CHAPTER II

REVIEW OF THE LITERATURE

As previously mentioned, the objectives of this study were: to find out the proper conditions in the preparation of Raney nickel catalysts and, then, also the suitable conditions for the hydrogenation reaction using this catalyst; to investigate effects involving activity and selectivity when the Raney nickel catalyst was incorporated with palladium compound. The survey of pertinent literature is thus conducted in order to study previous work and, subsequently, to better define the scope of this work. Review of the literature is presented as follows.

Several methods of processing Ni-Al alloys to produce catalysts have been described in the literature. In the original process recommended by Raney [1] and developed by Covert and Adkins [2], a prolonged period of digestion of the alloy at 115 °C was mentioned. Mozingo [3] later improved the process, shortening and lowering the temperature of the digestion period. At the suggestion of Adkins, the catalyst used by Covert is known as W-1 and that of Mozingo is known as W-2, a similar designation being applied to the improved preparations described by Adkins and his co-workers [4,5]. The W-6 Raney nickel catalyst of Adkins and Billica [5] has been claimed to be the most active form of Raney nickel known. The leaching and the digestion processes are accomplished at about 50 °C, and the washing is done by a continuous flow method under hydrogen pressure.

ricinoleic acid molecule took place. They obtained products rich in hydroxyl groups by the hydrogenation of castor oil in the presence of a solvent (ethyl alcohol), at room temperature and a hydrogen pressure of 40 psig.

Zajcew [14] used a highly selective modified palladium catalyst to hydrogenate castor oil at 100°C and a hydrogen pressure of 45 psig. The product had an iodine value of 4, a hydroxyl value of 145 and an acid value of 1.8 and a capillary melting point of 86°C.

Hladik and Zajic [15] studied the hydrogenation of castor oil at atmospheric pressure and low temperatures (120 - 180 °C) in the presence of a nickel catalyst and found that optimal hydrogenation was achieved with 0.5% of nickel catalyst at 160 °C. Manerkar and Kane [16] found that the conditions for the hydrogenation of castor oil with very little dehydroxylation were determined by using ethyl alcohol as a solvent and a Raney nickel as catalyst. A product with an iodine value of 2 was obtained in 3 hours by the hydrogenation of ethyl alcohol: castor oil mixtures (3:1 and 5:1) at 75-100°C, 200-300 psig and using a 2% Raney nickel catalyst.

Kaezanowski and Jakabowski [17] investigated the hydrogenation of castor oil at 1.2 atm., 150°C, using a nickel catalyst. After a 5-hours passage of H_2 at a rate of 2 l/min, the product had an iodine value of 14.1, a saponification value of 184.8, an acid value of 2.28, a hydroxyl value of 163.3 and a melting point of 79.8 °C. Kane and Menerka [18] 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

Bernstein and Dorfman [6] have prepared a modified catalyst by allowing the reaction mixture to stand at room temperature overnight after the addition of the alloy. Bougault, Cattelain, and Chabrier [7] and Mozingo [8] have prepared similarly modified catalysts.

Delepine and Horeau [9] and Reichstein and Gatzi [10] obtained good results using small amounts of Raney nickel catalyst.

Bataafsche [11] prepared the nickel catalyst to hydrogenate castor oil without dehydroxylation at 175 °C under a hydrogen pressure of 100 atm, by adding 0.5 l of a solution of Na_2SiO_3 (containing 56 g SiO_2) to 420 g of NaOH in 4.5 l of water at 100 °C. Then after stirring for a short time, $Ni(NO_3)_2$ (containing 200 g of Ni) in 5 l of boiling water was added. The precipitate was filtered and washed with 24 l of water at 45 °C, dried 7 hr at 110 °C, pulverized to 0.4 mm mesh size and reduced. The powder was mixed with 231 g of white Surinam bauxite preheated 2 hr at 500 °C and 6.5 g of graphite and compressed into tablets, which were then reduced at 275 °C and a normal pressure in a stream of hydrogen.

Kobayashi and Kyokaishi [12] used a Raney nickel to hydrogenate castor oil at 68 atm. and 50-95 °C to give a product which was presumed to consist chiefly of 12 hydroxystearic acid and prepared dibasic acids from its hydrogenated castor oil. Srivasan et al. [13] studied the hydrogenation of castor oil and methyl ricinoleate at atmospheric pressure using a 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 temperatures, whereas at low temperatures simple hydrogenation of hydrogen and not on the total pressure, P_o. At a total pressure, 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 a temperature an increase in P was accompanied with increase in r_h up to an ethyl alcohol concentration of 90% vol./vol. The presence of solvent also insured only a small percentage of dehydroxylation of the oil.

Van Loon [19], using 3% reduced nickel from nickel keiselguhr catalyst, found that at 5-120 atm. of hydrogen pressure and at temperatures 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 deposited 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 [20] examined the effect of a Raney nickel catalyst and compared it 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, and amounts of catalysts above 1% did not speed up the hydrogenation, and agitation markedly increased hydrogenation.

Rao et al. studied the hydrogenation of castor oil in several aspects; influence of variables on hydrogenation efficiency [21], process development, project costs and pilot plant study [22] and storage studies for nickel catalyst [23]. They found that the optimum conditions were at a temperature 150°C, a hydrogen pressure of 10 kg/cm^2, 5 hours of reaction time and concentration of 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 its activity.

Schmidt et al. [24] examined the effect of various solvents on the hydrogenation of castor oil at 50 °C and a hydrogen pressure of 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 a hydrogen pressure of 40 kg/cm^2 in ethyl alcohol using Raney nickel as catalyst. Maskaev et al. [25] 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 the hydrogenation of castor oil at 70-80 °C and a hydrogen pressure at 2-5 kg/cm^2.

Bronfen [26] used a nickel catalyst deposited on kieselguhr for the hydrogenation of castor oil at 125-128 °C and a hydrogen pressure of 12 atm. This catalyst could be used repeatedly 4-5 times.

From the literature, a number of articles mention methods for preparation of Raney nickel catalysts, varying from simple preparation methods to the complex ones. However, there have been many conflicting statements concerning the effects of parameters such as the concentration of aqueous NaOH solution, temperature of digestion, ratio of the alloy to NaOH (anhydrous), etc. Thus, in this study the effects of these parameters to the activity of Raney nickel will be studied.

Palladium has never been reported used in the hydrogenation of castor oil as a catalyst. However, even in those few studies, it can be clearly seen that the activity of palladium catalysts is greater than that of nickel, owing to reduced operating temperatures and pressures. The question as to why it was not commercially used was discussed by Rylander [27] and it was concluded that this was due to economic considerations.

There was an interesting study, investigated by Brown [28], that the activity of nickel catalysts could be enhanced by the presence of up to 2% Pd. But this happened in the hydrogenation of soyabean oil. However, this reference initiated the idea of incorporating Pd into the Raney nickel catalyst in order to study the effect on activity and selectivity of nickel catalyst in the hydrogenation of castor oil. The percentage of palladium incorporated was also varied up to 2%.