The Hydrogenation Process

S. G. SOURELIS, Wurster and Sanger Inc., Chicago, Illinois

S. G. Sourelis

THE HYDROGENATION PROCESS is commercially very important to the fatty-oil industry. By hyrogenation, liquid oils such as cottonseed and soybean are converted into plastic fats. These fats are used in the manufacture of shortenings, margarine, and in a variety of other edible and industrial fat products.

Hydrogenation involves the chemical addition of hydrogen to the unsaturated carbon - to - carbon double bonds in a fatty-oil or fatty-acid molecule. The reaction is carried out by mixing the heated oil and hydrogen gas in the presence of a catalyst.

In this paper a brief review of the technology of this hydrogenation reaction is presented. Other reactions sometimes referred to as "hydrogenations" involve also the splitting of the fatty-oil or fatty-acid molecule, and the term "hydrogenolysis" is more applicable in describing them. The preparation of fatty alcohols by hydrogenolysis of the carboxyl group of a fatty acid is a good example of such a reaction.

General Considerations

Selectivity

Under proper conditions the hydrogenation reaction takes place readily and can be continued until the oil is completely hydrogenated, *i.e.*, until all of the double bonds are saturated. In such a case a relatively hard fat is produced. In the manufacture of most products however softer fats are required, and oils are only partially hydrogenated.

The objective in partial hydrogenation is to establish certain conditions for the reaction in order to hydrogenate selectively certain double bonds and not others.

Selectivity in a general sense can be defined as the preferential reduction of the more unsaturated molecules in the fatty oil (2). Complete selectivity has never been achieved. In practice the conditions established for the hydrogenation allow certain reactions to proceed at a faster rate than others and in this way provide some degree of selectivity. When a hydrogenation reaction is said to be selective therefore, it is necessary to state the chemical or physical properties that are selectively achieved. In other words, these properties measure the degree of selectivity and also serve to define it.

A variety of reactions will take place at the same time because fatty oils are really complex mixtures of different triglycerides. The properties of these triglycerides before and after hydrogenation depend upon the particular structure and position of their fatty acid radicals. Their fatty acids will vary in size and degree of unsaturation and will also exist in isomeric forms which are greatly influenced by hydrogenation. We can actually think of hydrogenation as a combination of hydrogen addition and isomerization of these fatty acid radicals.

Figure 1 represents the structure of a typical mixed triglyceride, such as is found in many fats and oils. In this particular molecule each of the fatty acid radicals contain 18 carbon atoms which differ only in their degree of unsaturation. When this triglyceride is completely hydrogenated, both the linoleic and oleic radicals are converted to stearic. This results in a completely saturated molecule known as tristearine.

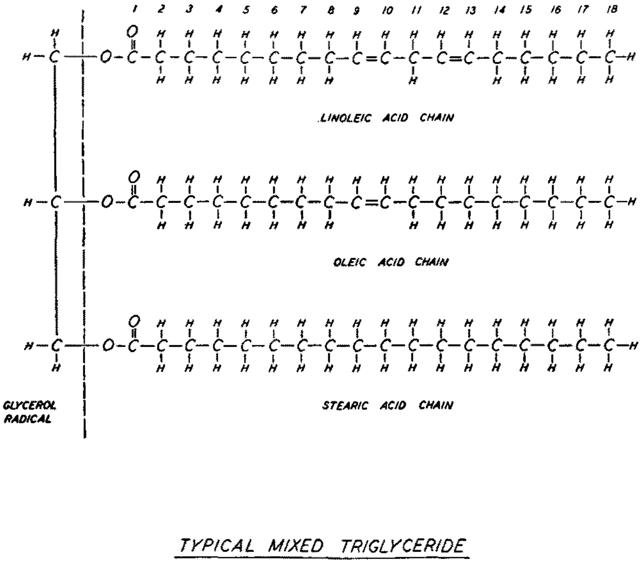

FIG. 1. Typical mixed triglyceride β-oleolinoleostearin.

However when the triglyceride is only partially hydrogenated, a variety of products are formed, depending upon which of the double bonds are saturated, and depending also upon which isomers are formed among the remaining unsaturated acids.

Theoretically the double bonds can exist anywhere in the fatty acid chains. For example, linoleic acid has double bonds at the 9:10, 12:13 position as shown in the figure. Two other isomeric acids are also found: one with double bonds at the 9:10, 15:16 position and another with double bonds at the 12:13, 15:16 position. Each fatty acid with a double bond can also exist in either a *trans*- or *cis*-configuration, that is, the chain can be straight somewhat as shown for oleic acid or folded back on itself at the double bond. With two or more double bonds there can be a combination of *cis*- and *trans*-arrangements.

Many different configurations are possible therefore in this one triglyceride, each with somewhat different properties and each influencing the hydrogenation either directly or through the formation of isomers. All of these possible forms multiplied by the number of different triglycerides present in fatty oil make a direct chemical approach to hydrogenation very difficult. In practice we have to depend upon a great deal of experience in order to establish the best conditions for carrying out any particular hydrogenation.

In general, the more unsaturated acids are usually the first to be hydrogenated, and the reaction tends to be selective in this way (2). This kind of selectivity is very important since the more unsaturated acids are the least stable, and their reduction improves the stability of the product. A selective reaction is therefore desirable. At the same time however it is necessary to control the formation of isomers among the unsaturated acids. The isomers produced by hydrogenation are usually of higher melting point than their normal forms. In this respect the *trans*-isomers of oleic acid are of particular concern, and all isomers produced are often referred to as "iso-oleic" isomers even though they may be isomers of other unsaturated acids.

An oil partially hydrogenated to a certain degree of unsaturation, as measured by its iodine value, will therefore show wide variations in its composition and physical properties, depending upon which of the many possible reactions predominated. The technology of hydrogenation is concerned with the control of these reactions in order to achieve certain characteristics in the product.

The over-all rate at which hydrogenation takes place and the composition and characteristics of the final product depend upon the following factors: the type of catalyst used, the catalyst concentration in the oil, the hydrogen gas pressure, the temperature of the reaction, and the degree of hydrogen gas dispersion. The most important factor perhaps is the type of catalyst used. Finely divided nickel metal catalysts are commonly used in commercial hydrogenation.

The accepted theory is that the reaction takes place on the surface of the catalyst where the oil and gas molecules are adsorbed and brought into close contact (1). It is understandable therefore that any condition which affects the catalyst surface or which controls the supply of gas to the catalyst surface will in turn affect the course and rate of the reaction.

In examining the methods and results of practical hydrogenations, it is generally concluded that the selectivity of the reaction is favored by low pressure, high catalyst concentration, high temperature, and low degree of gas dispersion in the oil. To explain this, it has been suggested that the selectivity of the reaction is favored by a low concentration of hydrogen gas on the surface of the catalyst (3). Apparently a limited supply of hydrogen gas tends to react with the more unsaturated molecules.

This explanation is certainly reasonable but it may not apply in all cases. Some investigators have reported results that appear to contradict a relationship between selectivity and the concentration of hydrogen gas on the catalyst surface (6, 12). It should be realized that the theoretical aspects of hydrogenation are not very well established and that in practice hydrogenation is as much an art as it is a science.

Differences in the design of equipment, variations in catalyst activity and selectivity, and the type of oil and its pretreatment make it necessary for the operator to vary the conditions of the hydrogenation based also upon his specific experience. It is common to find somewhat different conditions employed in different plants for the production of almost identical products.

As a rule, commercial hydrogenations are carried out with a fixed, high degree of gas dispersion and a catalyst concentration somewhere between 0.05 to 0.15% of nickel based upon the weight of the oil charge. Adjustments of the temperature and pressure are depended upon to give the various degrees of selectivity required for different products. At temperatures below 200°F. the reaction proceeds too slowly, and such operation is uneconomical. To minimize decomposition of the oil and sintering of the catalyst, the maximum temperature used rarely exceeds 425°F. Pressures in the range of 0–100 p.s.i.g. are commonly employed, and in certain cases the reaction may even be conducted under a slight vacuum. The advantage of using pressures above 100-lbs. gauge is usually offset by higher equipment and operating costs. However, for fatty acids and other inedible materials which are difficult to hydrogenate, it is common to use pressures of up to 400 p.s.i.g. in order to accelerate the reaction.

Type of Catalyst

Nickel metal catalysts sometimes promoted with copper or aluminum oxide are commonly used in commercial hydrogenation. These catalysts are prepared by special methods in order to provide an extended surface which is highly active and as selective as possible.

The catalyst surface is envisioned as consisting of active centers where nickel atoms are presumed to extend beyond the surface (1). It is these active centers that attract and hold the oil and gas molecules, causing their reaction. The number, activity, and space relations of these active centers establish the properties of the catalyst and differ with the methods of preparation. The manufacture of catalysts with uniform properties is very difficult, and even with careful control catalysts prepared by identical procedures will often exhibit some variation in their activity and selectivity (5).

Some catalysts cause the formation of iso-oleic isomers to a greater extent than others. Such catalysts are known as iso-promoting and are useful in the hydrogenation of margarine oils, for example. An iso-promoting catalyst may at the same time be nonselective. In other words, such a catalyst will cause the formation of isomers and also saturated acids to a greater extent than it brings about the reduction of highly unsaturated acids. This type of catalyst is undesirable for partial hydrogenation. It can, of course, be used for complete hydrogenation where the selectivity of the reaction is not a factor. Very selective catalysts which are also iso-suppressing are useful in the hydrogenation of shortening oils where the formation of isomers is undesirable.

Different types of catalyists are therefore prepared, depending upon their use. The most common method of preparation, known as wet reduction, involves the thermal decomposition of nickel formate salts. The nickel formate is mixed in oil and heated to 475°F., where it rapidly decomposes to form a finely divided nickel metal powder. Wet-reduced catalysts prepared by this method have good activity and are produced in various grades of selectivity (14).

In another method, nickel carbonate precipitated on diatomaceous earth is reduced with hydrogen gas in a furnace heated to as high as 1,000°F. Catalysts prepared by this method are known as dry-reduced. These catalysts are less active than the wet-reduced type but are somewhat more stable for high temperature use and are easier to filter from the hydrogenated oil product (2).

Some years ago it was common practice for the oil processor to prepare his own catalysts, usually from nickel formate by the wet-reduction method. Today however, catalysts of good quality and uniformity are available from chemical companies specializing in their manufacture. Generally it is more economical and preferable to purchase ready-made catalysts, which are available in the form of solid blocks or flakes containing about 25% nickel suspended in a hydrogenated oil.

Purity of the Materials

The purity of the oil and hydrogen gas is, in a sense, a condition of the hydrogenation reaction. Impurities affect the reaction chiefly by poisoning the catalyst surface. Certain impurities reduce the activity of the catalyst and its selectivity and may also increase its ability to form isomers.

Soaps, phosphatides, carbohydrates, and related compounds inactivate the catalyst by being permanently adsorbed on its surface. Fatty acids gradually destroy the catalyst by reacting with it to form nickel soaps. Oxidized glycerides and peroxides are also claimed to reduce catalyst activity and selectivity (9).

Careful refining and bleaching, and proper storage and handling of the oils prior to hydrogenation will therefore prolong the life of the catalyst and allow better control of the reaction.

Sulfur compounds and carbon monoxide which occur as impurities in hydrogen gas produced by the steam-iron or the steam-hydrocarbon process are strong catalyst poisons. Carbon monoxide is an unusual poison insofar as it does not permanently inactivate the catalyst and can be removed by high temperature or vacuum. Its poisoning effect therefore depends particularly upon the temperature of the hydrogenation. At 400°F. as much as 0.5% can be tolerated whereas at 200°F. a few thousandths of 1% of carbon monoxide will virtually stop the reaction (2). Other impurities found in commercial hydrogen gas, such as nitrogen and carbon dioxide, do not poison the catalyst, but if they are allowed to accumulate in the equipment, they will slow down the reaction by diluting the hydrogen gas. This is, of course, equivalent to reducing the hydrogen pressure and can also affect the selectivity of the reaction.

Products of Hydrogenation

The primary products of hydrogenation are margarines and shortenings. Many different fats and oils are used in their manufacture. The special characteristics of these products however depend mostly upon how the fats are prepared by hydrogenation.

Margarines

Margarine oils are hydrogenated to produce a fat similar in physical characteristics to butter-fat with some exceptions. Ordinary butter is too brittle at refrigerator temperatures and also gets too soft and oily at room temperatures.

Margarine is made therefore to be somewhat softer than butter at low temperatures but still firm at room temperatures. It is most important, of course, that margarine also melt completely at body temperatures in order to avoid a pasty sensation in the mouth.

These characteristics require that margarine oils be hydrogenated under highly selective conditions with low pressures, in the range of 0–5 p.s.i.g., and temperatures as high as 400°F., using 0.10–0.15% of a very selective catalyst, which is also iso-promoting.

These conditions are employed in order to produce large amounts of iso-oleic acids and to minimize the formation of high-melting saturated acids. The iso-oleic acids, which melt at near body temperature, also impart the required firmness in the product at room temperature.

Shortenings

The use of shortenings in baked goods requires that they have an extended plastic range. They should be soft and plastic at room temperatures and still possess some body at temperatures close to 100°F., with melting points in the range of 104° to 109°F. The stability of shortenings is very important since they are exposed to high temperatures in baking and frying and are not usually refrigerated.

In preparing shortening fats by straight hydrogenation, these characteristics impose a rather conflicting set of operating conditions. Selective conditions are desirable in order to convert all linolenic and linoleic acids to oleic and stearic for maximum stability. However selective conditions also favor the formation of iso-oleic acids. Iso-oleic acids are undesirable in shortenings. They have much higher melting points than normal oleic but do not offer any improvement in the stability of the product. Furthermore, since they are high-melting, they restrict the amount of saturated acids that could otherwise be formed with greater benefit to the stability of the product. Saturated acids also serve to extend the plastic range and provide the higher temperature body required.

In practice therefore the operator compromises by using moderately selective conditions, with relatively low temperatures in the range of 200–300°F., pressures as high as 60-lbs. gauge, and a catalyst concentration of 0.05 to 0.10%. Selective catalysts are used which are also iso-suppressing in order to minimize the formation of iso-oleic acids.

Some manufacturers hydrogenate the oil more selectively and add stearines to give the product the high temperature body required. With this method, of course, it is easier to control the consistency and plastic range by adjusting the amount of stearine used to compensate for variations in different hydrogenated stocks. Although the products are somewhat less stable than those prepared by straight hydrogenation to the same consistency, they are satisfactory for general-purpose shortenings.

Very often a blend is made of two or more stocks, each of which is hydrogenated to a different degree and selectivity. There is a further advantage in this method when making shortenings from soybean and cottonseed oils. The soybean oil is hydrogenated to the greater extent to stabilize it against flavor reversion and is blended with less hydrogenated but more stable cottonseed oil (2).

In the hydrogenation of special shortenings for deep fat frying and for biscuit and cracker manufacture, the highest possible stability is the first consideration. Since an extended plastic range is not too important, these products are prepared by straight hydrogenation and under more selective conditions than are used for general purpose shortenings.

Stearine

In the hydrogenation of oils to make stearines, selectivity is unimportant since the oils are almost completely hydrogenated. Both high temperatures, in the range of 400–425°F., and pressures, up to 100 p.s.i.g., are employed to make the reaction progress as rapidly as possible. Quite often, catalysts are used which have lost some selectivity from previous use on shortening or margarine stocks.

Stearines are mostly prepared for use in blended shortenings or for stiffening soft lards. In the early days of hydrogenation, shortenings were made by mixing various amounts of stearine with unhydrogenated vegetable oils. These products were known as "compounds" and are still very popular in many countries. Of course, they are not nearly as stable as the all-hydrogenated shortenings made in this country but are simple to make and less expensive.

Inedible Fats and Fatty Acids

Inedible fats and fatty acids are usually hydrogenated to a high degree of saturation. The hydrogenation of these materials is similar to that for edible oils except that high temperatures are avoided to prevent decomposition of the more sensitive fatty acids. The reaction is somewhat difficult because of the many impurities which cannot be economically removed from inedible stocks. Pressures as high as 400-lbs. gauge and catalyst concentrations of 1% or more may be required for such hydrogenations.

Miscellaneous

The foregoing applications of hydrogenation for which the process is most commonly used involve the conversion of oils into plastic fats of much higher melting points. Hydrogenation is useful also in some other respects which should be briefly mentioned.

Soft lards are often partially hydrogenated to improve their consistency and resistance to atmospheric oxidation. Partial hydrogenation of lard is carried out under selective conditions in order to reduce the more unsaturated and less stable fatty acids.

The effect of hydrogenation in improving the color of most oils, notably by the reduction of carotenoid pigments, has been developed into an interesting process known as "hydrobleaching." Even with the usual conditions of hydrogenation, substantial color reduction is effected. However, by using a special co-precipitated nickel-iron-copper oxide catalyst, remarkable bleaching takes place. In a recent patent granted to Paterson of Lever Brothers Company an example is given, using such a catalyst (10). The color of a cottonseed oil sample was reduced from 35 yellow—6.5 red to 2 yellow—0.2 red. The hydrobleaching was carried out at 1,800 p.s.i.g. and close to 400°F., using 0.2% of this special catalyst. It is not known to what extent the process is used industrially. If the exceptional results reported in the patent are typical and the operation is economically favorable, hydrobleaching should find wide use.

Hydrogenation destroys most of the natural odor of fats and oils. The process is used for this purpose to reduce the strong odors of many fish oils, which cannot be removed by ordinary steam deodorization. Very mild conditions are employed to minimize hydrogenation of the oil, and the operation is carried out at temperatures slightly above 200°F. and under slight vacuum (11).

The Plant and Equipment

Complete plant facilities for the manufacture of hydrogenated fats will normally include most of the unit processes and operations familiar to the fat and oil industry. A typical plant will consist of the following sections: 1. storage, measuring, and handling facilities for crude, intermediate, and finished oil; 2. refining and bleaching equipment for preparing the oils for hydrogenation; 3. equipment for the generation, storage, and handling of the hydrogen gas required; 4. the hydrogenation equipment proper, consisting essentially of the reaction vessel or convertor, and auxiliary equipment for the handling and removal of catalyst from the hydrogenated oil; and 5. deodorizing equipment for the removal of undesirable odor and flavor in the hardened oil.

Gas Generating

Hydrogen gas is generated by various methods, depending upon the size of the installation and the relative operating costs. For capacities under 75,000 standard cu. ft. per day it is generally economical to produce hydrogen gas by the electrolytic method, except perhaps in areas where electricity is relatively expensive. Many small installations use gas purchased in cylinders or tank trucks. This is very convenient and sometimes more economical.

For capacities of 75,000 S.C.F. and over, the equipment and operating costs generally favor the steam-iron or steam-hydrocarbon process.

All commercial processes are automatic and continuous in operation and provide for some variation in capacity. In this respect electrolytic generating equipment is most versatile. Newly-developed, high-amperage electrolytic cells used in conjunction with selenium rectifiers can be started up in a half-hour from complete shutdown. The capacity of such an installation can be adjusted down to 25% of full load without affecting the operating efficiency.

Gas requirements vary with the particular oils processed and the degree to which they are hydrogenated. Theoretically 14.8 S.C.F. of hydrogen gas are required for each iodine value reduction per 1,000 lb. of oil. Allowing for venting and other losses, a practical figure of 16.5 S.C.F. is used for sizing the gas-generating facilities. This is equivalent to about 1,000 S.C.F. of gas per iodine value reduction per tank car (60,000 lb.) of oil hydrogenated.

The usual hydrogenation installations in this country range in size from about one tank car to 10 tank cars in daily-production capacity. For the manufacture of shortenings and margarine in these capacities gas generation facilities will range in size from about 50,000 to 500,000 S.C.F. per day.

A low-pressure gas-holder is used to receive the gas as it is generated. Since large volumes of gas are handled, it is customary to compress and store the gas at high pressure in a number of storage tanks, from which it is used directly in the hydrogenation plant.

The gas-generating and handling facilities are best located in an isolated area some distance away from the plant buildings, with most of the equipment installed out in the open.

Hydrogenation Equipment

The equipment required for the hydrogenation of oils is relatively simple. Although there have been some continuous and many different batch systems developed and used in the past, there is a definite preference today for the so-called dead-end system, employing a mechanically agitated, batch-type convertor.

Continuous Systems. Continuous systems have been developed and are used to a limited extent. Their general use has been restricted because of the wide variety of products normally hydrogenated, each of which requires somewhat different but precise control of selectivity.

The well-known continuous process developed by Bolton and Lush has found some use in Europe and South America, where it is reported that more than 40 installations have been made (11). These installations are very small and are apparently used for the production of stearine where control of the selectivity is not a factor.

In this country the Procter and Gamble Company has developed and is understood to be using, in at least one of their plants, a continuous process employing a powdered nickel catalyst. Patents issued in 1950 indicate that they may be using their process for partial hydrogenation of oils to shortening consistency.

The Kahn Company of Cincinnati, O., also has a continuous unit for the hydrogenation of lard, which has been in operation for several years. The equipment consists of a tall, vertical cylinder fitted with multiple turbine agitators, which provides about one hour hold-up at a capacity of 1,000 lbs. per hour. Lard is reduced to very low iodine values for the production of lard flakes, which are used to stiffen soft lards. The reaction is conducted at 125-p.s.i.g. pressure, at 400°F., with 0.4% nickel catalyst concentration.

Similar equipment is used by Canada Packers Ltd. of Toronto, Canada. Contact times of about 20 min. are provided with pressures as high as 250 p.s.i.g. for the partial hydrogenation of tallow and fatty acids used in soap manufacture.

Many other companies are undoubtedly experimenting with continuous methods and probably have small production installations. As experience is gained, continuous methods may be improved and become more popular. At the present time however batch methods of hydrogenation are required and are used exclusively by nearly all processors.

The Dead-End Batch System. A schematic arrangement of the basic equipment used with the dead-end batch system is shown in Figure 2. A catalyst mixer is provided for preparing a slurry of catalyst, filter aid, and oil, sometimes with the addition of activated carbon. This tank is fitted with an agitator and a jacketed bottom for steam heating. The catalyst slurry is transferred without the need of a pump since the convertor is under vacuum at the start of the operating cycle.

The evacuator, usually a single-stage steam ejector, is used for deaerating and drying the oil before it is heated to operating temperature.

The hydrogenated oil is pumped through a plate and frame filter press for removal of the catalyst. In operation the oil is initially circulated through the press and back to the convertor in order to build up a proper cake of catalyst and filter aid. The clear oil is then collected in an intermediate holding tank and may be treated with citric or phosphoric acid for complete removal of the nickel.

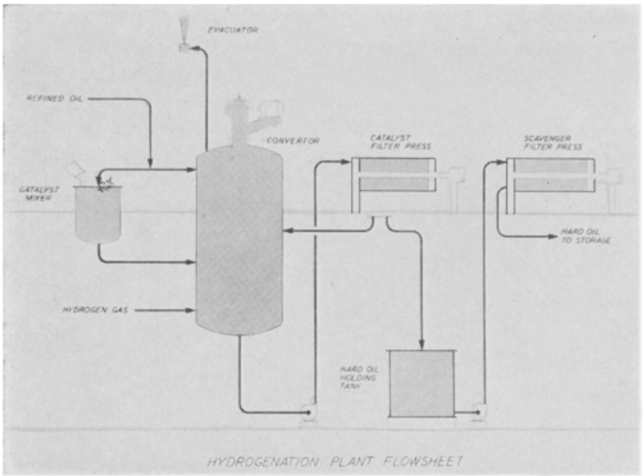

FIG. 2. Hydrogenation plant flowsheet.

The convertor is a closed, vertical, cylindrical pressure vessel constructed of high quality carbon steel or sometimes of stainless steel. Stainless steel construction is necessary however for the hydrogenation of fatty acids since they are very corrosive to plain steel at elevated temperatures. Dead-end convertors are designed for a maximum working pressure of about 100 p.s.i.g. in capacities of 5,000 to 40,000 lb. of oil. They are called dead-end convertors because the hydrogen gas is allowed to accumulate in the head space above the oil instead of being continuously recycled by an external blower or compressor.

Figure 3 shows the important features provided in

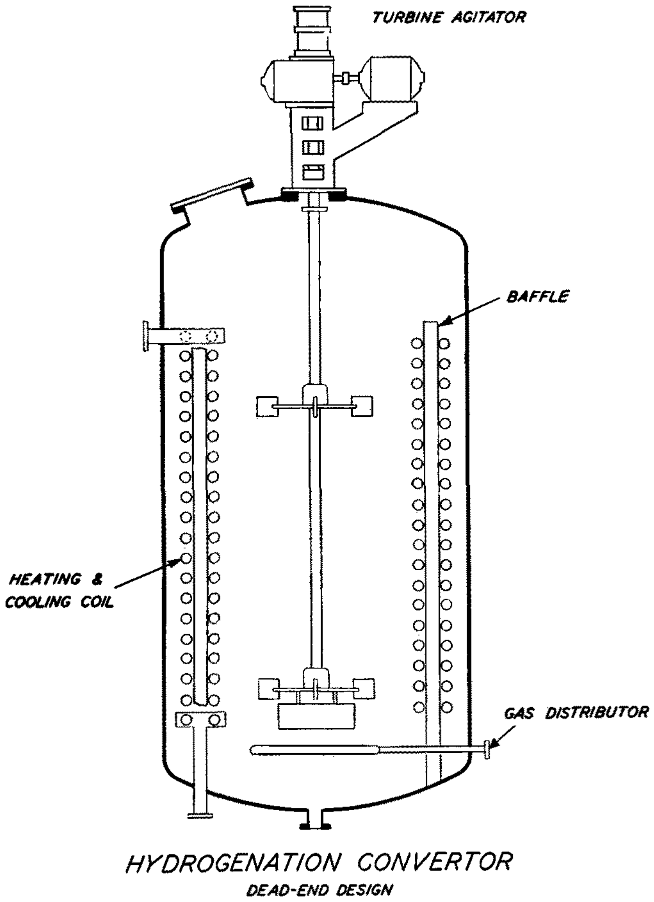

FIG. 3. Hydrogenation convertor dead-end design.

a modern convertor design. In this design a helical pipe coil is used for steam-heating and water-cooling. Proper agitation is provided by means of a turbine type of agitator, employing two or more impellers. Many different arrangements for agitating have been used successfully in the past. The turbine agitator however has been most successful and is popular today. The impeller of a turbine agitator consists of curved, vertical pieces attached to the rim of a flat, horizontal disc. Impellers are sometimes shrouded to increase the shearing effect on the gas in order to improve the dispersion. However it has been shown that shrouds restrict the circulation of oil and the fine bubbles of gas formed coalesce as soon as they leave the impeller, thereby defeating the purpose (8).

In order to avoid internal foot bearings to guide the long shafts required in large convertors, a stabilizing ring has been developed which prevents excessive shaft deflection (8). This is shown attached to the lower impeller.

The hydrogen gas is distributed, by means of a perforated pipe ring, to the outer periphery of the bottom impeller. Here the gas runs into a high velocity stream of oil to be dispersed and rapidly circulated. Vertical baffles, attached to the coil, cause the very high degree of turbulence desired.

Proper agitation is extremely important for the efficient operation of the convertor. Agitation is required not only for the rapid solution of hydrogen gas in the oil but also for adequate circulation of the oil to effect uniform and efficient heat transfer during the reaction, and for proper suspension and mixing of the catalyst solids throughout the oil batch.

Prior to the development of modern turbine agitators, designers often employed two or more separate means for insuring proper agitation.

A popular design years ago employed a propeller agitator and provided a pump to circulate the oil and catalyst from the bottom of the convertor into the head space (14). This arrangement also allowed the use of external exchangers for heating and cooling. In other designs the gas was also circulated.

The gas recirculation system with or without mechanical agitation is still commonly used in this country. The system was very popular prior to the development of modern gas purification methods for the steam-iron process. At that time considerable quantities of inert gases were carried over with the hydrogen. Such gas made it necessary to vent a dead-end convertor so often during the run that the operation was expensive, inconvenient, and lengthy. Large volumes of gas were therefore circulated through the oil by means of external compressors in order to absorb as much hydrogen as possible. In this way a small amount of gas could be vented continuously. With this arrangement the circulated gas provided the agitation and separate agitators were not required. This was a particular advantage since agitator stuffing boxes were difficult to keep in good working condition.

Today inert gases in hydrogen are kept well under 0.5% and a dead-end convertor normally does not require any venting at all during the run. The use also of improved seals for agitator shafts has eliminated the difficulties of older designs.

The dead-end system of hydrogenation is particularly advantageous since it provides more positive control of the reaction and allows the selectivity to be varied by pressure as well as temperature adjustments. Furthermore the equipment is less expensive and simpler to operate.

Figure 4 shows the auxiliary items required for operating the dead-end convertor. The pressure control valve is set to deliver hydrogen gas at the rate necessary to maintain the desired pressure in the convertor. A pressure-vacuum-temperature recorder keeps an accurate account of the operating conditions throughout the cycle. Such a record is useful for control of the reaction and also provides a means for evaluating the results of a particular run. The relief valve for protecting the equipment is piped to some safe point outside of the building. The lubricator shown supplies oil to the double mechanical seals on the agitator shaft. With this arrangement, gas leakage is completely eliminated.

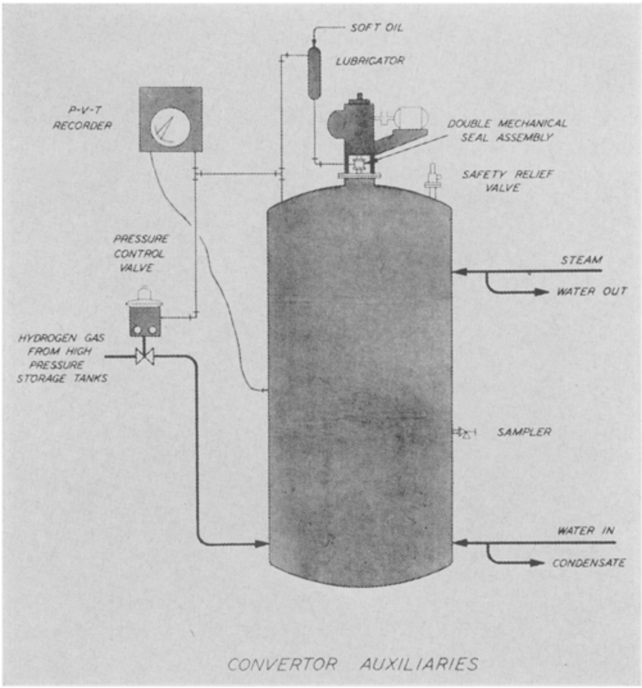

Fig. 4. Convertor Auxiliaries.

The hydrogenation equipment is usually installed in the plant building with walls isolating it from all other equipment and with doors leading to the outside only.

Operation of the Equipment

In operation, refined oil is charged from a measuring tank or through a batching meter into the convertor, which is under vacuum. The agitator is started as soon as oil covers the bottom impeller, and the required amount of catalyst slurry is then added. As the convertor is being filled, the agitated oil is thoroughly deaerated under the influence of vacuum. After the convertor has been charged with the oil and catalyst, the steam is turned on to heat the oil and to remove any moisture and volatile impurities present. When the temperature reaches about 275°F., the evacuator is shut and the hydrogen gas is run in.

The reaction is exothermic, and each pound of oil reduced one iodine unit will produce 1.7 B.t.u. of heat. This amount of heat will raise the temperature of the batch about 3°F. for each unit of iodine value reduction. Since hydrogenation will take place quite rapidly at the beginning, a great deal of heat will be generated and the temperature will rise quickly. The heating steam is therefore shut off, and it is often necessary to control the operating temperature by circulating cold water in the coil.

Different methods are used to follow the course of the hydrogenation. As a general guide, samples are withdrawn and their iodine values are determined either directly by some fast approximate method or indirectly from refractive index readings which can be correlated to iodine values. Iodine values can also be estimated, without taking samples, from the amount of gas used as indicated by the pressure drop in the hydrogen supply tank. As the desired degree of hydrogenation is approached, it may be necessary to check quickly some critical characteristic of the oil such as the micropenetration, congeal-point, or cloud-point. The micropenetration test has the advantage of being an actual measure of the consistency. Cloud- and congeal-points are not direct measures of the consistency, and their relationship to consistency depends upon the selectivity of the reaction.

When these quick tests and the experience of the operator indicate that the end-point has been reached, the gas supply is shut off and the hydrogen in the convertor is vented immediately to stop the reaction. At this point it is usually necessary to send samples of the oil to the laboratory for accurate testing to confirm the results.

When the tests show that the desired hardness has been reached, the charge is cooled to about 150°F. and is filtered to remove the catalyst. The clear oil is dropped into an intermediate oil-receiving tank, and the filter press cake is transferred to the catalyst-mixing tank for further use.

The catalyst cannot be used indefinitely since it gradually loses both its activity and selectivity. In addition, it is noted that as a catalyst is used it tends to become more iso-promoting (2). This is a particular disadvantage in the hydrogenation of shortening stocks. It is common therefore to use catalysts a few times for shortening hydrogenation, then for margarine, and finally for stearine before they are discarded.

A typical operating cycle for hydrogenating an oil, such as cottonseed, to shortening consistency would be as follows:

for charging the convertor with oil and catalyst slurry	¼ hr.
for deaerating, heating to 275°F. and drying the oil under vacuum	1¼ hrs.
normal reaction time @ 325°F	2 hrs.
time required by laboratory for making the final tests	½ hr.
for cooling the oil to 150°F	¾ hr.
for circulating cloudy oil and for the actual filtration	1¼ hrs.
or a total time of	6 hrs.

For complete hardening an additional two hours may be required for the reaction, and the equipment is usually sized on the basis of an 8-hr. cycle.

Post-Bleaching. Normally as much as 50 parts per million of nickel catalyst, mostly in colloidal form, will remain in the hydrogenated oil following the usual filtration. Years ago many processors considered this satisfactory. Today, of course, a much more complete removal of nickel is essential for producing a high quality product. Trace amounts of nickel metal remaining in the oil will affect the stability of the product by accelerating the auto-oxidation of the oil.

There are two practical alternatives for removing this nickel. The oldest method known as "post-bleaching" involves a separate bleaching operation, usually with acid activated clay. Acid clays also remove the green color deriving from chlorophyll pigments, which predominate following the reduction of carotenoid pigments during the hydrogenation. This operation however is relatively expensive and involves substantial oil losses in the discarded bleaching clay. For this reason many processors add activated carbon to the oil, which is very effective in removing the chlorophyll pigments, and they treat the filtered oil with citric or phosphoric acids to reduce the nickel metal content to well under 1.0 p.p.m.

Conclusion

It should be stressed again that successful hydrogenation depends upon the careful preparation and handling of all materials, the accurate control of the reaction, and the use of efficient equipment and operating procedures. Our understanding of the reaction and the chemistry involved is far from complete and present methods of controlling the results are, by necessity, indirect and time-consuming.

The critical problem of hydrogenation has to do with the selectivity of the reaction. Improvements in the process therefore will depend largely upon the preparation of better and more selective catalysts. Perhaps when catalysts are developed which will provide very precise selectivity, continuous methods for hydrogenation may be used to much greater advantage.

REFERENCES

1. Adkins, Homer, Ind. & Eng. Chem., *32*, 1189–1192 (1940).
2. Bailey, A. E., "Industrial Oil and Fat Products," 2nd ed., Interscience Publishers, New York (1951).
3. Bailey, A. E., J. Am. Oil Chemists' Soc., *26*, 644–648 (1949).
4. Bailey, A. E., J. Am. Oil Chemists' Soc., *26*, 596–601 (1949).
5. Bailey, A. E., Ind. & Eng. Chem., *44*, 990–994 (1952).
6. Beal, R. E., and Lancaster, E. B., J. Am. Oil Chemists' Soc., *31*, 619–625 (1954).
7. Dean, G. J., Ind. & Eng. Chem., *44*, 985–990 (1952).
8. Fuente, H., private communication, Mixing Equipment Coompany, Rochester, N. Y. (1956).
9. Markley, K. S., "Soybeans and Soybean Products," vol. II, Interscience Publishers Inc., New York (1951).
10. Paterson, W. J., U. S. Pat. 2,437,706 (1948).
11. Schwitzer, M. K., "Continuous Processing of Fats," Leonard Hill Ltd., London (1951).
12. Sims, R. J., J. Am. Oil Chemists' Soc., *29*, 347–350 (1952).
13. Waterman, H. I., "Hydrogenation of Fatty Oils," Elsvier, New York (1951).
14. Wurster, O. H., Ind. & Eng. Chem., *32*. 1193–1199 (1940).