Effect of Agitation in the Hydrogenation of Castor Oil

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ABSTRACT: Castor oil was hydrogenated to evaluate the effect of agitation during hydrogenation. The turbine and propeller impellers were evaluated during hydrogenation of castor oil at various temperatures, pressures, and catalyst concentrations. The effect of impeller position in the agitator at definite oil depth was also evaluated. Hydrogenation of castor oil at 130°C, 2.0 kg/cm^2 hydrogen gas pressure with 0.5% Ni catalyst for 6 h while using two turbine impellers fitted in an agitator, one close to the reactor bottom and another at a height just below the top oil layer, revolving at 350 rpm, resulted in a product of a iodine value of 4.1, hydroxyl value of 156.4, and slip point of 84°C.

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KEY WORDS: Agitation, castor oil, hydrogenation, impellers, hydroxyl value, mass transfer coefficient, pressure, temperature, catalyst.

Hydrogenation of oils is a typical gas-liquid reaction in industry. It is a complicated process that involves not only several simultaneous and consecutive chemical reactions but also a great deal of mass transfer operations. Oil hydrogenation is primarily done in the presence of nickel catalyst at 120–200°C at 2–10 kg/cm^2 hydrogen pressure in an agitated reactor. In simple chemical engineering terms, it is the mass transfer of gaseous hydrogen into liquid oil at the oil–gas interface and further through to the solid–liquid interface of the catalyst, on which the rate and selectivity of hydrogenation greatly depends. The contacting operation is, however, influenced by the mode of dispersion of one phase into another (agitation and gas pressure) and the solubility of one phase into the other (temperature and pressure).

The influence of various parameters on the rate of hydrogenation has been reviewed by Allen (1). Much work has been reported on the effect of hydrogen pressure, temperature, and catalyst concentration on the rate of hydrogenation (2,3). However, only a few investigations (4–8) have been reported on the effect of the type of agitator and mode of agitation on the overall rate of hydrogenation. The object of the present study has been to study the effect of mixing on mass transfer rates between the gaseous hydrogen and the liquid oil. The mixer can affect the mass transfer rate in three ways. It can affect the driving force ΔC by controlling the rate of distribution of the components, it can affect the interfacial area A by influencing the size of the gas bubbles and their hold-up time, and it can affect the mass transfer coefficient K in the liquid phase by the turbulence and flow produced in the liquid. The simple mass transfer rate equation

$$W = KA\,\Delta C \qquad [1]$$

shows that the mass-transfer rate W is proportional to the interfacial area and the driving force due to the concentration gradient. The proportionality constant K is the overall mass-transfer coefficient. It is generally more convenient to use ΔC for the concentration gradient in the bulk phase; if this is done, the coefficient will be based on that phase only. Therefore, Equation 1 can be written as

$$W = K_L A\,\Delta C \qquad [2]$$

where K_L applies to the liquid-phase mass transfer, and hence, concentration gradient ΔC also applies to the liquid. By substituting $A = aV$ in Equation 2, where a is the specific area per unit liquid volume V, the resultant equation will be

$$W = K_L aV\,\Delta C \qquad [3]$$

The group $K_L{\cdot}a$ will be a function of gas dispersion, bubble size, liquid phase turbulence, and any other phase present and can therefore be used as a measure of the performance of a mixer. Hydrogen is first dissolved in the oil; then it travels to the layer of oil surrounding the catalyst. The hydrogen penetrates the oil layer through its interfacial resistance and enters the catalyst surface to saturate the double bond. Therefore, external resistance against hydrogen transport from the gas phase to the oil phase is related to the thin oil interface near the gas bubbles and the surface of the catalyst. However, the hydrogen transport resistance near the catalyst surface may be neglected owing to the high surface area of the catalyst compared to the interfacial gas–oil surface and the low relative velocity between catalyst particles and the oil. Thus, mass transfer Equation 3 becomes

$$V\,\Delta C = C_o\,C$$

where C_o = hydrogen concentration in the gas–oil interface, equal to the solubility of hydrogen in mol/L oil, and C = hydrogen concentration in the bulk oil in mol/L oil. If $C_o \gg C$,

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the mass-transfer coefficient may be calculated from Equation 3 as follows:

$$K_L a = W/C_o \qquad [4]$$

The value of solubility concentration C_o may be calculated from the reported relationship (9):

$$C_o = 0.0203\, P \exp(-710/T) \qquad [5]$$

where T is the absolute temperature in Kelvin and P is hydrogen pressure in gas outflow in atm. Also, the rate of hydrogen transfer may be calculated from the following equation:

$$W = 0.039\, (\rho/60)\, \mathrm{d(IV)}/\mathrm{d}t \qquad [6]$$

where ρ = density of the oil in g/cm^3, and d(IV)/dt = change in iodine value (IV) per unit time.

Finally, the value of mass transfer coefficient $K_L a$ will be

$$K_L a = 0.032\, (\rho/P) \exp(710/T)\, \mathrm{d(IV)}/\mathrm{d}t \qquad [7]$$

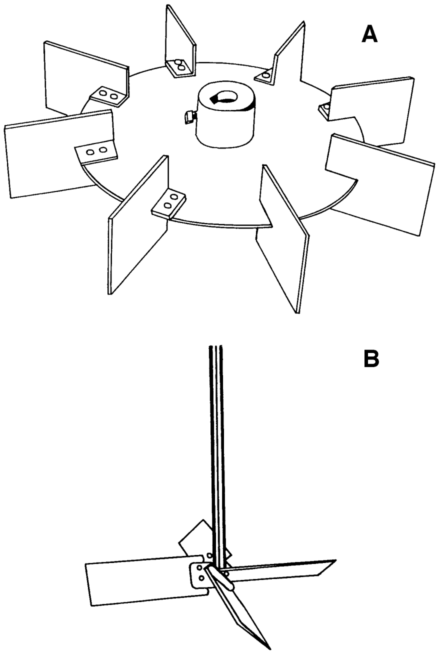


FIG. 1. (A) Radial-flow flat-blade turbine. (B) Axial-flow flat blade.

HYDROGENATION EQUIPMENT AND MIXING

Industrial hydrogenations are chiefly of the dead-end type in which the gas is bubbled in at the bottom of the reactor. Part of the gas is absorbed, while the rest goes to the headspace of the reactor. The agitation level must comply with two basic conditions. First, it must provide translational motion that is sufficiently intense to create, in every point of the liquid, a velocity higher than that of catalyst sedimentation and to originate a mixing action that will keep the mixture uniform. Second, a turbulence regime must be established that will provide appropriate mass transfer for the overall chemical reaction.

Agitation is usually provided by one or more impellers located on a central shaft. The impellers of both axial and radial flow flat-blade turbines are used for agitation in hydrogenators (Fig. 1). Some earlier workers (10,11) have shown that, for viscous fluids, the stirrer design and its speed play an important role in chemical reactions. A good deal of work on gas–liquid mixing systems (12,13) suggested that turbines are the best stirrers in such reactions. It has been suggested that a turbine stirrer just below normal oil operating levels is helpful in drawing hydrogen that has escaped to the reactor headspace back into the oil, thus preventing pressure from building up.

For castor oil several limiting factors, particularly when performing the reaction at low temperatures to avoid simultaneous dehydroxylation and production of high-viscosity oil, result in less net agitation. More emphasis has to be placed on the net IV and hydroxyl value reduction under specific reaction conditions rather than isomerization and selectivity of the hydrogenation reaction.

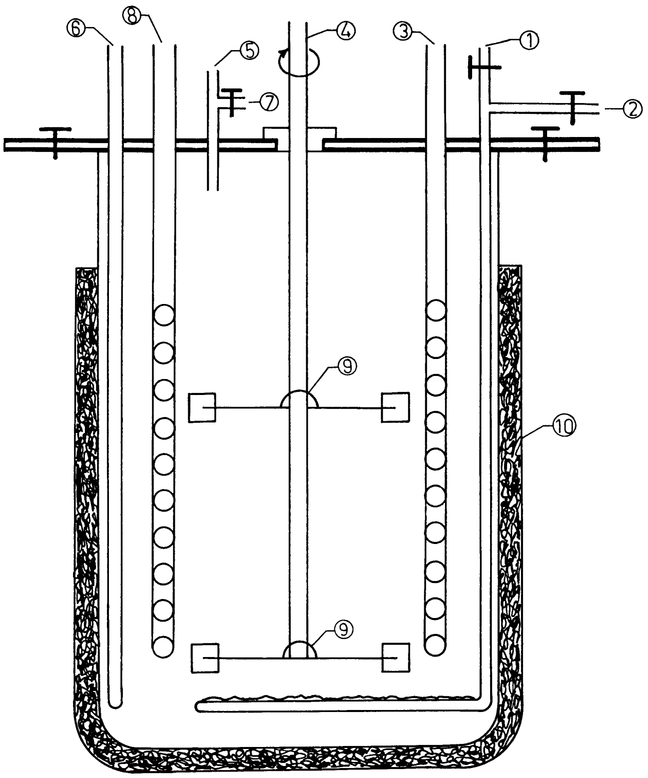


FIG. 2. Hydrogenation reactor: (1) hydrogen gas inlet; (2) sample-taking device; (3) cooling water inlet; (4) stirrer shaft; (5) pressure gauge; (6) thermometer pocket; (7) vacuum; (8) cooling water outlet; (9) impeller; (10) electrical heater. Dimensions: volume of vessel, 5.5 L; diameter of vessel, 14.6 cm; volume of oil, 2.07 L; height of vessel, 33.0 cm; diameter of impeller rotation, 8.6 cm; width of impeller blades, 2 mm; length of impeller blades, 10 mm; number of blades in each impeller, 4; distance of first impeller from tank bottom, 3 cm; shaft speed, 160–350 rpm.

The geometry and details of the hydrogenation reactor are given in Figure 2. The hydrogen was supplied through a perforated ring inlet underneath the bottom impeller. The volumetric gas flow rate was measured at the gas inlet. The gas flow rate and the hydrogen pressure in the reactor were calculated on the assumption that the reactor performed as an ideal stirred tank reactor concerning the mixing of the continuous gas flow (14). The stirrer shaft had arrangements for fixing impellers at different heights.

MATERIALS AND METHODS

The characteristics of the castor oil used in the experiments were determined by standard AOCS procedures (15). The oil had the following characteristics: specific gravity (30°C) 0.956, refractive index (25°C) 1.4790, color (Lovibond, 1" cell, Y + 5R) 2.8, acid value 1.4, IV (Wijs) 87.6, and hydroxyl value 163.0. The hydrogenation catalyst used in the experiments contained 22% nickel and was obtained from M/s. General Chemical Company, Bombay, India.

A weighed quantity of castor oil was transferred to the reactor and heated under vacuum to the desired temperature. The catalyst, dispersed in oil, was sucked into the reactor. Hydrogen was introduced, and the desired pressure was maintained. The temperature was controlled by circulating cooling water. Samples were withdrawn at specific intervals and analyzed for IV, hydroxyl value, and slip point. Different sets of experiments were conducted with varying stirring arrangements to make a comparison of the performance of the turbine and propeller agitators.

RESULTS AND DISCUSSION

The two types of agitators that were used in the present study for evaluation of stirring effects in hydrogenation are shown in Figure 1. The typical performance of flow patterns resulting from these stirrers is shown in Figures 3 and 4. When two turbines are on one shaft and are sufficiently far apart, a flow pattern will result that approximates that shown in Figure 5. Each turbine operates essentially independently of the other. Each turbine has a radial or axial flow pattern, depending on its construction. When two turbines are close together, there is an interaction between the flows and peculiar and unexpected flow patterns will result; this is evident from Figure 5 where the lower turbine appears to give axial flow and drives liquid through the blades toward the bottom of the tank. The upper turbine gives radial flow and acts more nearly like a single turbine. Different turbine spacings and different turbine diameter/tank diameter ratios would show many unexpected results. In some positions, the interaction between the turbines causes the lower turbine to give an upward axial flow and the upper turbine to give a downward axial flow, resulting in a radial flow that occurs toward the wall at a point midway between the two turbines. From the flow pattern studies one would expect that various reaction rate results might easily occur from the effect of turbine spacings.

The results of experiments conducted to optimize hydrogen pressure, catalyst concentration, and temperature for castor oil hydrogenation in the reactor with twin impellers of the propeller or turbine type are depicted in Tables 1 and 2. The results of Runs 1–4 clearly indicate that, for the propeller agitator, increased pressure helped the castor oil hydrogenation in two ways, first by increasing the rate of hydrogenation, and

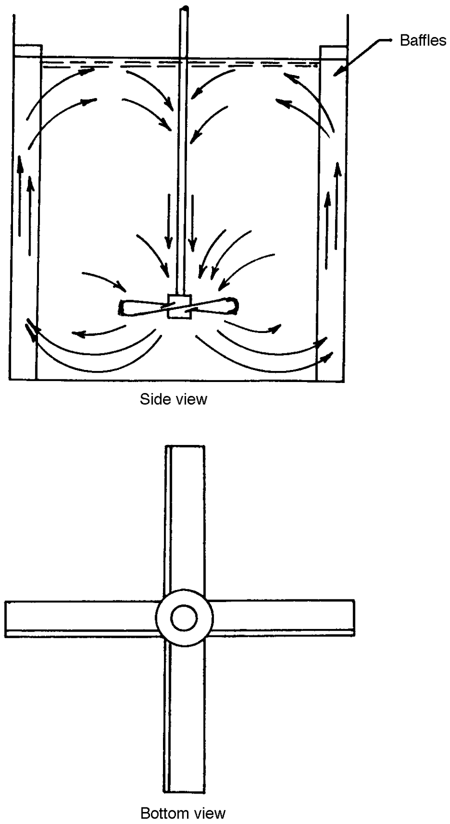


FIG. 3. Flow pattern for a single-propeller agitator.

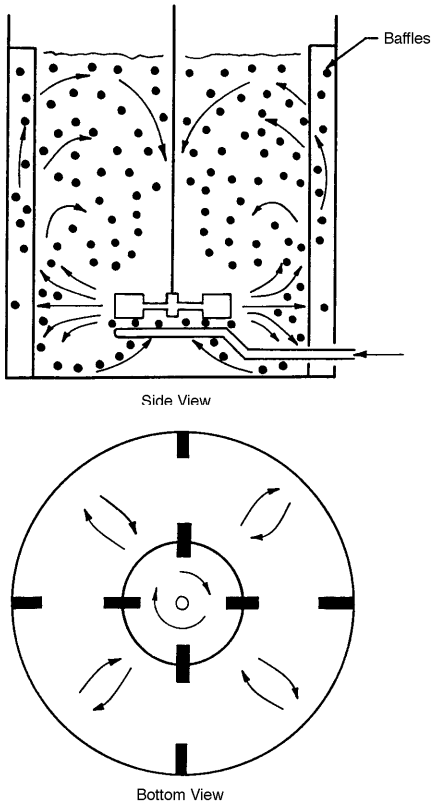
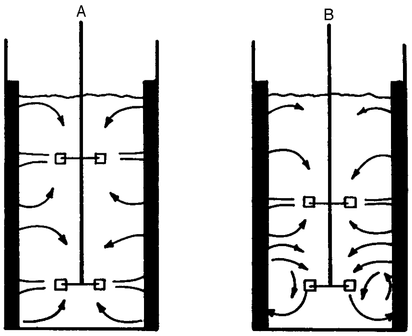


FIG. 4. Flow pattern for a single-turbine agitator.



Separate flow patterns

Combined flow patterns

FIG. 5. Flow patterns of dual turbines.

second by protecting the hydroxyl group. However, for the turbine agitator (Runs 13–16), the hydrogenation was almost complete in all runs while better protection of the hydroxyl group with increased hydrogen pressure was also observed. Because of the limitations of the present study to low-pressure (<5 kg/cm^2) hydrogenation, the effect of further increase in pressure could not be studied. The rate of hydrogenation decreased slightly as the catalyst concentration decreased, but no marked effect on hydroxyl group protection was observed (Runs 4–6 and 16–18). The study indicated that a nickel catalyst concentration of 0.5% is the optimal level for castor oil hydrogenation. Therefore, further studies on the effect of temperature on castor oil hydrogenation were carried out at 1.35–4.7 kg/cm^2 pressure and 0.5% catalyst concentration with both types of agitators.

The effect of temperature is obvious from the results of Runs 6–8 with the propeller agitator and of Runs 18–20 with the turbine agitator. Better protection of the hydroxyl group was possible at low-temperature hydrogenation at the cost of a slightly lower rate of hydrogenation. Satisfactory results with respect to hydrogenation rate, as well as protection of the hydroxyl group, were obtained at 130°C with the turbine agitator. The turbine agitators yielded products of much lower IV, compared to the propeller agitators under identical reaction conditions. This could possibly be due to the profound decrease in the concentration gradient of mass transport of the gaseous hydrogen phase to the liquid oil phase.

Some runs were conducted at 130°C and 0.5% catalyst concentration with varying pressure, mainly because of the emphasis of this study on low pressure. The results of Runs 8–11 with the propeller and Runs 20–23 with the turbine impeller indicated an optimal pressure for castor oil hydrogenation of 2.0 kg/cm^2. Run 12 was performed to determine the effect of reaction time for completion of hydrogenation with a propeller impeller agitator, and the results were not encouraging. However, the reaction almost reached the completion stage in 6 h when the turbine impeller was used. In all these experiments, the mass transfer coefficient could not be calculated, primarily because of simultaneous hydrogenation and dehydration reactions in the castor oil. To make a comparison between the performance of the turbine and propeller agitators, a hydrogen pressure of 2.0 kg/cm^2, catalyst concentration of 0.5% Ni, and temperature of 130°C were considered optimal.

The parameters related to agitator dimensions, the number, speed, and position with respect to height of oil, were varied and the results of the experiments are given in Table 3. The mass-transfer coefficient was calculated by putting the values for $T = 403$ K, $P = 1.96$ atm, and $\rho = 0.95$ at 130°C into Equation 7:

$$K_La = 0.0903\ \mathrm{d(IV)}/\mathrm{d}t$$

The results clearly show that the rate of hydrogenation was better for twin impellers compared to a single impeller at both agitator speeds (Runs 24–31). The results also indicate that turbine impellers are better for castor oil hydrogenation compared to propeller impellers (Runs 24–27 and 28–31). At 350 rpm, a higher rate of hydrogenation was observed compared

TABLE 1
Effect of Operating Parameters on Castor Oil Hydrogenation with an Agitator of Two Propeller Impellers[a]

Run number	Pressure (kg/cm^2)	Catalyst conc. (%Ni)	Temperature (°C)	Reaction time (h)	Iodine value	Hydroxyl value	Slip point (°C)
1	1.35	1.0	200	6	26.2	90.2	70-71
2	2.0	1.0	200	6	18.4	91.3	72–73
3	2.70	1.0	200	6	15.2	100.2	73–74
4	4.70	1.0	200	6	8.3	124.6	78–79
5	4.70	0.3	200	6	24.2	118.2	72–73
6	4.70	0.5	200	6	13.0	127.3	77–78
7	4.70	0.5	160	6	14.5	138.2	76–77
8	4.70	0.5	130	6	16.6	158.0	79–80
9	2.70	0.5	130	6	18.2	157.4	78–79
10	2.0	0.5	130	6	19.5	156.5	78–79
11	1.35	0.5	130	6	30.6	143.8	70–71
12	2.0	0.5	130	8	14.7	154.2	80–81

[a] Speed 350 rpm and two impellers in the shaft at 3- and 12-cm height from the reactor bottom.

TABLE 2
Effect of Operating Parameters on Castor Oil Hydrogenation with an Agitator of Two Turbine Impellers[a]

Run number	Pressure (kg/cm^2)	Catalyst conc. (%Ni)	Temperature (°C)	Reaction time (h)	Iodine value	Hydroxyl value	Slip point (°C)
13	1.35	1.0	200	6	2.2	95.6	80–81
14	2.0	1.0	200	6	2.9	96.3	80–81
15	2.70	1.0	200	6	3.6	105.4	80–81
16	4.70	1.0	200	6	2.8	122.0	81–82
17	4.70	0.3	200	6	12.3	120.8	76–77
18	4.70	0.5	200	6	4.2	128.0	81–82
19	4.70	0.5	160	6	3.9	142.8	81–82
20	4.70	0.5	130	6	2.8	157.0	84–85
21	2.70	0.5	130	6	3.5	156.4	83–84
22	2.0	0.5	130	6	4.1	156.4	83–84
23	1.35	0.5	130	6	11.2	147.2	78–79

[a] Speed 350 rpm and two impellers in the shaft at 3- and 12-cm height from the reactor bottom.

to lower speeds, but speeds greater than 350 rpm were not used owing to higher loads on the stirrer motor. Combinations of propeller and turbine impellers were also tried in Runs 32–33, and the results showed that the presence of a turbine impeller near the reactor bottom helped increase the rate of hydrogenation, while when reversed, it showed poor results. Finally, Run 34 was carried out at optimized parameters with a reduced height of the upper turbine impeller to observe the effect of impeller position. The lower reaction rate shows that the position of the second turbine close to the surface of the oil had helped increase the rate of hydrogenation, possibly owing to formation of a peculiar flow pattern. The gaseous hydrogen at the reactor headspace was drawn back continuously into the reaction phase, and only a minimal quantity of hydrogen bubbled out from the oil into the headspace. Therefore, maximum contact of reactive material at the active surface was possible; hence, it increased the rate of reaction.

The results of this study suggest that hydrogenation of castor oil at 130°C, 2.0 kg/cm^2 hydrogen pressure, with 0.5% Ni catalyst is best to yield a product rich in hydroxy stearic acid with a slip point of 84°C in 6 h while using an agitator with two turbine impellers on its shaft, one close to the reactor bottom and another at a height just below the top oil layer, to obtain a favorable agitation flow pattern.

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TABLE 3
Effect of Mode of Agitation on Hydrogenation[a] of Castor Oil[b]

Run number	Number of impellers	Type of impeller[c] and height from reactor bottom (cm)		Agitator speed (rpm)	Iodine value	Hydroxyl value	Slip point (°C)	Volumetric mass transfer coefficient K_La, ($\times 10^{-4}$)
		(I)	(II)					
24	1	T,3.0	—	350	16.4	155.8	79–80	179
25	2	T,3.0	T,12.0	350	4.1	156.4	83–84	209
26	1	T,3.0	—	160	20.4	157.2	78–79	169
27	2	T,3.0	T,12.0	160	7.1	158.0	82–83	202
28	1	P,3.0	—	350	24.3	154.3	76–77	159
29	2	P,3.0	P,12.0	350	19.5	156.5	78–79	171
30	1	P,3.0	—	160	28.8	157.4	74–75	147
31	2	P,3.0	P,12.0	160	21.3	155.2	77–78	166
32	2	T,3.0	P,12.0	350	6.6	156.0	82–83	203
33	2	P,3.0	T,12.0	350	17.4	156.4	79–80	176
34	2	T,3.0	T,10.0	350	15.8	156.6	79–80	180

[a] At 130°C, 2.0 kg/cm^2 hydrogen pressure, and 0.5% Ni catalyst for 6 h.
[b] 2 kg castor oil, giving 12.5 cm oil depth in the reactor.
[c] P, propeller impeller; T, turbine impeller.

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