

Hydrogenation of Fatty Oils

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IN a broad sense the term "hydrogenation" may be applied to any reaction in which molecular hydrogen is caused to react with an organic compound. So defined, the term covers a number of diverse reactions; for example, reductions, such as the conversion of acids or esters to alcohols, or even to hydrocarbons, additions which change cyanides or nitriles to amines, molecular splitting or hydrogenolysis reactions, dehalogenizations, and a number of others. A common factor in all such reactions is the necessity of providing a catalyst to bring about the reaction.



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The term "hydrogenation" is used by Adkins in a more limited sense to indicate only those reactions in which hydrogen is catalytically added directly to a multiple linkage within a molecule, without cleavage of the molecule. Examples of reactions of this type are conversions of carbonyl to carbinol compounds, of imines to amines, of benzenoid to cyclohexanoid compounds, and of saturation of unsaturated hydrocarbon chains by hydrogen addition at the carbon to carbon double bonds. The latter, as applied to the ethylenic linkages of fatty acids and more particularly the glyceride oils, is, of course, the reaction generally thought of when the fats and oils chemist speaks of hydrogenation. It is in this sense that the term is used in the present paper.

Historical

According to Ellis, the first reporting in the literature of the catalytic hydrogenation of an organic compound was made by Debus in 1863. Using platinum black as a catalyst, hydrocyanic acid was hydrogenated to methyl amine. A few similar references are found in the following 30 or so years. However in 1897 Sabatier and his co-workers began the publication of a series of papers covering researches on hydrogenation, using reduced nickel as a catalyst. In these now classic works it was demonstrated that the carbon to carbon double bonds could easily be saturated under relatively mild conditions of temperature and pressure. These works were not directly applicable to the hydrogenation of fatty oils since the methods used were limited to hydrogenation in the vapor phase. Nevertheless their publication led others to work along similar lines, with the result that Normann in 1903 took out an English patent covering the hydrogenation of fats in the liquid phase with nickel as the catalyst.

The Normann patent was acquired by an English firm and was put into practice on a commercial scale

by 1906. The American rights to use this patent were obtained by The Procter and Gamble Company in 1909. In 1911 this company marketed its hydrogenated shortening "Crisco." Apparently in these early days the goal of hydrogenation was substantially complete saturation of the treated oil. The resulting "stearine" was used as a substitute for hard fats of animal origin as the stiffening agent in shortenings. Improvements in the original process in the form of partial hydrogenation, or hydrogenation to a given end-point, were developed and made the basis of a patent granted in 1915 and assigned to Procter and Gamble. The validity of this patent was later attacked in the courts, and after prolonged litigation the patent was held to be invalid. This action opened the way for rapid and extensive development of the hydrogenation process throughout the whole edible oil industry in the United States.

As stated by Bailey, it is almost impossible to overestimate the importance of the process of hydrogenation in modern oil and fat technology and to modern agriculture as well. To it almost alone of the basic oil and fat processes we owe the substantial interchangeability of our oil and fat resources. Out of it grew the substantial increase in the economic value of cottonseed oil, and to it is due in large part the more recent development of the huge soybean industry.

Nature of the Hydrogenation Process

The hydrogenation of fatty oils, like all other hydrogenations, is a catalytic reaction; that is, the reaction does not proceed at a demonstrable rate without the influence of a catalyst. While platinum and other noble metals can catalyze the reaction, nickel is universally used for reasons of both economy and efficiency. For the reaction to take place, there must be present an oil, hydrogen gas, and nickel catalyst. Since these materials are present as a liquid, a gas, and a solid, the hydrogenation of oils is said to be a case of a three-phase heterogenous catalysis.

According to modern concepts, heterogenous catalytic reactions proceed through the formation of unstable complexes of the reactants and the catalyst, which are adsorbed on the catalyst surface. Decomposition of the complex follows, freeing the reaction products and regenerating the catalyst to its original condition, permitting the cycle to be repeated. In the case of the hydrogenation of a fatty oil, adsorption on the catalyst surface causes the formation of a hydrogen-nickel-unsaturated fatty acid radical complex, which upon desorption breaks down, releasing the nickel and a fatty acid radical of one degree greater saturation. Since the adsorption of the reactants probably takes place on surface areas of molecular proportions, it follows that the activity of a catalyst depends on the submicroscopic structure of the surface of the catalyst particles. This in turn is determined by the conditions under which the catalyst itself is produced and reduced.

For hydrogenation to take place, hydrogen and the fatty material to be hardened must be brought to-

gether at a suitable temperature at the catalyst surface. This is no problem so far as the fat is concerned because the catalyst is uniformly suspended in it. For hydrogen to reach the site of reaction, it must be in solution in the oil. Contrary to the solution of gases in water, the solubility of hydrogen in oil becomes greater as the temperature of the oil is increased. Similarly the solubility of hydrogen in oil is enhanced by increased pressure. It follows that temperature and pressure therefore affect the speed with which the reaction progresses. As hydrogen is removed from solution in the oil by reaction with the fat, it must be constantly replaced and brought to the renewed catalyst surface. Both solution and transportation are obtained by agitation of the charge, either by mechanical means or by blowing the charge with a current of hydrogen. Agitation also serves to keep the catalyst suspended in the oil. In general, increase in agitation serves to hasten the reaction; however in actual practice it is generally not a controllable variable, particularly in mechanically agitated reaction vessels, because the rate of agitation is fixed by the design of the agitator.

Preparation of Materials Used in Hydrogenation

As stated before, three materials are required to be brought together in carrying out the hydrogenation of an oil; namely the catalyst, hydrogen gas, and the oil to be hardened. Preparation of these materials in suitable condition is the first consideration in the practical process of hydrogenation.

1. *Catalyst Preparation.* The ultimate end-product of catalyst preparation is a finely divided reduced active powder of pure nickel, or of nickel containing small amounts of copper, alumina, or possibly other materials as "promoters." However the activity and selectivity of the catalyst depend upon the starting materials used and the method of preparation and reduction.

In general, catalysts are prepared by reduction of organic or inorganic salts of nickel and are classed as supported or unsupported catalysts depending upon whether or not the nickel is carried on the surface of particles of refractory materials such as kieselguhr. A further classification refers to the conditions under which the nickel salts are reduced. "Dry" reduced catalysts are produced by grinding the nickel salts to a fine powder, which is then reduced by exposure to an atmosphere of hydrogen in a retort heated to 425 to 500°C. until reduction is complete. "Dry" reduced catalysts must be immediately suspended in oil, without access to air, to protect them from oxidation by atmospheric oxygen. An active dry reduced catalyst is pyrophoric; that is, upon exposure to air it will oxidize so rapidly as to glow. Almost without exception, dry reduced catalysts are of the supported type and are prepared from inorganic salts of nickel, usually precipitated as the carbonate or the hydroxide.

"Wet" reduced catalysts, on the other hand, are prepared by suspending the powdered nickel salts in an oil and subjecting the mixture to heating in the presence of an atmosphere of hydrogen. In general, organic salts of nickel are used, and the catalysts are of the non-supported type. Nickel formate is the most widely used compound of nickel for preparation of catalysts of this type. Upon heating the nickel formate-oil mixture to 150 to 200°C., the formate decom-

poses with the liberation of hydrogen, carbon dioxide, and water, leaving the reduced nickel. Simultaneously, as the nickel becomes active, hydrogenation of the oil carrier occurs. The reaction is allowed to go on until the oil is completely saturated. Catalysts of this type are prepared on a commercial scale and are sold as flakes or solid blocks of completely hardened oil carrying the reduced nickel in suspension. Because the original oil used in the reduction usually suffers some degree of thermal decomposition, it is the general practice to remove it from the reduced nickel and to replace it with oil hardened under less drastic conditions prior to flaking or casting into blocks.

In past years it was common practice for each processor to prepare his own catalyst by methods developed within his own organization and generally held secret. However the very considerable difficulty in producing catalysts of uniform activity and selectivity, even with constant attention and supervision, together with the development of reliable commercially available catalysts produced by organizations specializing in that field, has resulted in the abandonment of catalyst-making activities by a large number of processors. While some organizations continue to prepare their own catalysts for reasons of economy or special properties, the trend today is toward purchase of catalyst supplies from the firms specializing in this field of endeavor.

In passing, mention should be made of Raney catalyst, a catalyst prepared from a powdered alloy of nickel and aluminum. This material was formerly widely used in oil hardening and is used extensively in the hydrogenation of organic compounds both in the laboratory and on a plant scale. This material is reduced by dissolving the powder in moderately strong caustic soda solutions. The aluminum portion of the alloy is converted to sodium aluminate, with the evolution of hydrogen, leaving the reduced nickel as a sludge. The latter is washed free of caustic and is taken up in oil by boiling away the water in which it is suspended. When properly prepared, Raney nickel produces hydrogenated oils equal to those made by good quality wet or dry reduced catalysts but is generally not quite as active.

2. *Hydrogen Manufacture.* The production of hydrogen gas of sufficient purity and in sufficient quantity is one of the major considerations in the hydrogenation of fats. Since one molecule of hydrogen is added for each double bond saturated, the degree of hydrogenation is directly related to the iodine value of an oil. It is hence possible to calculate the theoretical amount of hydrogen required to harden a known quantity of oil a given interval of iodine value drop. For 1,000 lbs. of oil to be hardened, one iodine value unit requires .0795 lb. of hydrogen, or just under 15 standard cu. ft., as measured at 14.7 lbs. per sq. in. pressure and 60°F.

A typical commercial installation for the hydrogenation of domestic vegetable oils may accommodate a batch of 25,000 lbs., which will on the average be reduced about 50 iodine value units. The theoretical hydrogen demand to harden such a batch would be 18,750 cu. ft.; in actual practice somewhat more would be required. Assuming that the turn-over time is six hours per batch, a daily hydrogen production of some 80,000 cu. ft. would be necessary. This will give some idea of the magnitude of the hydrogen production problem attendant upon hydrogenation.

In addition to the quantity of hydrogen required, its quality is of paramount importance. Particularly, the hydrogen used for hydrogenation must be free from sulfur compounds and from carbon monoxide for these cause rapid poisoning of the hydrogenation catalyst. In some types of hydrogenation small quantities of inert gases may be tolerated, but it is desirable that their concentration be kept as low as practically possible.

Hydrogen production for the hydrogenation of fatty oils in the United States is generally accomplished by one of three systems; namely, by electrolysis, by the steam-iron ore process, or by hydrocarbon reforming, or the steam-hydrocarbon process. A number of factors influence the choice of process for a given installation. Some of these are capacity required, power cost, availability and cost of raw materials, whether operation will be continuous or intermittent, and of course the capital investment required.

Electrolytic Hydrogen. Electrolytic hydrogen is produced when direct current electricity is passed through an aqueous electrolyte, two volumes of hydrogen evolving for each one volume of oxygen. Theoretically 9.4 standard cu. ft. of hydrogen are produced per kilowatt-hour of current passed; in actual practice less than this amount is produced, depending on the cell efficiency. Commercial electrolytic cells are operated at 2.0 to 4.0 volts per cell and at a current density of about 75 amperes per sq. ft. of electrode area. The direct current is produced by a motor-generator set or by large capacity rectifiers. Allowing for losses in conversion and resistance of the system, each 1,000 cu. ft. of hydrogen produced requires 150 to 165 kilowatt hours overall expenditure of electric power.

The electrolyte used is usually a solution of caustic soda or caustic potash of such strength as to afford maximum conductivity, about 25% to 30%. To keep this concentration relatively constant, the water electrolyzed into gases must be replaced with distilled water. This water usage amounts to about six gallons per 1,000 cu. ft. of hydrogen produced.

From the quantity of current required it is readily apparent that except in cases of exceedingly cheap electricity, the electrolytic system is a relatively expensive source of hydrogen. Nevertheless it has distinct advantages, particularly for small installations and intermittent operation. With careful operation a very pure hydrogen is produced, 99.8%, with oxygen as the remaining 0.2%, and hence requires no purification. The electrolytic system can be started up or shut down in minimum of time as compared to other systems. For these reasons in capacities of 2,500 cu. ft. per hour or below it is probably the system of choice even though power must be obtained at the usual industrial rates.

In passing, it might be mentioned that hydrogen is also produced as a by-product in the electrolysis of brines to produce chlorine and caustic soda. At least one U. S. plant situated near a chlorine plant has made use of by-product hydrogen obtained in this manner in the past.

Steam-Iron Ore Process. This process is widely used in the United States for the production of hydrogen. The basic raw material required is coke of good grade, preferably as low in sulfur content as possible. The process proceeds in two steps: first,

water gas manufacture, and second, hydrogen production.

Water gas is produced by passing steam through incandescent beds of coke and is stored in a holding tank. This gas is then used as the reducing gas in the reduction cycle of the hydrogen generator. The latter is originally packed with pieces of iron ore of suitable size. While some domestic ores have been used for this purpose, the preferred ores are the spathic, or carbonate ores imported from England, possibly because reduction of the carbonate ore affords greater porosity and hence greater area of active surface.

In operation, water gas is passed through the heated iron ore, reducing it to active metallic iron. Above the ore bed, air is introduced to burn the spent reducing gas in a refractory checker-work superheater. Steam is then admitted through the superheater. The super heated steam oxidizes the previously reduced iron, freeing hydrogen, which is passed to a gas holder for storage prior to purification. The cycle is then resumed. Between the 10- to 15-minute reduction and hydrogen-making cycles a short purge period is provided to vent reducing gas to the atmosphere, and following the hydrogen-making cycle, a short burn-off period is provided to burn off sulfur and carbon which accumulate in the checker work.

The hydrogen produced by this process is 98-99% pure and contains both sulfur compounds and carbon monoxide, which must be removed by further purification. The sulfur compounds are removed by absorption on iron oxide in lux boxes or in amine solutions at somewhat elevated temperatures and pressures. The carbon monoxide is removed by the water gas shift reaction, one molecule of monoxide uniting with one molecule of water to form carbon dioxide, thus freeing one molecule of hydrogen. The carbon dioxide is then removed by absorption in an amine solution. In some systems the final traces of carbon monoxide are removed by methanation, which is simply hydrogenation over nickel catalyst to methane, which is inert to hydrogenation catalysts.

In efficiently operated steam-iron ore systems about 45 to 50 lbs. of coke are consumed for each 1,000 cu. ft. of hydrogen produced.

Hydrocarbon Reforming Process. This process of hydrogen manufacture is also often referred to as the steam-hydrocarbon process. In recent years it has gained a wide acceptance in the fats and oils industry primarily because of its economy of operation, the high purity of hydrogen produced, its cleanliness, and the fact that with suitable instrumentation it can be made fully automatic in operation.

The raw material is a gaseous hydrocarbon, either natural gas or liquefied petroleum gas, such as propane or butane, which serves both as feedstock gas and as fuel gas to heat the reforming catalyst tubes. The choice of raw material is dependent on availability, cost, and analytical characteristics of the hydrocarbon. Natural gases of high nitrogen content are generally undesirable because the nitrogen appears as inert gas in the finished hydrogen.

The first step in the process is the removal of sulfur compounds from that portion of the gas used as feedstock. If sulfur is present as hydrogen sulphide or as mercaptans, the latter often being added to natural gas as an odorant, adsorption on activated carbon in so-called carbon drums or scrubbing with caustic solution serves to remove it. Certain other sulfur com-

pounds are first broken down by passing the feedstock gases over metallic oxide catalysts at about 375°C. prior to adsorption or scrubbing. Complete removal of sulfur compounds is essential to avoid the poisoning of catalysts subsequently used in the system.

The desulfurized process gas is then mixed with steam in definite proportions, and the mixture is passed through catalyst-packed furnace tubes maintained at about 815°C. Assuming for purposes of illustration that the hydrocarbon is methane, one molecule of the hydrocarbon reacts with one molecule of water to form three molecules of hydrogen and one of carbon monoxide. Simultaneously a portion of the carbon monoxide undergoes the water gas shift reaction, reacting mol for mol with water to form an additional mol of hydrogen and one of carbon dioxide. The gases issuing from the reforming tubes are thus a mixture of hydrogen, carbon monoxide, and carbon dioxide. Additional steam is metered into the stream, cooling it to about 375°C., after which the mixture is passed through a catalyst bed different from that of the reformer tubes. During this passage about 95% of carbon monoxide present is converted to the dioxide, freeing hydrogen.

The gas stream is then cooled to about 38°C., and the carbon dioxide is removed by scrubbing with a cool monoethanolamine solution. The reaction by which this solution absorbs carbon dioxide is reversible at temperatures of around 100°C. This permits regeneration of the solution by heating to that temperature and scrubbing with steam. The released carbon dioxide is discharged to the atmosphere, and the stripped solution is cooled through heat exchangers for recycling.

In some steam-hydrocarbon systems further removal of carbon monoxide is accomplished by using two more cycles of the water gas shift reaction, with amine scrubbing following each cycle. In others one additional cycle is employed, followed by a methanation step as discussed under the steam-iron ore process to convert the remaining small amount of monoxide to inert methane. In general, if the feedstock gas contains appreciable quantities of nitrogen, methanation is the cheaper final step, and the quantity of inert gas in the finished hydrogen is only slightly raised thereby.

Steam-hydrocarbon plants may be built for any capacity required but are generally considered economically feasible in capacities of 120,000 cu. ft. per day or higher. These plants possess considerable flexibility as to capacity of operation without affecting the operating economy. It is stated that they may be run as low as 75% of rated capacity and can probably be operated well above it; however licensing arrangements limit maximum production in accordance with the schedule of fees charged.

Other Processes of Hydrogen Production. In passing, three other processes for the production of hydrogen will be commented on briefly. The water gas catalytic process employs purification of water gas directly by means of repeated cycles of water gas shift reaction followed by carbon dioxide absorption. This method is used to furnish hydrogen for ammonia synthesis and similar uses but is not used much in the hydrogenation of fats since it is difficult to prepare a very pure gas by this means.

A more recent development is the production of hydrogen by the catalytic dissociation of ammonia at

high temperatures. The gas produced is a mixture of 75% hydrogen and 25% nitrogen. This method is said to be advantageously used in the hydrogenation of oils to stearines and in the hardening of inedible stocks. However it is not suitable for the hydrogenation of edible stocks in which careful control of selectivity is required.

A third development is the production of hydrogen by a method making use of elements of both the hydrocarbon reforming and the steam-iron ore processes. Mixed gases consisting mainly of hydrogen and carbon monoxide in roughly the same proportions as in water gas are produced by the catalytic reforming of hydrocarbons. These gases are employed as the reducing gases in the reduction cycle of the steam-iron ore process, as previously described, and thus serve the same function as water gas produced from steam and coke.

Several advantages are claimed for this process. Natural gas of relatively high content of nitrogen or other inert gas may be used as the feedstock since inert gases do not pass through to the finished hydrogen. Where natural gas is not available, liquid hydrocarbons of lower purity and cost than the relatively pure propane or butane required in the hydrocarbon reforming process may be employed. A further advantage over the straight steam-iron ore process is the elimination of the dirt and manual labor involved in the charging of coke to the water gas generators.

3. Preparation of Oil Stocks for Hydrogenation.

As a general requirement, fatty oils which are to be hydrogenated should be dry, free from soaps, and low in free fatty acids, phosphatides, and related materials. This is particularly true of fats to be hydrogenated for edible purposes. The presence of moisture, soaps, and phosphatides interferes with the usual hydrogenation reaction, possibly by poisoning or otherwise interfering with the functioning of the catalyst. The presence of excessive amounts of fatty acids tends to form nickel soaps, which are difficult to remove from the finished oil. These latter materials are detrimental to the color and stability of the hardened oils.

For these reasons it is the general practice to use fully refined oils having free fatty acid contents of .05% or lower. Almost invariably these refined oils are bleached with natural or acid activated clays prior to being charged to the hydrogenation converter. Bleaching prior to hydrogenation serves the dual purpose of reducing the color of the oil and of removing traces of soap which may have been left in the oil as a result of caustic refining.

Hydrogenation Equipment

Aside from a source of hydrogen the basic equipment in any batch hydrogenation system comprises a mixing tank in which the catalyst is slurried with a portion of the oil charge, the vessel in which the hydrogenation reaction actually takes place, generally called a converter, and a filter for the removal and recovery of the catalyst from the hardened oil charge. The design of the hydrogenation converter, which is the heart of the system, is subject to a wide degree of variation depending on which of several hydrogenation "systems" is employed in the plant, and on the ideas of the designer. However, regardless of system

or design, there are certain features common to all. Since the charge must be heated to initiate the reaction, which once initiated is exothermic, provisions must be made for both heating and cooling the reaction mixture. This is generally accomplished by means of a common coil of suitable area into which either high pressure steam or cooling water may be introduced. To renew the supply of hydrogen to the catalyst surface and to keep the catalyst in suspension, agitation is provided, either by mechanical means or by recirculation of hydrogen at such a rate as to cause vigorous agitation due to bubbling.

For the hardening of glyceride oils the converter is generally constructed of mild steel and is designed to withstand pressures of around 100 p.s.i.g. and in some instances the application of full vacuum as well, at temperatures ranging upward to 200° to 225°C. Capacities range generally from 10,000 lbs. to 40,000 lbs., with provisions being made for some 20% to 30% of free headspace above the design capacity. For the hydrogenation of fatty acids, vessels of similar capacity are used but are designed for around 300 p.s.i.g. pressure, and are constructed of Type 316 stainless steel or other alloys which will resist the corrosive effects of the fatty acids at elevated temperatures.

1. *Systems of Hydrogenation.* The two basic hydrogenation systems are named for early practitioners of the art. These are the Wilbuschewitsch system, in which the oil-catalyst mixture is sprayed into an atmosphere of hydrogen, and the Normann system in which hydrogen is bubbled into the oil-catalyst charge. The latter is the system which is almost universally used in this country today. Within the Normann system two pairs of more or less opposing subsystems are generally recognized by hydrogenation technologists. These are a) the so-called "intermittent vacuum" system as opposed to the "sustained pressure" system and b) the so-called "dead end" system as distinguished from the hydrogen recirculation system. Each has its proponents, each has its own application, and each has its advantages and disadvantages.

The Intermittent Vacuum System. In the "intermittent vacuum" system the hydrogenation converter is connected to a source of moderately high vacuum, such as a two- or three-stage ejector system or a wet vacuum pump. In operation the charge is heated up under vacuum, the catalyst slurry is drawn or pumped in, the vacuum broken by hydrogen, and hydrogenation proceeds. At the end of the run vacuum is again pulled on the converter, either before or after cooling, the vacuum is broken with air and the charge filtered. Advantages claimed for this system are ability to dehydrate a wet oil charge in the unit, greater safety in that air or hydrogen, as the case may be, is substantially removed from the vessel before the other gas is admitted, and better control of end-point by completely removing hydrogen at the end of the run. Disadvantages are the greater equipment cost, due to provision of vacuum equipment and internal bracing of the converter to withstand external pressure.

The Sustained Pressure System. On the other hand, in the "sustained pressure" system the converter is kept under at least slight hydrogen pressure at all times. The charge as well as the catalyst slurry is pumped in against the 3 to 5 p.s.i.g. hydrogen pres-

sure maintained in the vessel during periods of inactivity by means of an adjustable regulating valve. The charge is then heated, the pressure brought up to operating conditions, and hydrogenation proceeds. When end-point is reached hydrogen pressure is reduced to resting level, the charge is cooled and filtered. Advantages claimed for this system are lower cost due to less equipment being needed, and greater safety since with slight positive pressure of hydrogen in the vessel no air can enter to form explosive mixtures in the confined space. A disadvantage is the inability to prevent slight hydrogenation during heating and cooling the charge, which complicates somewhat the control of end-point.

The Dead-End System. As the name implies, the dead-end hydrogenation system makes no provision for recycling hydrogen gas from the head space of the converter. All gas fed to the vessel except that which maintains pressure in the head space must be absorbed. This obviously implies a very pure hydrogen gas, with no inert gas content to speak of. In actual practice, if reaction slows or stops, hydrogen supply is cut off, the head space is evacuated, and the hydrogen is readmitted. Dead-end systems are invariably also of the intermittent vacuum type, and evacuation during the run as just described is in effect a purge system. In this respect and also in the use of turbine type agitators which draw gas from the head space and redistribute it through the system, the dead-end system overlaps functionally at least with re-cycling or purge type systems.

When operating with very pure hydrogen and with a suitable high pressure hydrogen storage system, the dead-end system does have the advantage of quite precise control of iodine value reduction since the amount of hydrogen absorbed by the charge can be calculated from the pressure drop of an isolated high pressure storage tank.

The Recirculation System. In all hydrogenation systems discussed up to this point mechanical agitation of some type, employing paddles, propellers, or turbines attached to a shaft entering the vessel through a stuffing box located in the top is used to provide for dispersion of hydrogen and suspension of the catalyst. The recirculation system however obviates the need for mechanical agitation by recycling large volumes of head space gas by means of a blower or pump, returning it to the sparger in the bottom of the converter. In this manner vigorous agitation as well as abundant hydrogen is supplied to the catalyst-oil mixture. Hydrogen to replace that absorbed by the oil is fed into the suction side of the recycling blower or pump while gases abstracted from the head space may be subjected to purification processes before being recycled. The accumulation of inert gases is taken care of by periodically purging to the atmosphere.

Among advantages claimed for this system are freedom from bearing and stuffing box trouble inherent in mechanical agitators, good gas economy, a high degree of selectivity, and ability to distil out and remove moisture and volatile impurities with the recycled gas stream. In addition, recirculation systems operate at near atmospheric pressure and hence can operate with blowers or circulating pumps from low pressure hydrogen storage of the gas holder type, eliminating the need for high pressure compressors and storage tanks. Just what proportion of U. S. hy-

drogenation plants uses the recirculation system is not definitely known, but there are some quite extensive installations of this type.

The Constant Purge System. Related to the recirculation system is one frequently employed particularly with sustained pressure systems in cases where the hydrogen supply contains sizeable quantities of inert gases but is otherwise of suitable purity. In this system head space gas equal to some 10% of the hydrogen fed into the stock through the spargers is purged from the converters. This purged gas may be returned to the gas plant and a portion of it fed to the purification system while the remaining portion is discharged to the atmosphere. The ratio of revert gas recycled to the system to that discharged is adjusted to keep the inert gases in the finished hydrogen below a pre-determined level. The purging of gas from the converter head space prevents build-up of inerts in the head space and provides for the maintenance of a steady flow of fresh gas from the spargers into the charge in the converter.

Continuous Hydrogenation. Before going on, mention should be made of continuous hydrogenation. From the literature it appears that there has been very little development of continuous hydrogenation of fats and oils. The Bolton and Lush process, developed in England some 25 years ago, appears to have had little commercial application. Attempts were at one time made by a West Coast engineering firm to develop the process in this country, but apparently the results were not encouraging.

The process employs fixed catalyst in the form of reduced nickel oxide coatings deposited electrically on the surface of nickel turnings loosely packed in cages of metal screen. The cages are contained in tubes through which oil is pumped or flowed counter-current to the flow of hydrogen gas. Lack of selectivity and difficulty of reactivating the fixed catalyst is generally referred to as the reasons for the lack of success with the method.

Some three years ago a series of patents assigned to The Procter and Gamble Company were issued, covering a continuous hydrogenation process employing a powdered nickel catalyst, but no additional information on the development has been published. Another company in the industry has been reported to be conducting work on a continuous hydrogenation process but so far is stated to be using it only for stearine production due to inability to attain suitable selectivity.

While continuous hydrogenation would seem a fruitful field for investigation, the fact remains that the hydrogenator is called upon for such a wide range of products of such precise specifications that the problem of adequate control to produce them in a continuous system looks well nigh insurmountable.

Operational Aspects of Hydrogenation

In the earlier discussion of the nature of the hydrogenation reaction it was stated that it is classified as a heterogenous or contact catalytic reaction involving the addition of hydrogen at the carbon to carbon double bonds in unsaturated fatty acid chains. The reaction is exothermic, the heat of reaction being about 25 kilogram calories per mol of double bond saturated. This is sufficient to raise the temperature of the stock being hydrogenated 1.6 to 1.7°C. for each

unit drop in iodine value in hydrogenations conducted in the range of 130° to 200°C. Owing to the fact that the temperature at which the reaction is carried out affects both its speed and its course, the heat of reaction poses one of the primary control problems in practical hydrogenation.

The simple statement that hydrogenation consists of the addition of hydrogen at the double bonds and that fats may be hardened or raised in melting point thereby occurs in many textbooks of organic chemistry. This is likely to leave the novice entering the field of practical hydrogenation totally unprepared for the surprising complexity encountered in the partial hydrogenation of glyceride oils. These complexities stem from two factors: the tremendous possibilities for isomerization encountered in the hydrogenation of oils and the factor of selectivity in the reaction.

1. *Isomerization in Hydrogenation.* The isomeric possibilities encountered in glyceride oils, particularly as regards partial hydrogenation are too extensive and involved to permit full treatment in a paper of this length; however an attempt will be made to outline their scope.

In considering triglyceride oils containing unsaturated fatty acids, three types of isomerization are possible. The first of these is concerned with the position a fatty acid may occupy as regards its attachment to the glycerol molecule. If the glyceride contains two or three different fatty acid groups, that is, if it is not a simple tri-glyceride, a given fatty acid may be attached to the middle or β carbon atom, or to either of the outside or α carbon atoms.

A second type is positional isomerism, by which is meant isomerism due to the location of the double bond in the carbon chain of the fatty acid. As an illustration, normal oleic acid contains a double bond between the ninth and tenth carbon atoms of its 18 carbon chain, counting from the carboxyl carbon, and it is identified as 9-10 octadecenoic acid. A positional isomer of oleic acid, 6-7 octadecenoic acid, is known as petroselenic acid, and the 11-12 isomer as vaccenic acid. Each of these differs from oleic acid in its physical and chemical properties. In like manner linoleic acid or octadecadienoic acid, a two double bond, and linolenic or octadecatrienoic acid, a three double bond acid, have a very large number of possible positional isomers.

A third type of isomerism is also possible at every point in a fatty acid chain at which a double bond occurs. This type is known as *cis-trans* isomerism. For purposes of illustration let it be assumed that one end of a fatty acid chain with respect to the double bond may rotate 180°, with the double bond as a pivot. When rotated so that the carbon chains are adjacent to each other, the molecule is said to be in *cis* configuration. Obversely, when the rotatable end of the chain is in opposite position to the fixed end, the configuration is said to be *trans*. Very nearly all naturally occurring unsaturated fatty acids occur in *cis* configuration; however under conditions of hydrogenation *trans* acids may be formed in the reduction of more unsaturated *cis* forms. In general, the *trans* isomers of a given unsaturated fatty acid are higher melting than the *cis* form. For example, oleic acid or *cis* 9-10 octadecenoic acid is normally liquid while its *trans* isomer, called elaidic acid, is solid at room temperature.

In illustrating the great diversity of possible reactions in the hydrogenation of glycerides, Bailey, in his book "Industrial Oil and Fat Products" considers a glyceride molecule made up of linolenic acid in the α position, linoleic acid in the β position, and oleic acid in the α' position, the whole containing 6 double bonds. He points out that at the first contact between this molecule and hydrogen on an active catalyst surface there is the possibility of forming one of no less than eight different glyceride molecules, depending only on which of the six double bonds present is first hydrogenated. Whichever of these eight possible molecules occurs, there will still exist a multiplicity of possibilities on the second contact, and similarly on each subsequent contact until but two double bonds remain. Even at this point there is still opportunity for variation in the reaction unless the remaining double bonds occur in symmetrical steardiolein.

With the foregoing in mind, when it is considered that naturally occurring fats or oils contain numbers of different glycerides rather than a single one, and may in the aggregate be made up of five or more different fatty acids, it becomes at once apparent that the overall hydrogenation reaction can be exceedingly complex. No methods of analysis exist which would permit following the whole of the reaction, and, as a matter of fact, it is only with considerable difficulty that the main trends of it may be discerned. It is for this reason that practical control of hydrogenation rests largely on physical measurements of the end-product rather than in its chemical structure.

2. *Selectivity in Hydrogenation.* Although no mention was made of it in the foregoing discussion of the possibilities of isomerization in the hydrogenation of fats, it must be obvious that some isomers will be formed more readily than others; that is, there will be a definite trend in the course of the reaction. It is rather to be expected that the most highly unsaturated fatty acids will be hardened preferentially to those of lesser unsaturation. The degree to which such preferentiality is manifest in a reaction is related to the factor called selectivity.

As originally used by Richardson and his co-workers in 1924, selectivity referred to the conversion of linoleic acid to oleic acid preferentially to the conversion of oleic acid to stearic acid. More recent work by Hilditch indicates that selectivity is related to the hydrogenation of acids containing active methylene groups preferentially to acids which do not. In a theoretical sense an oil hardened with perfect selectivity would first have all of its linolenic acids reduced to linoleic before any linoleic was reduced to oleic; then all linoleic acids would be reduced to oleic before any oleic acids were saturated. Of course, in actual hydrogenation nothing of this sort happens; however, by suitable operating conditions and catalysts, it is possible to vary the ratio of the hydrogenation rate of linoleic acid to that of oleic acid over the range of 4 to 1 in a very nonselective reaction to 50 to 1 in a very selective one. Selectivity as defined in a theoretical sense does not specifically refer to hydrogenation carried out in such a manner as to attain the lowest iodine value for given melting point or congeal point although this may parallel true selectivity.

From a practical point of view the hydrogenation of oils is always accompanied by the formation of various amounts of the higher melting isomers of oleic acid which are grouped together in hydrogenation

parlance as "isooleic acids." The amount of these isooleic acids formed is in direct proportion to the true selectivity of the reaction. It is for this reason that reactions which result in a product having its congeal point close to its melting point—a condition resulting from the presence of relatively large amounts of isooleic acids as compared with the amount of saturated acids—is called "selective" by the practical hydrogenation technologist. However, at the same level of selectivity, different catalysts may vary widely in the amount of iso acids formed at the same degree of iodine value drop. For example, catalysts self-poisoned with sulfur are known to promote the formation of isooleic acids to a much greater degree than normal catalysts when hardening the same oil to the same iodine value.

Selectivity in hydrogenation is affected by conditions aside from the nature of catalyst used. In general, increasing the temperature increases the selectivity of the reaction and at the same time increases the formation of isooleic acids. Decrease of hydrogen pressure increases selectivity. Using the same conditions, increase of catalyst concentration increases selectivity. While the degree of agitation in a hydrogenation converter is generally fixed, and therefore not a factor, it has been shown experimentally that selectivity is increased by less vigorous agitation and is decreased by more vigorous agitation, other conditions remaining constant.

In the foregoing there is one common factor which tends toward selectivity of hydrogenation, and that factor is the limitation of the amount of dissolved hydrogen adsorbed at the active catalyst surface. It appears that under conditions in which the active catalyst centers are "starved" for hydrogen, the hydrogen is preferentially directed to the more reactive positions in the oil molecule, or toward the more unsaturated of the fatty acids. That decrease of hydrogen pressure or decrease in the rate of agitation will cause hydrogen "starving" of the active centers is obvious because solution of hydrogen in the oil is slowed thereby. Also if an increased number of active centers are made available, that is, catalyst concentration is increased, without increasing the dissolved hydrogen supply (which depends on temperature and pressure, assumed to be constant in this instance), then "starvation" results because a greater number of active centers compete for the available hydrogen supply. Increasing temperature, all other factors remaining constant, increases reaction speed, which has the same effect as increasing catalyst concentration, since it increases competition for the available supply of hydrogen; hence "starving" with respect to dissolved hydrogen at the active catalyst centers results.

3. *Control of Selectivity in Practical Hydrogenation.* In practical hydrogenation the operator makes use of the factors of hydrogen pressure, reaction temperature, and the activity and concentration of the catalyst to produce the desired or specified qualities in the final product. The control of all of these except catalyst activity is obvious. Of the latter perhaps some mention should be made.

The original activity of a catalyst can be measured by suitable laboratory test, taking into consideration the speed with which a test oil may be hardened a given degree under standard conditions. It is well known, of course, that catalysts show more or less rapid decrease in activity and selectivity upon use,

due probably to slow poisoning by products of side reactions in the oils or to traces of catalyst poisons in the hydrogen. However, no matter how pure the hydrogen or how well refined the oil, catalyst deterioration inevitably occurs with repeated usage. For this reason it is common practice in the industry to employ new catalyst for products requiring the greatest degree of selectivity. These once-used catalysts are then generally segregated or combined in lots of suitable size to permit identification. They are then re-used by lots, care being taken to maintain the identity of each. Depending on the activity shown in the last previous reaction the lots are graded downward through several grades. Each succeeding grade is used for products requiring a lower degree of selectivity, until finally the nearly spent lot is used for the hardening of stearine. In the latter usage selectivity is of no consequence since the final aim is substantially complete saturation, and it makes no difference if it is arrived at by a selective or a nonselective route.

4. Practical End-Point Control in Hydrogenation. In any hydrogenation operation except those carried out to make stearines, the ultimate aim is to produce a partially hardened stock of a definite preconceived consistency at room temperature or thereabout, or a stock suitable for blending with other stocks to produce such a product. Because of inevitable variations in the oils used, and in catalyst activity and selectivity, batch to batch variations in composition and consistency are encountered even when precisely the same hydrogenation conditions are maintained from one lot to the other. It therefore becomes of paramount importance to devise some means of control which will permit the reaction to be stopped at a point which will provide the desired consistency. As was pointed out earlier, because of the great complexity of the hydrogenation reaction, physical rather than chemical methods are relied upon to provide this control. These are generally applied toward the end of the hydrogenation run although means related to iodine value may be used in the earlier stages.

Control by Refractive Index. Because iodine value decreases directly with hydrogen absorption, extrapolation of a time-iodine value curve could serve to follow the course of a hydrogenation. However even the most rapid iodine value method is too slow to keep up with a rapidly moving reaction. In a dead-end type of system, free from appreciable leakage, the actual absorption of hydrogen may be used as a control although this is not possible in a recirculation or purge type system. In any type of hydrogenation system though, advantage can be taken of the fact that for a given oil the relationship between its iodine value and refractive index at different degrees of hydrogenation is essentially a straight line curve. It is therefore possible to follow the course of hydrogenation by following the change in refractive index of an oil, providing that the refractive index-iodine value curve for that particular oil is known.

The instrument generally chosen for this application is the butyro or the dipping refractometer. The latter, when equipped with heated split prisms, is particularly well adapted for hydrogenation work because of its high degree of precision. The direct reading Abbé instrument is not suitable because it is incapable of the required degree of resolution. Both the butyro and the dipping refractometers read in arbitrary units, the scale being graduated from 0 to

100, with provision for vernier reading of tenths of units. Actual refractive indices with these instruments must be determined by reference to tables although it is the usual practice merely to relate the iodine value curves to the arbitrary scale units. One readily becomes accustomed to thinking of refractive index in terms of these scale units, and it is likely that some hydrogenation plant operators are unaware that these arbitrary scale readings are not actually refractive index values.

In operation, the course of a hydrogenation reaction is followed by means of the refractometer until a value is reached at, or a little short of that which experience indicates to be the highest iodine value at which the desired consistency will be attained. The reaction is then halted while other physical tests which correlate more closely with consistency are applied.

Physical Tests Related to Consistency. A number of physical tests related to consistency by experience are used throughout the industry, with more or less minor differences from operator to operator. One such test is the congeal or setting point. The general nature of this test is as follows. A definite quantity of the clear, melted fat is cooled under standardized conditions with vigorous stirring until a certain degree of clouding occurs. The clouded fat is then allowed to stand quiescent in an air bath at or near room temperature. The degree of temperature rise due to the heat of crystallization of the supercooled fat is noted, the highest point reached, or the temperature at which the rising curve levels out being the congeal point or setting point. This value, in general, is somewhat more closely related to the consistency of a fat than is its melting point.

A variation of the congeal-setting test is the cloud point test, in one version of which the fat under test is stirred mechanically while being simultaneously cooled by streams of chilled water. A light beam of known intensity passes through the fat, falling on a photo cell, the output of which is read on a microammeter. The cloud point is the temperature at which the intensity of the light beam is reduced to 20 foot candles by the clouding of the fat in the light path, the original illumination having been 120 foot candles when the fat was completely liquid. In this method the temperature rise upon crystallization is not noted.

A third method, described by Harrington in 1945, is known as the "C" number test. In this method the molten fat in a tube of definite dimensions and weight is subjected to an up-and-down stirring by means of a dasher type stirrer, while being cooled under controlled conditions. When the fat increases in viscosity due to partial solidification to the extent that the tube rises with the plunger, an electrical contact signals the end-point. The "C" number is the temperature at that point.

All of these methods have in common the fact that they are related to actual consistency through extensive past experience and must be constantly verified by continuing subsequent check against consistency as determined by penetration or similar tests of the finished product. Bailey, on the other hand, used a micro-penetration technique which actually measured the consistency of very small samples chilled, tempered, and penetrated under controlled conditions. Even so, the micro-penetrations must finally be justi-

fied by comparison with the consistency of the final product.

It goes without saying that all such tests must be capable of performance in as short a time as possible and, in general, require from 10 to 40 minutes. During this time operations are at a standstill awaiting the results of the tests. Upon these results the operator projects further hardening as his judgment indicates. Of course, the smaller the steps of final hardening and the more frequent the final testing, in general the more accurately the batch may be brought off within the desired limits. Against this is balanced the loss of operating time while awaiting analysis.

Dilatometry as a Hydrogenation Control. The use of dilatometric measurements by means of which the actual solids content of a fat at any temperature up to its melting point may be determined has intriguing possibilities as a means of hydrogenation control. The solids content of a fat over this range of temperature is directly related to its consistency. At the present, so far as is known, no system of dilatometric measurement sufficiently rapid to permit its use for direct control of hydrogenation has been devised. To obtain reliable results with this method certain elements of time are involved which appear to be very difficult of abridgement. As a result the method is generally of more use in controlling the consistency of blends made up of hydrogenation batches controlled by more conventional methods.

5. Postbleaching of Hydrogenated Stocks. While bleaching following hydrogenation is not, strictly speaking, a part of the hydrogenation process, it is directly related thereto and often is physically a part of the hydrogenation plant. For this reason it will be discussed briefly.

Postbleaching following hydrogenation is generally done for one or both of two reasons: a) to remove traces of nickel, often colloidal in nature, which escape the catalyst recovery filtration, and b) to remove undesirable colors, generally of greenish hue. Traces of nickel are removed to prevent subsequent deleterious effects on the oil due mainly to oxidative effects catalyzed by the nickel. Simple filtration with diatomaceous earths usually suffices for the removal of nickel.

Green colors emerge in hydrogenated oils because of the reduction of yellowish or reddish masking pigments in the course of hydrogenation. It frequently occurs that oils, particularly soybean stocks, appear to be light-colored due to a balance of mutually cancelling reddish carotenoid and green chlorophyllic pigments. In the course of hydrogenation the carotenoid pigments are reduced to a colorless form while the chlorophyllic pigments merely have their absorption maxima shifted from 660 to 640 μm . With the removal of the masking reddish pigments, the greenish pigments predominate, resulting in a greenish-colored oil. These greenish pigments are readily removed by adsorption on acid activated clays, which incidentally serve to remove traces of nickel. Postbleaching may be done by atmospheric batch bleaching methods; however advantages in lower earth usage and protection of the stock from atmospheric oxidation accrue from the use of vacuum postbleaching.

Hydrogen Safety

The process of hydrogenation always presents a potential hazard due to the wide limits of flammabil-

ity of mixtures of hydrogen and air. For this reason it seems desirable to close this discussion with a brief consideration of safety in the hydrogenation plant.

1. Limits of Flammability of Hydrogen-Air Mixtures. In any mixture of flammable gas with air there is always an upper limit of the concentration of the flammable constituent above which the mixture is too rich to burn, and a lower limit below which the flammable component is too diluted to support combustion. In the case of the system of hydrogen and air these limits are quite wide, the upper limit occurring at 75% of hydrogen in the mixture and the lower at 4%, under conditions of atmospheric temperature and pressure.

Increase of pressure above atmospheric at first narrows these limits slightly, but on further increase the limits become widened. At subatmospheric pressures the limits show little change until an absolute pressure of 300 mm. is reached. From this point further decrease in pressure narrows the limits of flammability until at 50 mm. absolute pressure no mixture of hydrogen and air will propagate flame. Increase of temperature widens the flammability limits, the lower limit dropping at about 0.83% per 100°C. rise, while the upper limit increases at about 2.75% for the same temperature increase.

The sustained pressure system of hydrogenation operation, in which at least some positive hydrogen pressure is maintained in the converters at all times, makes sure that a hydrogen content well above the upper limits of flammability is maintained in the closed vessel. The vacuum system on the other hand removes either hydrogen or air so completely that when the opposite gas is admitted to the vessel, the mixture will be well above or below the limits of flammability, as the case may be.

2. Safety Precautions in the Plant. Safety considerations in the plant hinge on two basic tenets. First of these is the avoidance of the formation of flammable mixtures at any time in the plant, and since flammable mixtures, if formed, do not ignite spontaneously, the second is the avoidance of sources of possible ignition.

Outside of the hydrogenation equipment, the next most likely cause of the formation of flammable mixtures is the pocketing of hydrogen released by leakage or faulty operation in the surrounding building. Because of the very low density of hydrogen the best defense against this is adequate ventilation. The roof above hydrogenation apparatus may be provided with adequate louvered openings which cannot be shut. If the vessel extends through floors, the area immediately surrounding the openings may be made of open gratings. The matter of ventilation as a safety measure is so well regarded that hydrogenation plants are now being built completely in the open, with only the controls and instrumentation being housed.

In the matter of avoidance of possible ignition of pocketed flammable mixtures, the prohibition of smoking or the carrying of matches and lighters in the hazardous area is obvious. The matter of ignition from electrical equipment is apparently viewed differently by different companies in the field. Some adhere strictly to explosion-proof wiring and electrical equipment, some use only explosion-proof agitator motors, and others use conventional wiring and depend on efficient ventilation of the surrounding area. In general, the hazard must be balanced against the

cost of installation and maintenance of explosion-proof electrical equipment.

3. *Safety in Mechanical Work.* Most hydrogenation plants have experienced small "pop" explosions of hydrogen at one time or another. These often are caused by welders or other mechanics in the course of repair work on hydrogenation equipment. The safest procedure if hydrogen-containing vessels must be worked on is to isolate the vessel, fill it completely with water, and empty it before entering it or working on it. In this regard it is advisable to break all hydrogen connections to the vessel because valves cannot be depended upon to hold hydrogen without some leakage, due to its tenuous nature.

Aside from the mechanical aspects of safety the thorough indoctrination of both supervisory and operating personnel in safe operating practices and safety consciousness is extremely important. Surveys of accidents incidental to the handling of hydrogen indicate that many more such accidents were attributable to operator mistakes than to mechanical causes.

Conclusion

In the brief space available an attempt has been made to survey the theoretical and practical aspects of the hydrogenation of fatty oils. That the view of the field presented was necessarily abridged becomes obvious when it is considered that hydrogenation has become almost a sub-science of its own. However, de-

spite the large amount of developmental work which has been done on the process and the magnitude of the commercial operations carried out with it, the published literature on hydrogenation is surprisingly meager.

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Deodorization

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DEODORIZATION implies steam stripping of preredefined glyceride oil at elevated temperature under low absolute pressure to produce a bland or palatable edible oil. This is a simplified modern definition. For a more inclusive and general meaning, as well as for historical background and additional details, there are three recent references which can be used (1, 2, 3). Within the limits set by this simplified definition, there are three main categories: Theoretical Approach to Deodorization, Deodorization Systems in Current Use, and Engineering Aspects of Deodorization Equipment.



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Theoretical Approach to Deodorization

As stated in the definition, deodorization implies stripping or distillation of volatile undesirable constituents from a preredefined

temperature. However the principal measurable difference is the reduction in free fatty acid content of the oil. This measurement of reduction in free fatty acid content has generally been used as a yardstick by which progress of deodorization may be estimated. Yet it is not a perfect yardstick since oil stability does not improve indefinitely with reduction in free fatty acid content. The stability may actually increase at the start of deodorization and decrease toward the finish (4).

Thus deodorization is an operation which principally removes volatile materials from the oil which are undesirable in the finished product. It may also change the chemical nature of trace constituents. With this background we can set down the various factors which influence the quality of finished deodorized oil.

a) The preparation of oil for the deodorizer has a significant effect upon the finished deodorized product. Needless to say, if the refining and bleaching operations leave appreciable amounts of non-volatile metallic soaps in the oil, the deodorized oil will contain most of these and will be subject to whatever effects these contaminants have on the oil. Thus the first requirement of good deodorization is to make sure that the refining and bleaching steps preceding deodorization are properly carried out. The complete chemistry of edible oils has not been fully worked out although the procedure needed to change a crude oil into finished deodorized products has been well de-

edible oil. During this operation it is possible that the chemical nature of some constituents in the oil may be changed as a result of the treatment at high