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Operating Variables in Hydrogenating Cottonseed Oil

A mechanism for selectivity is proposed, based on preferential physical adsorption of linoleic instead of oleic acid

MOST COTTONSEED oil produced in this country is hydrogenated to oleomargarine and shortening (3). In this process, selectivity, iso-oleic acid formation, and rate of hydrogenation are affected by operating conditions (3-6, 9, 15, 16, 18). Selectivity is defined here as the preferential hydrogenation of polyunsaturated acid groups such as linoleic and linolenic acids, as compared to mono-unsaturated groups, such as oleic acid.

Iso-oleic acids are considered as only those acids which contain trans configurations of the double bond, although it is recognized that isomers of oleic acid also occur with the double bond in the cis configuration at other than the usual 9, 10 position. Since acids with trans configurations have much higher melting points than *cis*-oleic acids, the amount of iso-oleic acid in the fat is important to softening point. Rate of hydrogenation is considered here as the decrease in iodine value for a given time. The iodine value is essentially proportional to the total number of ethylenic double bonds in the oil.

Previous studies (6, 9, 16, 18) have determined the effect of various operating variables on these factors for vegetable oils and animal fats, and show that increase in temperature, hydrogen pressure, nickel catalyst concentration, and agitation increases rate of hydrogenation. Bailey (5) presented data showing that operating conditions which favor selectivity also favor iso-oleic acid formation. Selectivity and isomerization increase with increased temperature and catalyst concentration and with decreased pressure and agitation. All of these studies, however, used what are now considered (8, 20) obsolete and relatively inaccurate analytical methods for measuring selectivity and/or isomerization.

Since hydrogenation can occur only when hydrogen and the unsaturated fatty acid radical are brought together

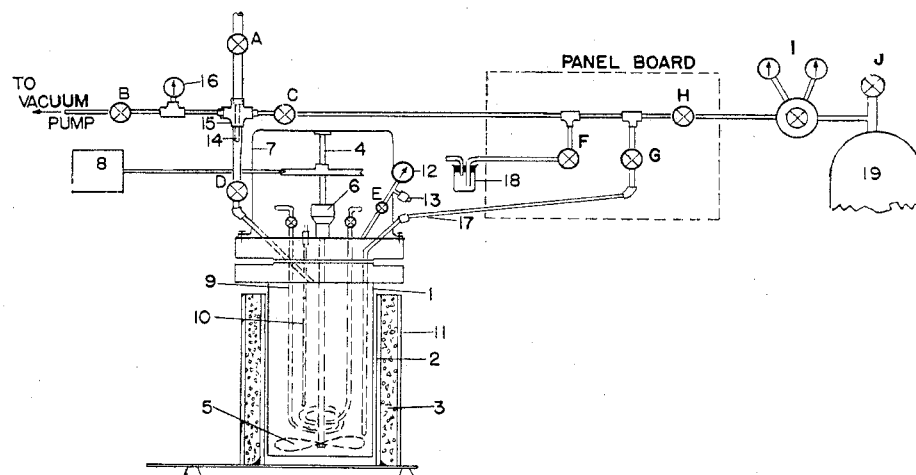
on or in close proximity to the catalyst surface, mass transfer mechanisms are important. Rates of hydrogenation were affected to a significant extent by changes in agitation rate. As a result, mass transfer resistances must have been important in most, if not all, previous studies. Therefore, it is impossible to determine the effect of the operating variables on the chemical steps of the reactions for those studies.

Krane (14), who hydrogenated ethyl oleate, reports that relative importance of the mass transfer resistances and chemical rate-controlling steps varies as the operating conditions change. He thinks that ethyl oleate is physically adsorbed on the nickel catalyst and hydrogen is chemisorbed. The adsorbed reactants then react, and ethyl stearate is desorbed. Gol'danskiĭ and Elovich (11) hydrogenated oleic acid in both alcohol and acetic acid solutions. They used a platinum catalyst, and vigorous agitation essentially eliminated mass transfer resistances. When mass transfer resistances were low, rate of

hydrogenation was directly proportional to amount of catalyst used and to pressure.

The action of atomic hydrogen on 1-hexadecene, hexadecane, and linseed oil has been studied by Boelhouwer, Heertjes, Houtman, van Steenis, and Waterman (7). They found with hexadecane that higher molecular weight hydrocarbons were formed. With 1-hexadecene and linseed oil, both hydrogenation and polymerization occurred. They proposed that hydrogen atoms first reacted with the hydrocarbons to form free radicals which then reacted either with each other to cause polymerization or with more atomic hydrogen to complete the hydrogenation process.

Recently Allen and Kiess (7) proposed the same free radical mechanism to explain positional and geometrical isomerizations during hydrogenations when a nickel catalyst is used. They thought that the free radical was unstable and might decompose into a hydrogen atom plus an acid group containing an ethylenic double bond. The



Hydrogenation apparatus

- | | | |
|----------------------|-------------------------|--------------------------|
| 1. Reactor shell | 7. Support for agitator | 14. Catalyst funnel |
| 2. Reactor support | 8. Motor | 15. Cross |
| 3. Electrical heater | 9. Cooling coil | 16. Vacuum pressure gage |
| 4. Agitation shaft | 10. Thermocouple well | 17. Hydrogen-sample line |
| 5. Propeller | 11. Asbestos shell | 18. Sample receiver |
| 6. Stuffing box | 12. Pressure gage | 19. Hydrogen cylinder |
| | 13. Safety valve | |

Valves are lettered

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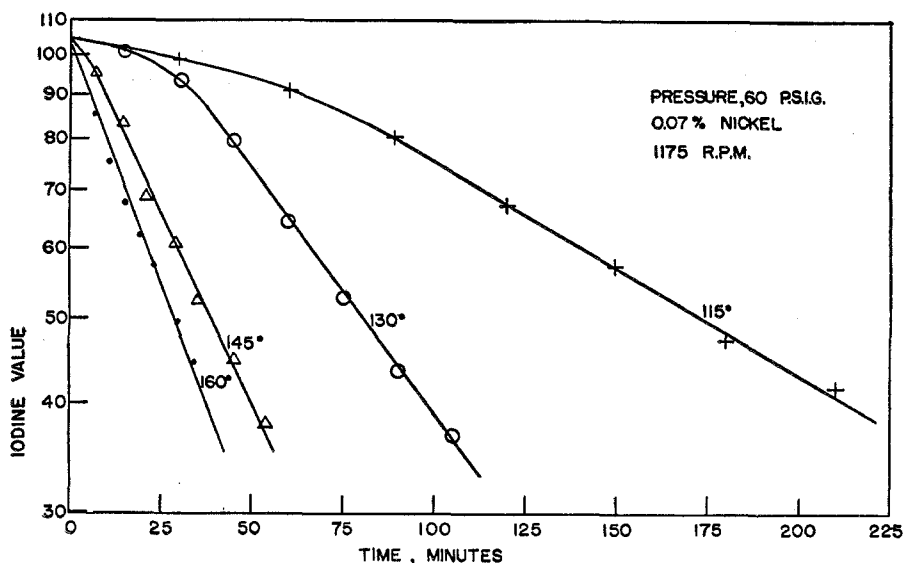


Figure 1. Effect of temperature on hydrogenation rate

released hydrogen atom had been bound to a carbon atom next to the free radical carbon. The double bond formed might have a different position than the original double bond and might have a trans configuration. This explanation seems consistent with their data. They do not suggest, though, how the atomic hydrogen was produced. A similar hydrogenation mechanism was proposed earlier for ethylene by Horiuti and Polanyi (12) and Twigg and Rideal (27).

Because reliable methods for measuring selectivity and isomerization are now available (8, 17, 20), it was decided to study the effect of temperature, pressure, concentration of the nickel catalyst, and agitation on the hydrogenation of cottonseed oil. Vigorous agitation was used to eliminate mass transfer resistances in most of the hydrogenation runs. Effects of operating variables on chemical reactions were observed over a wide range of operating conditions.

Equipment and Materials

The dead-end hydrogenator having a capacity of about 2 liters, was constructed of plain carbon steel to withstand pressures up to 400 pounds per square inch. The reactor, 1, fitted snugly inside a steel reactor support, 2, wrapped with insulated Nichrome wires. These wires served as heaters, 3, and the power input to them was controlled manually with Variacs. The agitator, 5, in the reactor was driven with a constant-speed 1/4-hp. electric motor. Pulley arrangements were used to change the speed of the agitator. The cooling coil, 9, in the reactor was connected to low pressure steam and was used for temperature control purposes. Valves A and D and the catalyst funnel, 14, were arranged so that solutions of oil and catalyst could be introduced to the reactor without allowing air to enter the system. The hydrogen-sample line, 17, was used both to bubble hydrogen

into the oil and to withdraw oil samples through valves G and F. An iron-constantan thermocouple in the thermocouple well, 10, was used to measure temperature in the reactor. Pressure gages, 12 and 16, indicated pressure in the reactor and vacuum pump line.

The refined and bleached cottonseed oil had an iodine value of 103.5 and contained 25.6% saturated acids customarily referred to as stearic acid 27.0% *cis*-oleic acid, 0.4% iso-oleic acid, and 47.0% linoleic acid. The electrolytic hydrogen gas was reported by the vendor to be 99.9% pure. Rufert catalyst flakes containing 24.5% nickel were used.

Operating Technique

A total of 1400 grams of cottonseed oil was added to the reactor and then deaerated by applying a vacuum for at least 10 minutes. Hydrogen gas was introduced to the hydrogenator until the desired pressure was reached. The pressure was maintained automatically for the remainder of the run by means of the pressure-regulating valve. The agitator and heaters were then started. When the reactor temperature reached a point about 10° C. below the planned operating temperature, the desired amount of catalyst was dissolved in 50 grams of hot deaerated cottonseed oil. The mixture was introduced to the reactor through valves A and D and the catalyst funnel. Another 50 grams of hot oil were used to wash out the lines. The valves were operated during catalyst introduction so that no air entered the reactor. Introduction of the catalyst was considered the start of the run. As soon as the catalyst was added to the oil, the oil temperature quickly rose several degrees. Within the first few minutes of the run, the temperature was controlled within 5° to 10° C. of that desired. For the remainder of the run, temperatures were controlled within about 1° to 2° C.

Six to seven fat samples were collected during each run at intervals of about 10 to 15 iodine value units. Samples were obtained by closing valve H and cracking valve F. The initial 10 cc. of oil collected were discarded, and the next 20 cc. saved as the sample. After the sample was collected, the hydrogen supply valve, H, was opened and all the lines were flushed out with hydrogen. While a sample was being taken, the hydrogen pressure decreased no more than 2 to 3 pounds per square inch. The fat samples were filtered to remove the catalyst. Iodine values were determined by the Wijs solution method (13), iso-oleic acid by an infrared absorption method (20), and linoleic acid by an ultraviolet absorption method (8). The isomerization period in the last analysis was modified from 30 to 45 minutes as suggested by O'Connor and

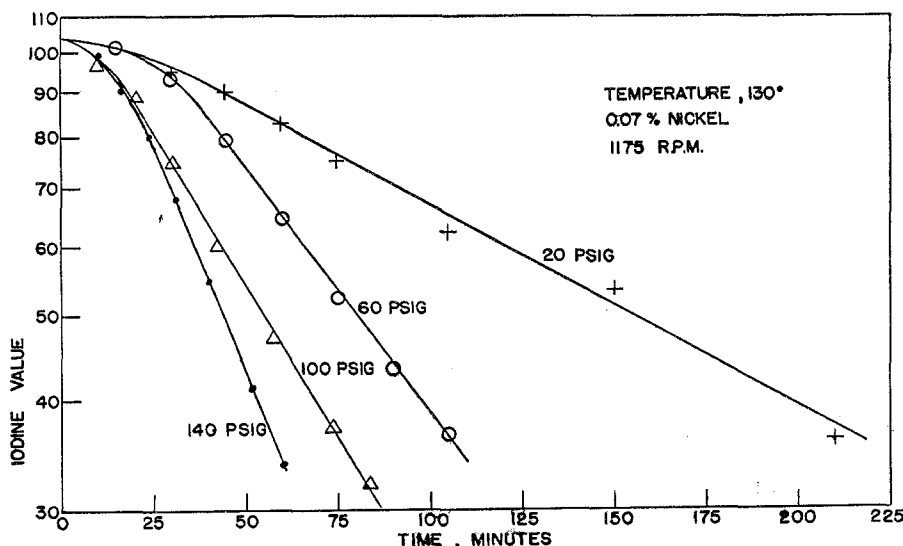


Figure 2. Effect of pressure on hydrogenation rate

others (17). *cis*-Oleic and stearic acids were calculated by difference (3).

Results

Thirteen hydrogenation runs were made over a temperature range of 115° to 160° C.; pressure, 20 to 140 pounds per square inch gage; catalyst concentration, 0.03 to 0.15% nickel by weight; and agitation, 550 to 1760 r.p.m. When one operating condition was being studied, all others were held constant.

Logarithmic plots of the iodine value *vs.* time are shown in Figures 1 to 4. Runs 1 and 11 were both made at average operating conditions—i.e., 130° C., 60 pounds per square inch gage, 0.07% nickel, and 1175 r.p.m. Results of these two runs are similar, and the average is shown on these graphs. Iodine values below at least 80 for all runs, are represented with experimental accuracy by straight lines. The negative slopes of the straight lines are equal to the pseudo first-order reaction rate constant, k' , in the equation,

$$r = k' (\text{I.V.}) \quad (1)$$

Experimental values of k' for each run are shown in Table I.

Linoleic and iso-oleic acid values were plotted *vs.* iodine values (Figures 5 to 9). Figure 5 indicates good reproducibility of the two average runs (1 and 11).

Temperature. Values of the experimental pseudo first-order reaction rate constant, k' (Table I), for runs 1 and 11, 2, 3, and 4 when plotted *vs.* temperature are represented essentially by a straight line whose values increase with temperature. This indicates that the over-all rate of hydrogenation was linear with temperature. An extrapolation of the plot shows that k' would be zero at 103° C. Figure 6 indicates relatively little change in linoleic acid values (selectivity) with temperature. Slightly more iso-oleic acid was formed at higher temperatures, however.

Pressure. Values of k' (Table I), for the pressure runs 1 and 11, 8, 9, and 10 when plotted *vs.* absolute pressure indicated that rate of hydrogenation was directly proportional to absolute pressure. Both selectivity and isomerization (Figure 8) decreased with increased pressure from 20 to 100 pounds per square inch gage. A pressure increase from 100 to 140 pounds per square inch gage, however, had only a small effect on either factor.

Nickel Catalyst Concentration. Values of k' (Table I), for runs 1 and 11, 5, 6, show the reaction rate to be directly proportional to the catalyst concentration. Selectivity and isomerization (Figure 8) were not significantly affected by increases in catalyst concentration. The

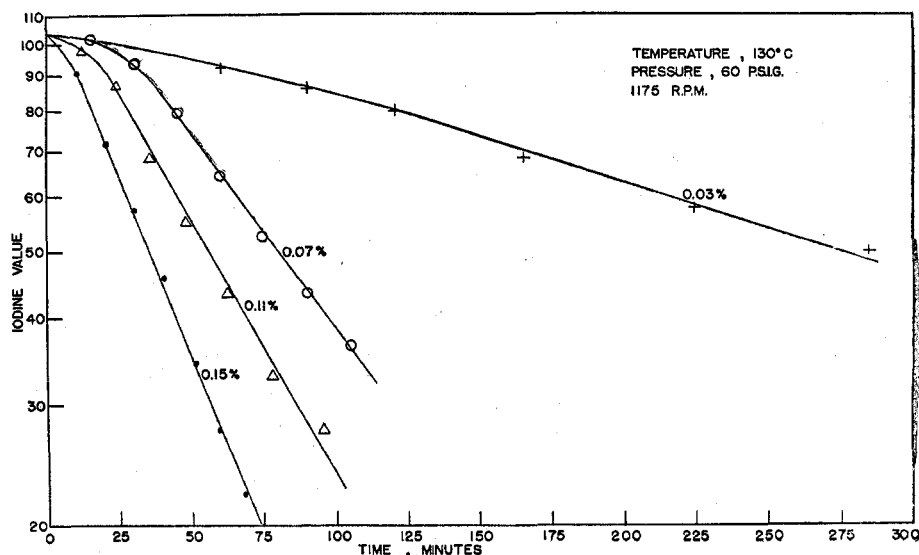


Figure 3. Effect of catalyst concentration on hydrogenation rate

Table I. Experimental and Calculated Values of Reaction Rate Constants

Run No.	Descriptive Parameter	k' , Exptl.	k' , Calcd.	Deviation, %
1, 11	Average	0.0128	0.0116	- 9.4
2	145° C.	0.0184	0.0180	- 1.7
3	160° C.	0.0253	0.0241	- 0.3
4	115° C.	0.00557	0.00516	- 7.9
5	0.03% Ni	0.00295	0.00496	+ 68.0
6	0.11% Ni	0.0169	0.0182	+ 7.4
7	0.15% Ni	0.0239	0.0248	+ 3.8
8	20 lb./sq. in. gage	0.00559	0.00539	- 3.6
9	100 lb./sq. in. gage	0.0163	0.0178	+ 8.9
10	140 lb./sq. in. gage	0.0238	0.0240	+ 0.8
12	550 r.p.m.	0.00653	0.0116	+ 79.5
13	1760 r.p.m.	0.0119	0.0116	- 2.5

only exception is the run at low (0.03% nickel) catalyst concentrations. Iso-oleic acid formation of this run was higher than that of the other runs. Also, the k' value of the run did not follow the linear relationship between k' and catalyst concentration.

Agitation. The over-all rates of hydrogenation for the middle (1175 r.p.m.) and high agitation (1760 r.p.m.) runs were almost identical (Figure 4). The low (550 r.p.m.) agitation run, however, had a considerably slower rate. Figure 9 shows that middle and high agitation

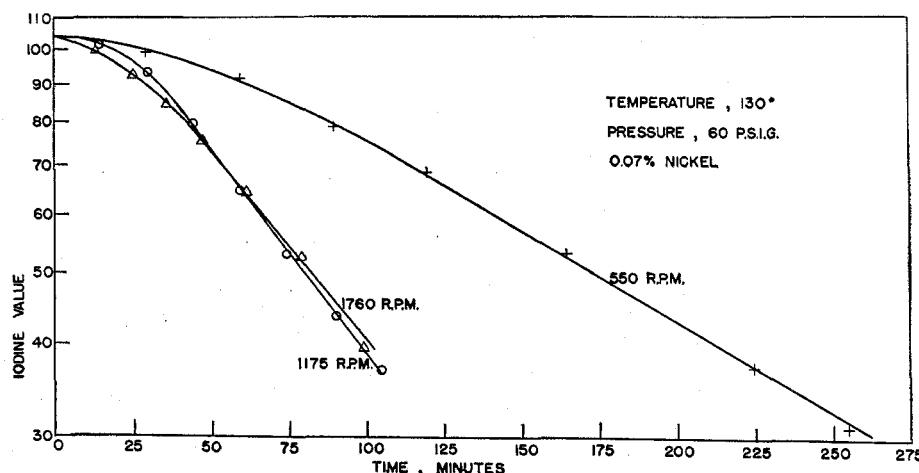


Figure 4. Effect of agitation on hydrogenation rate

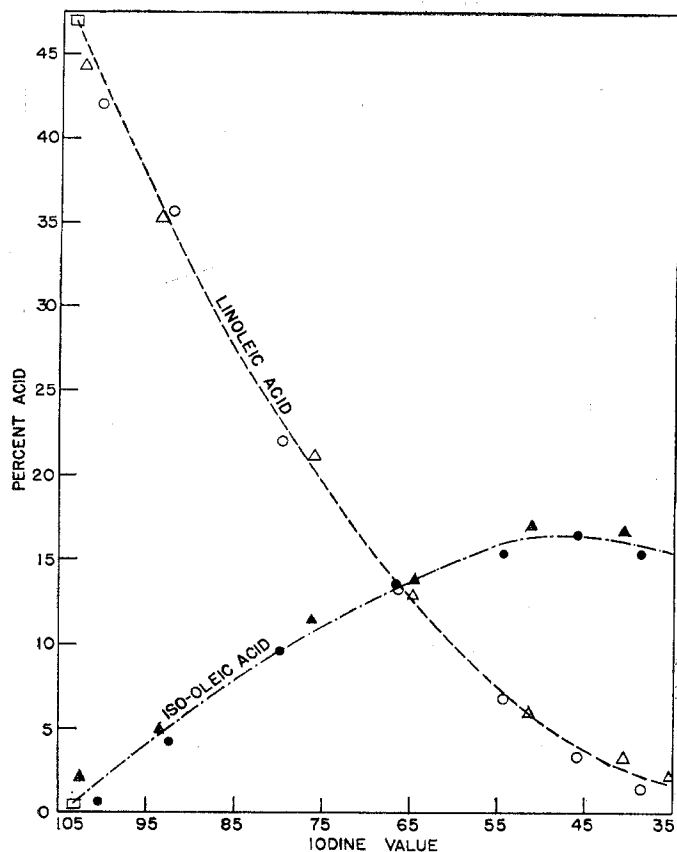


Figure 5. Reproducibility of average runs (1 and 11)

Temperature, 130 C.; pressure, 60 pounds per square inch; catalyst, 0.07% nickel; agitation, 1175 r.p.m.

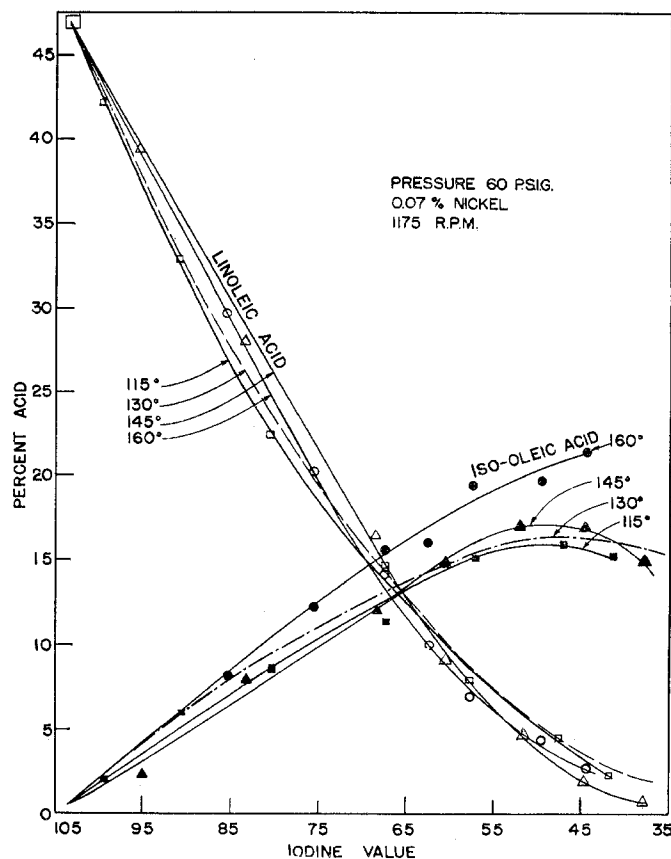


Figure 6. Effect of temperature on selectivity and isomerization

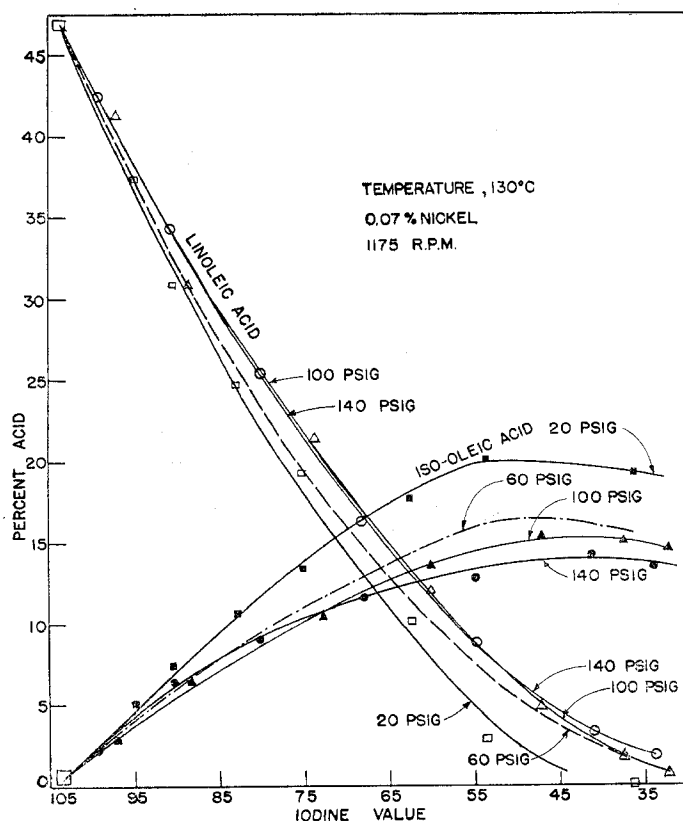


Figure 7. Effect of pressure on selectivity and isomerization

had almost the same effect on selectivity and iso-oleic acid formation. Low agitation resulted, however, in more selective hydrogenation and increased iso-oleic acid content.

Correlation of Rate Data. Since correlations of k' for temperature, pressure, and catalyst concentration runs are straight lines, the following rate equation can be developed:

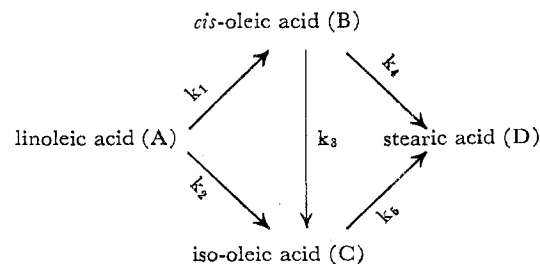
$$r = 0.0000821 (T-103) (P) (W) (I.V.) \quad (2)$$

In this equation,

$$k' = 0.0000821 (T-103) (P) (W) \quad (3)$$

Calculated values of k' are compared to experimental values as shown in Table I. The agreement is within 10% except for low catalyst and low agitation runs.

Correlation of Composition Data. The main reactions in hydrogenation of cottonseed oil are probably as follows:



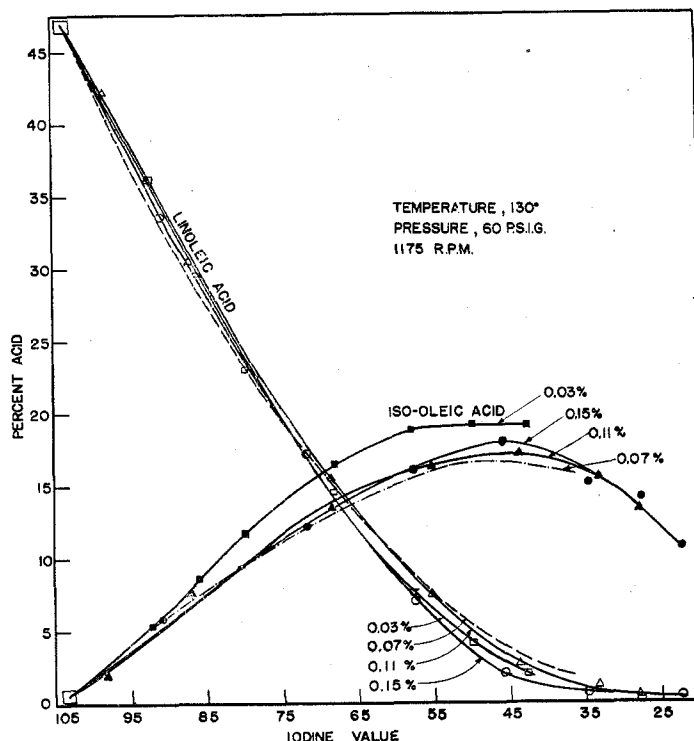


Figure 8. Effect of catalyst concentration on selectivity and isomerization

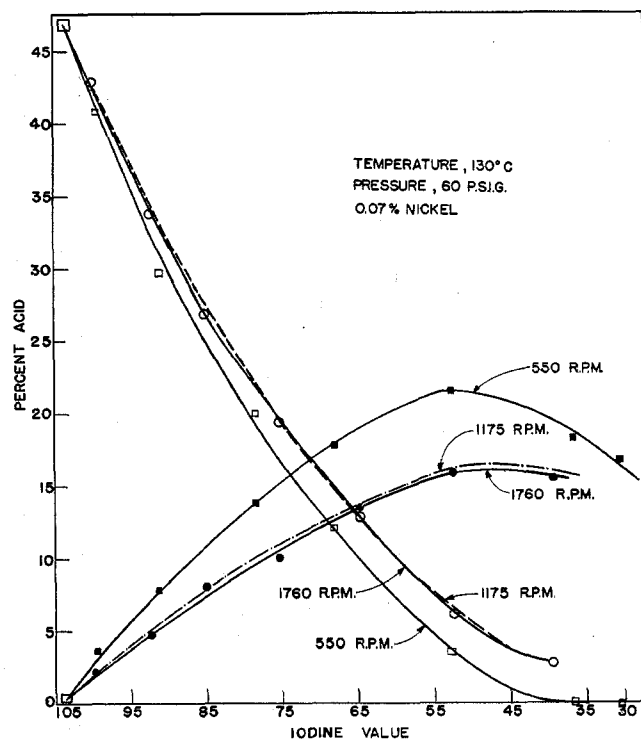


Figure 9. Effect of agitation on selectivity and isomerization

It was assumed that each of the reactions is irreversible and first order. Using the method outlined by Frost and Pearson (10), the following equations were developed to represent concentration of acids as a function of time:

$$n_A = n_{A0} e^{-(k_1 + k_2)t} \quad (4)$$

$$n_B = n_{B0} e^{-(k_3 + k_4)t} +$$

$$n_{A0} \left(\frac{k_1}{k_3 + k_4 - k_1 - k_2} \right) [e^{-(k_1 + k_2)t} - e^{-(k_3 + k_4)t}] \quad (5)$$

$$n_C = n_{C0} e^{-k_5 t} +$$

$$n_{A0} \left(\frac{k_2}{k_5 - k_1 - k_2} \right) [e^{-k_5 t} - e^{-(k_1 + k_2)t}] + n_{A0} \left[\frac{k_2(k_3 + k_4 - k_1 - k_2) + k_1 k_3}{(k_3 + k_4 - k_1 - k_2)(k_5 - k_1 - k_2)} \right] [e^{-(k_1 + k_2)t} - e^{-k_5 t}] +$$

$$n_{B0} \left(\frac{k_3}{k_5 - k_3 - k_4} \right) [e^{-(k_3 + k_4)t} - e^{-k_5 t}] \quad (6)$$

$$n_D = 1 - n_A - n_B - n_C \quad (7)$$

It was assumed that the weight fraction of the acid was equal to the mole fraction. The k values were calculated using a trial and error solution and pseudo times of reaction. Bailey (5) had used such a procedure with somewhat different equations. Our equations correlated the composition data of several runs, generally within experimental accuracy. The k values are relative reaction rate constants and a relative measure of the reactivity of each acid radical (Table II).

Discussion of Results

Several mass transfer steps are involved in the hydrogenation process—transfer of hydrogen from gas to liquid phase, absorbed hydrogen in the liquid phase to the catalyst surface, unsaturated fatty acid radical to the catalyst surface, and saturated fatty acid radical at the catalyst surface to the main body of the liquid. In this investigation, mass transfer resistances were essentially eliminated in most of the runs. This is demonstrated for the middle and high agitation runs by the fact that both rate and type of hydrogenation were similar. For pressure and catalyst concentration runs, the following conclusions seem justified.

1. Mass transfer of hydrogen from the gas to the oil phase was not controlling, because rate of hydrogenation was proportional to the amount of catalyst.
2. Mass transfer of hydrogen from the oil phase to the catalyst surface was not controlling, because rate of hydrogenation for a given run was proportional to the iodine value.
3. Mass transfer of unsaturated oil

to the catalyst surface was not controlling, because rate of hydrogenation was directly proportional to the hydrogen pressure.

4. Mass transfer of saturated oil from the catalyst surface to the main body of the oil was not controlling, because rate of hydrogenation for a given run was proportional to the iodine value.

Rates of hydrogenation for the temperature runs were similar to those for the pressure and catalyst runs. As a result, it is probable that mass transfer resistances in the temperature runs were also eliminated. In addition, the high temperatures which caused rapid reaction rates resulted in lower viscosities for the oil. Hence, the mass transfer resistances were probably low. The only run in which mass transfer resistances were significant was probably the low agitation run.

Results of the present study were compared to those of earlier hydrogenation investigations. There is general qualitative agreement (6, 9, 11, 14, 16, 18) on the effect of various operating variables on the over-all rate of hydrogenation.

Table II. Relative Reaction Rate Constants for Various Runs

Run No.	k_1	k_2	k_3	k_4	k_5
1, 11	0.80	0.20	0.30	0.075	0.60
3	0.55	0.45	0.10	0.10	0.33
5	0.50	0.50	0.15	0.05	0.40
8	1.00	0.00	0.55	0.00	0.60
10	0.65	0.35	0.12	0.24	0.40
12	1.00	0.00	0.46	0.00	0.33

tion. Krane (14), who used a catalyst similar to that in this investigation, also obtained rate data that extrapolate to zero at 103° C. Two investigators (6, 17) also found that rate of hydrogenation was essentially proportional to pressure. Also, studies (19, 22) of the gas phase hydrogenation of propylene and ethylene indicate that rates were proportional to pressure. Gol'danskiĭ and Elovich's results (17) agree quantitatively with those of this study in regard to effect of catalyst concentration on rate. This is probably because they, too, eliminated mass transfer resistances. For selectivity and isomerization, however, the general consensus (5, 6, 9, 16, 18) is that temperature and catalyst concentration affect these variables significantly. This work, however, indicates little or no effect, probably because mass transfer resistances were significant in the other studies.

For three catalyst runs (1 and 11, 6 and 7) and the high agitation run (run 13), concentrations of reactants and products at the catalyst surface were similar at a given iodine value, as mass transfer resistances were negligible. In all of these runs, both selectivity and isomerization were similar and also rates per unit amount of catalyst defined as the iodine value drop per time per unit amount of catalyst were essentially equal. For runs at other pressures and low agitation, concentrations of materials at the catalyst surface were undoubtedly different. Selectivity, *cis-trans* isomerization, and rate per unit amount of catalyst were also different. Possibly then, these three factors do not actually depend on pressure, amount of catalyst, and agitation, but rather on how these operating variables affect concentrations on the surface of the catalyst. Allen and Kiess (7) made a similar conclusion to explain isomerization. With such reasoning, Bailey's results (6) seem to agree with those of this study in all respects.

Selectivity by definition results in higher reaction rates for linoleic acid than for oleic acids. Rates for the surface reaction of linoleic acid can be represented as

$$r_A = k_A a_A C_H \quad (8)$$

and for oleic acids as

$$r_O = k_O a_O C_H \quad (9)$$

Hydrogen concentration, C_H , is constant at a given time for both the linoleic and oleic hydrogenations. Then if r_A is greater than r_O —i.e., selectivity prevailing— k_A must be bigger than k_O when $a_A = a_O$; or a_A must be greater than a_O when $k_A = k_O$. Since k' in Equation 1 is a constant for most iodine values, it is probable that $k_A = k_O$. If this is true, the linoleic acid must be preferentially absorbed as compared to oleic acid.

This work and that of Bailey (5) indicate that increased selectivity and

iso-oleic acid content occur simultaneously. Selective adsorption of linoleic acid as compared to oleic acids might be used to explain this phenomenon. It could be reasoned that, when linoleic acid displaces oleic acid on the catalyst surface, *cis*-oleic acid will in most cases be converted to iso-oleic acids. Positional isomerization, however, probably cannot be explained by this mechanism. The Allen and Kiess (7) theory postulating a hydrogenation-dehydrogenation mechanism of a free radical seems to explain satisfactorily both positional and geometrical isomerization. This mechanism for hydrogenating a liquid oil is the same as that for hydrogenating gaseous ethylene (12, 27).

The low catalyst run (run 5) was the only run in which higher iso-oleic acid formation was not accompanied by appreciably higher selectivity. The amount of hydrogenation in this run for a given amount of catalyst was, however, at least twice as great as for any other. As a result, catalyst activity probably had changed more than for other runs. This change of activity was probably the cause of the higher iso-oleic acid content and the relatively low rate of hydrogenation. In addition, any catalyst poisons in the oil would affect this run most.

When Equations 4 to 7 were developed to represent acid concentrations as a function of time, all hydrogenation and isomerization steps were assumed irreversible. It is probable, however, that the isomerization step is reversible and the proposed reactions are too simplified. Allen and Kiess (7) have, for example, presented data that indicate some double bonds of linoleic acid or methyl linoleate may wander on the chain and, in addition, *cis-trans* isomerization of some double bonds may occur before either double bond hydrogenates.

Equations 4 to 7 do represent the experimental data of most runs, with at least fair accuracy. The relative reaction rate constants (Table II) of these equations, therefore, should be useful for determining probable course of the reactions. For example, the values of k_1 and k_2 indicate that linoleic acid is generally hydrogenated preferentially to a *cis*-oleic acid. Allen and Kiess have also made a similar observation for nonselective hydrogenation. k values of Table II indicate in addition that *trans*-oleic acids hydrogenate more readily than *cis*-oleic acids, and that most are produced by isomerization of *cis*-oleic acids.

The data of Allen and Kiess, however, indicate that while linoleic acid is present in a mixture of linoleic and oleic acids, all *trans* isomers of oleic acid are obtained by partial hydrogenation of linoleic acid. Rather surprisingly, their results do not show any geometrical or positional isomerization occurring in the oleic acid groups produced from linoleic

acid. When tallow or greases are selectively hydrogenated, the amount of *trans*-oleic acids produced are sometimes greater than the original amounts of linoleic and linolenic acid groups. In this case at least, a considerable portion of *trans*-oleic acid must result from isomerization of *cis*-oleic acid. The mechanism of this isomerization is presumably explained by the partial hydrogenation-dehydrogenation theory of Allen and Kiess. It appears that more studies will be necessary before the mechanism for producing *trans*-oleic acids in oils such as cottonseed oil can be definitely determined.

Rate Equation 2 is considered empirical, but it represents most of the rate data of this investigation. In addition, this equation would probably be useful for predicting rates over an operating range somewhat larger than that of this investigation. It is limited, however, to runs in which mass transfer resistances are negligible and to runs in which catalyst activity does not change appreciably. The equation does not represent most rate data above an iodine value of 80, probably because an induction period resulted when the catalyst was added to the oil. During this time, hydrogen and unsaturated fats were transferred to the catalyst surface. Also, colored and odoriferous materials in the oil poison the catalyst until they are destroyed or hydrogenated. For a constant temperature Equation 2 can be written as

$$\frac{r}{W} = C'(P)(I.V.) \quad (10)$$

The hydrogen behaves at hydrogenation conditions essentially as an ideal gas. If it is assumed that the iodine value is proportional to activity of the unsaturated fat, Equation 10 can be written as:

$$\frac{r}{W} = C'(a_H)(a_U) \quad (11)$$

A plot of k' vs. pressure shows k' to be linear with pressure. However, if k' deviates with pressure, it decreases slightly with increased pressure; this same relation applies to C' as a function of pressure. If C' deviates with a_U , it decreases slightly as the iodine value decreases (Figures 1 to 4).

To propose a reaction mechanism for the present hydrogenation, Equation 11 was compared to the rate equations developed by Hougen and Watson (13) for 17 possible mechanisms (a to q). These mechanisms were originally considered for hydrogenating codimer (13), but they should also be applicable for hydrogenating cottonseed oil. In this study, reverse rates of hydrogenation can be considered negligible because of the high equilibrium constant (5). The equations of Hougen and Watson then simplify to the general forms,

$$r = \frac{\text{kinetic term}}{\text{adsorption term}} (\text{driving force term}) =$$

$$\frac{B}{Y^n} a_H, \text{ or } \frac{B}{Y^n} a_U, \text{ or } \frac{B}{Y^n} a_H a_U \quad (12)$$

The driving force term is probably $a_H a_U$. Those equations (mechanism a , b , e , f , i , l , and q) in which the driving force terms were a_H or a_U were eliminated.

The mechanisms in which desorption of the saturated product is controlling contain the over-all equilibrium constant in the adsorption term (Y^n). As a result, the adsorption term of these equations will increase rapidly with increased pressure or increased iodine value. This means that B/Y^n would change significantly with pressure or iodine value changes. Equation 11 indicates only small changes of C' . As a result, mechanisms c , g , j , m , and p were eliminated.

If the unsaturated fat is chemisorbed on the catalyst, the adsorption equilibrium constant for linoleic acid would probably be greater than that of oleic acid. This seems necessary if linoleic acid adsorbs preferentially to oleic acid. In addition, the chemisorption equilibrium constant of stearic acid would probably be smaller than that of oleic acid. As hydrogenation occurs, a_U will decrease and a_S will increase. The result, a decrease of the adsorption term, will cause an increase of B/Y^n . This seems inconsistent with Equation 11; so mechanisms d , h , and o were eliminated. This leaves mechanisms k and n —i.e., reactions of chemisorbed molecular hydrogen (mechanism k) and atomic hydrogen (mechanism n) with unadsorbed (not chemisorbed) unsaturated in which the surface reaction is controlling.

If the unsaturate is not chemisorbed, it is improbable that the saturate would be to any extent. Hence, k_s for the saturate would be small. If ($K_H a_H$) is also small, then either mechanism k or n could fit the data of this investigation. In such a case, the adsorption term remains essentially constant or increases slightly as the hydrogenation progresses or as the hydrogen pressure increases. The increase would be greater for mechanism n , since the adsorption term is squared. Mechanism n is preferred, however, since atomic hydrogen is involved in the mechanism proposed by Allen and Kiess (7). Since mechanism n indicates the unsaturate is not chemisorbed and since the selectivity mechanism indicates preferential adsorption of linoleic acid, the adsorption is apparently physical. Krane (14) has also proposed a similar mechanism for hydrogenating ethyl oleate.

It is suggested that molecular hydrogen is adsorbed and dissociated on the nickel catalyst. Double bonds of the fat react with either adsorbed atomic

hydrogen or atomic hydrogen desorbed from the catalyst. Selective hydrogenation is then explained by the fact that atomic hydrogen has a greater probability of meeting and reacting with a polyunsaturate, because of selective adsorption, than monounsaturates. The proposed role of the catalyst is to produce atomic hydrogen either on or near the catalyst surface, and to cause selective adsorption of the acids so that selectivity occurs. The hydrogenation mechanism proposed here is also probably applicable to related oils such as soybean and peanut oils.

Cottonseed oil was hydrogenated over a wide range of operating conditions. The over-all rate was represented within 10% by the equation, $r = 0.0000821 (T-103) (W) (P) (I.V.)$. This equation was generally limited to oils at an iodine value of 80 or less. Further, it applied only if mass transfer resistance were eliminated and if activity of the catalyst did not change during a run.

When mass transfer resistances were eliminated—it was in most of the runs—selectivity was not appreciably affected by temperature, but iso-oleic acid content increased slightly with temperature. Both decreased with pressure increases. They increased with agitation until mass transfer resistances were eliminated. Selectivity and isomerization were unaffected by catalyst concentration.

Selectivity probably resulted from physical adsorption of linoleic in preference to oleic acid on the catalyst surface. Iso-oleic acid with trans configuration appeared to be formed predominantly by isomerization of *cis*-oleic acid. The surface reaction between atomic hydrogen and physically adsorbed unsaturate appeared to be the rate-controlling step.

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Nomenclature

- a = activity of component at catalyst surface
- B = kinetic term, constant at a given temperature, containing forward rate and equilibrium constants
- c = concentration of component at catalyst surface
- C' = 0.0000821 ($T-103$)
- I.V. = iodine value
- k, k' = forward rate constants
- n = mole fraction of acid in fat
- P = hydrogen pressure, lb./sq. inch
- r = over-all rate of hydrogenation, I.V. drop per minute
- t = time

- T = temperature, °C.
- W = weight per cent of nickel in oil
- Y^n = adsorption term, a function of equilibrium constants and activities of products, reactants, and inerts

Subscripts

- A, B, C, D , and O = linoleic, *cis*-oleic, iso-oleic, stearic, and total oleic acids, respectively.
- o = original compositions
- H = hydrogen
- S = saturated fats
- U = unsaturated fats

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