# Reaction Rates of Simultaneous Dehydration and Hydrogenation of Castor Oil

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ABSTRACT: The reaction rates of simultaneous dehydration and hydrogenation of castor oil to make tallow-like hard fat were calculated through a simplified procedure which makes use of a new variable derived from the incremental change in hydrodxyl value and iodine value.
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KEY WORDS: Castor oil, simultaneous hydrogenation and dehydration, solid fat from castor oil.
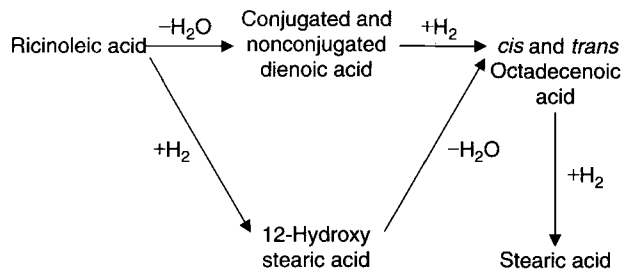
Castor oil, a nonedible vegetable oil, is produced abundantly in India and can be converted into a number of industrially useful products. Tallow-like hard fat is one such product that is useful as a hard component in soap manufacture. This product can be prepared by a number of different procedures, such as by dehydration followed by hydrogenation or vice versa (1). The process of dehydration followed by hydrogenation is uneconomical because of high consumption of nickel catalyst due to the presence of residual dehydrating acidic catalyst. This process yields poor quality products (2,3). The process of hydrogenation followed by dehydration often necessitates rehydrogenation, and is also uneconomical (4).

To overcome the limitations of these two- or three-step processes, a single-step simultaneous hydrogenation–dehydration to yield a tallow-like product has been developed (5). The intermediates that are formed during simultaneous dehydration and hydrogenation of castor oil are conjugated and nonconjugated dienoic acids and 12-hydroxy stearic acid (6).

The composition of the product depends on the relative rates of the different reactions shown in Scheme 1.
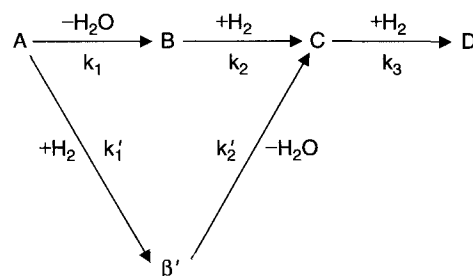
The following differential equations result on the basis of a first-order mechanism:

$$\frac{-dC_A}{dt} = r_0 = k_1 C_A + k_1' C_A \quad [1]$$

$$\frac{+dC_B}{dt} = r_1 = k_1 C_A - k_2 C_B \quad [2]$$

$$\frac{+dC_{B'}}{dt} = r_2 = k_1' C_A - k_2' C_{B'} \quad [3]$$

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SCHEME 1

Symbolically, the reactions can be written as:

SCHEME 2

$$\frac{+dC_C}{dt} = r_3 = k_2 C_B + k_2' C_{B'} - k_3 C_C \quad [4]$$

$$\frac{+dC_D}{dt} = r_4 = k_3 C_C \quad [5]$$

The solution of these differential equations for kinetic parameter estimation is possible only with the data concerning the variation of concentration of various species with time. Procuring these data will involve detailed experimental work.

The overall process is monitored by noting the variation in hydroxyl value (HV) and iodine value (IV). To characterize the process in terms of overall rates, it is both necessary and convenient to have a single variable. A new variable $(IV)_T$ that incorporates incremental changes in HV and in IV has been derived for this purpose.

The IV_T and calculation of overall reaction rates. The process of preparing "hard fat" from castor oil involves simultaneous dehydration and hydrogenation of castor oil. The rate of the overall process is monitored by noting the variation in HV and IV with time. The former is a measure of dehydration, and the latter is a measure of unsaturation. It is necessary to monitor both because the two reactions are occurring simultaneously and are dependent upon each other. Thus, the reaction product can be characterized only by taking into account both variables.

If the two reactions were to take place independently (i.e., saturation of double bonds initially present and dehydration, which results in creation of fresh double bonds that remain intact until the process of hydrogenation is completed), then there would be no need to evaluate $(IV)_T$ to calculate the overall reaction rate.

The objective of this paper is to calculate the overall rate of the process by using a single variable $(IV)_T$, which is derived by incorporating the change in HV and IV. $(IV)_T$ indicates the level of overall unsaturation that results from the dehydration plus the initial unsaturation level of the oil. The new variable $(IV)_T$ is therefore necessary to represent the overall hydrogenation rate.

The overall reaction rates r_1 and r_2 were calculated from the three-point central difference formula for all the intermediate points. The forward difference formula has been used for the first and last points. Thus, the overall rates of hydrogenation were calculated by incorporating the new variable $(IV)_T$ from:

$$\frac{d(IV)_{T,t}}{dt} = \frac{(IV_{T,t+1} - IV_{t-1})}{2\Delta t}(5.909 \times 10^{-7}) \text{moles / mL / min} \qquad [6]$$

and the rate of dehydration has been calculated from:

$$\frac{d(HV)_t}{dt} = \frac{(HV_{t+1} - HV_{t-1})}{2\Delta t}(2.67 \times 10^{-7}) \text{moles / mL / min} \qquad [7]$$

EXPERIMENTAL PROCEDURES

The present analysis was made on the basis of data obtained from pilot-plant and bench-scale experiments. The basic units of the equipment in which the pilot-plant runs were conducted were of Wurster and Sanger design and were supplied by Powergas Corporation (Stockton-on-Tees, England). A stainless-steel reactor with a working capacity of 25 kg of oil per batch and electrically heated with three sets of heating coils, each of a 3.75 KW capacity, was used. The reactor is provided with a feed inlet for the oil–catalyst mixture, and a hydrogen inlet, which extends almost to the bottom so that hydrogen can be bubbled through the oil–catalyst mixture. An electrically-driven stainless-steel, turbine-type stirrer is provided.

Other accessories include a cooling coil in the reactor, a gauge to indicate internal pressure, a pressure regulator, a gas outlet to vent air or hydrogen during initial flushing and to release the pressure at the end of hydrogenation, and a rupture disc.

Experiments of simultaneous hydrogenation and dehydration of castor oil were conducted by heating the oil (15 kg) with the required amount of nickel catalyst and attapulgite while stirring under hydrogen atmosphere. The hydrogen was let in after attaining the temperature, which was 20°C less than the reaction temperature. The reaction was allowed to proceed for the required reaction time while letting out the hydrogen gas continuously during the reaction, mainly to eliminate the water formed due to dehydration. The results obtained from these experiments are summarized in Table 1.

The following variables were studied in pilot-plant experiments: (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, 10–27 L/h/kg oil; and (vi) reaction time, 4–6 h.

The bench-scale experiments were performed in a similar fashion in a 2-L capacity Parr Autoclave (Parr Instrument Co., Moline, IL) with a batch size of 500 g while maintaining the following conditions: (i) stirrer speed, 465 rpm; (ii) hydrogen outlet flow rate, 125 L/h; (iii) nickel catalyst concentration, 0.5% Ni; (iv) temperature, 180– 255°C; and (v) reaction time, 6 h. The results are summarized in Table 2. Materials, analytical methods, and experimental procedures have been described previously (7).

Data analysis. During the simultaneous dehydration and hydrogenation of castor oil, elimination of every hydroxyl group will generate a new double bond, and these newly created double bonds, along with the original double bonds in the oil molecule, would be saturated during hydrogenation. Therefore, a single variable to represent both dehydration and hydrogenation reactions has been derived in terms of HV and the IV of the product.

The number of double bonds generated due to dehydration can be calculated from:

$$(n_1 - n_2) = (HV_1 - HV_2) \times M_{wt/56100} \qquad [8]$$

where n_1 and n_2 are the number of hydroxyl groups per molecule before and after the dehydration, respectively, and (n_1-n_2) is the number of double bonds generated after dehydration. The corresponding IV value becomes:

$$\begin{aligned}(IV)_{new} &= 2 \times 127 \times 100 \ (n_1 - n_2)/M_{wt} \\ &= 2 \times 127 \times 100 \ (\Delta HV)/56100 \\ &= 0.453 \ \Delta HV \qquad [9]\end{aligned}$$

The enhanced IV after the dehydration step is:

$$\begin{aligned}(IV)_T &= (IV)_{initial} + (IV)_{new} \\ &= (IV)_0 + 0.453\Delta HV \qquad [10]\end{aligned}$$

TABLE 1
Rate Data on Simultaneous Dehydration and Hydrogenation of Castor Oil on a Pilot-Plant Scale[a]

Reaction time (h)	Hydroxyl value (HV)	Iodine value (IV)	$(IV)_T$	Rate of dehydration based on HV (g moles)/(min) (mL) $r_1 \times 10^6$	Rate of overall hydrogenation based on new variable (gmoles)/(min) (mL) $r_2 \times 10^6$	Temperature[f] (°C)
0	165.10	85.0	133.63	0.477	0.512	
1	57.74	81.90	93.22	0.294	0.290	
2	32.76	75.00	77.72	0.069	0.149	
3	26.76	63.14	75.02	0.022	0.144	220
4	22.55	48.55	49.29	0.013	0.166	
5	20.91	41.48	44.06	0.016	0.056	
6	15.20	37.97	37.97	0.025	0.060	
0	165.10	85	114.49	0.289	0.44	
1	100	70	81.32	0.200	0.28	
2	75	57	66.97	0.104	0.169	
3	53	47	49.26	0.060	0.128	200
4	48	41	42.36	0.077	0.070	
5	45	35	38.17	0.022	0.056	
6	38	31	31.00	0.031	0.071	
0	165.10	85	105.88	0.205	0.365	
1	119	69	78.97	0.151	0.244	
2	97	56.50	65.56	0.093	0.158	
3	77	47	49.72	0.058	0.126	180
4	71	40	42.26	0.024	0.073	
5	66	35	39.53	0.033	0.061	
6	56	30	30.00	0.045	0.094	

[a]Batch size, 15 kg; rpm, 775; H2 gas rate, 27 L/h • Kg; catalyst concentration (Ni) by weight, 0.1%; attapulgite concentration by weight, 3%.

TABLE 2
Rate Data on Simultaneous Dehydration and Hydrogenation of Castor Oil on a Laboratory Scale[a]

Reaction time (h)	Hydroxyl value (HV)	Iodine value (IV)	$(IV)_T$	Rate of dehydration based on HV (g moles)/(min) (mL) $r_1 \times 10^6$	Rate of overall hydrogenation based on new variable (gmoles)/(min) (mL) $r_2 \times 10^6$	Temperature (°C)
0	165.10	85	117.21	0.316	0.417	
1	94	75	91.94	0.241	0.270	
2	56.60	62.6	65.14	0.094	0.219	
3	51.00	47.50	49.09	0.020	0.187	255
4	47.50	27.30	27.53	0.009	0.131	
5	47.00	22.50	22.50	0.001	0.041	
6	47.00	19.30	19.30	0	0.032	
0	165.10	85	114.26	0.287	0.309	
1	100.50	83	98.90	0.221	0.179	
2	65.40	78	84.52	0.110	0.242	
3	51	50	54.53	0.054	0.326	235
4	41	18.6	19.28	0.025	0.190	
5	39.50	16	16.68	0.006	0.023	
6	38	14.6	14.60	0.006	0.021	
0	165.10	85	107.24	0.218	0.245	
1	116	82.5	97.45	0.182	0.144	
2	83	78	85.70	0.112	0.210	
3	66	55	59.98	0.062	0.300	220
4	55	25	26.54	0.032	0.197	
5	51.60	20.1	21.28	0.013	0.037	
6	49	19	19.00	0.011	0.225	
0	165.10	85	97.28	0.121	0.156	
1	138	81.5	90.56	0.105	0.105	
2	118	76	83.25	0.080	0.146	
3	102	61	65.53	0.057	0.224	200
4	92	38	40.49	0.034	0.210	
5	86.5	23	24.13	0.017	0.141	
6	84	12	12.00	0.111	0.120	
0	165.10	85	90.00	0.049	0.069	
1	154	83	87.98	0.049	0.054	
2	143	79	83.98	0.048	0.116	
3	132	64.50	67.67	0.040	0.128	180
4	125	58	60.94	0.030	0.115	
5	118.5	44.5	46.09	0.022	0.163	
6	115	28	28.00	0.015	0.179	

[a]Batch size, 500 g; rpm, 465; H_2 gas rate, 125 L/h; catalyst concentration by weight, 0.5%.

In these calculations, the molecular weight of the fat component is assumed to be constant because the error involved in this assumption is negligible. This is demonstrated in the following section. Thus, for practical purposes, $(IV)_T$ as a single variable can be used to represent the overall process of simultaneous dehydration and hydrogenation.

The overall reaction rates of simultaneous dehydration and hydrogenation of castor oil, from the data obtained from bench-scale, as well as from pilot-plant experiments, are shown in Tables 1 and 2.

Effect of molecular weight. During the process of simultaneous dehydration and hydrogenation, there will be a reduction in molecular weight due to dehydration, and this reduction in molecular weight would be limited to the extent of dehydration.

To evaluate the effect of molecular weight on the calculation of the new variable, $(IV)_T$, using the newly generated double bonds due to dehydration, the variation in molecular weight of fat should be considered. The relationship for calculating the number of double bonds generated can be derived by considering the difference in initial and final values of HV during the process. Thus:

$$HV_1 = n_1 \times 56100/298$$
$$HV_2 = n_2 \times 56100/M_{wtv}$$
$$\Delta HV = n_1 \times 56100/298 - n_2 \times 56100/M_{wtv} \qquad [11]$$

Rearranging, Equation gives:

$$n_2 = (n_1/298 - \Delta HV/56100)M_{wtv} \qquad [12]$$

where $M_{wtv} = [298 - 18(HV_1 - HV_2)/HV_1]$, and 298 and 18 are molecular weights of ricinoleic acid and water, respectively.

Equation 12 takes into account the variation in molecular weight during the process.

Consider, for example, that ricinoleic acid has an IV of 85.23 and an HV of 188.255 and is subjected to simultaneous dehydration and hydrogenation. The overall difference in HV is 60.

The number of double bonds generated can be calculated from:

$$n_2 = (n_1/298 - \Delta HV/56100)M_{wtv} = 0.6682 \qquad [13]$$

and the number of double bonds generated on the basis of constant molecular weight are:

$$n_2 = n_1 - (\Delta HV \times 298)/(56100) = 0.6813 \qquad [14]$$

As can be seen, the difference in the value of n_2 is marginal, i.e., the value is overestimated by 1.96%.

This clearly shows that the new variable, $(IV)_T = (IV)_o + 0.453\ (\Delta HV)$, can be safely used to calculate the reaction rates.

RESULTS AND DISCUSSION

The single-step process for preparing tallow-like hard fat from castor oil consists of mainly dehydration and hydrogenation in the presence of nickel catalyst and attapulgite (naturally occurring bleaching earth, 200 mesh).

The new variable, which is derived by incorporating the change in HV and IV during the simultaneous dehydration and hydrogenation of castor oil, appears to be suitable for calculating the apparent reaction rates of the overall process.

The following are some of the general conclusions drawn from the experimental results. Table 1 shows that, at low temperatures, the rate of overall hydrogenation is predominant, and the reaction rates r_1 and r_2 decrease with time and temperature. Dehydration was low at 180 and 200°C. A reaction temperature of 220°C yields a product of low HV. A nickel concentration of 0.1% was necessary to get a product with an IV of 42 in 4 h of reaction time. Low catalyst concentrations gave products with comparatively higher HV and IV, and with higher concentrations of nickel the drop in IV was fast. The concentration of attapulgite may be fixed, depending upon the quality of castor oil to be used and the characteristics of the product desired.

The results obtained from the bench-scale experiments show that higher temperatures, i.e., beyond 220°C, are necessary to get products with an IV of 20 and an HV of 41 in 4 h of reaction time. At low temperatures of 180, 200, and 220°C, saturation of the double bonds appears to be the predominant reaction.

Comparatively, reaction rates r_1 and r_2 are low in bench-scale experiments, probably due to the absence of the dehydrating agent and the poor mixing conditions in the reactor.

The main advantages of new variable, $(IV)_T$, are that (i) it represents a measure of dehydration and simultaneous overall hydrogenation, and (ii) the overall reaction rate, based on this new variable, $(IV)_T$, is useful for the evaluation of the mass transfer resistances in a three-phase slurry reactor.

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