A Process for Solid Fat from Castor Oil by Simultaneous Hydrogenation and Dehydration

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A single step process has been developed on a pilot plant scale (15 kg/batch) for simultaneous hydrogenation and dehydration of castor oil using nickel catalyst and attapulgite to yield solid fats having a hydroxyl value of 7–33 and an iodine value of 41–56. The polymer and keto fatty acid contents in the products were up to 2% and 3.2%, respectively. The product can be used in the manufacture of soap as the hard fat component and in textile sizing.

KEY WORDS: Castor oil, simultaneous hydrogenation and dehydration, solid fat from castor oil.

India is short of both animal and vegetable solid fats which are needed in soap manufacturing as the hard component. The indigenous production and import of tallow and other animal fats are practically negligible due to both socio-economic reasons and government policies. Hence, several nonedible vegetable oils are hydrogenated to meet the demand. Among these, castor oil is produced abundantly in India, the production being 150,000 metric tons in 1988–89 (1). After meeting the export demand of about 50% of the production, the remainder of the oil is available for indigenous use at a relatively cheaper price. Since the castor oil as such gives a soft nonlathering soap as it contains 85–90% of 9-*cis*, 12-hydroxyoctadecenoic (ricinoleic) acid (2), it is converted to a solid fat by dehydration followed by hydrogenation or *vice-versa* (3). The process of dehydration followed by hydrogenation is not only costly because of high consumption of nickel catalyst due to the presence of residual dehydrating acidic catalyst (4), but also yields poor quality product because of the formation of polymeric compounds during dehydration (5). The process of hydrogenation followed by dehydration often necessitates rehydrogenation involving the same difficulties and also leads to the keto acid formation during hydrogenation (6). Both these multistep processes lead to high cost of production.

To overcome the limitations of these two- or three-step processes, we have developed a single step simultaneous hydrogenation-dehydration process to yield a product of low hydroxyl value and of iodine value comparable to that of tallow for use in soap manufacture. This process has been patented (7). The details of the process developed on 15 kg oil/batch scale and the product characteristics are reported here.

MATERIALS AND METHODS

Commercial grade castor oil (Indian Standard 435-1973, Bureau of Indian Standards, New Delhi), which was treated with oxalic acid (6) and had a hydroxyl value (HV) of 166, an iodine value (IV) of 85 and an acid value (AV) of 3.3, was obtained from Tata Oil Mills Company Ltd. (Bombay, India). Untreated commercial grade (HV 165, IV 81 and AV 1.8) and Firsts grade (IS:435-1973) (equivalent to British Standard 650:1977; HV, 160–165; IV, 84–87; and AV, 1.27) castor oils were purchased from local mills. Nickel catalyst (16% nickel) was obtained from Hindustan Lever Ltd. (Bombay, India). Korvi and Timsanpalli attapulgites (naturally occurring bleaching earths, 200 mesh) were purchased from Korvi Fullers Earth Processing Industry, located in Gulbarga, Karnataka and Timsanpalli, Vikarabad, Andhra Pradesh, respectively. Electrolytic hydrogen was used.

Simultaneous hydrogenation and dehydration of castor oil was carried out (7) on 10 to 20 kg-batch size in a 25-liter capacity hydrogenation unit (Power Gas Corporation Limited, England). A Parr autoclave of 2-liter capacity was used for 1 kg-batch size experiments. The oil, nickel catalyst and attapulgite were charged and heated with stirring under hydrogen atmosphere to study the effect of various parameters. Samples were collected at hourly intervals. Analyses for HV, IV, AV and titer were done according to the *Official and Tentative Methods of the American Oil Chemists' Society* (8). Fatty acid composition was determined by gas-liquid chromatography (GLC) of acetylated methyl esters using 1.2 m × 3 mm column packed with 5% SE-30 on 40–60 mesh Chromosorb P and 2.4 m × 6 mm column packed with 15% EGSS-X on Gaschrom Q (80–100 mesh). The columns, injector and FI detector were maintained at 200, 250 and 300°C, respectively. The flow rate of nitrogen was 30 mL/min. Keto (6) and hydroxyl fatty acid contents were calculated from SE-30 column chromatograms and the other fatty acid contents from EGSS-X column chromatograms. Polymers present in the sample were separated (9) as non-urea adducting methyl esters and estimated by GLC on SE-30 column. The polymers, which were not eluted from the GLC column, were estimated by using methyl heptadecanoate as an internal standard.

RESULTS AND DISCUSSION

The following parameters were studied: i) nickel catalyst, 0.05 to 0.2% Ni; ii) temperature, 180–220°C; iii) stirrer speed, 550 and 775 rpm; iv) attapulgite, 1–4%; v) hydrogen outlet flow rate, 10 to 27 L/hr/kg oil; and vi) reaction time, 4–6 hr (Tables 1–3). A nickel concentration of 0.1% was found to be necessary to get a product with iodine value of 42 in 4 hr (Table 1). Low concentration gave products with comparatively higher hydroxyl and iodine values, and with higher concentration of nickel the drop in iodine value was fast. The effect of temperature on the reaction is shown in Table 1. At 180°C and 200°C dehydration was slow. A reaction temperature of 220°C was found to yield a product with low hydroxyl value. Stirrer speeds of 550 and 775 rpm gave similar results (Table 1). The results obtained with 2, 3 and 4% Korvi attapulgite are given in Table 2. The concentration of attapulgite may be fixed depending upon the quality of castor oil to be used and the characteristics of the product desired (Tables 1–4). For the untreated commercial

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TABLE 1

Simultaneous Hydrogenation and Dehydration of Commercial Grade Castor Oil Treated with Oxalic Acid: Effect of Parameters[a]

		Reaction time (hr)			
		3	4	5	6
A. Effect of Ni concentration[b]					
Expt. 1 - 0.05% Ni	HV		49	42	38
	IV		67	64	60
	AV		7.6	6.6	7.0
Expt. 2 - 0.1% Ni	HV		30	28	25
	IV		42	35	30
	AV		5.8	6.6	6.4
Expt. 3 - 0.2% Ni	HV		21	—	16
	IV		16	—	7.4
	AV		6.8	—	7.2
B. Effect of temperature[c]					
Expt. 4- 180°C, attapulgite 3%	HV	77	71	66	56
	IV	47	40	35	30
	AV	4.2	4.3	4.2	4.6
Expt. 5 - 200°C, attapulgite 3%	HV	53	48	45	38
	IV	47	41	35	31
	AV	4.1	4.5	4.6	4.6
Expt. 6 - 220°C, attapulgite 2%	HV	25	23	19	19
	IV	51	44	35	29
	AV	5.8	5.7	5.8	5.8
C. Effect of stirrer speed[d]					
Expt. 7 - 550 rpm	HV	44	38	33	29
	IV	71	68	59	52
	AV	9.2	8.2	8.4	8.7
Expt. 8 - 775 rpm	HV	46	39	32	28
	IV	69	61	53	45
	AV	8.5	9.2	9.4	9.5

[a] Batch size, 15 kg; H_2 flow rate, 27 L/hr/kg oil.

[b] 220°C; Karvi attapulgite, 2%; stirrer speed, 775 rpm.

[c] Ni, 0.1%, stirrer speed, 775 rpm; Timsanpalli attapulgite.

[d] Ni, 0.1%; Korvi attapulgite, 2%; 220°C.

TABLE 2

Simultaneous Hydrogenation and Dehydration of Commercial Grade Castor Oil: Effect of Korvi Attapulgite Concentration[a]

		Reaction time (hr)			
		3	4	5	6
Expt. 1 - attapulgite 2%	HV	58	51	48	43
	IV	58	48	41	36
	AV	5.5	5.3	5.7	5.6
Expt. 2 - attapulgite 3%	HV	37	32	27	23
	IV	69	61	55	48
	AV	6.5	6.5	6.6	7.0
Expt. 3 - attapulgite 4%	HV	20	13	10	7
	IV	83	76	63	55
	AV	8.1	8.5	8.7	8.6

[a] Batch size, 15 kg; H_2 flow rate, 27 L/hr/kg oil; Ni, 0.1%; stirrer speed, 550 rpm; 220°C.

TABLE 3

Simultaneous Hydrogenation and Dehydration of Firsts Grade Castor Oil: Effect of Hydrogen Gas Flow Rate[a]

Batch kg	Hydrogen outlet flow rate (L/hr/kg oil)	Analysis of final product		
		HV	IV	AV
1	20	9.9	85	11.4
1	20	18.0	78	10.0
1	20	7.4	77	9.5
10	10	21.0	92	9.9
10	15	11.0	81	11.1
10	20	14.5	62	8.6
15	10	17.5	81	10.2
15	15	8.6	67	10.4
15	20	10.5	67	9.8
15	27	10.2	53	8.5
20	10	17.6	82	8.6
20	15	12.9	72	10.0
20	20	8.8	63	8.8

[a] Ni, 0.1%; Korvi attapulgite, 2%; 220°C; stirrer speed, 480 rpm for 1 kg batch and 550 rpm for 10-20 kg batch; reaction time, 4 hr.

TABLE 4

Optimum Conditions (15 kg Batch) for Simultaneous Hydrogenation and Dehydration of Castor Oil

Castor oil grade	Product specification		Nickel (%)	Korvi attapulgite	Temperature (°C)	Stirrer speed (rpm)	Hydrogen flow rate L/hr/kg oil	Reaction time hr
	HV	IV						
Commercial treated with oxalic acid	20-40	40-60	0.1	2	220	550	27	4
Commercial	below 20	40-60	0.1	4	220	550	27	6
Firsts	below 20	30-60	0.1	2	220	550	27	4

TABLE 5

Analytical Data on Solid Fats Obtained from Castor Oil Under Optimum Conditions[a]

		Reaction time (hr)					
		1	2	3	4	5	6
A. Commercial grade castor oil treated with oxalic acid							
Expt. 1	HV	89	59	36	33		
	IV	80	73	66	41		
	AV	6.0	6.9	7.1	9.8		
Expt. 2	HV	81	52	38	29		
	IV	88	81	73	50		
	AV	6.1	7.6	8.1	10.8		
Expt. 3	HV	90	57	40	30		
	IV	82	78	64	45		
	AV	6.0	8.3	9.4	10.5		
B. Commercial grade castor oil							
Expt. 4	HV	46	32	20	13	10	7
	IV	100	89	83	76	63	55
	AV	5.5	6.5	8.1	8.5	8.7	8.6
Expt. 5	HV	85	73	36	27	20	15
	IV	82	73	73	62	56	47
	AV	3.5	5.1	7.4	8.4	8.8	8.3
C. Firsts grade castor oil							
Expt. 6	HV	59	27	15	10		
	IV	82	75	63	53		
	AV	5.1	7.3	8.5	8.5		
Expt. 7	HV	67	47	22	10		
	IV	90	77	71	56		
	AV	4.6	5.8	7.3	8.1		
Expt. 8	HV	74	48	23	13		
	IV	80	70	67	54		
	AV	3.9	6.1	8.7	9.3		

[a]See Table 4 for details.

TABLE 6

Analysis and Composition of Two Typical Products of Solid Fat from Castor Oil

	Sample 1	Sample 2
HV	12	11
IV	60	50
AV	10.0	8.9
Titer, °C	52.3	57.5
Fatty acid (wt. %)[a]		
Palmitic	0.8	0.7
Stearic	22.7	36.8
Oleic/isooleic	72.2	57.3
Hydroxy	1.2	1.6
Keto	2.5	3.2
Unknown	0.6	0.4

[a]Also contained 1-2% polymers.

TABLE 7

Reuse of Catalyst for Solid Fat from Castor Oil[a]

	Reaction time (hr)			
	1	2	3	4
Expt. 1 (fresh catalyst: Ni 0.1%, Korvi attapulgite 2%)				
HV	70	25	15	11
IV	93	87	74	59
AV	5.6	7.2	7.9	8.7
Expt. 2 (75% fresh catalyst + 25% spent catalyst from Expt. 1)				
HV	64	28	18	12
IV	90	83	72	61
AV	5.1	6.9	7.6	8.2
Expt. 3 (75% fresh catalyst + 25% spent catalyst from Expt. 2)				
HV	77	35	22	16
IV	87	84	81	66
AV	4.5	6.5	7.7	8.2
Expt. 4 (75% fresh catalyst + 25% spent catalyst from Expt. 3)				
HV	71	33	23	16
IV	94	86	77	68
AV	4.0	6.1	8.3	8.2

[a]Firsts grade castor oil; batch size, 15 kg; 220°C; stirrer speed, 550 rpm; H_2 outlet flow rate, 27 L/hr/kg oil.

grade castor oil, a higher concentration was found to be necessary than the oxalic acid-treated commercial grade castor oil or Firsts grade castor oil. Both Korvi and Timsanpalli attapulgite gave similar results (Tables 1 and 2). Hydrogen outlet flow rates of 10 to 27 L/hr/kg oil were examined using 1, 10, 15 and 20 kg-batch sizes (Table 3). For 15 kg-batch size 27 L/hr/kg oil was found to be satisfactory. For commercial scale operation 20 ± 5 L/hr/kg oil hydrogen outlet flow rate is recommended. Reaction time up to 6 hr was used (Tables 1-3 and 5). Depending upon the characteristics of the final product desired and castor oil used, the reaction time can be varied from 4-6 hr (Table 4).

The optimum conditions established on 15 kg-batch size for three types of oil, namely commercial grade castor oil treated with oxalic acid, commercial grade castor oil and Firsts grade castor oil, are shown in Table 4 along with the product characteristics, and the results obtained under such conditions are shown in Table 5. The optimum conditions and product specifications are: i) commercial grade castor oil treated with oxalic acid to get a product with HV 20-40 and IV 40-60: Ni, 0.1%; Korvi attapulgite, 2%; temperature, 220°C; stirrer speed, 550 rpm; hydrogen flow rate, 27 L/hr/kg oil; and reaction time, 4 hr; ii) commercial grade castor oil to get a product with HV below 20 and IV 40-60: Ni, 0.1%; Korvi attapulgite, 4%; temperature, 220°C; stirrer speed, 550 rpm; hydrogen flow rate, 27 L/hr/kg oil; and reaction time, 6 hr; and iii) Firsts grade castor oil to get a product with HV below 20 and IV 30-60: Ni, 0.1%; Korvi attapulgite, 2%; temperature, 220°C; stirrer speed, 550 rpm; hydrogen flow rate, 27 L/hr/kg oil; and reaction time, 4 hr. Under these optimum conditions, products with HV below 40 and IV 30-60 were obtained (Table 5). These products were found suitable for soap making by a commercial manufacturer (personal communication). Flexibility in varying the characteristics of the product such as IV and HV, and titer is inherently present in the process described here since the operating conditions can be changed as desired.

The analysis and fatty acid composition of two typical final products are shown in Table 6. The keto fatty acid content was low (2.5% and 3.2%). Shitole and Baliga (6) observed the formation of a substantial amount of keto acids when castor oil was hydrogenated using only nickel catalyst. The polymer content in our products was also low (1–2%). The keto fatty acid and polymer contents were low because of the simultaneous hydrogenation-dehydration process using both hydrogenation catalyst nickel and dehydration catalyst attapulgite and, consequently, minimum occurrence of side reactions.

Catalyst reuse was examined by hydrogenating Firsts grade castor oil (Table 7). The reuse of spent catalyst was not very satisfactory in spite of the addition of 75% fresh catalyst and therefore is not recommended. The fat and the nickel in the spent catalyst can be recovered by suitable processes. Excess hydrogen passing out of the reactor can be dried and recirculated by installing a recirculation pump. This will help to bring down the process cost considerably.

The process is useful to obtain solid fat with low HV (40) and moderate IV (30–60) suitable as hard fat component in soap manufacture from castor oil. The process can be adapted by organizations engaged in hydrogenation of oils, fats and fatty acids.

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