Mechanism of Hydrogenation of Triglycerides

L. F. ALBRIGHT, Purdue University Lafayette, Indiana

Abstract

Factors affecting the rate of hydrogenation, selectivity, and isomerization are discussed in detail. The proposed mechanism for the reaction involves transfer steps for the reactants and products to and from the catalyst surface and the chemical steps occurring on the catalyst surface.

Introduction

When vegetable oils or animal fats are hydrogenated, at least three different types of reduction can occur. The type that will be considered in detail in this paper consists of the reduction of carbon-carbon double bonds in the fatty acid chains of the triglyceride and which results in the reduction of the iodine value (I.V.). As practiced commercially, this hydrogenation involves three phases: the gas phase (hydrogen), the liquid phase (triglycerides plus dissolved hydrogen), and the solid phase (metallic catalyst). In all cases, isomerization accompanies the type of hydrogenation being considered, therefore, any discussion of the mechanism must explain both. In addition, selectivity is an important part of the reaction.

During reduction of the I.V., the color and odor of the triglycerides are improved, indicating that at least some of the trace-quantity materials are being hydrogenated. These materials contain carbonyl, quinone-type, etc. structures. The mechanism for this second type of hydrogenation is not well understood, partly because of the large and probably variable number of trace materials present in the oils or fats. Although hydrogenation processes for reduction of the I.V. are somewhat effective in improving the color and odor, processes for getting, primarily, color and odor improvements without significant reduction of the unsaturation in the fatty acid chains are known. For example, hydrobleaching processes have been patented (19). This reduction uses metal oxide catalysts with hydrogen pressures up to perhaps 1500–2500 psi.

The third type of hydrogenation that is possible for oils or fats involves the production of fatty alcohols and glycerine. (This type of reduction is sometimes called hydrogenolysis.) The reduction occurs at high pressures from about 2500–4000 psi, at temperatures from approximately 250–400C, and in the presence of solid catalysts such as copper chromite (9). The mechanism for this type of reaction has not been reported in the literature, but is obviously considerably different than that for the reduction of the carbon-carbon double bonds. Work in progress will help elucidate the mechanism. No further attention will be given in this paper to this type of reduction since it does not occur to any measureable extent during I.V. reduction.

Hydrogenation of the carbon-carbon double bond as practiced commercially generally involves a nickel catalyst. Palladium catalyst is apparently used to a limited extent commercially (22), and platinum is sometimes used in the laboratory. The approximate range of commercial operating variables is as follows:

Temperature, 110–190C.
Pressure, 0–300 psi.
Catalyst concentrations, 0.01–0.15% by wt nickel.
Agitation, mechanical or gas bubbles through liquid.

The main effort of this paper will be to develop the mechanism for reduction of carbon-carbon double bonds in this range of operating variables.

Importance of Mass Transfer Steps in Hydrogenation

Transfer of the reactants to the catalyst surface and of the products away from the catalyst, has long been recognized as being important in the hydrogenation reaction. For example, Bailey (6), in 1949, outlined several transfer steps that must occur. Since hydrogenation and isomerization occur simultaneously and both on the catalyst surface, a restatement and enlargement of steps involved during hydrogenation seem necessary:

(1) Transfer of hydrogen from gas to liquid phase.
(2) Transfer of hydrogen from liquid phase to catalyst surface.
(3) Transfer of unsaturate group (carbon-carbon double bond) from liquid phase to the catalyst surface.
(4) Chemical reactions on or near the catalyst surface. (Such reactions include adsorption of reactants, surface reactions, and desorption of product for *both hydrogenation and isomerization.*)
(5) Transfer of product from catalyst surface to the main body of liquid.

The last step (#5) needs discussion since several alternatives are possible. In the case of hydrogenation of an oleic acid group, the stearic acid group would be transferred. If one of the double bonds of a linoleic acid group is hydrogenated, however, the monounsaturated acid group can be transferred to the main body of oil. As an alternative, the monounsaturate can remain at the catalyst surface until it is hydrogenated or isomerized; then the stearic acid group or the isomer is transferred to the liquid phase. Of course, the isomer can remain near the catalyst surface until it is reduced. In the case of just isomerization, the positional or geometrical isomer is transferred to the liquid.

Since there are several transfer steps, it is obvious that the amount of interfacial area is important plus the degree of agitation. Bailey (6) had indicated that the transfer of the hydrogen from the gas to the liquid phase was often the single most controlling step. Recent work (21) has verified this postulate. Much of the hydrogenation data reported in the literature were obtained using operating conditions such that, transfer steps were controlling to at least a considerable degree. Such data frequently are not as valuable as would be liked in studying the kinetics and chemistry that occur at the catalyst surface.

Chemical Selectivity

Selectivity as used in this paper, is defined on a chemical basis as being the preferential hydrogenation of polyunsaturate acid groups of the triglyceride, as compared to monounsaturate groups. Many investigators have reported on the effect of operating variables on selectivity. For example, when the degree of agitation is rather low (i.e. when mass transfer resistances are at least partially controlling), selectivity increases with decreased pressure and agitation, and increased temperature and amounts of catalyst (7). When agitation rates are so high that mass transfer resistances are negligible, selectivity decreases with pressure; however, selectivity is unaffected by changes in catalyst concentration or increased agitation, and is essentially unaffected by temperature (3,13,21). Selectivity has generally been characterized on a qualitative basis. Some attempts have been made to define it quantitatively but in general they were rather inadequate for the more complicated triglycerides. Recently (3) a method has been reported which is based on a rather complicated hydrogenation sequence.

Because polyunsaturate groups hydrogenate preferentially to monounsaturate groups (and they do, even for quite non-selective hydrogenation) does not necessarily mean that the rate of hydrogenation for a double bond in a polyunsaturate acid group (such as linoleic acid) is faster than for the double bond in a monounsaturate acid group (such as oleic acid). In this respect, when a mixture of acetylene and ethylene are hydrogenated, the acetylene hydrogenates preferentially (10). Yet the rate of hydrogen uptake is less while acetylene is being reduced than when ethylene is. The literature concerning triglyceride hydrogenation seems to offer conflicting evidence in regards to this problem. Figure 1 of Eldib and Albright (13) indicates that at 160C, the rate of hydrogenation is essentially directly proportional to the I.V. regardless of the amount of linoleic or oleic acid groups present in the cottonseed oil. In this case, at least, linoleic and oleic acid groups seem to hydrogenate at the same rates. Figure 2 of Albright, Wei, and Woods (2), however, indicates that the rate of hydrogenation is somewhat faster for linoleic acid groups. (There is a break in the curves at about 60 I.V. at which point the linoleic acid groups are essentially depleted.)

Induction Period

The induction period that occurs in many hydrogenation runs often occupies a major portion of the time the triglycerides are in the reactor. Wisniak and Albright (21) reported induction periods from 10–80 min for batch runs at 100–130C. The induction periods at these temperatures decreased with increased temperature, pressure, and amount of nickel catalyst. A somewhat comparable run at 160C showed little or no induction period (13). The cause of the induction period is not known definitely, but it is probably related to some extent at least with selective adsorption but slow hydrogenation of the trace-quantity polar materials of the oil such as those materials which are colored or odoriferous. Presumably more effective bleaching or refining operations would decrease the induction period. It might be mentioned here that there are significant differences of the hydrogenation characteristics of refined and bleached cottonseed oils as obtained from various companies (see Fig. 5 of Albright, Wei, and Woods [2]). Any manufacturer contemplating low temperature hydrogenation should determine carefully if the induction period is an excessive portion of the residence time of the triglycerides in the reactor system. Certainly more research attention needs to be devoted to the induction period and methods of eliminating it.

Isomerization of Double Bonds

Two types of isomerization always occur during hydrogenation. Geometrical isomerization involves the *cis-trans* isomerization of the double bonds. Up until about 1950, the so-called "lead salt" method was used to analyze the *trans* double bonds. Infrared spectrophotometric method of analysis was developed about this time, and it was found to give a much more accurate analysis. Within the last few years, gas chromatographic techniques have also been developed for separating the *cis* and *trans* isomers.

Differences in the physical properties of the *cis* and *trans* isomers are most significant for partially hydrogenated oils used for oleomargarine, shortening, or soap stocks. Higher amounts of the *trans* isomer increase the softening temperature significantly.

From a thermodynamic standpoint, the *cis* and *trans* isomers reach an equilibrium ratio of approximately 2:1. Naturally occurring fats or oils exist predominantly in the *cis* configuration, and during partial hydrogenation, a large portion of the unsaturated double bonds are converted to the *trans* form. The question has been raised several times if the ratio of *trans* to *cis* double bonds in hydrogenated oils approaches and remains at 2:1. Some results in the literature indicate that such a ratio is not only reached but maintained at all I.V. less than 30–50 (1,4,16, 21). When Cousins and Feuge (11) hydrogenated methyl oleate in solvents at 30C in the presence of palladium and Raney nickel catalysts, a *trans/cis* ratio greater than 2:1 was obtained. Perhaps the higher ratio resulted from the low temperature or the solvents used during this hydrogenation. The author has also seen commercial hydrogenation data in which a *trans/cis* ratio of greater than 2:1 was obtained. In this latter case, the analysis may have not been too accurate, which could account for the higher ratio. Assuming that a 2:1 ratio is approached during most hydrogenations, then the *cis* and *trans* isomers adsorb on the catalyst and hydrogenate with equal facility. Presumably higher temperatures should promote such an occurrence.

Positional isomerization in which the double bonds migrate in both directions along the fatty acid chain also occurs during hydrogenation (4,5,8,11,12). In several cases, the *trans/cis* ratio of the migrated double bonds was 2:1 (4). Cousin and Feuge (11) in the investigation already mentioned found ratios that were sometimes greater than 2:1. More investigations are needed to clarify this point. Based on the available data for runs that approximate commercial operating conditions, apparently the ratio approximates 2:1 and the double bonds migrate with relatively equal facility in both directions along the fatty acid chain.

When polyunsaturates are hydrogenated, conjugation of the double bonds may be an intermediate step. There may be difficulty in conclusively proving this, since, even if conjugation did occur, the conjugated double bonds might be so strongly adsorbed to the surface that there would be no method to desorb them in significant quantities. In which case, only trace quantities of the conjugated groups would be found in the main body of the liquid.

Mechanism of Hydrogenation and Isomerization

The mechanism for hydrogenation and isomerization was published quite some time ago for light olefins (10,14,15). More recently Allen and Kiess (4) postulated a similar mechanism for triglycerides which are really complicated olefins. This mechanism does an excellent job explaining both hydrogenation and isomerization. The steps in the reaction are as follows:

1. Hydrogen is sorbed on the catalyst surface and is dissociated into two hydrogen atoms (H*).
2. Hydrogenation and isomerization of the double bond (Fig. 1).

Strong evidence indicates that hydrogen molecules are dissociated on the catalysts to hydrogen atoms (14,15). The mechanism as shown indicates the relationship between hydrogenation and isomerization. It will be noted that a single "activated" hydrogen atom (H*) attacks the double bond to produce an unstable partially unsaturated complex. If a high concentration of hydrogen is present on the surface, the complex will probably react with another hydrogen atom (H*) to complete the hydrogenation. If a low concentration of hydrogen is present on the catalyst surface, one of the hydrogen atoms of the complex will probably dissociate from the complex to reform a double bond. Since four hydrogen atoms can dissociate from the complex, both geometrical and positional isomers can be

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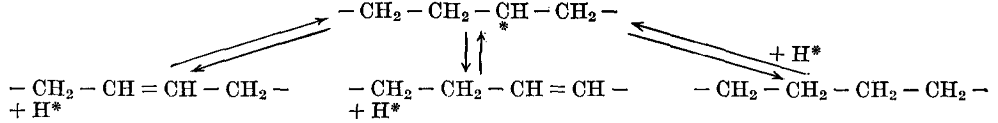

$$-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-+H^*$$

$$-CH_2-CH_2-\underset{*}{C}H-CH_2-$$

$$-CH_2-CH=CH-CH_2-+H^* \qquad -CH_2-CH_2-CH=CH-+H^* \qquad -CH_2-CH_2-CH_2-CH_2-$$

Geometrical isomers formed

Positional and geometrical isomers formed

Hydrogenation step

FIG. 1.

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formed. Hence, the degree of either positional or geometrical isomerization can be predicted to a large extent on the concentration of hydrogen at the catalyst surface.

Mechanism of Selectivity (13)

Changes in the operating variables which increase isomerization also generally increase selectivity and vice versa. Although the mechanism for selectivity is known with less certainty than that for isomerization, the following mechanism explains the available data (3,7,13,21). Both the monounsaturates and polyunsaturates can be absorbed (probably physically rather than by chemisorption) on the catalyst surface. The polyunsaturates tend to be more strongly adsorbed than the monounsaturates, and if time is available, the polyunsaturates will displace all or most of the monounsaturates on the surface. If a high concentration of hydrogen is present on the catalyst surface, hydrogen atoms will tend to react with the first double bond that approaches the catalyst; the attack will be random and non-selective. If the concentration of hydrogen on the catalyst surface is low, time will probably be available for polyunsaturates to concentrate at the catalyst surface. In which case, most of the double bonds that hydrogenate or isomerize are those of the polyunsaturate fatty acid groups; selectivity will hence be high. As was also the case with isomerization, hydrogen concentrations at the catalyst surface are hence most important in predicting selectivity.

Engineering and Chemical Factors of Importance in Partial Hydrogenation of Triglycerides

When a reactor is designed for partial hydrogenation, control of the overall rate of hydrogenation, of selectivity, and of isomerization are all obviously of importance. These three factors depend on the following:

1. Temperature.
2. Concentration of hydrogen, unsaturate groups, saturate groups, "inerts," catalyst poisons, etc. at the catalyst surface.
3. Type of catalyst such as nickel, palladium, platinum, etc. The activity of the catalyst and how the activity changes with use or catalyst poisons are also of importance.

Temperature increases the rate of hydrogenation in the temperature range of commercial interest. Several investigators (3,7,13,21) have obtained data which indicates that the rate is linearly proportional to temperature. Such an observation for a catalytic reaction is surprising, since several consecutive reactions are occurring, such as chemisorption, surface reactions, and desorption. Probably over a larger temperature range, the rate-temperature relationship is essentially an S-shaped curve, and the range from about 100–190C is essentially the straight line portion of the total curve.

For many years, it was accepted that increased temperature increased selectivity and isomerizations. When mass transfer of hydrogen is a controlling step, as is the case in most, if not all, commercial reactors, the above conclusion is correct. In such a case, as the temperature increases, the overall reaction rate increases which results in drastically decreased hydrogen concentrations at the catalyst surface. When mass transfer of hydrogen is not a controlling step, however, temperature has little effect on either selectivity or isomerization (3,13,21). Actually the solubility of hydrogen increases slightly with temperature (see solubility data of Wisniak and Albright [21]). Based only on such solubility information, one might guess that selectivity and isomerization would actually decrease slightly with temperature. However, temperature must have slightly different relative effects on the kinetics of the various reactions so the net effect is that temperature per se changes neither significantly.

For hydrogenations with a given catalyst at isothermal conditions, the concentrations of the reactants, products, etc. at the catalyst surface, control the reactions occurring there. Since the amount of catalyst used is small, it can be assumed that each catalyst particle is completely unaffected by the other catalyst particles. Changing operating variables such as pressure, agitation, and catalyst concentration affect the reactions on a given catalyst particle *only* as they cause changes in the concentrations at the catalyst surfaces.

Increasing hydrogen *pressures* results in a larger driving force to solubilize the hydrogen in the oil. As a result, the hydrogen concentration in the liquid and at the catalyst surface is always increased regardless of the degree of agitation. The overall rate of hydrogenation increases; at lower pressures, the rate of hydrogenation is almost directly proportional to the absolute hydrogen pressure (7, 13,21). Selectivity and isomerization always decrease with increased pressure.

Agitation helps overcome the resistance for the transfer steps of the reactants and products in the mixture. Since hydrogen transfer is generally a controlling step, increased agitation results in higher hydrogen concentrations at the catalyst surfaces. Consequently in such a case, the overall rate of hydrogenation increases but selectivity and isomerization decrease. At very high rates of agitation in which the resistances for all transfer steps are eliminated, further increases of agitation have no effect on the rate, selectivity, or isomerization since there are no changes in the concentrations at the catalyst surface (3,13,21).

As the *amount of catalyst* used is increased, the *overall* rate of hydrogenation always increases (assuming a relatively good suspension of the solid catalyst in the oil). When a hydrogen diffusion step is controlling, the rate of hydrogenation per unit weight of catalyst decreases (7). However, since the hydrogen concentration at the catalyst surface decreases, consequently, selectivity and isomerization increase. When no diffusion steps are controlling, the concentration at the catalyst surface is unchanged. Consequently there are no changes (3,13,21) in selectivity, isomerization, or rate of hydrogenation per unit weight of catalyst (i.e., the overall rate is directly proportional to the amount of catalyst).

Catalyst preparation is still largely an art. Since the reaction occurs on the catalyst surface, catalyst manufacturers attempt to have large surface areas for a given weight of catalyst. Small size particles are therefore desired, but too small a size would result in poor filtration. Many claims and counterclaims have been made on increased catalyst activity, ability to obtain high selectivity, filterability, etc. Comparing the various catalysts is not always easy. For example, the surface areas and the porosities of the various catalysts are presumably of much more importance than the weights of the catalysts. Larger surface areas per given weight of catalysts will tend to cause more active catalysts (i.e. produce higher rates of reaction). In addition, claims are often made that active catalysts result in selective hydrogenation. When hydrogen diffusion to the catalyst surface is controlling, the hydrogen concentration at the surface will decrease with increased catalyst activity; so the above-mentioned claim can be explained in part at least on the basis of hydrogen concentration.

Raney nickel is thought to be a porous catalyst as compared to most commercial nickel catalysts. In this case, diffusion inside the pores might be controlling and presumably diffusion of the unsaturate groups might be controlling. If so, one could reason that selectivity and isomerization would be much different than for other catalysts.

Most catalysts are reused several times, and the activity decreases with time as the active sites are poisoned or "wear out." Since the triglycerides and hydrogen often contain poisons, continued use of the catalyst may mean increased poisoning. Hence the refining and bleaching steps for the oils and the purification operations for the hydrogen are important in regards to catalyst activity and performance. If catalyst poisons are eliminated from the oil and hydrogen, presumably the catalyst could be used a large number of times with good hydrogenation charac-

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• *New Products*

Consolidated Vacuum Corp., Rochester, N. Y., now offers a new vacuum pumping system. The system is designed for maximum flexibility with many standard accessory options.

General Electric, Silicone Products Dept., Waterford, N. Y., has announced the development of four new silicone defoamers for improved economy in food processing and general industrial use. Some of the materials are effective in concentrations as low as 0.1 part per million.

Analytical Engineering Laboratories, Inc., Hamden, Conn., has developed five new temperature-stabilized polyesters for use as stationary phases in the gas chromatograph analysis of fatty acids. The phases are capable of operating efficiently at temperatures up to 250–270C.

Buss Ltd., Basle, Switzerland, announced the development of a novel continuous process for the refining of vegetable or animal oils and fats. The Buss-Semco process uses centrifuges. Its principal advantages lie in very little loss of neutral oil, perfect lighting up of oil tints, plain servicing, quick change over to other types of oils, great flexibility regarding capacities, and important reduction of capital cost.

F & M Scientific Corp., Avondale, Pa., has introduced a new Model 700 Dual Column Gas Chromatograph into its line of research instruments. Its low mass oven permits rapid heating and cooling and ease of column changing. It will also be useful as a teaching instrument. In addition, they announced their Model 810 Dual Column Flame Ionization Gas Chromatograph with a new versatility in injection port design, fully automatic temperature programming, and multiple detection system.

Barber-Colman Co., Rockford, Ill., announced a new Selecta-System Gas Chromatograph, designed with a unit concept and featuring component selection with a flexibility which makes approximately fifty different systems available.

Frenkel C-D Central Co., Ltd., Basle, Switzerland, has made available a Research Unit which for the first time makes new product formulation, design, and testing a continuous, one-step process. They claim that the only other step required to specifying production is virtually reading from a graph the size and hp of C-D Units required to handle the production outputs. The complete control and automation system and components for the actual production can be designed in conjunction with and tested on the C-D Research Unit directly, and need only be hooked up to the Production Units hereafter.

Scientific Products, Division of American Hospital Supply Corp., Evanston, Ill., now produces moisture dishes, designed in accordance with specifications outlined in procedure for flour determinations. "Cereal Laboratory Methods," American Association of Cereal Chemists, 6th Ed., 1957. They are supplied with slip-in covers for tight fit, and made of spun aluminum, measuring 55 mm in diameter and 15 mm deep. The Company has also released a flash heater unit, designed to confine heat concentration, enabling an instant rise in temperature. Polished chrome housing measures 6 x 6 in.; height 6½ in. Tapered openings for round bottomed flasks measure 4 in. or more.

Archer-Daniels-Midland Co. has developed a new method of controlling chemical reactions by means of "timed release" particle coatings. The first application of the technology has been to fertilizer, to control the release of plant nutrients. Research scientists are now seeking to apply the coatings technology in other areas.

• *Obituary*

Ernest Schlenker (1951) passed away January 10, 1963. Dr. Schlenker was a consulting chemical engineer in Marseille, France.

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teristics. Catalyst poisons, when present, are generally thought to poison the most active sites first. Consequently, not only is the activity of the catalyst decreased, resulting in slower rates of hydrogenation, but, in addition, selectivity and isomerization characteristics may be changed. Any decreased selectivity and isomerization of used catalyst (with decreased activity) can often be explained, in part at least, by increased hydrogen concentrations on the catalyst surface.

Changes at the catalyst surface with use, such as changes of the type and number of active sites, are important. The literature gives some information pertinent to this. Bailey (6,7) for example indicates that sulfur-poisoned catalysts are less selective. His use of the term selectivity as applied to catalysts is rather ambiguous; however, one of his graphs indicates that either the iso-oleic (or *trans*) acid content increases for a given saturated acid content or the saturated content increases for a given iso-oleic content. He reported a similar finding when a catalyst was used in oils at very low concentrations. At such conditions, the catalyst is "more used" to perform the necessary hydrogenation than when larger quantities of catalyst are used. The type or quality of the oil also appears to be important. Eldib and Albright (13) found, for example, that when they used 0.03% nickel in cottonseed oil, selectivity (as defined by polyunsaturate and saturate contents) was unchanged but isomerization was increased as compared to runs at 0.07–0.15% nickel. On the other hand, Wisniak and Albright (21), who used what was probably a more highly purified cottonseed oil, found that selectivity and isomerization both decreased as the catalyst concentration was decreased from about 0.04–0.07% to 0.02% nickel. In each of the above two series of runs, the rate of hydrogenation (hence the activity of the catalyst) was much lower for the runs made at low catalyst concentrations, than would have been expected as compared to the runs with higher catalyst concentrations. It is hoped that research now in progress will help give information pertaining to used catalysts.

In some continuous flow reactors, possibly the only controlling diffusion step involves an unsaturate or saturate group of the triglyceride. In which case, increased catalyst concentrations would decrease selectivity and isomerization. There may be other reactors in which both diffusion steps for the hydrogen and the unsaturate are partially controlling. Then the ratio of the hydrogen to the unsaturate groups on the surface of a specific catalyst would be most important. Increasing this ratio (caused by changed operating conditions) would result in less selectivity and less isomerization. The results of Sims (20) can be explained by such reasoning. He had hydrogenated at high pressures with probably moderate agitation. Quite possibly in this case mass transfer steps for the unsaturated acid groups were controlling. Hence increased agitation would increase selectivity as occurred in his study.

Increased interest has been shown in the last few years in continuous flow hydrogenators. Procter and Gamble Co. is, however, the only American company that is known to be using such a reactor for partial hydrogenation. In their reactor (18) the oil, catalyst, and hydrogen are contacted at or near the reactor inlet. Obviously some of the hydrogen is dissolved in the oil, but presumably three phases (gas, liquid, and solid) are present at the reactor inlet. As the hydrogen is reacted, possibly the gas phase disappears leaving only liquid and catalyst phases; presumably the controlling diffusion resistances would then involve unsaturated groups rather than hydrogen. Solubility data such as obtained by Wisniak and Albright (21) should be most helpful in designing such a reactor and estimating the selectivity and isomerization characteristics of the resulting hydrogenation.

Mechanism of Catalytic Reactions

Various combinations of adsorption, surface reaction, and desorption steps have been considered for the hydrogenation of light olefins (17) and later for triglycerides (13,21). Experimental data were needed in which mass transfer resistances were essentially eliminated since it was necessary to know the concentrations of reactants at the catalyst surface. Such data were obtained for hydrogenation runs of triglycerides over wide ranges of operating variables (13,21). These kinetic data indicate that the probable reaction mechanism involves the reaction between the unsaturated group, which is physically adsorbed, and atomically chemisorbed hydrogen. The surface reaction is the controlling step. It is of considerable interest to find that a comparable mechanism has been earlier postulated for the hydrogenation of light olefins (14,15).

REFERENCES

1. Albright, L. F., L. J. Harrison, and A. Sesonske, JAOCS *35*, 240 (1958).
2. Albright, L. F., C. H. Wei, and J. M. Woods *Ibid.*, *37*, 315 (1960).
3. Albright, L. F., and J. Wisniak, *Ibid.*, *39*, 14 (1962).
4. Allen, R. R., and A. A. Kiess, *Ibid.*, *32*, 400 (1955).
5. Allen, R. R., and A. A. Kiess, *Ibid.*, *33*, 355 (1956).
6. Bailey, A. E., *Ibid.*, *26*, 644 (1949).
7. Bailey, A. E., "Industrial Oil and Fat Products," 2nd Ed., Interscience Publishers, Inc., New York (1951).
8. Chahine, M. H., E. R. Cousins, and R. O. Feuge, JAOCS, *35*, 396 (1958).
9. Church, J. M., and M. A. Abdel-Gelil, Ind. Eng. Chem., *49*, 813 (1957).
10. Corson, B. B., "Catalytic Hydrogenation of Olefinic Hydrocarbons" pp. 79–108 in "Catalysis," Vol. III, P. H. Emmett, Editor, Reinhold Publishing Corp., New York (1955).
11. Cousins, E. R., and R. O. Feuge, JAOCS, *37*, 435 (1960).
12. Cousins, E. R., W. A. Guice, and R. O. Feuge, *Ibid.*, *36*, 24 (1959).
13. Eldib, I. A., and L. F. Albright, Ind. Eng. Chem., *49*, 825 (1957).
14. Eley, D. D., "*Catalytic Activation of Hydrogen*," pp. 157–159 *in* "Advances of Catalysis," W. G. Frankenburg et al., Editors, Academic Press Inc., New York (1948).
15. Eley, D. D., "Catalytic Hydrogenation of Ethylene," pp. 49–77 in "Catalysis," Vol. III, P. H. Emmett, Editor, Reinhold Publishing Corp., New York (1955).
16. Feuge, R. O., M. B. Pepper, R. T. O'Connor, and E. T. Field, JAOCS, *28*, 420 (1951).
17. Hougen, O. A., and K. M. Watson, "Chemical Process Principles," Vol. III, pp. 943–958, John Wiley and Sons, Inc., New York (1947).
18. Mills, V., J. H. Sanders, and H. K. Hawley, U. S. Pats. 2,520,423 and 2,420,424 (1950).
19. Patterson, W. J., U. S. Pats. 2,307,065 (1943), and 2,437,705 and 2,437,706 (1948).
20. Sims, R. J., JAOCS, *29*, 347 (1952).
21. Wisniak, J. and L. F. Albright, Ind. Eng. Chem., *53*, 375 (1961).
22. Zajcew, M., JAOCS, *37*, 11 (1960).

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New Solvent Process Announced at A.I.C.E. Meeting

A process for exacting gossypol from cottonseed by a solvent process was announced at the 49th National Meeting of the American Institute of Chemical Engineers. It was the subject of a paper, "Chemical Engineering Development of a Mixed Solvent—Extraction Process for Cottonseed," authored by E. A. Gastrock (1941), E. L. D'Aquin (1938), E. Keating, and H. L. E. Vix (1946) of the Southern Regional Research Laboratory, U.S.D.A., New Orleans.

The problem was to remove as much gossypol as possible, This toxic material "derived originally from small oval-shaped glands" in cottonseed and "responsible for certain toxic and antinutritional properties which limit the use of cottonseed meal as feed for poultry and swine."

In contrast to contemporary commercial extraction processes, this mixed solvent process is reported to use a mixture of hexane, acetone, and water and is designed to: remove most of the gossypol from the meal along with the oil; yield an extracted meal with not over 1.5% residual oil; use processing conditions that will not harm the meal by heat damage, reduction of epsilon-amino-free lysine content or other causes.

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