



## CHAPTER IV

### REVIEW OF LITERATURE

The methyl 12-hydroxystearate, the hydrogenated methyl ricinoleate, is a product with high hydroxyl value and low iodine value. It is prepared from hydrogenation of esterified castor oil or from esterification of hydrogenated castor oil. The most researches are related to castor oil esterification and castor oil hydrogenation. The abstract of some articles are.

Brown and Green (16) prepared a methyl ricinoleate by fractional crystallization procedure. Castor oil was esterified with methyl alcohol containing 2% dry hydrogen chloride by refluxing on a hot water-bath for twenty-four hours. The crude esters were then distilled at a pressure of 2-3 mmHg, the boiling point range being 185 to 212 °C. After standing, the solution of ester dissolved in acetone at -20 °C for seventy-two hours, the solution was cooled with constant stirring to -50 °C at which point a small precipitate was obtained. Methyl ricinoleates were given the iodine value 80.71-82.43 and the acetyl number 133.75-137.05.

Srivasan et al. (17) saponified 100 g of castor oil by refluxing for 3 hours with a solution of 40 g of potassium hydroxid in 400 ml of methanol and then cooled to room temperature. The soap solution thus obtained was acidified by adding 240 ml. of methanolic hydrochloric acid (122.9 g HCl/litre) portionwise with continuous shaking. Esterification was achieved by refluxing for 3 hours or

allowing the mixture to stand over night at room temperature, after which about 80% of the alcohol was distilled off. The residue was diluted with 250 ml of water, and extracted with 500 ml of ether. The extract was washed with water until free from hydrochloric acid then with four 200 ml portions of 2% aqueous potassium carbonate, and finally with water. After the extract had been dried with anhydrous sodium sulphate, ether was distilled off. The last traces of ether were removed by heating the methyl esters under vacuum (2-3 mmHg) on a water bath. The yield was 94-95% with the iodine value 80.3, and the hydroxyl value 162.0.

McCormack and Balley (18) studied the separation of castor oil methyl esters by means of liquid-liquid extraction, using methyl alcohol and heptane at 8.4 °C and 24 °C. It was observed that the hydroxyl value of ester in the methanol phase was greater than that of esters in the hydrocarbon phase. Lakshmanan and Laddha (19) also studied castor oil methyl esters obtained by the methylation of castor oil using HCl as catalyst. The phase distribution data for the systems of castor oil methyl esters-furfural-hexane and of castor oil methyl esters-nitromethane-hexane at 30 °C were determined. The estimated plait point for the system of methyl esters-furfural-hexane, corresponds to 27.2% methyl esters, 29.4% furfural, and 43.4% hexane while for the system of methyl esters-nitromethane-hexane, it corresponds to 24.2% methyl esters, 64.9% nitromethane, and 10.9% hexane.

Cotes and Wenzel (20) studied kinetics of the transesterification of castor oil in MeOH to give methyl ricinoleate with the variation of concentrations of castor

oil, methanol, hydrochloric acid, and the variation of temperature from 8° to 30°. A 3 step mechanism involving cationic intermediate was proposed.

Lakshminarayana et al. (21) analyzed seventeen newer varieties of castor seed grown in different parts of India and the oils extracted therefrom. Castor oil was converted to methyl esters by refluxing with methanolic sodium methoxide as described by Schneider et al. Gas liquid chromatography was carried out using a Hewlett-Packard 5840A unit coupled with a flame ionization detector and a data processor. A stainless steel column (0.6 m x 6 mm) packed with 5% SE-30 on chromosorb W, AWDMCS 80-100 mesh was used for analysis of methyl esters. The column temperature was maintained at 200°C and the flow rate of nitrogen at 30 ml/min. Ricinoleic acid varied from 87.4% to 90.4%.

Deryabin and Petrov (22) prepared a dielectric material by hydrogenation of castor oil at 140-150°C in the presence of active Ni or Ni-Co catalyst until the product did not melt below 75°C and an iodine value did not exceed 8. Paquot and Richet (23) found that the preferred conditions for total hydrogenation castor oil without dehydroxylation were hydrogen pressure 100-150 kg/cm<sup>2</sup> and 100-110°C or at 50 kg/cm<sup>2</sup> and 150°C, 230-240°C dehydroxylation occurred. Gupta and Aggarwal (24) found that in the process of hydrogenation of castor oil with 2% Rufert nickel catalyst, low temperature (150-160°C) and high pressure (200 lb/sq.in.) retarded the reduction of the OH group, which at high temperature (250°C) and low pressure (70-75lb/Sq.in.) almost complete dehydroxylation occurred.

Bataafsche (25) prepared the nickel catalyst to

hydrogenate castor oil without dehydroxylation at  $175^{\circ}\text{C}$  and hydrogen pressure 100 atm by adding to 420 g NaOH in 4.5 L water at  $100^{\circ}\text{C}$ , first 0.5 l of a solution of  $\text{Na}_2\text{SiO}_3$  (containing 56 g  $\text{SiO}_2$ ), then after stirring for a short time,  $\text{Ni}(\text{NO}_3)_2$  (containing 200 g Ni) in 5 L boiling water, filtering the precipitate, washing with 24 L water at  $45^{\circ}\text{C}$  drying 7 hrs. at  $110^{\circ}\text{C}$ , pulverizing to 0.4 mm mesh size and reducing this powder (421 g). The powder was mixed with 231 g white Surinum bauxite preheated 2 hrs at  $500^{\circ}\text{C}$  and 6.5 g graphite and compressed into tablets which were then reduced at  $275^{\circ}\text{C}$  and normal pressure in a stream of hydrogen, other catalyst carriers could also be used.

Kobayashi and Kyokaishi (26) used Raney nickel to hydrogenate castor oil at 68 atm. and  $50-95^{\circ}\text{C}$  to give a product which was presumed to consists chiefly of 12-hydroxystearic acid and prepared dibasic acids from this hydrogenated castor oil. Srivasan et al (27) studied the hydrogenation of castor oil and methyl ricinoleate at atmospheric pressure using Raney nickel and 20% dry-reduced nickel catalyst, which was prepared by precipitating  $\text{NiCO}_3$  in the presence of "Hyflo-super-cell" (Celite), in amounts of 0.1 and 1.0% at temperature from 80 to  $240^{\circ}\text{C}$ . They found that products with low hydroxyl value were obtained at higher temperature, where as at low temperature simple hydrogenation of ricinoleic acid molecule took place. They obtained products rich in hydroxyl group by hydrogenation of castor oil in the presence of a solvent (ethyl alcohol), at room temperature and hydrogen pressure 40 psig.

Zajcew (28) used highly selective modified palladium catalyst to hydrogenate castor oil at  $100^{\circ}\text{C}$  and hydrogen pressure 45 psig. The product had are iodine value of 4, a

hydroxyl value of 145 and an acid value of 1.8 and a capillary melting point of  $86^{\circ}\text{C}$ .

Van Loon (29) using 3% reduced nickel from nickel keiselguhr catalyst, found that at 5-120 atm. of hydrogen pressure and temperature below  $200^{\circ}\text{C}$ , all the unsaturation of castor oil and only 15-20 % of the hydroxyl groups were removed. Above  $200^{\circ}\text{C}$ , the rate of hydroxyl reduction was increased. Using palladium deposit on carbon catalyst for hydrogenation of castor oil and its ethyl esters, the main centre of hydrogenation activity was found to be the double bond.

Hladik and Zajic (30) studied the hydrogenation of castor oil at atmospheric pressure and low temperature ( $120-180^{\circ}\text{C}$ ) in the presence of nickel catalyst and found that the optimal hydrogenation was achieved with 0.5% nickel catalyst at  $160^{\circ}\text{C}$ . Kane and Menerka (31) studied the influence of temperature, pressure, type and concentration of catalyst on the hydrogenation of castor oil and found that the rate of hydrogenation  $r_{\text{H}}$  depended on the partial pressure of the hydrogen and not on the total pressure,  $P_0$ . At an overall P of 6.8 atm.  $r_{\text{H}}$  has a maximum at  $170^{\circ}\text{C}$ , and when  $P=20.4$  atm., the maximum  $r_{\text{H}}$  occurred at  $125^{\circ}\text{C}$ . At constant temperature, an increasing in pressure was accompanied that ethyl alcohol increase  $r_{\text{H}}$  upto ethyl alcohol concentration of 90% vol./vol. The presence of solvent also insured that only a small amount of dehydroxylation of the oil was decreased. They (32) also found that the conditions for the hydrogenation of castor oil with very little dehydroxylation were determined by using ethyl alcohol as solvent and Raney nickel as catalyst. A product with an iodine value of 2 was obtained in 3 hours by hydrogenation of ethyl alcohol :

castor oil mixture (3:1 and 5:1) at 75-100°C, 200-300 psig. and using a 2% Raney nickel catalyst.

Kaczanowski and Jakabowski (33) investigated the hydrogenation of castor oil at 1.2 atm., 150°C, using nickel catalyst. After a 5-hours passage of H<sub>2</sub> at a rate of 2 l/min, the product had an iodine value 14.1 saponification value 184.8, acid value 2.28, hydroxyl value 13.3 and melting point 79.8°C.

Rao et. al studied the hydrogenation of castor oil in several parts ; Influence of variables on hydrogenation efficiency (34). Process of development, project costs and pilot plant study (35) and storage studied on nickel catalyst (36). They found that the suitable conditions were at temperature 150°C, hydrogen pressure 10 kg/cm<sup>2</sup>, 5 hours and used Raney nickel catalyst at the 2% level. The catalyst could be used indefinitely and only 25% of fresh make-up catalysts was needed for each run. The catalyst stored in hydrogenated castor oil retained their activity.

Nachaev (38) examined the effect of Raney nickel catalyst and compared with that of the Cu-Ni catalyst commonly used in the hydrogenation of vegetable oils and found that the suitable temperature for castor oil was 150°C, amount of catalyst over 1% did not speed up the hydrogenation and agitation markedly increased hydrogenation.

Shmidt et.al (38) examined the effect of various solvent on the hydrogenation of castor oil at 50°C and hydrogen pressure 1 atm and found that; a) the hydrogenation curve in polar solvents indicated a 1st order reaction, b) changing to nonpolar solvents decreased the starting rate of

reaction, c) suitable conditions were attained at 80 °C and hydrogen pressure 40 kg./cm<sup>2</sup> in ethyl alcohol using Raney nickel as catalyst. Maskaev et.al (39) used the Ni-Ti-Al alloy with a particle size of 3-8 mm, which was activated with 8% aq.NaOH at 80 -90 °C, washed and dried in a hydrogen current at 120 °C, as a catalyst for hydrogenation of castor oil at 70-80 °C and hydrogen pressure at 22-25 kg/cm<sup>2</sup>.

Bronfen (40) used a nickel catalyst deposited on kieselghur for hydrogenation of castor oil at 125 -128 °C and hydrogen pressure 12 atm, this catalyst could be used repeatedly 4-5 times. Vangmaneerat (15) studied the hydrogenation of castor oil under varying reaction condition using nickel catalyst G53D. The suitable condition was 140 °C, H<sub>2</sub> pressure 175 psig, concentration of catalyst 0.2% Ni/oil, agitation 800 rpm., and hydrogenation time 2 hours. Several alumina supported nickel catalysts were prepared in-house. The best in-house catalyst was a 325-400 mesh size catalyst with 9.3% nickel loading. Its activity was nearly the same as the G 53D catalyst under the following industrial condition ; temperature 140 °C, H<sub>2</sub> pressure 150 psig., concentration of catalyst 0.2% Ni/oil, agitation 800 rpm., and hydrogenation period 2 hours. The resulting castor wax had an iodine value of 4.68, a hydroxyl value of 139.11, an acid value of 0.99, and melting point at 84 °C.

From the articles shown in the review, nickel catalysts were most widely used in the hydrogenation of castor oil, and the suitable hydrogenation conditions were 150 °C, H<sub>2</sub> pressure 150 psig and concentration of catalyst 0.2 - 2%. Several investigators hydrogenated castor oil in ethyl alcohol to protect hydroxyl group. The nickel catalysts were Raney nickel, precipitated nickel and supported nickel

catalyst. For Methyl ricinoleate, there were a few articles in hydrogenation. Because of having the same functional group as castor oil, methyl ricinoleate could be studied in the same condition range as castor oil hydrogenation. In the present study, the commercial nickel catalysts in Catalysis Laboratory were used to hydrogenate methyl ricinoleate. The best commercial catalyst was chosen to determine the suitable operating condition in different concentration from 0.01% to 0.5% at various temperatures from 110 to 200 °C, H<sub>2</sub> pressure from 100 to 175 psig., agitation from 200 to 800 rpm., and reaction time from 1 to 5 hours. In addition, the effect of hydrogen gas feeding and of the storage time of methyl ricinoleate on hydrogenation were studied. The hydrogenated products at various studied condition were analyzed for their iodine value (I.V.), hydroxy value (OH.V.), acid value (A.V.) and melting points (m.p.).