Hydrogenation

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THE LIQUID PHASE, catalytic hydrogenation of oils is one of the most important chemical reactions that are carried out in the production of edible fats. Because of the large number of papers on this subject, this presentation will not give credit to those whose work is quoted nor will a bibliography be included. There are several good books on the subject and the interested student can readily find references to specific papers.

Since hydrogenation is a very broad subject, this presentation will attempt to give only a very general view. The purpose is not to present the specific conditions required to obtain a specific product since this involves a myriad of details, but to furnish a simplified theory of hydrogenation that will perhaps offer some guides when a specific product is desired.

From the basic patent on liquid-phase hydrogenation issued to Normann in 1902 and its introduction in this country in 1911, few chemical processes have had such a great economic impact on an industry. Not only has this process changed the shortening and margarine industry but it has also had a far-reaching effect on agricultural practices. It is almost impossible to imagine the fat and oil industry without hydrogenation, although it would seem that some nutritionists would like to see us try it. At the present time some three billion pounds of edible oils are hydrogenated in this country annually, which uses some 2.25 billion cubic feet of hydrogen.

General Considerations of the Reaction

The purpose of hydrogenation is to change a normally liquid oil into a semisolid product that has the desired consistency over a certain temperature range. A secondary purpose is to reduce the diene and triene contents of the product to a minimum, for this will contribute to the stability of the product in regard to oxidative rancidity. Thus the "selectivity" of the reaction is important. In this presentation, selectivity is defined as "chemical selectivity," the complete reduction of a diene to a monoene before any saturated material is produced.

The achievement of the desired consistency of the hydrogenated product, which is usually measured by the "solids index" at several temperatures, has been the subject of many investigations. The products of hydrogenation are a very complex mixture because of the several simultaneous reactions that occur. Not only are double bonds saturated with hydrogen but some of the remaining double bonds are isomerized. This isomerization is both geometrical, a change from the low-melting *cis* form to a high-melting *trans* form, and positional, a shift of the bond away from its natural position in the chain. Extensive geometrical or *trans* isomerization tends to give products that are hard at low temperatures but soft at high temperatures. A lesser but significant effect on melting points is contributed by the positional isomerization, since the shift of a double bond in a carbon chain affects the melting point of the material. Since the bonds that are shifted can be in either the *cis* or *trans* form, a hydrogenated oil is an extremely complex mixture. For example, the hydrogenation of linoleic acid, which is the main component reacted during the hydrogenation of vegetable oils, results in the production of 18 isomeric monoenes, the *cis* and *trans* forms of nine positional isomers. Thus hydrogenated cottonseed oil would contain 18 different monoenes, some dienes, myristic, palmitic, and stearic acids, a total of 22 different acids. This number of acids could form about 5,000 different triglycerides. When one considers the possibility of the solubility of glycerides in each other at various temperatures, the problem of exact control of consistency becomes impossible.

However there are several empirical rules that may be followed to give a product of the desired properties.

Effect of Operating Variables

The equipment for hydrogenation consists of a reaction vessel and some means to bring together the three components: the catalyst, oil, and hydrogen. There may be many variations in the physical equipment which will have an effect on the course of the hydrogenation reaction. However the variables that may be changed at will, temperature, pressure, and catalyst concentration, are used to obtain a product of the desired characteristics using the available equipment.

Countless investigations have been made on the effect of the operating variables, most of which have not been published. However from the material that has been published, a number of generalized conclusions can be drawn, although there will perhaps be some disagreement.

In general, the higher the temperature of hydrogenation, the more selective the reaction becomes and the more iso-oleic *trans* acids are formed, and the speed of the reaction increases.

The higher the pressure of the reaction, the less selective the reaction becomes with less *trans* formation, and the speed of the reaction is increased.

The higher the catalyst concentration, the more selective the reaction with an increase in *trans* formation, and again the speed of the reaction increases.

Of course the effects of these three variables are not exclusive but all tend to affect each other. However a very simplified theory may be advanced to account for the effect of the operating variables.

There seems to be considerable evidence that the concentration of hydrogen in or on the catalyst is the factor that determines the selectivity and isomer formation of the reaction. Thus at a fixed pressure and catalyst concentration, there would be an equilibrium amount of hydrogen per catalyst site as the hydrogenation reaction proceeded. However an increase in temperature would probably decrease the solubility of the hydrogen in oil and also increase the speed of the reaction and this would cause a faster removal of hydrogen from the catalyst and thus there would be less hydrogen on the catalyst, resulting in high selectivity and isomer formation.

Also the effect of pressure may be explained. At a fixed catalyst concentration and temperature, an increase in pressure will increase the concentration of hydrogen in the oil and cause a decrease in the selectivity, and less isomers will be formed. Thus if the catalyst concentration is increased at a fixed temperature and pressure there would be less hydrogen per catalyst site, and an increase in selectivity and isomer formation results.

Thus it would seem that the operating variables all affect the concentration of hydrogen on the catalyst, and this one factor in turn determines the selectivity of the reaction.

There is a fourth factor that is usually fixed in the equipment but has a great effect on the reaction and that is the rate of agitation. Agitation of the mixture must accomplish a number of jobs. The catalyst must be kept suspended in a uniform dispersion throughout the liquid. Since the density of the catalyst is considerably higher than the density of the oil, it tends to settle under low agitation, thus effectively decreasing the catalyst concentration in part of the oil. Heat must be dissipated throughout the mixture in order to prevent hot spots with consequent differences in the reaction. Not only must the external heat be dissipated, but since the formation of a carbon hydrogen bond is exothermic, this heat must be removed from the site of the reaction. Hydrogen must be supplied to all parts of the mixture at a uniform rate to replace that used during the reaction. Apparently the solution of the maximum amount of hydrogen in the oil is seldom if ever achieved in plant-size batch equipment in spite of internal baffling and the admission of the hydrogen through a spider in the bottom of the vessel in the form of small bubbles.

The efficiency of agitation, which in turn affects the solution of hydrogen in oil, is probably the major cause for the differences in products from different convertors under the same conditions as well as differences in laboratory or pilot-plant-scale and plant-scale hydrogenations.

Catalyst poisons are a factor that can have a great effect on the product. The poisons, which effectively reduce catalyst concentration with a consequent change in the selectivity and rate of reaction, may arise from many sources. The hydrogen gas may contain sulfur compounds, carbon monoxide, or ammonia, all of which are effective poisons. The oil may contain soaps, water, phosphatides, partial glycerol esters, mineral acids from the use of high-acid bleaching clays, and a host of other materials which could change the catalyst. Most of the troubles experienced in commercial hydrogenations can be traced to catalyst poisons. The best method to prevent trouble is to make sure of the quality of the hydrogen and the oil.

Isomerization

The formation of the high-melting unsaturated fats or *trans* isomers always accompanies hydrogenation and seems to be in direct proportion to the selectivity of the reaction. Along with the formation of *trans* or geometrical isomers there is considerable positional isomerization or shifting of the double bond from its normal position in the carbon chain. Some work has indicated that the two types of isomerization occur at the same time during the hydrogenation. These isomerizations can be explained by a half hydrogenation-dehydrogenation concept of atomic hydrogenation. If on the catalyst molecular hydrogen is dissociated to hydrogen atoms and a hydrogen atom is added to one end of a double bond, a free center is produced. If a hydrogen atom is then removed from either side of the free center, a double bond is formed either in the original position or in the adjacent position and the double bond that is reformed may be in either the *cis* or *trans* form. Of course the new double bond can go through this reaction sequence and be moved still farther from the "natural" position. Under conditions which cause high isomerization, high-temperature, low-pressure, high-catalyst conditions which permit low concentrations of hydrogen on the catalyst, the isomerization reaction is preferred over saturation. It would follow that if only a few of the "active sites" on the catalyst were covered with hydrogen, the exchange of hydrogen atoms between the carbon atom and the catalyst would proceed at a greater rate than the addition of two atoms of hydrogen to a double bond.

This reaction sequence would also serve to explain the selective hydrogenation of linoleic over oleic acids. Thus under conditions which permitted low concentrations of hydrogen on the catalyst, selective conditions, it would be possible to cause extensive positional isomerization of the two double bonds in the linoleic, and at least part of the resulting diene isomers would have the two double bonds conjugated, which is a very stable structure. This material would presumably hydrogenate to a monoene much faster than the nonconjugated material or isolated double bonds. Thus the linoleic would disappear before the monoenes were saturated to stearic. If the hydrogenation conditions were changed to permit a high concentration of hydrogen on the catalyst, less isomerization would take place and the methylene-interrupted diene and the monoene would hydrogenate at about the same rate, and selectivity would be decreased.

This extremely simplified theory of selectivity, although it is based on the available information, is still a theory and much more research is necessary before a complete explanation of the selectivity of the hydrogenation reaction can be made.

Hydrogenation and Nutrition

The practice of hydrogenation is receiving considerable criticism at the present time from those concerned with the relationship of diet and disease.

Not only has the amount of saturated fat been questioned but also the presence of the isomers of the natural fatty acids. Although a number of studies have shown that the *trans* fatty acids are metabolized quite efficiently and are in the depot fat of man, they just "aren't natural" and are therefore suspect. Of course a charcoal broiled steak is not "natural" either. Just or not, this seems to be causing some changes in hydrogenation practices. The trend seems to be to attempt to produce plastic fats with as high as possible "essential fatty acid" content, principally for use in margarine. Of course this requirement is rather difficult to obtain because of the isomerization.

Margarine oils in the past have been produced under very selective conditions, with a resulting high content of *trans* isomers. These isomers cause the product to be relatively hard at low temperatures with a melting point slightly below body temperature. However to produce a margarine fat that contains a high proportion of "essential fatty acids," the *cis-cis* 9,12-octadecadienoic acid, the isomerization must be kept low. This of course results in a nonselective hydrogenation with the product being waxy. Therefore some compromise must be made and the hydrogenations are carried out under conditions that do not cause too much isomerization or produce too much saturated material.

Recent Progress in Hydrogenation Processes

Most of the edible oil hydrogenation is carried out by a batch process. However a number of studies have been made and patents issued covering the continuous hydrogenation process. In one variation of this process, the catalyst is mixed with oil and the mixture pumped or sprayed into a reaction chamber that contains the hydrogen under pressure. The oil-catalyst slurry may be agitated in the reactor. The catalyst is filtered from the oil continuously and the catalyst may be returned to the start of the cycle for reuse. Another process involves the use of a fixed catalyst bed. The oil and hydrogen are pumped through the bed, where the reaction takes place. There are several difficulties involved in the use of a continuous process, not the least being analysis and control. A continuous reading of the refractive index will indicate the iodine value of the stream of hydrogenated product. However since the iodine value is not the only criterion for the hardness of the oil, some other measurement should be made. It has been reported that a continuous measure of the *trans* acids may be performed on the oil stream by the infrared absorption at 10.36 microns. This would give a somewhat better indication of the consistency of the product. However it would appear that perhaps a combination of refractive index and *trans* content would permit very close analytical control over the product stream. In the operation, various catalyst poisons may alter the catalyst efficiency for both hydrogenation and isomerization, so both types of measurement appear to be necessary.

Hydrogenation in solution seems to be of considerable interest. Solvent extracted oils are becoming more prevalent and since micella refining has several obvious advantages, it should be possible to hydrogenate the oil in the extracting solvent. There have been many claims as to the superiority of the products by solvent hydrogenations but one advantage apparent from the studies is that the reaction may be carried out at a much lower temperature. There are also other advantages such as less oil loss on the catalyst filters and easier filtering because of lower viscosity. Among the disadvantages would be the increased bulk of material for a given amount of oil and the possibility of catalyst poisons in the solvent. The continuous hydrogenation of fats in the extracting solvent should be an efficient process since the process could be operated at low temperatures and in a fixed-bed operation would permit faster reaction because of the decreased concentration of oil compared to catalyst. These are only suggestions of the possibilities that exist in the field of edible-oil hydrogenation.

For almost fifty years the fat and oil industry has hydrogenated, using empirical conditions with very little understanding of the reaction. Research investigations were limited because there was very little incentive to change a process that worked and was very cheap compared to the raw-material cost. Lack of good analytical methods also deterred research. The latter problem has now been largely solved and work in the field of nutrition has given an impetus to the study of the reaction, so that the future should bring a complete picture of the most important chemical reaction the industry performs, hydrogenation.

Emulsifiers[1]

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THE TREND of modern technology is to use newer techniques and newer materials to provide more desirable items for the consumer. Food technology, even food emulsion technology, is no exception even though it has been with us as long as any, and even though it is subject to as many restrictions as any. Presumably man drank milk very early in history, and milk is certainly a complex food emulsion. Interestingly, milk and milk derivatives are among the more highly regulated of our food products.

The regulations which affect edible emulsifiers, and of course all foods, are based on the factors of safety, food identity, and economic protection. Perhaps the most important Federal regulation affecting all three factors is the Food, Drug, and Cosmetic Act of 1938 and amendments, especially the Food Standards provisions and the Food Additives Amendment of 1958. State regulations, governing intrastate commerce not subject to Federal regulation, are sometimes diverse and nonuniform as would be expected by their origin.

Acceptable Emulsifiers and Stabilizers

The above preamble on regulations recognizes that the very definition of "edible" emulsifier requires a knowledge of the Food Additives Amendment of 1958. In fact the lists of materials published in the Federal Register serve as guides to acceptable food emulsifiers and are used for that purpose here. Tables I through V show listed materials which are indicated as emulsifiers or stabilizers, and which are direct additives to foods. No attempt has been made to assemble a list of indirect additives (e.g. via packaging materials). Materials under "prior sanction" do not appear on these lists, and therefore have been omitted from this compilation.

Table I shows the emulsifiers and stabilizers which were on the original list of materials "generally recognized as safe." The first three classes of materials contain the terminology ". . . from the glycerolysis of edible fats or oils." This terminology is due, in part, to an earlier unrecognized contaminant in certain fatty acids which could cause a pericardial edema in young chickens. Steps are underway to

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[1] Communication No. 270 from the Research Laboratories of Distillation Products Industries, Division of Eastman Kodak Company, Rochester, N.Y.