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Practical Aspects of Hydrogenation

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The hydrogenation of fats and oils remains the largest single chemical reaction of the industry. The purpose of the reaction is two-fold. First, a liquid oil is converted into a semisolid or plastic fat and secondly, since the unsaturation of the oil is reduced, the rate of reaction with oxygen is decreased.

The reaction has been carried out for many years with very little change. Converters holding 10,000 to 60,000 lb. of oils are used, heated with internal coils and agitated mechanically using usually a flat blade or turbine agitator. The oil and catalyst are mixed in the converter, heated near operating temp and hydrogen admitted through a spider in the bottom of the vessel. The temp increases rapidly due to the exothermic reaction and may or may not be controlled during the reaction. Excess hydrogen may be allowed to accumulate in the head space of the tank and may or may not be purged, depending on the type of system used. The reaction is followed usually by a change in refractive index of the oil which can be related to the iodine value. When the desired end point is reached, the hydrogen flow is stopped and the charge cooled, filtered to remove the catalyst and then can be bleached with a small amount of clay to remove the last traces of catalyst.

There are three parameters that may be changed to give different characteristics to the products, catalyst, temp and hydrogen pressure. These three parameters cause changes in the rate of hydrogenation, ratio of the rate of saturation vs. isomerization of the double bonds and the selectivity, i.e., the rate of reduction of polyenes to monoenes vs. the rate of reduction of monoenes to saturated.

TABLE I

Composition of Two Hydrogenated Soybean Oils

	I	II
% Solids at 50 F	12.0	12.3
70 F	5.1	3.8
80 F	2.9	0.8
92 F	0	0
Essential fatty acids, %	19.0	11.7
Trans, %	27.8	36.1
Palmitic, %	11.7	11.8
Stearic, %	8.1	5.7
Oleic, %	57.1	61.5
Linoleic, %	22.1	20.1
Linolenic, %	1.0	1.0

I—Hydrogenated at 285 F, 30 psig to 92 IV.
II—Hydrogenated at 330 F, 10 psig to 92 IV.

With the increasing supply of soybean oil with its linolenic acid which presumably gives it a flavor defect, the question of selectivity has received much attention.

Figure 1 shows the analytical characteristics at the same IV of a soybean oil hydrogenated with the same catalyst under two different reaction conditions that may be used in commercial equipment. It is apparent the reaction at high temp and low pressure (II) is more selective, lower linoleic and lower stearic but has more trans isomers and thus a somewhat steeper solids slope. Also, the more selective reaction (II) has a smaller proportion of the linoleic acid in the cis cis methylene interrupted system as shown by the analysis for "Essential Fatty Acids" using lipoxidase.

The effects of the operating parameters on selectivity and isomerization are: increased pressure decreases selectivity and trans isomers, increased temp under low agitation, increases selectivity and isomerization. However, under very efficient mixing of the oil and hydrogen, the temp effect on selectivity is slight and only an increase in the reaction rate occurs.

From a study of the reaction rates of hydrogenation of cottonseed oil, Wesniak and Albright (10) concluded the mechanism was the reaction between unsaturated in the liquid phase and atomically chemisorbed hydrogen with the surface reaction controlling. This mechanism is consistent with other observations. Kokes and Emmet (7) have shown Raney nickel catalysts hold 45–100 cc of hydrogen/g. catalyst as hydrogen atoms in a substitutional solid solution. Also Beek (2) has shown the hydrogenation of ethylene occurs when it approaches a catalyst film that holds two atoms in a favorable geometric position.

When a catalyst is saturated with hydrogen as in relatively high pressure hydrogenations, most of the "active" sites will hold hydrogen atoms and the probability is large that two atoms are in the correct geometrical position for reaction with any double bond as it approaches the catalyst. Conditions which favor a continuous saturation of the catalyst will thus favor low selectivity because any unsaturated bond that approaches the two hydrogen atoms will be saturated. Also, the isomerization is low since the rate of saturation of a bond is high compared to the rate of isomerization. If the catalyst is sparsely covered with hydrogen atoms, which obtains at low pressure, low transport of hydrogen from the oil to the catalyst, a high probability exists for only single hydrogen atoms to react with the double bond since very few sites have two hydrogens in the correct position to react with a double bond. This reaction with a single hydrogen atom can then lead to a half hydrogenation–dehydrogenation of the double bond which results in positional and geometric isomerization (4). If linoleic acid is being hydrogenated, presumably part of the diene system going through this hydrogenation–dehydrogenation reaction sequence will be conjugated and for some reason hydrogenate faster than the isolated double bonds of oleate. It has been shown (5) that isomerization during hydrogenation of linoleate results in high concentrations of monoenes with double bonds in the 10 and 11 positions which would result from conjugation of the 9,12 diene system, followed by rapid hydrogenation of one bond of the conjugated diene.

From these data and others, it is becoming apparent the selectivity of a hydrogenation and the formation of trans isomers are inexorably tied together under the present conditions of hydrogenation and catalysts. This of course means one must make a compromise between selectivity and isomer formation when setting conditions for hydrogenation to prepare various base stocks.

Catalysts

Nickel catalysts are used almost exclusively for food fat hydrogenations. The usual nickel catalyst is prepared by the reduction of a nickel salt and is usually supported on an inert solid or flaked in hard fat or a combination of the two. Traces of other metals may be added to the nickel to prepare special catalysts.

The only other metal that has been studied to any great extent is palladium. It was found by Zajcew (11) that if palladium was modified by the addition of silver and bismuth, castor oil could be hydrogenated to a low IV at 100 C, 45 psig with 0.0055% Pd with no loss of hydroxyl. Also, using a 2% and 5% Pd on carbon at a level of 0.0005% Pd, shortening base stocks were prepared (12). The products were slightly more selective, contained more linoleic and more trans, than the equivalent stocks prepared by the use of nickel. By repeated reuse of the catalyst one gram of 5% Pd on carbon would hydrogenate about 18 kg of oil to a satisfactory product while 1 gm of the 2% Pd on carbon would hydrogenate about 11 kg. Also, margarine base stocks were prepared that were equivalent to those prepared using nickel (13). By an increase in temp, lower pressure and lower rate of agitation over the conditions used to prepare shortening bases, the necessary trans were produced to make a satisfactory margarine base.

For the hydrogenation of tall oil fatty acids using members of the platinum group metals palladium was found to be the most selective and economical. Also the more dispersed the metal was on the carrier the more selective it became (14).

Unfortunately, fatty acid compositions of periodic samples during the triglyceride hydrogenations were not published so no selectivity measure of palladium for triene unsaturation may be made. However, from the trans contents and fatty acid compositions of the final stocks, the catalyst is believed to be about equivalent to nickel in this respect.

These palladium catalysts are somewhat remarkable when one considers that 6 ppm palladium in oil is sufficient to give rather rapid hydrogenation rates compared to nickel which requires at least 200 ppm. This would indicate palladium is some thirty times as active as nickel. This difference in activity has been related to the inter-atomic spacing in the lattice (3).

Hydrogenation in solvent as practiced in the laboratory has the possibility of changing the properties of the system so that more selective hydrogenation may result. With the advent of micella refining and winterization, hydrogenation in solvent should also be a possibility. The presence of solvent should decrease the viscosity of the liquid phase, modify the solubility of hydrogen, while reducing the concentration of double bonds. Also, the presence of solvent would change the absorption characteristics of the reactants on the catalyst surface. A patent has been issued (9) which claims increased selectivity without extensive isomerization. Later work by Albright et al (1) indicated the presence of solvent had no effect on the selectivity of the reaction. The rates of hydrogenation were found to decrease in the order, non solvent, hexane, isopropyl alcohol and di isopropyl ether. Although different reaction conditions, particularly agitation and catalyst, were used in the two studies, it would appear the presence of solvent could have little or no effect on the relationship of selectivity and isomerization in view of the atomic theory of hydrogenation.

Since most natural fats are somewhat non random in the distribution of fatty acids among the three positions of the glycerine molecule, some consideration has been given to the possible difference in hydrogenation rates of fatty acids in the different positions. If there were differences that could be exploited, various non random fats such as cocoa butter could be duplicated.

Mattson (8) by hydrogenation of randomly rearranged soybean oil followed by analysis of the various fractions produced by lipase hydrolysis of the fats showed the hydrogenation was completely random. The fatty acids found in the 2 position of the samples were the same as those in the 1 and 3 positions. No consideration was given to the possibility of acyl migration during the hydrogenation which would tend to produce a random rearrangement even if there was a difference in hydrogenation rate between the 1 and 2 positions. However, Feuge (6) hydrogenated olive oil and found no intermolecular rearrangement and showed the hydrogenation was random among the three positions of the triglyceride molecule.

Thus it seems hydrogenation today is a somewhat uncontrollable random process with isomerization and selectivity tied together. If, as accumulating evidence indicates, hydrogenation using a heterogenous system of oil, hydrogen and catalyst is an atomic hydrogenation, this may be explained. However, this theory would also indicate there is no possibility of hydrogenating a food fat to the extent of oxidative flavor stability and still retain the cis configuration of all the remaining double bonds.

At present, manufacturers of food fats and oils can live with this because they must. However, a major research effort on hydrogenation using some new approach would be most welcome to the industry.

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Fat Chemistry—Past, Present, Future

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FAT CHEMISTRY, the chemistry of triglyceride fats and oils and the fatty acids derived therefrom, had its beginning in antiquity with the preparation of soap from tallow and wood ashes. The Egyptians produced alkali soaps and used lime soaps to lubricate chariot wheels. Fat technology, as the term is used today, had its origin in the discovery by Chevreul in 1811 that fats were composed of fatty acids and glycerol. And probably the first major contribution of fat technology to better living arose through the substitution of solid fatty acids (produced by fractional crystallization) for tallow in the manufacture of candles, thus eliminating the acrid fumes which are produced when tallow candles are burned. The first synthetic surface-active agent (Turkey-red oil) was produced in the late 19th century by the sulfation of castor oil and was used in textile processing and as an emulsifying agent. It was the first hard-water-stable surfactant.

At the turn of the century, Twitchell discovered his process for the catalytic splitting of fats, thus simplifying the manufacture of fatty acids through elimination of the two-step saponification-acidulation process. Not long thereafter, Sabatier's procedure for catalytic hydrogenation was applied commercially for the hardening of liquid fats in the production of the so-called vegetable shortenings. This development had a tremendous adverse impact upon the animal-oil shortening industry. The relatively low stability of animal fats contributed to their loss of popularity.

The fatty chemical industry, as we know it today, probably began in the 1920's with the catalytic hydrogenation of fatty acids or esters to produce fatty alcohols. Introduction of salts of fatty alcohol sulfates in the early 1930's marked the beginning of the synthetic detergent industry.

Also in the early 1930's commercial fractional distillation of fatty acids provided a means for separating fatty acids according to chain length, and the consumer was then able to select the specific fatty acid best suited to his application. Heretofore, mixtures of solid and liquid fatty acids, such as are obtained by the old panning and pressing process, constituted the selections available. Solvent crystallization, first applied commercially in the 1940's, offers a substantial improvement over panning and pressing. Separation of solid and liquid acids is accomplished much more efficiently, thus making available fatty acids of relatively high purity.

A second important development occurred in the food-fat field in the middle 1930's with the introduction of a shortening containing fatty acid monoglycerides (actually predominantly a mixture of mono- and diglycerides). These shortenings made it possible to use a much higher ratio of sugar to fat in bakery goods.

The fifth decade of this century saw a number of significant developments in the field of fat and fatty-acid technology. Continuous, high-temp, high-pressure splitting of fats was introduced. This process adds both speed and economy to the splitting process. Also introduced commercially during the 1940's were the nitrogen-containing derivatives of the fatty acids based upon the reaction of the acids with ammonia to yield amides and nitriles. The latter were hydrogenated to amines which were converted to quaternary ammonium salts and other derivatives.

Two industrially important dibasic acids are produced from fats. Sebacic acid is manufactured by the alkaline fusion of ricinoleic acid from castor oil and azelaic acid by the oxidative cleavage of oleic acid with ozone. These products assumed commercial importance during the 1950's. Also during this period, epoxidation of unsaturated fats was applied on a commercial scale.

Having reviewed some of the highlights in the growth of the fatty chemical industry, it is appropriate to survey the areas in which fatty chemicals find application today. These areas are very extensive; in fact, it probably is safe to state that a fatty chemical has played an important role somewhere in the course of the manufacture of most of those items and goods which are essential to our way of life. Items with which we come in daily contact and which are based wholly or in part upon fat-derived materials include soaps and synthetic detergents, cosmetics, and pharmaceuticals. Even in our food products and especially bakery goods and prepared mixes, both chemically modified fats and emulsifiers produced from fatty acids are essential.

Although lime soaps have been used as lubricants for centuries, the use of metallic soaps in this application has expanded tremendously in recent years. Soaps not only of calcium, but also of barium, aluminum, and lithium find specialized applications. Also, an entirely different type of fatty chemical, a combination of a fatty quaternary ammonium compound with an acid clay such as bentonite, is being employed in certain grease formulations and other applications.

Fatty chemicals are widely used in petroleum technology. Cationic surface-active agents based upon fatty acids are employed in "down-the-hole" operations in secondary oil recovery. The function of the fatty chemical is three-fold. It assists in the penetration of water into the oil-bearing sandstone; it serves as an anti-microbial agent which inhibits the growth of sulfate reducers and other organisms which