is applicable to the sample which is insoluble in water and hardly pulverized such as fats, fatty acids, paraffin and waxes.

