Hydrogenating Cottonseed Oil at Relatively High Pressure

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This identification of the correct reaction mechanism will be of major importance to the fat and oil industry

HYDROGENATION of triglyceride oils is obviously a complicated reaction involving not only several simultaneous and consecutive chemical steps but also physical transfer steps of the reactants and products to and from the catalyst surface. Factors of importance during hydrogenation include the following:

• Rate of hydrogenation expressed as the rate of decrease of the iodine value, which is essentially directly proportional to the unsaturation.
• Hydrogenation selectivity defined as the preferential hydrogenation of polyunsaturated acid groups, such as linolenic and linoleic, relative to the monounsaturated groups, such as oleic acid.
• Isomerization. Cis-trans geometrical isomerization has been demonstrated (5) to have a significant effect on the softening point and consistency of the fats. In addition, positional isomerization also occurs in which the double bonds migrate along the fatty acid chain (2, 3, 10, 11). The effect of this latter type of isomerization on the physical properties of the product is not definitely established as yet.

Eldib and Albright (9) and Albright, Wei, and Woods (7) have made the only known investigations in which sufficient agitation was employed to minimize and probably essentially eliminate mass transfer resistances during the hydrogenation of triglycerides. Their results indicate that the effects of operating variables on selectivity and isomerization are quite different than the results obtained by investigators who used relatively low degrees of agitation

(5). Except for the investigations of Sims and Hilfman (20, 21), which employed low rates of agitation, all hydrogenation studies of triglycerides reported in the literature have been at relatively low hydrogen pressures, up to about 150 p.s.i. Since the true effects of operating variables on the chemical reactions per se cannot be determined unless mass transfer resistances are minimized, additional kinetic information is still required over an extended range of operating variables, especially at higher pressures, to clarify the reaction mechanism.

The standard method, until recently, for determining the composition of polyunsaturate groups in triglycerides was ultraviolet spectroscopy; it is not only a tedious method but may have poor accuracy for hydrogenated oils (4). Gas-liquid chromatography is apparently more reliable than the ultraviolet method (8, 12) and provides more information. As yet the chromatographic technique has not been perfected for separation of the cis and trans isomers so that infrared spectroscopy must still be employed for this analysis.

Hydrogenation runs were made in the present investigation over a wide range of operating variables using the best analytical techniques available. The over-all rate of hydrogenation was directly proportional to the degree of unsaturation and to the amount of nickel catalyst; the rate increased with pressure and temperature. The reaction on the catalyst surface is apparently between chemisorbed hydrogen atoms and physically adsorbed unsaturate groups in which the surface reaction is controlling. Selectivity and isomerization decreased with pressure but were little affected by temperature and catalyst

concentration when mass transfer resistances were eliminated.

Experimental Details

Hydrogenation runs were made in a dead-end batch hydrogenator which was manufactured by Struthers-Wells Corp. for a working pressure of 7500 p.s.i. The agitator and baffles in the hydrogenator were of standard dimensions for optimum agitation (19). The equipment and its operation were similar to those used previously (7). One liter of cottonseed oil was used during most runs, and temperature control was achieved during a run to within ±2° C. by manual control of the cold water or steam lines. The oil was hydrogenated to an iodine value below 40, and six samples were collected at intervals during most runs.

Hydrogen solubilities measurements were made in an apparatus similar to that used by Wiebe and Gaddy (24) for the determination of the solubility of hydrogen in water at high pressures. The hydrogenator served as the equilibrium cell, and it was connected to the solubility apparatus by a high pressure line. The hydrogenator was loaded with cottonseed oil and hydrogen, and agitation was provided for at least 15 minutes at constant temperature and pressure. Since the connecting high pressure line was at a different temperature than that of the hydrogenator, it was flushed with about 20 ml. of oil. The buret system was adjusted to atmospheric pressure and a small sample of solution was then allowed to flow from the hydrogenator autoclave to the oil buret. The sample size varied between 20 and 50 ml., depending on the pressure of the autoclave. Hydrogen began

flashing immediately from the oil, and about 15 to 30 minutes were necessary to flash off the excess hydrogen. Then the buret system was readjusted to atmospheric pressure. The levels of liquid in both burets were recorded together with barometric pressure, atmospheric temperature (actually the temperature of the waterjacket surrounding the burets), and the autoclave temperature and pressure. The amount of hydrogen in excess of the equilibrium amount dissolved at atmospheric pressure and temperature was then calculated. The amount of hydrogen dissolved at atmospheric conditions was determined by extrapolation of the data obtained at various pressures to zero absolute pressure. This extrapolation is considered accurate since the curves found were straight lines up to about 700 p.s.i.a. and since the curve at atmospheric temperature must pass through zero at atmospheric pressure. Since the solubility changes only slightly with temperature, the extrapolation of all temperature curves passed through zero at essentially atmospheric pressure. The solubility value at atmospheric conditions was then added to the solubility data obtained experimentally; this correction was relatively small in all cases.

Gas chromatography analyses (8, 12) were made with a Perkin-Elmer Vapor Fractometer, Model 154-C, using a 2-meter column packed with a succinate polyester of diethylene glycol on Cromosorb R and 60/80 mesh fire brick. Before injecting the fatty materials into the chromatography column, the glycerides were converted into methyl esters (18) by refluxing with sodium methoxide dissolved in methanol (1.3 grams sodium per liter of absolute methanol) for 40 minutes followed by the addition of 0.1 ml. of glacial acetic acid and 2 ml. of carbon tetrachloride. The column was operated at 205° C. with a helium flow of 80 ml. per min., measured at the outlet, and a sample size of 10 μl. A Perkin-Elmer Infrared Spectrophotometer, Model 221, was used for the

Reaction Rate Constants and Induction Periods

Run No.	Pressure, P.S.I.G.	Temp., ° C.	Catalyst, % Ni	k', Min.$^{-1}$	Induction Period, Min.
26	150	115	0.05	0.0140	22
40	150	115	0.04	0.0118	27
46	150	115	0.02	0.0044	80
89	150	110	0.05	0.0091	60
43	300	120	0.04	0.0207	14
45	300	110	0.04	0.0111	35
49	300	130	0.04	0.0298	10
80	300	105	0.05	0.0101	52
91	300	110	0.05	0.0133	37
65	600	110	0.04	0.0114	32
71*	600	110	0.04	0.0114	32
79	600	105	0.05	0.0145	36
87	600	110	0.05	0.0211	24
88	600	110	0.10	0.0427	19
92	600	110	0.15	0.0578	13
78	1,000	105	0.05	0.0193	35
90	1,000	110	0.05	0.0264	25
81	1,500	105	0.05	0.0254	38
82	1,500	105	0.10	0.0504	20
83	1,500	110	0.05	0.0316	24
84*	1,500	105	0.05	0.0254	38
86	1,500	100	0.05	0.0141	53

All runs at 1700 r.p.m. except those marked* which were made at 1250 r.p.m. Batch A: Runs 25 to 50. Batch B: Runs 60 to 92. Runs 60 to 76 were made with the portion of batch B that hydrogenated slower.

quantitative analysis of trans bonds (14), and the iodine values were determined by the Wijs method (4).

Two batches of refined and bleached cottonseed oil were used. Batch A, with a Wijs iodine value of 114.0 and a calculated gas-liquid chromatography iodine value of 110.5, had the following composition as determined with the Vapor Fractometer: 0.97% myristic acid, 24.3% palmitic acid, 1.0% palmitoleic acid, 2.15% stearic acid, 17.0% oleic acid, and 54.4% linoleic acid. Batch B, with a Wijs iodine value of 108.4 and a gas-liquid chromatography iodine value of 105.1, had the following composition, as determined by the Vapor Fractometer: 0.99% myristic acid, 27.3% palmitic acid, 2.5% stearic acid, 17.0% oleic acid, and 52.2% linoleic acid. Infrared spectroscopy showed both oils contained 3.1% of trans acid. Electrolytic-type hydrogen was used

and the Rufert catalyst flakes (Harshaw Chemical Co.) contained 25.3% nickel.

Results

Forty-eight hydrogenation runs were made at pressures, 150 to 1,500 p.s.i.g.; temperatures, 100 to 135° C.; catalyst concentrations, 0.02% to 0.15% nickel by weight; and agitation rates, 1250 and 1700 r.p.m. Five pressure levels of 150, 300, 600, 1000, and 1500 p.s.i.g. were selected, and the effect of the remaining three variables was studied at each level.

The hydrogenation reaction was followed in each case by plotting the logarithm of the Wijs iodine value (I.V.) of the oil vs. the time (t) of reaction. These plots were essentially straight lines after initial induction periods, which are defined here as the times at which the straight lines extrapolate back to the initial iodine value. As an example (Figure 1), Runs 65 and 71 had an induction period of 32 minutes. After the induction period, the over-all rate (r) can be represented by the following first order equation:

$$r = \frac{d}{dt}(I.V.) = k'(I.V.) \tag{1}$$

The value of the over-all reaction rate constant (k') was obtained in each case by multiplying the negative slope of the straight line by 2.3. The table indicates the values of k' and induction period for different runs.

Analytical Techniques. The iodine values of the samples as determined by the Wijs method were compared to the values calculated from gas-liquid chromatographic results. In most cases, the
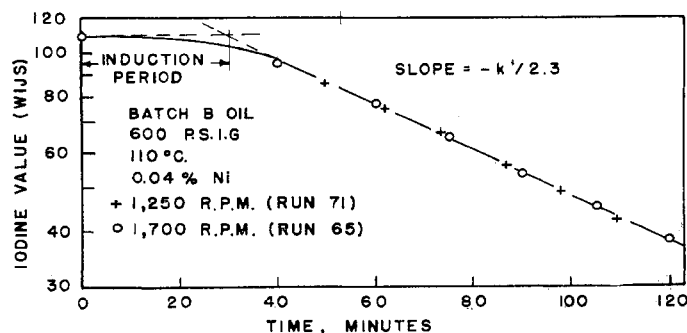

Figure 1. Hydrogenation is first order reaction after induction period

iodine values determined by the latter method were 3 to 5% lower than the Wijs iodine values. The difference in iodine values would affect the over-all rate constant by at most only a small factor since the slopes of the curves are almost identical.

Repeat chromatographic analyses of an oil indicated that the precision for a, given component is within 2% on an absolute basis. Proctor and Gamble Co. analyzed several samples of the present investigation using ultraviolet techniques, and their results agree well with those of the chromatographic method. Earlier comparisons of both analytical techniques had also shown (12, 16) relatively good agreement, but the respective accuracies of the two methods plus the Wijs analysis still remains to be proved, especially for hydrogenated oils.

Induction Period. The introduction period varied in this work from about 3 minutes to 80 minutes, decreasing with increased temperature and catalyst concentration. An increase in pressure up to about 600 p.s.i.g. decreased the induction period, but at higher pressure it remained fairly constant.

Most color improvement noted for the triglycerides occurred during the induction period. Although the rate of hydrogenation was low during this period, apparently the selectivity of hydrogenation and cis-trans isomerization that occurred were of the same order of magnitude as those occurring later. The probable cause of the induction period is the selective adsorption of catalyst poisons such as hydroperoxides and colored materials to reduce the number of catalytic sites. The adsorbed materials presumably hydrogenate slowly and are then no longer catalyst poisons. Additional information will be necessary before the causes of the induction period are definitely established, however.

Agitation. Preliminary runs indicated that the rate of hydrogenation depended on the volume of the oil in the autoclave. One liter of oil gave the highest rates of reaction, and corresponds to an impeller position at about two thirds of the liquid height. Thus, not only good internal mixing of the liquid-solid slurry but also adequate agitation at the gas-liquid interface is necessary. Probably then the resistance to transfer of the hydrogen from the gas to the liquid phase is more critical in most cases than resistance to transfer of reactants or products across the liquid-catalyst interface.

The over-all rates of hydrogenation at agitator speeds of 1250 and 1700 r.p.m. were identical within experimental accuracy in all cases for runs at 600 p.s.i. or greater when k' values were less than 0.05 min.$^{-1}$ (see Runs 65 and 75 of
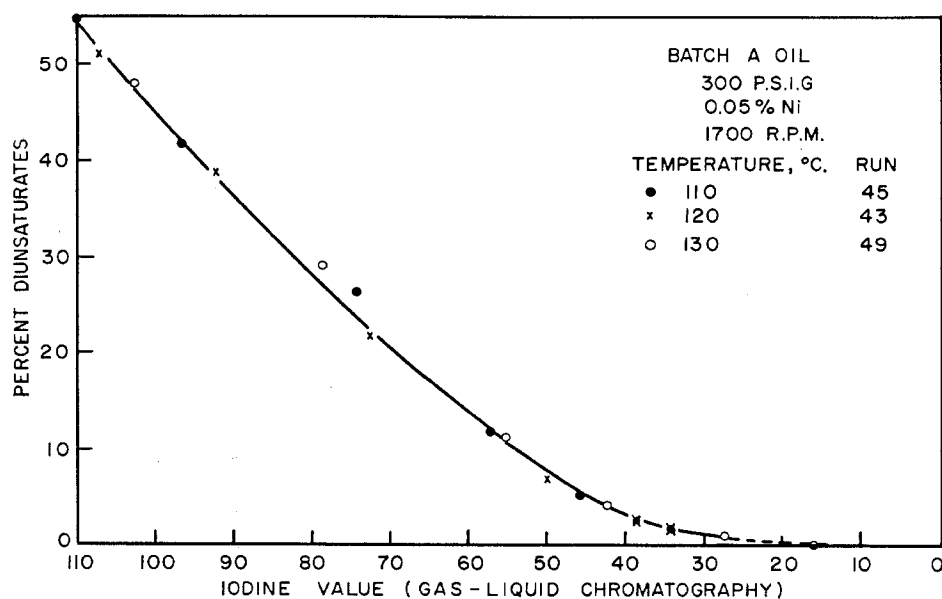

Figure 2. Temperature has little or no effect on selectivity at high rates of agitation
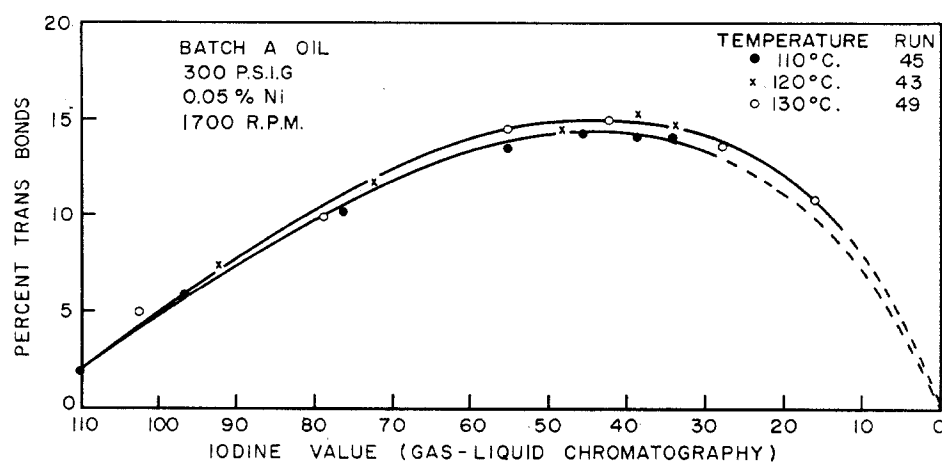

Figure 3. Temperature has only small effect on isomerization at high rates of agitation
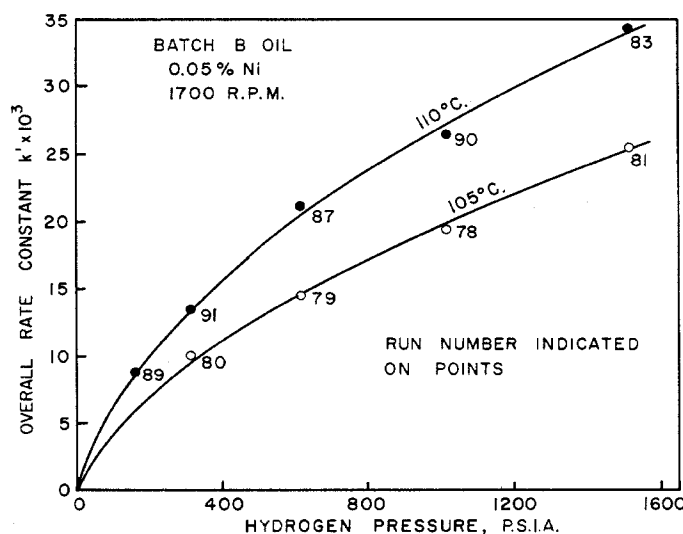
Figure 4. Rate of hydrogenation increases significantly with pressure and temperature
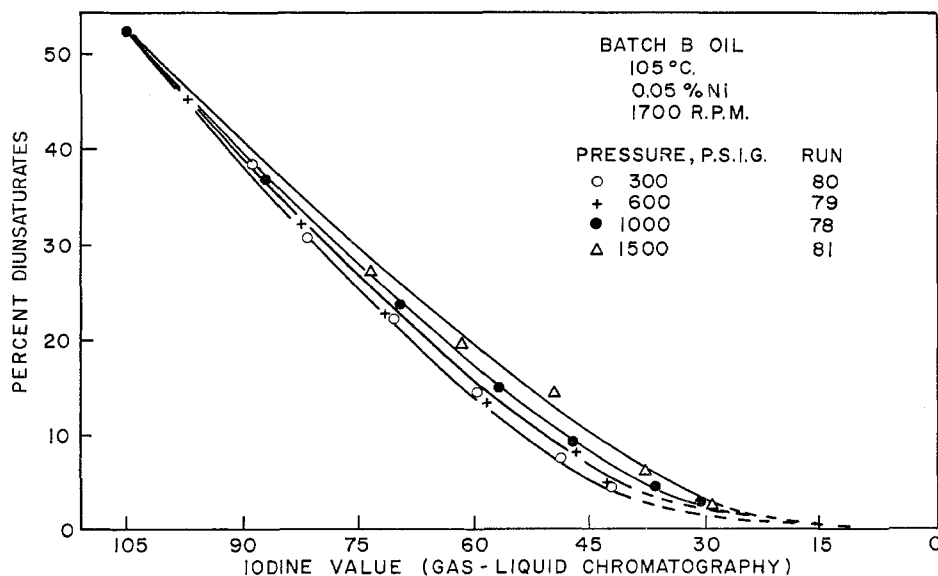
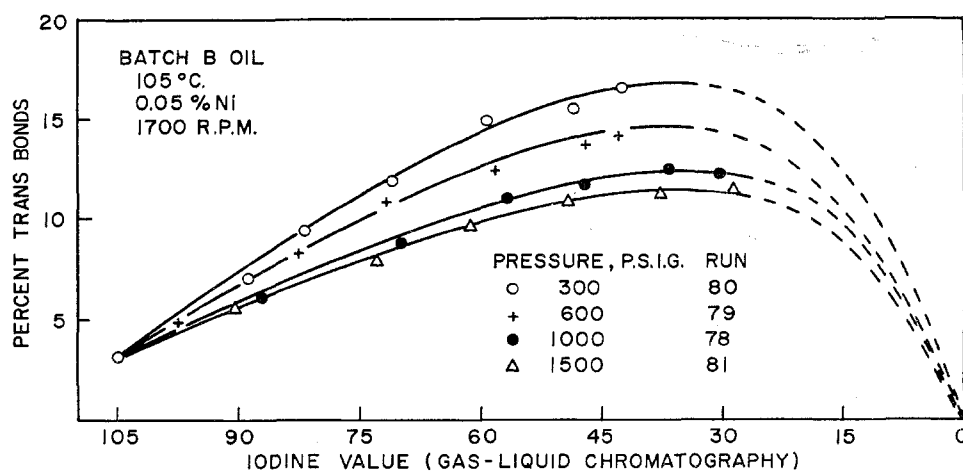Figure 5. Increased pressure causes decreased selectivity

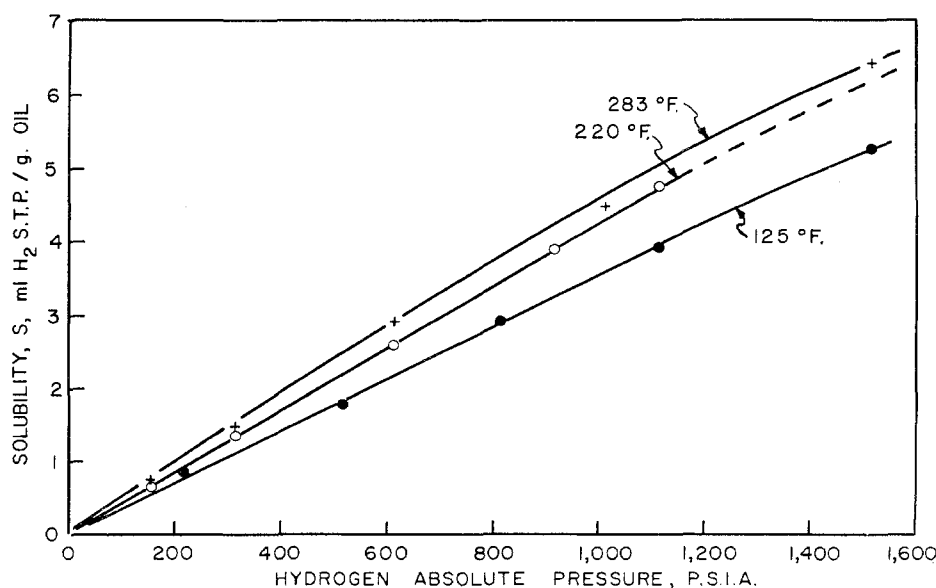Figure 6. Increased pressure decreases trans isomers formed

Figure 7. Hydrogen solubility in cottonseed oil increases with not only pressure but also temperature

Figure 1; and Runs 81, 84). Isomerization and selectivity as measured by the trans bonds and diunsaturated acid contents, respectively, were also not affected by agitation. Some differences in rate were noted, as agitation varied for runs at 150 and 300 p.s.i., but mass transfer resistances in runs with k' values less than 0.05 min.$^{-1}$ were minimized if not eliminated at 1700 r.p.m.

Temperature. The values of k' for the various pressure levels were plotted as a function of temperature (Runs 43, 45, 49; 81, 83, 86). Within the range being studied the data can be represented by straight lines—i.e., the rate of reaction was linearly proportional to the temperature. In most cases, the data were limited to relatively small temperature ranges because of experimental difficulties in maintaining isothermal conditions. Results for the 300 p.s.i. level showed a straight line extrapolation to $k' = 0$ at about 98° C.; the extrapolated temperatures for $k' = 0$ decreased slightly with pressure. Eldib and Albright (9) also found that k' vs. temperature gave a straight line relationship from 115 to 160° C. However, there is no known theoretical explanation for such a relationship. Probably the region investigated is the middle portion of a sigmoid curve where a straight line represents the data relatively well.

Relatively little change in diene values (selectively) was noted with changes of the operating temperature (Figure 2), but slightly more trans acids formed at higher temperatures (Figure 3). Although a lower temperature range (100° to 135° C.) was involved than previously reported, the temperature effects on the hydrogenation rate, selectivity, and isomerization are similar to those of Eldib and Albright (9), who investigated lower pressures but also used high agitation rates. Investigators who used relatively low degree of agitation found that selectivity and isomerization increased significantly with temperature (2, 5, 20, 21); mass transfer resistances were undoubtedly significant so that hydrogen transfer to the catalyst was slowed down. As discussed later, this phenomenon would increase selectivity and isomerization.

Catalyst Concentration. The values of k' were in most cases (see Runs 81, 82; 87, 88, 92) directly proportional to the amount of catalyst. However, catalyst concentration below 0.04% nickel gave in some cases lower rates than those predicted by a straight line relationship (see Runs 26, 40, and 46 at 150 p.s.i.g.).

The results indicate that transfer resistances were minimized in most runs since it varied linearly with the amount of catalyst. This latter observation is based on the assumption that the catalyst activity remained constant during the run and that catalyst particles were unaffected by each other. The low

rates observed with catalyst concentration below 0.04% may be explained by decreased catalyst activity during a low catalyst run (9).

The fact that selectivity and isomerization were unaffected by catalyst concentration or agitation also indicates that mass transfer resistances were probably eliminated. The concentration of the reactants on the catalyst surface was apparently identical in these runs.

Pressure. The effect of pressure, p, on the over-all rate constant is shown in Figure 4. A log-log plot of these data indicates that k' is essentially proportional to $p^{0.6}$. Eldib and Albright (9) over the range of 0–150 p.s.i. had found that k' was almost directly proportional to absolute pressure, but the present pressure results, which cover a much larger range, are most definitive. Figures 5 and 6 indicate that selectivity and isomerization both decrease with pressure increases up to 1500 p.s.i.g. Other investigators (2, 5, 9) also found similar results in regards to pressure.

Hydrogen Solubility. Hydrogen solubilities in cottonseed oil were determined in the range from 125° to 283° F. and from 150 to 1500 p.s.i.g. Figure 7 indicates hydrogen solubility expressed as ml. S.T.P./g. oil vs. the absolute pressure of hydrogen for 125° F. (51.8° C.), 220° F. (104.4° C.), and 283° F. (139.7° C.). Each point of Figure 7 is the average of three or more determinations. The resulting curves at each temperature are essentially straight lines at lower pressures—i.e., they follow Henry's law. The pressure range for linearity decreases with temperature. The solubility of hydrogen increases slightly with temperature.

The constants of the following empirical equation were obtained with a Datatron computer, and the equation represents the solubility data within ±5%:

$$S = -7.330(10^{-2}) + 2.208(10^{-3})P + 1.732(10^{-5})PT - 2.952(10^{-8})PT^2 - 2.924(10^{-7})p^2 \quad (2)$$

where

S = ml. hydrogen S.T.P./g. oil
P = p.s.i.a.
T = ° F.

This is an empirical equation and is obviously not accurate at low pressures. At zero pressure, the solubility must be zero, but the equation indicated a small positive value. Since the solubility vs. pressure plots up to 150 p.s.i.g. are essentially straight lines, it is recommended that for low pressure determinations the equation be used to calculate first the solubility value at 150 p.s.i.g. The solubility results at lower pressures can be calculated using a straight line interpolation.
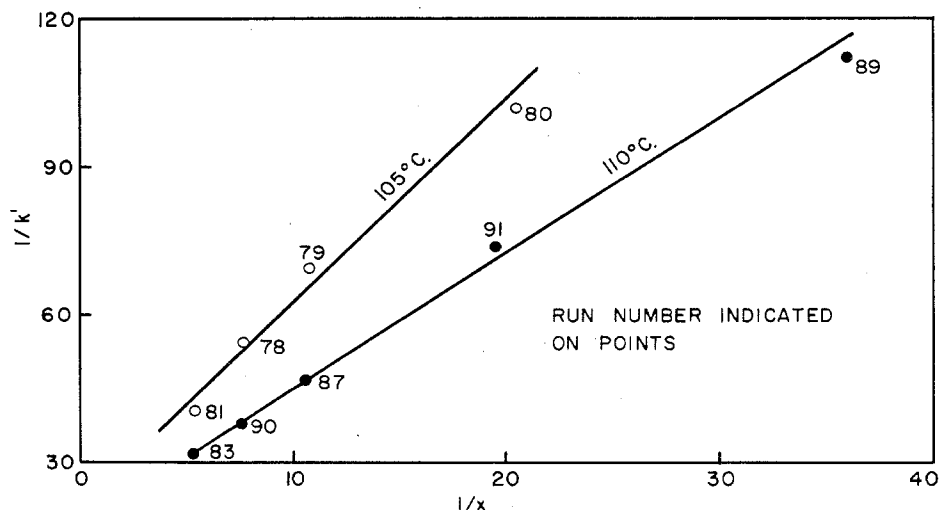

Figure 8. Data should be represented by straight lines if mechanism j is correct

Mechanism of the Reaction

Mass transfer of the reactants to the catalyst surface, or of hydrogen from the gas phase to the oil, occurs independently and simultaneously with the chemical steps; but at the high rates of agitation employed these steps are assumed to have offered negligible resistance. On the basis that only chemical steps offered resistance to reaction, the seventeen mechanisms proposed by Hougen and Watson (13) for catalytic hydrogenation were tested. Their equations were simplified and modified by the following assumptions: the over-all reaction is irreversible (22); the iodine value of the oil is directly proportional to the activity of the unsaturated, a_u; the activity of the dissolved hydrogen, a_H, is equivalent to the mole fraction, x, of the hydrogen in the oil (calculated from the hydrogen solubility data assuming a molecular weight of 860 for the oil); and the solubility of the hydrogen is not affected by the presence of the catalyst. Letters used for the mechanisms correspond to those employed by Hougen and Watson. Preliminary screening, such as previously outlined (9), leaves only mechanisms j, k, m, and n as the ones likely to represent the hydrogenation of cottonseed oil. A common characteristic of each is that the unsaturates are not chemisorbed in any of them, and the basic form of these four mechanisms is as follows (13):

$$r = \frac{(a_u)(a_H)}{(D + Ba_H^y + Ca_s^v)^w} \quad (3)$$

where the exponents v, w, and y depend on the particular mechanism; B, C, and D are constants and functions of the absorption and reaction rate constants; and r is the reaction rate. Since the over-all hydrogenation rate of a run

was proportional to the iodine value, Equation 3 can be reduced as follows:

$$k' = \frac{a_H}{(D + B\,a_H^y + Ca_s^v)^w} \quad (4)$$

Equation 4 can be rearranged into forms suitable for plotting for mechanisms j, k, m, and n as below:

Mechanism j: $\quad 1/k' = 1/a_H + B \quad (5)$

Mechanism k: $\quad 1/k' =$
$$(D + Ca_s)/a_H + B \quad (6)$$

Mechanism m: $\quad (a_H)^{1/2}/k' =$
$$D/(a_H)^{1/2} + B \quad (7)$$

Mechanism n:
$$(a_H/k')^{1/2} = B(a_H)^{1/2} + Ca_s + D \quad (8)$$

For mechanisms k and n, the activity of the chemisorbed saturated, a_s, was also assumed to be either zero, very small, or constant. The first possibility is probable since there is no chemisorption of the unsaturate in these mechanisms.

Equations 5 through 8 were plotted using the data from these investigations at 105° and 110° C. Equation 7 does not plot as a straight line so mechanism m is improbable. Equations 5 and 6 plot similarly, and Figure 8 indicates that the plots are almost straight lines. Equation 8, as shown in Figure 9, gives a good straight line fit at both temperatures. The screening process has left three of the original seventeen mechanisms.

Mechanism j. Reactant between unsaturated in the liquid phase and molecularly chemisorbed hydrogen, desorption of saturate controlling.

Mechanism k. Reaction between unsaturate in the liquid phase and molecularly chemisorbed hydrogen, surface reaction controlling.

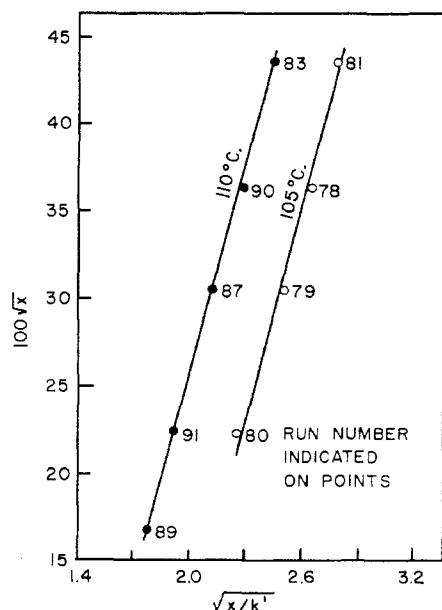**Mechanism n.** Reaction between unsaturated in the liquid phase and atomi-

Figure 9. The good fit of data by straight lines indicates mechanism *n* is probable

cally chemisorbed hydrogen, surface reaction controlling.

Final choice is for mechanism *n* on the basis of the following considerations:

- **Better fit of data to equation.**
- **Experimental evidence (6, 23) of the atomic behavior of hydrogen when chemisorbed on metals, particularly nickel.**
- **A hydrogenation-dehydrogenation step that involves atomic hydrogen (2, 3, 7).**

The slopes and intercepts of the straight lines of Figure 9 are as follows:

$$\text{Slope} = m = 1/(k\ C_t^2)^{1/2} \qquad (9)$$

$$\text{Intercept} = I = 1/(k\ K_H C_t^2)^{1/2} \qquad (10)$$

$$K_H = (m/I)^2 \qquad (11)$$

Values of K_H, as calculated from Figure 9 and Equation 11, are 2.26 for 105° C. and 3.62 for 110° C. K_H is expressed as a function of temperature:

$$\ln K_H = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (12)$$

Calculations indicate that $\Delta H = 27$ kcal. per g. mole. and $\Delta S = 70$ kcal. per g. mole ° K. The bond energy of a hydrogen molecule is about 103 kcal. (6); the hydrogen atom is bound to the catalyst surface with an energy of about 76 kcal.

The postulated mechanism is now compared with the known facts of ethylene hydrogenation. Beek's results (6) indicate that hydrogen adsorbs readily on catalytic films of nickel prepared by evaporation of nickel in vacuum. The heat of chemisorption is about 30 kcal. per g. mole for a sparsely covered surface, and decreases to a value of about 18 kcal. per g. mole when the surface is almost completely covered. Beek's results, together with those of others (15, 17), seem to indicate that the mechanism for the hydrogenation of ethylene involves the reaction between ethylene in the gas phase and atomically chemisorbed hydrogen. The reaction probably occurs when ethylene approaches the surface which holds two atoms in a favorable geometrical position (6).

Similar reasoning may be extended to nickel catalysts used in the hydrogenation of fats. When a catalytic nickel surface is saturated with hydrogen, each active site may hold a chemisorbed hydrogen, unless the site is preempted by some other material. A higher surface coverage with hydrogen atoms affords a large probability to pairs of hydrogen atoms being held in the right geometrical position for reaction with ethylenic groups in the unsaturated fatty acid radicals. Conditions which favor continued saturation of the catalyst surface with hydrogen will increase the rate of reaction and decrease selectivity, which is probably caused by preferential physical adsorption of linolein groups as compared to olein groups. Since hydrogen solubility depends mainly on pressure and increases slightly with temperature, pressure and temperature should increase the over-all rate of hydrogenation and decrease selectivity, if it is assumed that the relative rates of reaction on the catalyst surface do not change. The effect of temperature on the over-all rate will be much larger than that on selectivity because of the effect of temperature per se on reaction rates. It is not surprising then that under condition of minimum mass transfer resistances, selectivity should show little change with temperature.

When the catalyst surface is sparsely covered with hydrogen atoms, these atoms are held more strongly to the catalyst than when they are crowded by other hydrogen atoms; but not so strongly as to prevent their moving and taking positions relatively far from their neighbors (6). Under these conditions, the probability that the hydrogen atoms would be in favorable positions to react two at a time with ethylenic groups would be small. Thus neither the geometric nor energy relationship would be very favorable to hydrogenation, and adequate time would be allowed for the preferential physical adsorption of linoleic acid groups as compared to oleic acid groups. The selectivity and isomerization characteristics of the hydrogenation would then be higher.

When transport phenomena are critical, hydrogen can not be supplied to the catalyst surface rapidly enough to maintain a high hydrogen concentration. Since temperature rapidly increases the reaction rate constants for hydrogenation, hydrogen depletion at the catalyst surface will increase with temperature; the net effect will then be increased in selectivity and isomerization as has been found by several previous investigators (5).

Acknowledgment

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