Low Pressure Hydrogenation of Castor Oil

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Castor Oil was hydrogenated at low pressure (2.0–2.5 kg/cm^2) and low temperature (125–135 C) using nickel catalyst to obtain a saturated waxy product rich in hydroxy stearic acid. High catalyst concentration was required to obtain good results. However, the catalyst could be recycled. The final product had iodine value below 3.0, hydroxyl value 155, and slip point of 84 C.

Castor oil is a unique fatty oil containing a major amount of ricinoleic acid. The oil has three functional groups: a double bond, an ester and hydroxyl groups, which open numerous possibilities for chemical reactions. Complete hydrogenation of castor oil under conditions which protect the hydroxyl group results in a hard, brittle, waxy material rich in hydroxy-stearate. Such a product is in great demand in the world market for use in the manufacture of plasticizers, high pressure greases, cosmetics, and as a substitute for carnauba wax. The hydrogenation usually is done at pressures above 150 psi (1–4). Earlier attempts to hydrogenate the oil at low pressures resulted in the product having a low hydroxyl value (5–12). Also, some attempts have been made to hydrogenate the oil in the presence of solvents (2,3,8,13), but these have not been found commercially viable. Even at low temperatures Ueno (14) reported that the hydroxyl value of ricinoleic acid was reduced gradually depending on the rate of hydrogenation, and at complete saturation (IV, 2.0) the acetyl value was lower by about 40 units. Among the various catalysts used for hydrogenation, supported nickel catalysts have been reported (15,16) to be useful for castor oil.

Attempts were made to hydrogenate the oil at low pressure without any solvent while keeping the other operating conditions at a level that would keep the hydroxyl group intact. The present paper reports the findings of this work.

EXPERIMENTAL

Materials. The characteristics of the castor oil used in the experiments were determined by AOCS procedures (17). The oil had the following characteristics: Specific gravity (30 C) 0.956, refractive index (25 C) 1.4790, color (Lovibond, 1″ cell, Y + 5 R) 2.8, acid value 1.4, iodine value (Wijs) 87.6, hydroxyl value 163.0.

The stainless steel autoclave used for hydrogenation had a 5-kg capacity. It was electrically heated and fitted with a stirrer, thermometer and pressure gauge. The autoclave had arrangement for sparging hydrogen, using cooling water and withdrawing a sample.

Catalyst was commercially available wet reduced type catalyst obtained from M/s. General Chemical Company, Bombay, India, of ACS grade containing 22% nickel.

Methods. Castor oil in two-kg batches was transferred to the autoclave and heated to 110 C under reduced pressure of 30 mm Hg. The catalyst, dispersed in the oil, was sucked into the autoclave at the above temperature and pressure. The contents of the autoclave were heated to the required temperature, hydrogen was introduced and the desired pressure was maintained. Due to the high initial reaction rate and exothermic nature of the hydrogenation reaction, the temperature had to be controlled by circulating cooling water. Samples were withdrawn at specific intervals and analyzed for iodine value, hydroxyl value, acid value and slip point. For recycling of the catalyst, the cooled filter cake was scraped off the filter under atmospheric conditions, its nickel content determined (18) and the calculated amount of this used catalyst added to the fresh catalyst to make up to 0.8% Ni by weight of the oil charged.

RESULTS AND DISCUSSION

Initial experiments in the present work were conducted at 200 C while varying the other operating parameters of pressure and catalyst concentration. The results of the initial runs are shown in Table 1. These results indicate that during the hydrogenation of oil at 200 C, the reduction in the hydroxyl value of the oil, because of simultaneous dehydration (5–12), was more significant at lower pressure and higher catalyst concentrations. Reducing the temperature of hydrogenation also retards the reduction of hydroxyl value of the oil, which is evident from the results in Table 2. Further, no apparent drop in the rate of hydrogenation at 160 C was observed because the reduction in the rate of simultaneous dehydration reduced the rate of simultaneous increase in the iodine value of the oil. This was found encouraging and, therefore, further experiments were conducted at 130 C. Looking at the results of run 10 (Table 3) and comparing these with those of run 9 (Table 2) it is observed that the rate of dehydration was significantly reduced in run 10 at 130 C compared to that in run 9 at 160 C. This rate of hydrogenation was, however, still not as fast as desired. Therefore, run 11 was conducted at increased catalyst concentration, 0.8% by weight of oil. The rate of hydrogenation under the conditions of run 11 was rapid and, after five hr of hydrogenation, a product having I.V. 2.7 and H.V. 154.0 was obtained.

TABLE 1

Hydrogenation of Castor Oil at 200 C at Different Hydrogen Pressures and Doses of Fresh Nickel Catalyst[a]

Run no.	Hydrogen pressure (kg/cm^2)	Nickel catalyst (% Ni)	Reaction time (hr)	Iodine value	Hydroxyl value	Slip point (°C)
1	1.35	1.0	6.0	2.2	95.6	80-81
2	1.35	1.5	5.5	2.1	77.1	79-80
3	1.35	2.0	5.5	1.9	53.9	78-79
4	2.0	1.0	6.0	2.9	96.3	80-81
5	2.70	1.0	6.0	3.6	105.4	80-81
6	3.35	1.0	6.0	2.4	111.7	80-81
7	4.70	1.0	6.0	2.8	122.0	81-82
8	4.70	0.5	6.0	4.2	128.0	81-82

[a]Castor oil, I.V. 87.6, H.V. 163.0.

TABLE 2

Hydrogenation of Castor Oil at 160 C and 2.0 kg/cm^2 Pressure Using 0.5% Fresh Nickel Catalyst[a]

Run no.	Reaction time (hr)	Iodine value	Hydroxyl value	Slip point (°C)
9	1.0	54.6	151.2	56-59
	2.0	38.8	146.3	68-69
	3.0	24.3	140.3	73-74
	4.0	11.7	137.6	77-78
	5.0	7.8	137.0	80-81
	6.0	5.2	136.4	81-82

[a] Castor oil, I.V. 87.6, H.V. 163.0.

TABLE 3

Hydrogenation of Castor Oil at 130 C and 2.0 kg/cm^2 Pressure Using Fresh Nickel Catalyst[a]

Run no.	Catalyst concentration (% Ni)	Reaction time (hr)	Iodine value	Hydroxyl value	Slip point (°C)
10	0.5	1.0	63.0	163.0	47-48
	0.5	2.0	38.4	161.0	71-72
	0.5	3.0	21.8	160.7	77-78
	0.5	4.0	12.4	159.2	81-82
	0.5	5.0	6.2	157.4	82-83
	0.5	6.0	4.1	156.4	83-84
11	0.8	1.0	57.4	162.2	52-53
	0.8	2.0	33.2	159.4	73-74
	0.8	3.0	17.3	156.5	79-80
	0.8	4.0	6.9	155.3	82-83
	0.8	5.0	2.7	154.0	84-85

[a] Castor oil, I.V. 87.6, H.V. 163.0.

TABLE 4

Hydrogenation of Castor Oil at 130 C and 2.0 kg/cm^2 Pressure, Using Various Proportions of Recycled Catalyst[a]

Run no.	Catalyst concentration (% Ni fresh/used)	Reaction time (hr)	Iodine value	Hydroxyl value	Slip point (°C)
12	0.6/0.2	1.0	60.1	162.2	50-51
	0.6/0.2	2.0	35.8	159.7	72-73
	0.6/0.2	3.0	18.1	158.6	79-80
	0.6/0.2	4.0	7.4	157.2	82-83
	0.6/0.2	5.0	2.9	156.6	84-85
	0.6/0.2	5.5	2.2	156.6	85-86
13	0.4/0.4	1.0	62.1	163.0	49-50
	0.4/0.4	2.0	38.2	162.2	71-72
	0.4/0.4	3.0	19.8	160.0	78-79
	0.4/0.4	4.0	10.3	157.8	81-82
	0.4/0.4	5.0	4.7	156.2	83-84
	0.4/0.4	5.5	3.1	155.4	84
14	0.2/0.6	1.0	62.6	162.8	49-50
	0.2/0.6	2.0	40.7	-	70-71
	0.2/0.6	3.0	22.3	161.8	76-77
	0.2/0.6	4.0	11.2	160.2	81-82
	0.2/0.6	5.0	5.6	157.4	83-84
	0.2/0.6	6.0	2.8	156.0	84-85

[a] Castor oil, I.V. 87.6, H.V. 163.0.

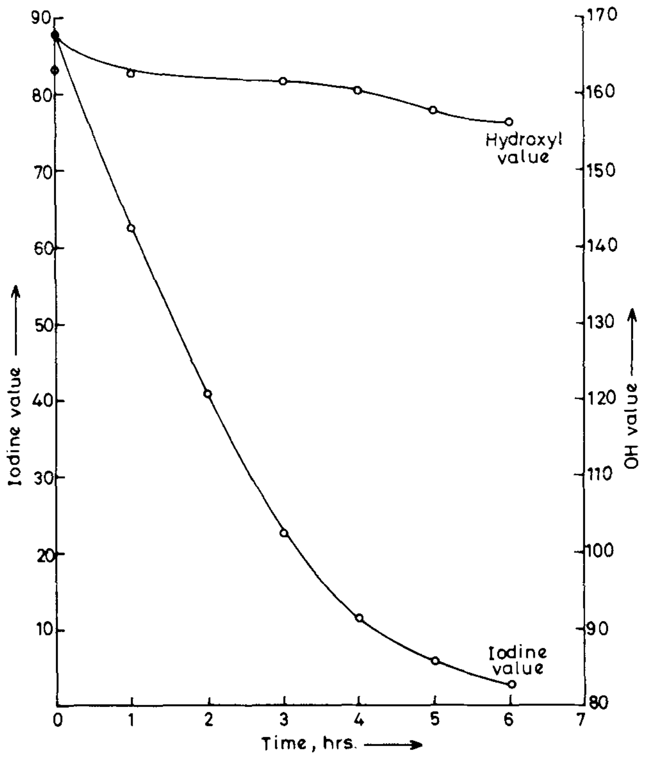

FIG. 1. Progress of hydrogenation reaction at optimum conditions.

TABLE 5

Suggested Operating Parameters of Castor Oil Hydrogenation and Product Characteristics

Suggested parameters	
Temperature	130±5 C
Hydrogen pressure	2.0±0.5 kg/cm^2
Catalyst concentration, % Ni 0.8	0.2 fresh 0.6 used
Product characteristics	
Specific gravity (25 C)	0.9990
Color (Lovibond, 5.25" cell as 10% alcoholic solution)	3.0 yellow 1.0 red
Acid value	2.1
Iodine value (Wijs)	2.8
Saponification value	182.4
Hydroxyl value	155.6
Slip point, °C	84-85
Titre, °C	71
Ash, ppm	76
Nickel, ppm	164

As the catalyst concentration required for a satisfactory rate of hydrogenation was high, recycling of the used catalyst was considered necessary. Table 4 shows the results of experiments carried out with part recycled catalyst at 130 C and 2.0 Kg/cm^2. Runs 12, 13 and 14 were conducted using 25% recycled catalyst, 50% recycled catalyst and 75% recycled catalyst, respectively. The results of these runs showed that the rate of hydrogenation and the rate of simultaneous dehydration were not very different in the three cases. Therefore, the conditions in run 14, when 75% recycled catalyst was used, were assumed to be optimum. The progress of hydrogenation reaction in run 14 is also depicted in Figure 1.

The suggested conditions of hydrogenation and product specifications are given in Table 5.

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