



REVIEW OF LITERATURE

The hydrogenation of castor oil to obtain a product with high hydroxyl value and low iodine value (the major product is 12-hydroxystearate) had been studied by many investigators under different reaction conditions. Most researches were conducted in India and Russia where most castor beans were produced. The abstract of some articles are

Deryabin and Petrov (13) 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 the iodine value did not exceed 8. Paquot and Richet (14) found that the preferred conditions for total hydrogenation castor oil without dehydroxylation were hydrogen pressure 100-150 kg./cm² and 100-110°C or at 50 kg/cm² and 150°C, while at atmospheric pressure and 230-240°C dehydroxylation occurred. Gupta and Aggarwal (15) found that in the process of hydrogenation of castor oil with 2% Ruffert 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 (70-75 lb/sq in) almost complete dehydroxylation occurred.

Bataashe (16) prepared the nickel catalyst to hydrogenate castor oil without dehydroxylation at 175°C and hydrogen pressure 100 atm. by adding to 420 g NaOH in 4.5 l water at 100°C, first 0.5 l

of a solution of Na_2SiO_3 (containing 56 g 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°C , drying 7 hrs at 110°C , pulverizing to 0.4 mm mesh size and reducing this powder (421 g). The powder was mixed with 231 g white Surinam bauxite preheated 2 hrs at 500°C and 6.5 g graphite and compressed into tablets, which were then reduced at 275°C and normal pressure in a stream of hydrogen other catalyst carriers could also be used.

Kobayashi and Kyokaishi (17) used Raney nickel to hydrogenate castor oil at 68 atm. and $50 - 95^\circ\text{C}$ to give a product which was presumed to consist chiefly of 12-hydroxystearic acid and prepared dibasic acids from this hydrogenated castor oil. Srivasan et al (18) 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 NiCO_3 in the presence of "Hyflo-super-cell" (Celite), in amounts of 0.1 and 1.0 % at temperature from 80 to 240°C . They found that products with low hydroxyl value were obtained at higher temperature, whereas 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 (19) used highly selective modified palladium catalyst to hydrogenate castor oil at 100°C and hydrogen pressure 45 psig. The product had an iodine value of 4, a hydroxyl value of 145 and an iodine value of 4, a hydroxyl value of 145 and acid value of 1.8 and a capillary melting point of 86°C .

Hladik and Zajic (20) studied the hydrogenation of castor oil at atmospheric pressure and low temperature (120-180°C) in the presence of nickel catalyst and found that the optimal hydrogenation was achieved with 0.5 % nickel catalyst at 160°C. Manerkar and Kane (21) 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 (22) investigated the hydrogenation of castor oil at 1.2 atm., 150°C, using nickel catalyst. After a 5-hours passage of H₂ 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. Kane and Menerka (23) 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_h depended on the partial pressure of the hydrogen and not on the total pressure, P_o . At an overall P of 6.8 atm. r_h has a maximum at 70°C, and when P = 20.4 atm., the maximum r_h occurred at 125°C. At constant temperature an increase in P was accompanied ethyl alcohol | increase r_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.

Van Loon (24), using 3 % reduced nickel from nickel keiselguhr catalyst, found that at 5-120 atm. of hydrogen pressure and temperature below 200°C, all the unsaturation of castor oil and only 15-20 % of the

hydroxyl groups were removed. Above 200°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.

Nechaev (25) 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 optimum temperature for castor oil was 150°C, amount of catalyst over 1% did not speed up the hydrogenation and agitation markedly increased hydrogenation.

Rao et. al studied the hydrogenation of castor oil in several parts; Influence of variables on hydrogenation efficiency (26), Process of development, project costs and pilot plant study (27) and Storage studied on nickel catalyst (28). They found that the optimum conditions were at temperature 150°C, hydrogen pressure 10 kg/cm², 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.

Shmidt et. al (29) 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 the reaction, c) optimum conditions were attained at 80°C and hydrogen pressure 40 kg/cm² in ethyl alcohol

using Raney nickel as catalyst. Maskaev et al (30) used the Ni-Ti-Al alloy with a particle size of 3-8 mm, which was activated with 8% aq NaOH at 80°C-90°C, washed and dried in a hydrogen current at 120°C, as a catalyst for hydrogenation of castor oil at 70°C-80°C and hydrogen pressure at 22-5 kg/cm²

Bronfen (31) used a nickel catalyst deposited on kieselguhr for hydrogenation of castor oil at 125°C-128°C and hydrogen pressure 12 atm, This catalyst could be used repeatedly 4-5 times.

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, H₂ pressure 150 psig and concentration of catalyst 0.5-2%. Several investigators hydrogenated castor oil in ethyl alcohol to protect hydroxyl group. The nickel catalysts were Raney nickel and precipitated nickel catalyst. No experimenter prepared nickel catalysts by impregnation. Therefore, in the present study, the in-house nickel catalysts were prepared by impregnation which was the easiest method of making a catalyst and leaching method (Raney nickel). They were compared to commercial catalysts. The optimum operating conditions were determined by using the best catalysts in different concentrations from 0.05% to 0.5% at various temperatures from 80 to 180°C, H₂ pressure from 75 to 175 psig, agitation from 200 to 800 rpm., and reaction period from 1 hour to 5 hours. The effect of hydrogenation under these conditions was studied by analyzing periodical samples for their acid values, iodine values, hydroxyl values and melting points.